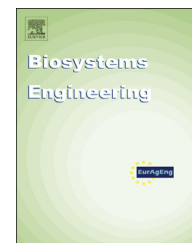


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## Research Paper

# Sensitivity analysis of mechanistic models for estimating ammonia emission from dairy cow urine puddles



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Ammonia (NH<sub>3</sub>) emission can cause acidification and eutrophication of the environment, is an indirect source of nitrous oxide, and is a precursor of fine dust. The current mechanistic NH<sub>3</sub> emission base model for explaining and predicting NH<sub>3</sub> emissions from dairy cow houses with cubicles, a floor and slurry pit is based on measured data from a limited number of studies. It requires input values for numerous variables, but the empirical equations for the model parameters in the literature vary. Furthermore, many of the input variables cannot be assessed accurately, and their actual influence on the prediction is unknown. We aimed to improve NH<sub>3</sub> emission modelling, by assessing the contribution to the variation in NH<sub>3</sub> emission of each input variable and each model parameter related to a single urine puddle. We did so for 27 candidate models, created by each possible combination of three equations per model parameter: the acid dissociation constant, Henry's law constant, and the mass transfer coefficient. After analysing each candidate model with a Global Sensitivity Analysis we found that at least 71% of the model variation in NH<sub>3</sub> emission for each candidate model was explained by five puddle related input variables: pH, depth, area, initial urea concentration and temperature. NH<sub>3</sub> emission was not sensitive to the other four variables: air temperature, air velocity, maximum rate of urea conversion and the Michaelis–Menten constant for urea conversion. Based on these results we recommend simplifying the model structurally and reducing the number of input variables.

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Nomenclature	
$a_p$	area of a urine puddle [ $m^2$ ]
$c$	concentration of a solute [various]
$CO(NH_2)_2$	urea [ $mol\ m^{-3}$ ]
$D_{a,b}$	diffusivity of substance a in b [ $m^2\ s^{-1}$ ]
$d_p$	depth of a urine puddle [m]
et	emission duration [s]
$f$	fraction $NH_3$ [–]
$H$	Henry's law constant [various]
$H^{cc}$	Henry's law constant [–]
$H_{inv}$	inverse Henry's law constant [various]
$H_{inv}^{cc}$	inverse Henry's law constant [–]
$h_m$	mass transfer coefficient [ $m\ s^{-1}$ ]
$K_a$	acid dissociation constant [–]
$K_d$	dissociation constant [–]
$K_w$	dissociation constant for water [–]
$k_{gas}$	individual gas film mass transfer coefficient [various]
$K_{GAS}$	overall gas mass transfer coefficient [various]
$k_{liq}$	individual liquid film mass transfer coefficient [various]
$K_{LIQ}$	overall liquid mass transfer coefficient [various]
$K_m$	Michaelis–Menten constant [ $mol\ m^{-3}$ ]
$L$	characteristic length, fixed at 1.2 m
$M_{2N}$	mol mass urea nitrogen [28.01 g $mol^{-1}$ ]
$M_{H_2O}$	mol mass $H_2O$ [18.02 g $mol^{-1}$ ]
$M_{NH_3}$	mol mass $NH_3$ [17.03 g $mol^{-1}$ ]
$N$	number of simulations [100,000 #]
$NH_3$	ammonia [ $mol\ m^{-3}$ ]
$NH_3-N$	ammonia-nitrogen [ $mol\ m^{-3}$ ]
$NH_4^+$	ammonium [ $mol\ m^{-3}$ ]
$NH_4^+-N$	ammonium-nitrogen [ $mol\ m^{-3}$ ]
$p$	partial pressure of a solute [various]
$P_{atm}$	atmospheric pressure [ $1.01325 \times 10^5\ Pa$ ]
pH	pH of urine puddle [–]
$R$	gas constant [ $8.205746 \times 10^{-5}\ atm\ m^3\ mol^{-1}\ K^{-1}$ ]
$Sm$	maximum rate of conversion [ $mol\ m^{-3}\ s^{-1}$ ]
$t$	time [s]
$T$	temperature [K]
TAN	$NH_3-N + NH_4^+-N$ in the puddle [ $mol\ m^{-3}$ ]
$[U]$	urea-nitrogen concentration [ $mol\ m^{-3}$ ]
$[U_0]$	initial $[U]$ [ $mol\ m^{-3}$ ]
$v$	air velocity [ $m\ s^{-1}$ ]
$\mu$	viscosity [ $kg\ m^{-1}\ s^{-1}$ ]
$\rho$	density [ $kg\ m^{-3}$ ]
$\phi_{NH_3}$	$NH_3$ volatilisation rate [ $mol\ s^{-1}$ ]
Subscript	
air	air
bound	boundary layer urine puddle
gas	gas
inv	Inverse
liq	liquid

## 1. Introduction

Ammonia ( $NH_3$ ) emission can cause acidification and eutrophication of the environment.  $NH_3$  is also an indirect source of the greenhouse gas nitrous oxide ( $N_2O$ ) (IPCC, 1996) and is a precursor of fine dust particles. To lower  $NH_3$  emissions in the EU, member states are required to set a National Emission Ceiling (NEC) (EU, 2001; UNECE, 1999). Twenty-five of the 27 EU member states complied with the 2010 NEC set by the European Commission. The total emission of ammonia in the Netherlands in that year was 122 kt, which was 4.9% below NEC 2010 (EEA, 2012). However, local and regional emission and deposition still cause a high overload in the Dutch Natura2000 areas (Planbureau voor de leefomgeving, 2012). If, as expected, the NECs set for 2020 are lower than those set for NEC 2010, further mitigation of  $NH_3$  emission will be necessary in the EU.

In 2010, agriculture was responsible for 94% of all  $NH_3$  emission from the 27 EU member states (EEA, 2012). Of this, 80% was emitted from livestock production systems. Ammonia emission from cattle in the Netherlands fell from 184 kt in 1990 to 53 kt in 2009 (Van Bruggen et al., 2011), of which 34% originated from dairy cow houses and manure storage facilities. Monteny, Schulte, Elzing, and Lamaker (1998) considered a typical dairy cow house consisting of a living area with cubicles, plus walking and feeding-alleys, which together provide a total area of 3.5  $m^2$  per cow. There is a slurry pit underneath the whole house, and a slatted

concrete floor in the cow walking area. They estimated that one urine puddle occupies an area of 0.8  $m^2$ . In such a typical dairy cow house about 70% of  $NH_3$  emission is emitted from the slatted floor.

Monteny et al. (1998) developed a conceptual mechanistic computer model in order to understand and predict  $NH_3$  emissions from dairy cow houses. Called the Monteny model, it describes the physical and chemical processes involved and quantitatively determines the  $NH_3$  emission according to model parameters, using input variables related to the characteristics of a urine puddle, air, floor and pit. Similar mechanistic  $NH_3$  emission models have been developed and validated against measurements in a limited number of studies for cows (Elzing & Monteny, 1997; Montes, Rotz, & Chaoui, 2009; Muck & Steenhuis, 1981; Vaddella, Ndegwa, & Jiang, 2011; Vaddella, Ndegwa, Ullman, & Jiang, 2013), and for pigs (Aarnink & Elzing, 1998; Arogo, Zhang, Riskowski, Christianson, & Day, 1999; Cortus, Lemay, Barber, Hill, & Godbout, 2008; Liang, Westerman, & Arogo, 2002; Zhang, Day, Christianson, & Jepson, 1994). In this study we focus on the general mechanistic  $NH_3$  emission model theory.

The Monteny model is currently used by the Dutch Ministry of Infrastructure and Environment to assess the  $NH_3$  emission from dairy cow houses that are applying new  $NH_3$  mitigation techniques, and also to obtain preliminary emission factors that are used when granting permits. This assessment is later followed by full-scale measurements in commercial houses in accordance with a prescribed protocol,

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