

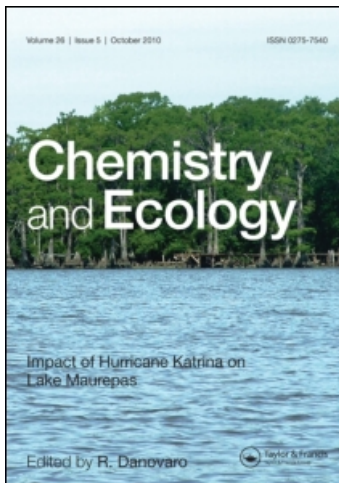
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A comprehensive model to estimate the simultaneous release of acidic and basic gaseous pollutants from swine slurry under different scenarios

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Swine slurry is a source of atmospheric pollutants. Emissions of basic and acidic compounds from slurry are largely dependent on the surface pH. In a storage system, the pH at the surface layers changes over time due to the volatilisation of ammonia (NH_3), carbon dioxide (CO_2) and acetic acid (HAc). In this article, a comprehensive gas emission–pH (GE–pH) coupled model is proposed to describe the simultaneous release of acidic and basic gaseous pollutants from swine slurry. The model was applied to describe the release of NH_3 , CO_2 , HAc and hydrogen sulphide (H_2S) from standard slurries stored in animal houses, outside storage tanks and lagoons. The modelled results agreed well with values reported in the literature and could be reasonably interpreted. The key parameters affecting the release of gases were: initial pH, initial concentration of total ammonium nitrogen and inorganic carbon, slurry temperature and air velocity. This study suggests that future modelling studies on gas emissions from animal slurry should consider the concentration of inorganic carbon and the frequency in which the slurry surface is mixed or altered, because they affect the surface pH and the release of gaseous pollutants from slurry.

Keywords: pH; hydrogen sulphide; ammonia; carbon dioxide; emission; model; slurry

1. Introduction

Animal production is a source of airborne contaminants that have a negative impact on the environment and human populations living in the surrounding areas [1]. Many of the noxious gases emitted from slurry are weak acidic or basic compounds. Ammonia (NH_3) is a basic gas which may cause eutrophication of natural ecosystems and indirectly lead to acidification of soil and vegetation [2]. Carbon dioxide (CO_2) is an acidic gas that contributes to the greenhouse effect. Odour emitted from animal facilities is a mixture of different compounds, such as acids, alcohols, aldehydes, amides, amines, aromatics, esters, ethers, halogenated hydrocarbons, hydrocarbons, ketones, nitriles, other nitrogen-containing compounds, phenols, sulphur-containing compounds and other compounds [3–5]. Despite this variability, several studies have shown that acetic acid (HAc) and hydrogen sulphide (H_2S) (both acidic compounds) are important odorants regarding odour intensity [6–9] and concentration [10,11].

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Noxious compounds are produced in slurry because of the anaerobic decomposition of organic substrates [12,13]. They are then transported from the slurry to the gas phase (air above slurry), across the air–liquid system, due to the difference in partial pressure of dissolved and gaseous compounds between the manure surface and the atmosphere. Transport across the air–liquid system may be referred to as ‘release’.

A difference in partial pressure is essential for the release of gases from a solution of dissolved gases to the atmosphere. So, the release is a function of the concentration of gas dissolved in the slurry surface. In their ionised form (i.e. charged or dissolved), chemical compounds cannot exchange between the liquid phase and the gas phase. Because many of the gases and odorous compounds released from slurry are weak acids or bases, the form of these compounds in the aqueous phase (and hence their potential to be released) will depend on chemical equilibria and will be affected by the pH.

Previous studies have shown that the main buffer components controlling the pH in the slurry are total inorganic carbon ($[TIC] = [CO_2] + [HCO_3^-] + [CO_3^{2-}]$), total ammonium nitrogen ($[TAN] = [NH_3] + [NH_4^+]$) and total acetic acid ($[TAc] = [HAc] + [Ac^-]$) [14–17]. In a storage system, the concentrations of buffer components controlling the pH in the surface layer of the slurry change over time due to microbial transformation [18] and the volatilisation of gases [19]. Volatilisation of acidic gases (e.g. H_2S , HAc , CO_2) tends to increase pH at the surface, and emission of bases (e.g. NH_3) tends to decrease it.

A correct estimation of the pH in the surface layers of slurry is essential to obtain more accurate gas emission estimations. Models predicting emissions of specific gases and odorous compounds from swine slurry have been developed in previous studies [20–28]. However, in these models, the buffer system controlling the slurry pH has not been thoroughly modelled and coupled with gas emission models.

In this article, a model that includes such an improvement is presented and discussed. The gas emission–pH (GE–pH) coupled model is comprehensive model that describes: (1) the simultaneous release of acidic (e.g. CO_2 , HAc and H_2S) and basic compounds (e.g. NH_3) from swine slurry; and (2) the effect of the release of these gases on the concentration of buffer components and pH in the slurry, which in turn, controls the release. The GE–pH coupled model presented here (which comprises the gas emission sub-model and the pH buffer sub-model) is applied to describe the release of NH_3 , CO_2 , HAc and H_2S from standard slurry stored in animal houses, outside storage tanks and lagoons, which constitute important continuous source of gases and odorants from farms.

2. The GE–pH coupled model

2.1. The gas emission sub-model

2.1.1. Description

The gas emission sub-model is based on the two-film theory [29], which assumes that the overall resistance to mass transfer across the air–liquid system results from resistance through two thin films (air and liquid) adjacent to the air–liquid interface. The gas emission sub-model is a gas transport model and does not consider the biological formation and consumption of compounds that occur in slurry. The transport of gases from the liquid slurry to the air can be illustrated as: (1) an upward transport of dissolved gases from the bulk slurry to the surface of the liquid phase, across a thin liquid film; (2) a transfer of gases between the surface of the liquid phase and the air phase immediately above the liquid (air–liquid interface); and (3) an upward transport of gas components from the air phase immediately above the liquid across the air film to the free

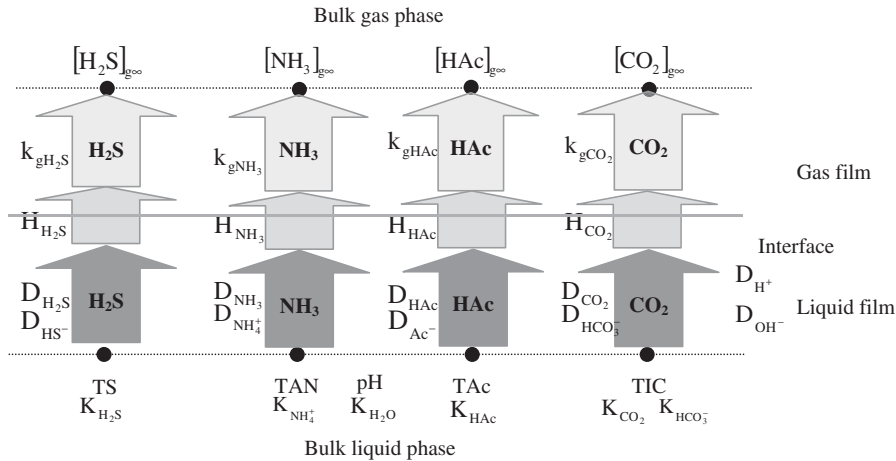


Figure 1. Layout of the gas emission sub-model in a gas–liquid interface, including the inputs of the model.

atmosphere (Figure 1). Above the air film, convection or turbulence created by wind over the liquid surface exists [30]. Below the liquid film (i.e. bulk slurry), turbulence can be created by the ebullition of gas produced in the anaerobic solution containing much degradable organic matter [31]. Turbulent transport is very efficient, and so, the concentration of gases above the air film and the concentration of buffer components below the liquid film are considered to be uniform.

The transport of gases across the liquid film is mediated by molecular diffusion. As a result of gas release and reversible dissociation reactions, steep concentration and pH gradients are likely to develop at the sub-millimetre scale, from the base of the liquid film, to the gas–liquid interface. At the gas–liquid interface, Henry’s constant (H , unitless, gas/liquid) controls the partitioning of the compound between the gas and liquid phases. Transport of gases across the air film occurs by molecular diffusion, which is influenced by local climate properties affected by convection or turbulence created by wind over the liquid surface [31–33].

2.1.2. Mathematical development and parameters estimation

The mathematical development of the gas emission model presented in this article is an application of the mass transfer chemical reaction (MTCR) model for the transfer of H_2S across the gas–liquid interfaces in an anaerobic swine waste treatment storage system developed by Blunden et al. [28]. In our study, the MTCR model was adapted and generalised for basic compounds and acidic compounds different from H_2S .

The equilibrium reactions for acids (HA) and bases (B) in the slurry can be represented by the following general forms (Equations 1 and 2, respectively):



In the gas emission sub-model, Fick’s first law diffusion equation (which results in Equation 3) was applied in the gas film, for each modelled compound:

$$F_a = -\frac{D_a}{t_a} \cdot ([G]_{a,\infty} - H \cdot [G]_{l,i}) = -k_a \cdot ([G]_{a,\infty} - H \cdot [G]_{l,i}), \quad (3)$$

where:

- F_a = Flux above the air film (or gas release) ($\text{mol} \cdot \text{m}^{-1} \cdot \text{s}^{-1}$)
- D_a = Diffusion coefficient in the air phase ($\text{m}^2 \cdot \text{s}^{-1}$)
- t_a = Thickness of the air film (m)
- k_a = Mass transfer coefficient for the transport in the air phase ($\text{m} \cdot \text{s}^{-1}$)
- G = Compound in the non-ionic form (HA or B).

In the liquid film, acid and basic equilibrium reactions (represented by Equations 1 and 2) are considered. Applying the mass balances and Fick's second law in the liquid film, the flux of gases at the gas–liquid interface can be calculated as (Equation 4) [34]:

$$F_{\text{int}} = \frac{1}{2 \cdot t_l} \cdot \left(2 \cdot D_G \cdot ([G]_{l,\infty} - [G]_{l,i}) + 2 \cdot D_{G_{\text{ion}}} \cdot [G_{\text{ion}}]_{l,\infty} - \beta - \sqrt{\beta^2 + 4 \cdot D_{G_{\text{ion}}} \cdot D_{W_{\text{ion}}} \cdot K \cdot [G]_{l,i}} \right), \quad (4)$$

where:

- F_{int} = Flux of gases at the gas–liquid interface ($\text{mol} \cdot \text{m}^{-1} \cdot \text{s}^{-1}$)
- t_l = Thickness of the liquid film (m)
- D_G , $D_{G_{\text{ion}}}$ and $D_{W_{\text{ion}}}$ = Diffusion coefficients of gases and species in the slurry ($\text{m}^2 \cdot \text{s}^{-1}$)
- $\beta = D_{G_{\text{ion}}} \cdot [G_{\text{ion}}]_{l,\infty} - D_{W_{\text{ion}}} \cdot [W_{\text{ion}}]_{l,\infty}$
- K = Equilibrium (dissociation) constant
- G_{ion} = Compound in the ionic form (A^- or BH^+)
- W_{ion} = Proton (H^+) or ions hydroxide (OH^-), depending on if G is an acid (HA) or a base (B).

The thickness of the liquid film can be calculated from:

$$t_l = \frac{D_G}{k_G},$$

where:

- D_G = Diffusion coefficient of the gas G ($\text{m}^2 \cdot \text{s}^{-1}$)
- k_G = Mass transfer coefficient of the gas G in the liquid film ($\text{m} \cdot \text{s}^{-1}$).

Under steady-state conditions, the flux at the interface (F_{int}) is equal to the flux at the top of the gas film (F_a); and so, the flux (or gas release) can be obtained from Equations (3) and (4).

The use of the gas emission sub-model requires knowledge of specific field conditions ($[G]_{a,\infty}$, $[G]_{l,\infty}$ and $[G_{\text{ion}}]_{l,\infty}$) and values of model parameters (k_a , H , D_G , $D_{G_{\text{ion}}}$, $D_{W_{\text{ion}}}$, k_G and K), at the case study being modelled. The concentration of the gas compound in the ionic ($[G]_{l,\infty}$) and non-ionic ($[G_{\text{ion}}]_{l,\infty}$) forms in the liquid film can be calculated from the pH, the total concentration of the buffer component in the liquid film ($[TG] = [G] + [G_{\text{ion}}]$), and the dissociation constants (K). For model parameter estimation, different equations in the gas emission sub-model can be used when modelling the release of gases from slurry stores. Mass transfer coefficients in the air phase (k_a) can be calculated using equations presented elsewhere [35–37], and mass transfer coefficients in the liquid phase (k_G) as shown previously [36,38,39]. Diffusion coefficients of gases and ionic species in the slurry (D_G , $D_{G_{\text{ion}}}$ and $D_{W_{\text{ion}}}$) can be calculated using equations developed previously [40–42]. The dissociation constant (K) and Henry's constant (H) can be estimated from the slurry temperature, using equations developed by different authors for each specific gas.

2.1.3. Application of the gas emission sub-model to model the release of H₂S, NH₃, HAc and CO₂

The general gas emission sub-model described in Equations (1) to (4) was applied to model the transport of three specific acids (H₂S, HAc and CO₂) and one base (NH₃) from the bulk slurry to the air (Figure 1). These gases were selected considering that: (1) H₂S and HAc contribute most to the obnoxious odour in the air from farms; (2) NH₃, HAc and CO₂ determine the pH in the surface of the slurry from where acidic and basic gases are released; and (3) H₂S, NH₃, HAc and CO₂ can act in the model as representatives of different chemical groups, among the wide range of compounds released from the slurry.

The concentrations of gases and ionic species in solution ($[G]_{l,\infty}$ and $[G_{ion}]_{l,\infty}$) were calculated considering the following dissociation reactions in the equilibrium system (Equations 5a, 5b, 5c, 5d, 5e) and equations presented in Table S1 (Supplementary content – available online only). The concentration of total sulphide ([TS]) was defined as $[TS] = [H_2S] + [HS^-]$. The concentration of dissolved sulphide as S²⁻ was not considered, because it is negligible when the pH < 11 [43]. Data on environmental parameters (air temperature, T_a ; slurry temperature, T_l ; relative humidity, RH; and air velocity, U_{10}) were used to estimate the mass transfer coefficients, Henry's constant, diffusion coefficients and dissociation constants in the gas emission sub-model, according to the equations from the literature, compiled in Supplementary Tables S2 and S3 (available online only) [44–54].



2.2. The pH buffer sub-model

The pH and concentration of buffer components (TG) at the surface layers in a mixed slurry is uniform with depth. However, when the slurry is left undisturbed, volatilisation of acidic and basic gases tends to modify the pH at the surface. Therefore, in stored (not recently mixed) slurry, the pH within 1 mm below the surface may be significantly different from the pH measured in deeper layers (centimetres below the surface) [31,55–57]. In this article, the initial conditions for the modelling process are those in which the very surface of the liquid slurry has been in some way disturbed or stirred by, for example, active mixing, emptying slurry pits, animals walking on wetted slats, rainfall, addition of new slurry, etc. These activities cause a disturbance/mixing in the surface layer of the liquid, and remove the differences in pH and concentrations at the surface layers. Immediately after these disturbances occur, the pH measured by conventional sensors at a few centimetres below the surface can be considered similar to pH at the surface.

The gas emission sub-model requires knowledge of the pH sub-millimetres below the surface of stored slurry, at each moment in time. The change in slurry pH can be estimated using a simple model, based on the fact that the charge of the liquid should be zero and including calculations of the equilibrium concentrations of charged species of HAc, NH₃ and CO₂, and the self-dissociation of water [16]. In this study, an extended version of the pH model described in Sommer and Husted [16] was implemented, considering as buffer components TIC, TAN, TAC and TS, and the ionisation reactions (Equations 5a, 5c, 5d, 5e, 5f, 5g).



The electroneutrality condition was formulated as follows (Equation 6). The concentrations of the gas compounds in the ionic form ($[G_{\text{ion}}]_{l,\infty}$) were calculated by the equations shown in Table S1 (Supplementary content – available online only), in which the equilibrium constants measured in an ideal solution (K) were replaced by the mixed equilibrium constants (K') in the non-ideal liquid solution, by considering the activity coefficients (γ) of the ions in solution (Equations 7a–e).

$$Z_{\text{system}} = ([\text{Na}^+] + [\text{K}^+] + 2 \cdot [\text{Ca}^{2+}] + 2 \cdot [\text{Mg}^{2+}] + [\text{NH}_4^+] + [\text{H}^+]) \\ - ([\text{Cl}^-] + [\text{OH}^-] + [\text{HCO}_3^-] + 2 \cdot [\text{CO}_3^{2-}] + [\text{HS}^-] + [\text{Ac}^-]). \quad (6)$$

$$K'_{\text{H}_2\text{S}} = \frac{K_{\text{H}_2\text{S}}}{\gamma_{\text{HS}^-}}, \quad (7a)$$

$$K'_{\text{NH}_4^+} = K_{\text{NH}_4^+} \cdot \gamma_{\text{NH}_4^+}, \quad (7b)$$

$$K'_{\text{HAc}} = \frac{K_{\text{HAc}}}{\gamma_{\text{Ac}^-}}, \quad (7c)$$

$$K'_{\text{CO}_2} = \frac{K_{\text{CO}_2}}{\gamma_{\text{HCO}_3^-}}, \quad (7d)$$

$$K'_{\text{HCO}_3^-} = \frac{K_{\text{HCO}_3^-} \cdot \gamma_{\text{HCO}_3^-}}{\gamma_{\text{CO}_3^{2-}}}. \quad (7e)$$

The activity coefficients were calculated from the Debye–Hückel equation (Equation 8) [16]:

$$\log \gamma = -0.509 \cdot Z^2 \cdot \left(\frac{I^{0.5}}{1 + 0.328 \cdot d \cdot I^{0.5}} \right), \quad (8)$$

where:

Z = Sign of the ion

d = Effective diameter of the hydrated ion (nm). The values for d used in the pH buffer sub-model were 4.5 (Na^+ , CO_3^{2-} , Ac^-), 9 (H^+), 2.5 (NH_4^+), 4 (HCO_3^-), 3.5 (OH^- , Ca^{2+} , Mg^{2+} , HS^-), 3 (Cl^-) [58]

I = Ionic strength of the buffer system (estimated by Equation 9):

$$I = 0.5 \cdot ([\text{Na}^+] + [\text{NH}_4^+] \cdot 1 + [\text{HCO}_3^-] \cdot 1 + 4 \cdot [\text{CO}_3^{2-}] + [\text{Ac}^-] + [\text{Cl}^-] + [\text{K}^+] \\ + 4 \cdot [\text{Ca}^{2+}] + 4 \cdot [\text{Mg}^{2+}] + [\text{H}^+] + [\text{OH}^-] + [\text{HS}^-]). \quad (9)$$

2.3. General structure of the GE–pH coupled model: coupling the model

The gas emission and pH sub-models were coupled in a comprehensive GE–pH coupled model, whose synthesised structure is summarised in Figure 2. The GE–pH model, applied for H_2S , NH_3 , HAc and CO_2 , was programmed in Matlab, and the length of time considered was 1 min (i.e. all mathematical computations, including the calculation of the gas release were performed on a 1 min basis).

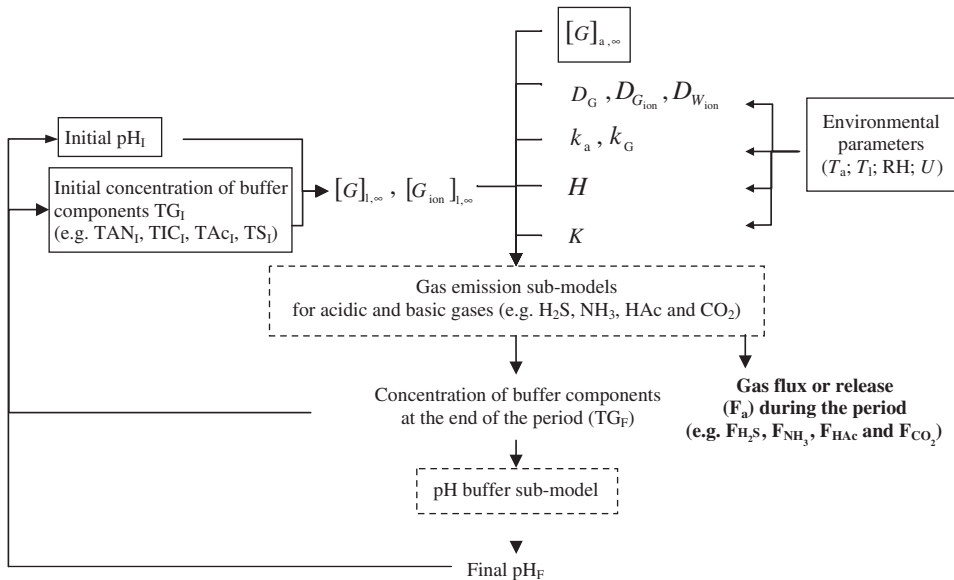


Figure 2. General structure of the GE-pH model. The inputs of the model are indicated inside continuous lined squares, the two sub-models are indicated inside dotted lined squares and the outputs of the model are marked in bold.

3. Applications to standard scenarios

The feasibility of the model is illustrated by modelling the release of H_2S , NH_3 , HAc and CO_2 in five different scenarios: (1) fresh slurry from farrowing sows (1FA), finishing pigs (1FI) and weaning pigs (1WE) stored in animal houses; (2) slurry stored in outside storage tanks (2ST); and (3) slurry stored in anaerobic waste lagoons (3LA). A review of environmental parameters (T_a , T_l , RH and U_{10}), and air concentration of gases ($[\text{H}_2\text{S}]_{g,\infty}$, $[\text{NH}_3]_{g,\infty}$, $[\text{HAc}]_{g,\infty}$ and $[\text{CO}_2]_{g,\infty}$) measured inside animal houses and above outdoor storage facilities, was carried out (Table 1) and typical values were used as inputs of the different scenarios.

Input data on dry matter (DM), pH, $[\text{TS}_l]$, $[\text{TAN}_l]$ and $[\text{TAC}_l]$ in slurry stored in animal houses (1FA, 1FI and 1WE) were taken from experimental data measured by Blanes-Vidal et al. [5], in slurry collected at different commercial pig farms (Table 2). Input data on $[\text{TIC}_l]$, K^+ , Ca^{2+} , Mg^{2+} , Na^+ and Cl^- for 1FA, 1FI and 1WE scenarios were inferred from typical values reported in the literature (Table 2). Data on DM, pH and composition of slurry stored in outside storage tanks (scenario 2ST) and anaerobic waste lagoons (scenario 3LA) were obtained from previous studies on pig slurry characterisation (Table 3). Data on slurry concentrations obtained from the literature (typically, in $\text{g}\cdot\text{L}^{-1}$ slurry) were converted to concentrations in $\text{mmol}\cdot\text{g}^{-1}$ DM by considering the reported data on DM. Averaged values were then converted to concentrations in $\text{mol}\cdot\text{L}^{-1}$ slurry by considering the different DM contents of each scenario (Tables 2 and 3). In all five scenarios, $[\text{TAN}_l] \geq [\text{TIC}_l]$, as obtained in previous studies reporting data on the concentration of TAN and TIC measured in swine slurry samples [15,19].

4. Results and discussion

4.1. Model results in different scenarios

Changes in surface pH, concentration of TIC, TAN, TAc and TS, and release of H_2S , NH_3 , CO_2 and HAc from undisturbed slurry were modelled on a 1 min basis during 10 days after

Table 1. Environmental parameters and concentration of gases in the air above slurry used for the following scenarios: fresh slurry in animal houses (1FA, 1FI, and 1WE), slurry stored in outside storage tanks (2ST) and slurry stored in anaerobic waste lagoons (3LA).

	Animal houses		Outdoor storage		
	This study	Other studies	This study	Other studies	
T_a (°C)	20	20 20.3 174 18–24.5	[21,59–61]	20 ^b	20 ^b
T_l (°C)	20	25 18.2	[21,60]	23	$T_{\text{air}} + 1 < T_l < T_{\text{air}} + 6$ [71]
RH (%)	65	60 58.9 71 65–70	[21,59–61]	65 ^b	65 ^b
U_{10} (V) ^a (m·s ⁻¹)	0.11 ^[1]	(0.12 at $z = 1.5$ m) (0.1–0.23 at $z = 1.5$ m) (0.05 at $z = 0.25$ m)	[59,62,63]	1.4 ^b	$1 > U_{10} > 2.5$ [28]
$[\text{H}_2\text{S}]_{\text{g},\infty}$	20.4 $\mu\text{mol}\cdot\text{m}^{-3}$ (0.5 ppm)	0.12 ppm 0.05–1.4 ppm	[64,65]	0.294 $\mu\text{mol}\cdot\text{m}^{-3}$	[28]
$[\text{NH}_3]_{\text{g},\infty}$	204 $\mu\text{mol}\cdot\text{m}^{-3}$ (5 ppm)	21.6 ppm 6–10 ppm 2.2–48.6 ppm 3.7 ppm 5–18 ppm	[60,62,65–67]	0.177 $\mu\text{mol}\cdot\text{m}^{-3}$	[72]
$[\text{HAc}]_{\text{g},\infty}$	1.3 $\mu\text{mol}\cdot\text{m}^{-3}$ (75 $\mu\text{mol}\cdot\text{m}^{-3}$)	281 $\mu\text{mol}\cdot\text{m}^{-3}$ 3.94–189 $\mu\text{mol}\cdot\text{m}^{-3}$	[8,65]	0.683 $\mu\text{mol}\cdot\text{m}^{-3}$	[73]
$[\text{CO}_2]_{\text{g},\infty}$	61,350 $\mu\text{mol}\cdot\text{m}^{-3}$ (1500 ppm)	1200–1500 ppm 858 ppm 1900 ppm 970–2600 ppm	[62,68–70]	14,300 $\mu\text{mol}\cdot\text{m}^{-3}$	[72]

Note: ^a U_{10} (necessary for k_G calculation) was calculated by considering a logarithmic velocity profile [74]:

$$U_{10} = V \cdot \frac{6.907}{\ln(z/0.01)}$$

where V (shown in parenthesis in the Table), is the air velocity at a certain height (z , in m) over the slurry surface. U_{10} was set at 0.11 m·s⁻¹, as calculated from an air velocity in the pit of 0.05 m·s⁻¹ at $z=0.25$ m (default in Monteny [63]). ^bMeteorological data assumed in the outdoor environment where the modelled storage tank and lagoon are placed.

the concentrations in the slurry surface were considered to be homogeneous (i.e. slurry surface mixing). In all five scenarios, variation in these parameters over time showed a similar pattern. Modelled surface pH, concentration of TIC, TAN, TAc and TS, and release of H₂S, NH₃, CO₂ and HAc, for scenario 2ST, are given as an example (Figures 3 and 4).

Because CO₂ is more volatile than NH₃, the decrease in TIC concentration was initially more pronounced than the decrease in TAN (Figure 3). Therefore, the pH at the slurry surface initially increased because CO₂ is an acidic gas, and NH₃ is a base. The rate of increase in slurry pH slowed over time, because the pH increase favours the emission of basic components and hinders the emission of acidic components. This, in turn, limits the pH increase, thereby constituting a negative feedback system. Emission of gases reduces the concentration of components (e.g. TIC, TAN and TS) in the liquid surface. Therefore, emission of gases (regardless whether they were acids or bases) decreased over time when pH was constant. The modelled concentration of TAc at the surface remained constant during the 10-day period, because no emission of HAc was obtained based on the model, probably because of the low Henry's constant of HAc and the high slurry pH.

Table 2. Input data on composition of slurry stored in under floor pits inside animal houses.

	Farrowing sows (1FA)			Finishing pigs (1FI)			Weaning pigs (1WE)		
	This study		Other studies	This study		Other studies	This study		Other studies
DM (%)	5.1		1.69 ± 3.11 [75] 3.5 [76] 3.3–13.2 [77]	7.1		3.10 ± 4.13 [75] 9 [76] 4.2–19.9 [77]	4.1		2.72 ± 4.41 [75] 4 [76]
pH _i	7		7.64 ± 0.16 [75] 6.23–8.65 [77]	7		7.54 ± 0.34 [75] 6.55–8.35 [77]	6.3		6.88 ± 0.63 [75]
Concentrations	mol·L ⁻¹	mol·kg ⁻¹ DM	mmol·g ⁻¹ DM	mol·L ⁻¹	mol·kg ⁻¹ DM	mmol·g ⁻¹ DM	mol·L ⁻¹	mol·kg ⁻¹ DM	mmol·g ⁻¹ DM
[TS _i]	0.005	0.1	0.12 [78]	0.007	0.1	0.12 [78]	0.004	0.1	0.12 [78]
[TAN _i]	0.133	2.6	0–2.7 [75] 4.5 [76] 0.7–2.8 [77]	0.183	2.6	0–3.5 [75] 3–9 [77]	0.122	2.5	0–2.5 [75] 5.7 [77]
[TAc _i]	0.035	0.7	0.2–3 [15]	0.082	1.2	0.2–3 [15]	0.017	0.4	0.2–3 [15]
[TIC _i]	0.091	1.8	0.3–13.2 [15] 5.2 [78] 1.8 [19]	0.12	1.8	0.3–13.2 [15] 5.2 [78] 1.8 [19]	0.087	1.8	0.3–13.2 [15] 5.2 [78] 1.8 [19]
[K ⁺]	0.042	0.9	0–1.1 [75] 1.3 [76] 0.5–1.2 [77]	0.067	1.0	0–1.3 [75] 0.8 [76] 0.7–2.1 [77]	0.025	0.5	0–1 [75]
[Ca ⁺²]	0.136	2.7	0–9.3 [75] 0.3–1.5 [77]	0.046	0.7	0–9.8 [75] 0.3–0.8 [77]	0.090	1.9	0–3.7 [75]
[Mg ⁺²]	0.025	0.5	0–1.4 [75] 0.1–0.5 [77]	0.023	0.3	0–1.2 [75] 0.2 [77]	0.021	0.4	0–0.9 [75]
[Na ⁺]	0.013	0.3	0.2–0.3 [77]	0.016	0.2	0.2–0.3 [77]	0.009	0.2	0.2 [78]
[Cl ⁻]	0.062	1.2	0.9–1.9 [15] 0.9 [78]	0.070	1.0	0.9–1.9 [15] 0.9 [78]	0.059	1.2	0.9–1.9 [15] 0.9 [78]

Note: Values of DM, pH, TS, TAN and TAc were measured in samples collected as reported in Blanes-Vidal et al. [5], and values obtained in other studies are shown for comparison in the reference column. Values of TIC, K⁺, Ca²⁺, Mg²⁺, Na⁺ and Cl⁻ used in this study were estimated from references. Concentration values wet basis from references were converted to mmol·g⁻¹ DM. Averaged values in mmol·g⁻¹ DM were then converted to concentrations in mol·L⁻¹ slurry by considering the different DM contents of each scenario.

Table 3. Input data on composition of slurry stored in outside storage tanks and anaerobic waste lagoons.

	Outside storage tanks (2ST)			Anaerobic lagoons (3LA)		
	This study		Other studies	This study		Other studies
DM, %	3.5		0.6–8.5 [79] 2.5–4.5 [80] 6.1[81] 10 [78] 2.6 [19] 1.5–2.0 [15]	0.4		0.3 [76] 0.4 [81] 0.6–1.3 [82] 0.5 [83] 0.4 [84]
pH _I	7.2		6.2–8.2 [79] 7.3 [78] 7.5 [19] 7.2–8.3 [15]	7.8		7.7–7.8 [82] 8.1 [83] 8 [84]
Concentrations	mol·L ⁻¹	mol·kg ⁻¹ DM	mmol·g ⁻¹ DM	mol·L ⁻¹	mol·kg ⁻¹ DM	mmol·g ⁻¹ DM
TS _I	0.004	0.1	0.12	0.0004	0.1	0.09–0.13 [82] 0.07 [84]
TAN _I	0.122	3.0	0.9–1.5 (FA) [79] 0.3–0.6 (FI) [79] 4.5–4.8 [80] 3.2 [81] 1.9 [78] 3.9 [19] 3.5–15.7 [15]	0.024	6.2	5.0 [76] 5.8 [81] 6.2–6.7 [82] 13.3 [83] 7.5 [84]
TAc _I	0.017	0.4	0.2–0.3 (FA) [79] 0.2 (FI) [79] 1.1 [19] 0.2–3 [15]	0.0027	0.7	0.7 [85]
TIC _I	0.122	3	5.2 (FI) [79] 1.8 [19] 0.3–13.2 [15]	0.02	5.1	5.2 [79] 1.8 [19] 0.3–13.2 [15]
K ⁺	0.06	1.5	1.0 [81] 1.0 [78] 0.2 [19] 1.7–3.6 [15]	0.022	5.7	4.6 [81] 4.9–7.7 [82]
Ca + 2	0.006	0.15	0.1–0.2 (FA) [79] 0.1 (FI) [79] 1.1 [81] 0.7 [78] 0.3 [19] 0.6–1.1 [15]	0.0055	1.2	0.6 [81] 0.8–2.1 [82]
Mg + 2	0.002	0.1	0–0.1 (FA) [79] 0.1 (FI) [79] 0.3 [78] 0.2 [19] 0.1–0.7 [15]	0.0022	0.6	0.6 [81] 0.3–0.8 [82]
Na ⁺	0.020	0.5	0.3 [81] 0.2 [78] 0.2 [19] 0.5–1.4 [15]	0.010	2.6	2.4 [81] 2.1–3.2 [82]
Cl ⁻	0.036	0.9	0.9 [78] 0.9–1.9 [15]	0.0035	0.9	0.9 [78] 0.9–1.9 [15]

Note: Values of DM, pH, TS, TAN and TAc were measured in samples collected as reported in Blanes-Vidal et al. [5]. Values obtained in other studies are shown for comparison. Values of TIC, K⁺, Ca²⁺, Mg²⁺, Na⁺ and Cl⁻ were estimated from references.

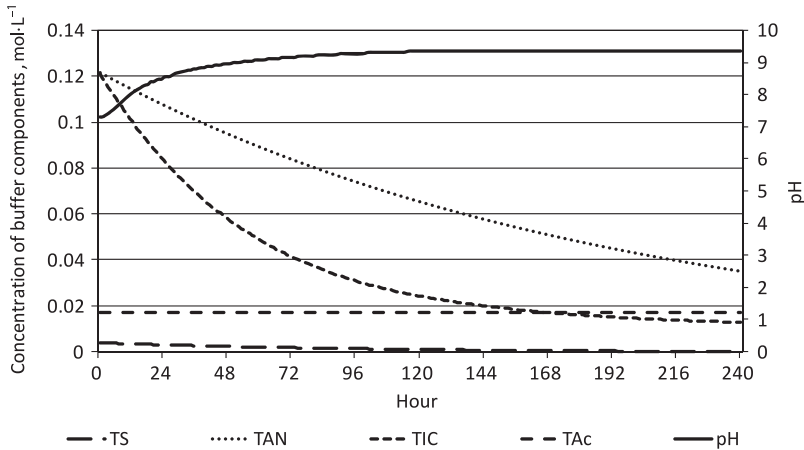


Figure 3. Modelled changes in concentration of buffer components (TIC, TAN, TAc and TS) and pH at the surface layers in an undisturbed slurry storage (2ST), over a 10 day period after slurry surface mixing.

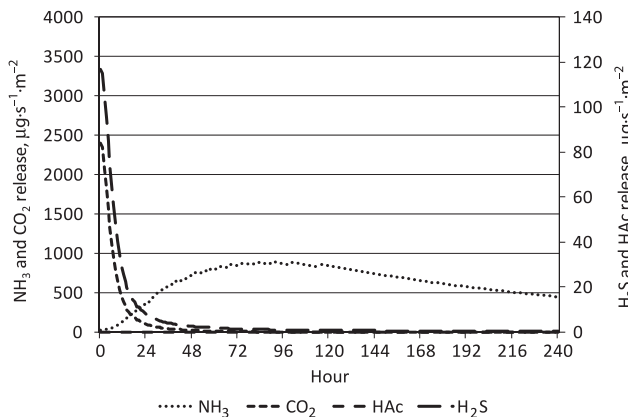


Figure 4. Modelled changes in the release of NH_3 , CO_2 , HAc and H_2S from undisturbed slurry storage (2ST) over a 10 day period after slurry surface mixing. The release of HAc was zero during the entire period.

The change of the average daily pH in the slurry surface over time, for each scenario is shown in Figure 5. In all five scenarios, the maximum pH was reached between day 4 and day 6. The performance of the modelled pH, concentration of buffer components and gas emissions shown in Figures 3–5 reflect the buffer capacity of the slurry [31,86]. In this respect, Sommer and Sherlock [19] also reported an initial increase in surface pH after mixing, which was followed by a period of stability or slight decrease in surface pH, owing to the slurry buffer capacity.

Daily averaged emissions of H_2S , NH_3 , CO_2 and HAc estimated by the GE–pH coupled model for each of the five different scenarios (Table 4) showed a different variation pattern over time. In all five scenarios, CO_2 release was maximum after mixing (at the beginning of the storage period), and it showed a marked decrease during the first two days, followed by a period of stable emission rate. For example, modelled hourly averaged CO_2 emissions in 2ST decreased in the ratio of 0.87 during the first day after mixing (i.e. emissions of CO_2 at each hour during the first day, were on average 87% of the CO_2 released during the previous hour). After this marked decrease, hourly averaged CO_2 emissions from day 3 to day 10 decreased in the ratio of 0.98. A high CO_2 release was also observed by Ni et al. [57], immediately after manure disturbances, followed by typical exponential decay and a period of steady release. The reason for the high initial CO_2

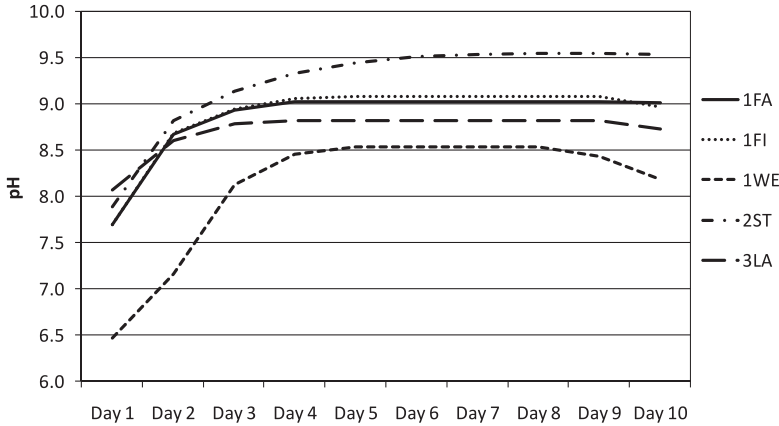


Figure 5. Modelled change in pH at the surface layer of undisturbed slurry, after slurry-surface mixing at the start of day 1, for all five scenarios: slurry from farrowing sows (1FA), finishing pigs (1FI) and weaning pigs (1WE) stored in animal houses; slurry stored in outside storage tanks (2ST); and slurry stored in anaerobic lagoons (3LA).

release is related to the low solubility of CO_2 (H_{CO_2} at $20^\circ\text{C} = 1.63$) in comparison to H_2S ($H_{\text{H}_2\text{S}}$ at $20^\circ\text{C} = 0.36$), NH_3 (H_{NH_3} at $20^\circ\text{C} = 5.4 \times 10^{-4}$) and HAC (H_{HAC} at $20^\circ\text{C} = 6.2 \times 10^{-6}$).

The increase in surface pH (Figure 5) caused by the CO_2 release can greatly accelerate NH_3 release, but is unfavorable for CO_2 , HAC and H_2S release. Therefore, emissions of H_2S and HAC followed a very similar pattern compared with CO_2 . In the 2ST scenario, hourly averaged H_2S emissions during day 1 decreased in the ratio of 0.89, whereas from day 3 to day 10, hourly H_2S emissions decreased in the ratio of 0.99. Modelled HAC emissions in the 2FI and 2WE scenarios were also maximum at the beginning of the storage period (0.11 and $0.7 \mu\text{g} \cdot \text{s}^{-1} \cdot \text{m}^{-2}$), and reached zero after 8 and 42 h of undisturbed storage, respectively. According to the model, no HAC emissions would occur in the 1FA, 2ST and 3LA scenarios. A previous study [102] showed that, as the manure ages, the emission rates of H_2S , volatile fatty acids and CO_2 decrease with increasing storage time, whereas emission rates for NH_3 increased.

Modelled emissions of NH_3 increased over time as the CO_2 emissions increased surface pH. From day 1 to day 4 NH_3 emissions showed a gradual increase after manure mixing, which could be explained by the change in pH. Hourly averaged NH_3 emissions reached maximum values (321 , 475 , 129 , 900 and $105 \mu\text{g} \cdot \text{s}^{-1} \cdot \text{m}^{-2}$) after 68, 80, 86, 90 and 60 h of storage, for the 1FA, 1FI, 1WE, 2ST and 3LA scenarios, respectively. Therefore, the GE-pH model showed a delayed response to slurry mixing. This response has been also documented in previous experimental studies [103].

Modelled emissions of H_2S , NH_3 , CO_2 and HAC obtained for the five different typical scenarios were within the range of values for gaseous emissions reported in previous experiments (Table 4). The agreement between modelled and measured emissions of H_2S and NH_3 in a specific slurry lagoon was also shown in Blanes-Vidal et al. [104]. In the current article, despite gross uncertainty associated with the field data, the GE-pH model could generally provide good predictions of the simulated variables in different scenarios. However, this study reveals the great importance of providing information regarding the frequency at which the slurry surface is mixed or altered, when reporting data on emissions of gases from slurry; as emissions can be very different depending on the time that has passed since the slurry surface was disturbed (Table 4). For example, in swine houses, animals defecate on the slatted floor throughout the day, and, because they develop well-defined dunging areas within a few days following birth, it is expected that the slurry surface under certain areas (those preferred by the animals) will be frequently altered; while other areas of the pit will contain undisturbed slurry at the surface. Regarding the slurry wetting the slat, this is frequently mixed or altered, due to the activity of the animals (e.g. walking or laying on the

Table 4. Modelled pH and release of H₂S, NH₃, CO₂ and HAc (in $\mu\text{g}\cdot\text{s}^{-1}\cdot\text{m}^{-2}$) from slurry stored under undisturbed conditions for 10 days for all five scenarios: slurry from farrowing sows (1FA), finishing pigs (1FI) and weaning pigs (1WE) stored in animal houses, slurry stored in outside storage tanks (2ST); and slurry stored in anaerobic lagoons (3LA).

		This study										Previous studies			
		Hour		Day		2	3	4	5	6	7	8	9	10	Refs
		1	1	1	1										
H ₂ S	1FA	230	94	7.6	3.2	2.0	1.6	1.3	1.0	0.8	0.6	0.5	0.167–8.19 [87]		
	1FI	332	131	10	4	2.6	2.0	1.6	1.2	1.0	0.8	0.8	1.93–26.9 [88]		
	1WE	453	378	170	24	8.8	5.7	4.5	3.6	2.9	2.8	4.0	0.0567–26.2 (FA) [89] 0.130–682 (FI) [89] 1.67–37.2 (WE) [89]		
	2ST	117	43	4.3	1.7	0.9	0.6	0.4	0.3	0.3	0.2	0.2	11 [8] 7.5–59 [89] 6.4 [90] 77.8–212 [89] 0.360–321 [89]		
	3LA	4.7	2.8	0.6	0.3	0.2	0.2	0.1	0.1	0.1	0.1	0.1	2.4–3.2 [8] 7.3–21.1 [91] 9.1 [83] 0.22 [84]		
	NH ₃	1FA	1.3	34	183	279	311	297	283	269	256	244	229	1.67–102 (FA) [89]	
		1FI	3.2	48	261	397	453	449	428	408	388	370	292	0–4980 (FI) [89]	
		1WE	0	0	5.3	59	112	123	118	112	107	84	46	7.34–261(WE) [89] 74.2–517 [88] 4.69–296 [87]	
		2ST	29	155	567	800	876	861	795	702	620	547	483	660–1667 [8] 367–734 [89] 42–106 [92]	
		3LA	17	33	80	98	92	78	69	64	56	50	38	2–69 [93] 5–67 [94] 891–1088 [8] 183 [91] 6–50 [95]	
		CO ₂	1FA	3326	1108	49	14.0	6.3	4.3	3.0	2.0	1.4	0.9	0.9	7167–32,889 [96]
	1FI		4388	1447	62	18.8	8.5	5.1	3.5	2.4	1.6	1.1	2.9	1886–8655 [97]	
1WE	9035		6341	1616	120	32	17	11	7.8	5.4	6.4	13			
2ST	2392		775	52	16	6.8	3.4	1.9	1.3	0.9	0.6	0.4	1.4–23 [98] 567–1065 [99] 1389 [100]		
3LA	131		71	11	4.4	2.6	1.5	1.1	0.8	0.6	0.4	0.7	440–671 [85] 852 [83]		
HAc	1FA	0	0	0	0	0	0	0	0	0	0	0	2.5 [101] ^a		
	1FI	0.11	0.02	0	0	0	0	0	0	0	0	0			
	1WE	0.7	0.50	0.07	0	0	0	0	0	0	0	0			
	2ST	0	0	0	0	0	0	0	0	0	0	0			
	3LA	0	0	0	0	0	0	0	0	0	0	0			

Note: ^aEmission from simulated slurry.

slat). In Denmark, slurry from the animal house is usually pumped to an outside storage unit every few weeks, where it is stored for up to 9 months before being land applied between March and May. Therefore, in this case, slurry at the surface in outdoor storages is aged, not recently mixed; because it is stored under undisturbed conditions for longer periods. The frequency at which the slurry surface is mixed or altered is important to consider, because according to the model (based on pH variations at the surface), recently mixed slurry will emit more H₂S, CO₂ and HAc, but less NH₃ than slurry that has been kept undisturbed for longer.

A limited number of values for emissions of CO₂ from slurry stored in swine houses and emissions of HAc have been found in the literature. Regarding data on CO₂ emissions from swine houses, most studies report total values for CO₂ emissions, which account for the addition of CO₂ released by the animals and CO₂ released from the slurry stored in the swine house, and these two sources are not usually distinguished. In this respect, it has been estimated that CO₂ emissions from slurry accounted for 38% of the total CO₂ emissions from swine houses with a slatted floor (i.e. 7167–32,889 μg·s⁻¹·m⁻²) [103]. However, in a recent review article [97], it was suggested that the contribution from manure to the total CO₂ emission from swine houses was ~10%. This corresponds to a CO₂ release from slurry of between 1886 and 8655 μg·s⁻¹·m⁻² according to Ni et al. [103].

4.2. Sensitivity analysis

Because model input estimation, and the sensitivity of the model to the estimated values, are important to the successful application of the GE-pH model, a sensitivity analysis was carried out for one of the modelled scenarios (2ST). The sensitivity analysis provided information regarding the percentage of change in the model outputs (release of H₂S, NH₃CO₂ and HAc) and initial pH at the surface, when model input variables were modified by 10% with respect to basic values (Table 5).

Sensitivity analysis showed that the key parameters affecting the release of H₂S, CO₂ and NH₃ were: pH_I, initial concentration of TAN ([TAN_I]) and TIC ([TIC_I]), slurry temperature (*T*_I) and air velocity (*U*₁₀). Surface pH had the highest effect on the emission of all modelled gases, because it controls the chemical equilibrium of the ionic and nonionic species in the slurry. Changes in HAc release were negligible when all model inputs were modified by 10%, except when the initial pH (pH_I) was decreased by 10%. In that case, the release of HAc ranged from 0.01 to 0.75 μg·s⁻¹·m⁻². Changes in the release of H₂S, NH₃, CO₂ and HAc were negligible when [TAC_I], *T*_a, RH, and the concentration of gases in the air were increased or decreased by 10%.

Sensitivity analysis confirmed that H₂S is not a main buffer component of the slurry, because changes in [TS_I] concentration had only a direct effect on the emission of H₂S, and a very limited effect on surface pH and the emission of NH₃ and CO₂. The analysis showed a linear relation between TS_I concentration and the emission of H₂S, as obtained by Blunden et al. [28].

The GE-pH model is a multiple input-multiple output model, in which the set of outputs (i.e. emission of each specific gas) has a feedback effect on one of the model inputs (pH). This model structure has two main consequences. First, model inputs may have a different direct effect on each of the outputs (i.e. emission of each specific gas), because the equations used to calculate intermediate variables (such as Henry's constant, dissociation constants and mass transfer coefficients) are specific for each gas. Second, the set of outputs (i.e. emission of the different gases) has a feedback effect on surface pH, which in turn, affects the emission of each of the gases differently. As a consequence, considering multiple outputs and their feedback effect may modify the influence of the model inputs on the outputs (even changing the sign of the effect, from positive to negative or vice versa), in comparison with the outputs that would be obtained if only one output (one gas) was considered in the model. The importance of considering this combined effect is illustrated when analysing the effect of [TAN_I] on NH₃ release. Daily averaged NH₃ emissions in the undisturbed slurry storage were lower when [TAN_I] was increased by 10%. The reason for this is the indirect effect of [TAN_I] on the slurry surface pH. Modelled gas emissions and pH on a 1-min basis for the first 12 h after slurry mixing (Figure 6) revealed that an increase in [TAN_I] caused a higher emission of NH₃ only during the first 8 h after mixing. The lower relation TIC/TAN led to a less pronounced increase in surface pH over time with respect to the results obtained from the original scenario 2ST, which resulted in a lower daily average NH₃

Table 5. Sensitivity analysis showing the percentage change in pH and release of H₂S, NH₃, CO₂ and HAc (daily averaged values on days 1, 3, 5, 7 and 9) when model inputs were varied by 10% with respect to basic values (2ST).

	Day 1		Day 3		Day 5		Day 7		Day 9	
	-10%	+10%	-10%	+10%	-10%	+10%	-10%	+10%	-10%	+10%
T ₁										
pH	0.8	-0.9	0.9	-1.1	0.9	-1.1	0.9	-0.4	0.9	-0.4
H ₂ S	-2.9	4.4	-11	17	-11	17	-10	1.9	-10	1.9
NH ₃	-4.9	4.7	-3.5	0.4	-2.1	-0.3	-0.9	4.7	0.9	2.8
CO ₂	-6.4	8.8	-16	25	-19	28	-18	-5.8	-18	-5.8
U ₁₀										
pH	-10%	+10%	-10%	+10%	-10%	+10%	-10%	+10%	-10%	+10%
H ₂ S	0.2	-0.2	0.2	-0.2	0.2	-0.2	0.4	0.0	0.4	0.0
NH ₃	-2.2	2.1	-4.1	4.0	-4.7	4.1	-8.8	0.0	-8.8	0.0
CO ₂	-0.7	0.8	-1.2	0.9	-0.2	0.1	3.1	0.9	4.5	-0.4
	-2.2	2.2	-4.6	4.5	-6.6	5.7	-16.5	-3.0	-16.4	-3.0
TAN ₁										
pH	-10%	+10%	-10%	+10%	-10%	+10%	-10%	+10%	-10%	+10%
H ₂ S	0.7	-0.7	0.9	-1.1	1.3	-1.4	1.3	-1.5	1.3	-1.8
NH ₃	-6.0	6.4	-17	24	-24	34	-24	38	-24	47
CO ₂	4.6	-4.5	1.1	-5.0	2.1	-6.0	1.6	-6.8	1.6	-9.9
	-6.0	6.4	-20	28	-34	48	-37	59	-37	91
TS ₁										
pH	-10%	+10%	-10%	+10%	-10%	+10%	-10%	+10%	-10%	+10%
H ₂ S	0.02	-0.02	-0.01	0.01	-0.04	0.04	0	0	0	0
NH ₃	-10	10	-10	9.7	-9.3	9.2	-10	10	-10	10
CO ₂	0.3	-0.3	-0.2	0.2	-0.4	0.4	0	0	0	0
	-0.3	0.3	0.3	-0.3	1.2	-1.1	-0.3	0.3	-0.3	0.3
TIC ₁										
pH	-10%	+10%	-10%	+10%	-10%	+10%	-10%	+10%	-10%	+10%
H ₂ S	-0.8	0.7	-1.4	1.1	-1.7	1.3	-1.9	1.5	-2.0	1.5
NH ₃	8.8	-6.8	33	-20	44	-23	51	-27	52	-27
CO ₂	-16	17	-18	14	-18	13	-20	15	-20	15
	-2.0	2.4	23	-14	43	-24	59	-35	63	-35
pH ₁										
pH	-10%	+10%	-10%	+10%	-10%	+10%	-10%	+10%	-10%	+10%
H ₂ S	-16	6.6	-13	2.0	-9	1.6	-10	2.0	-21	2.0
NH ₃	403	-72	1517	-34	587	-29	655	-35	6815	-35
CO ₂	-96	150	-90	27	-75	17	-76	20	-96	20
	751	-76	2002	-38	824	-39	1002	-57	16980	-57

Note: Basic values for environmental parameters and slurry concentrations are shown in Tables 1 and 3, respectively. Changes in output models are expressed as percentage change with respect to results shown in the basic 2ST scenario (Table 4). Changes in the release of H₂S, NH₃, CO₂ and HAc were negligible when TAC₁, T_a, RH and the concentration of gases in the air were increased or decreased by 10%. Changes in HAc release were negligible when model inputs were modified by 10%; except when the initial pH (pH₁) was decreased by 10%, in which case, the release of HAc ranged from 0.01 to 0.75 μg·s⁻¹·m⁻².

release, despite the initial higher TAN concentration. The results of the GE-pH model are in agreement with experimental results, as Sommer and Sherlock [19] found that there was a large increase in slurry surface pH over the first 8 h because of the release of CO₂ in slurry with the initial [TIC₁] > [TAN₁]; pH then increased steadily but slowly from 8 to 96 h. When the initial [TIC₁] < [TAN₁], pH initially increased, but decreased or did not change after 20 h incubation.

The buffer system controlling slurry pH has not been thoroughly modelled in previous studies. As a consequence, slurry characterisation and gas emissions studies have paid little attention to the concentration of TIC in the slurry, and so data on TIC concentrations are very scarce in the literature. However, our modelling study, together with previous experimental studies [19,103], revealed the importance of this parameter, which affects the emission not only of CO₂, but also of other important gases such as NH₃ and H₂S.

Determination of the model parameters (mass transfer coefficients, Henry's constants and dissociation constants) is necessary for modelling gas release. Equations for estimating model parameters are largely empirical because the processes are usually too complex to be analysed in detail. As a consequence, many equations (based on different laboratory or field experiments)

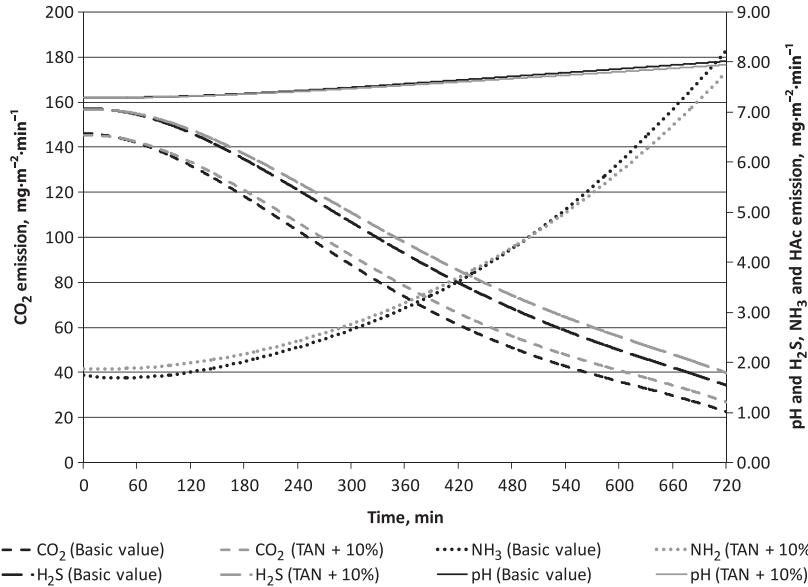


Figure 6. Modelled gas emissions and pH on a 1-min basis for the first 12 h after slurry mixing for scenarios 2ST and 2ST with a 10% increase in TAN_I concentration.

can be found in the literature [21,105]. The empirical equations selected to estimate the model parameters can also have an influence on the emissions estimated by the model.

The precision of the model can be improved by measuring slurry pH within 1 mm below the surface using microelectrode techniques, which would provide a scientific validation of the change in surface pH estimated by the model. However, when the slurry surface (~ 1 mm below the surface) has been initially disturbed, the pH gradient at the surface disappears, and pH measurements taken using a common pH meter at, for example, 2 cm below the surface, can be used as initial surface pH (input of the model). This model adds significant scientific value to previous gas emissions models because: (1) it contributes to the understanding of the underlying physical–chemical processes occurring at the surface of the slurry; and (2) it allows us to estimate changes in surface pH, which strongly affect the gas transport through the liquid–air interface, but are difficult to measure in practice.

5. Conclusions

A comprehensive gas emission–pH (GE–pH) coupled model has been presented. The GE–pH model describes: (1) the simultaneous release of acidic (e.g. CO_2 , HAc and H_2S) and basic compounds (e.g. NH_3) from swine slurry; and (2) the effect of the release of these gases on the concentration of buffer components and pH in the slurry, which in turn, controls the release. The main novelty of the GE–pH model in respect to previous gas emission models, resides in the fact that the GE–pH model presented here considers the simultaneous release of acidic and basic gases, the interaction among gas releases and the dynamic equilibrium of pH in surface slurry, in a single comprehensive model.

The GE–pH coupled model was applied to the release of NH_3 , CO_2 , HAc and H_2S from standard slurry stored in animal houses, outside storage tanks and lagoons. The results of the GE–pH model agreed well with values reported in the literature and could be reasonably interpreted. Sensitivity analysis showed that the key parameters affecting the release of H_2S , CO_2 and NH_3 were: pH_I ,

initial concentration of TAN ($[TAN_I]$) and TIC ($[TIC_I]$), slurry temperature (T_I), and air velocity (U_{10}). The effect of the TS_I concentration was confined to the H_2S release.

Finally, this modelling study showed the importance of determining the concentration of TIC_I in the slurries and having reliable data regarding this component, because the concentration of TIC_I (which has not received attention in previous emission studies and swine slurry characterisations), has a large effect on the release of CO_2 , NH_3 and H_2S from slurry. Besides, future modelling and measurement studies on gas emissions from animal slurry should consider the frequency in which the slurry surface is mixed or altered, when reporting data on emissions of gases from slurry; because surface pH and gas emissions are highly dependent on the time passed since the slurry surface was disturbed. Determination of these two variables (TIC and frequency of mixing) is feasible in commercial farms and allows estimation of changes in surface pH using the GE-pH model. Estimating variations in surface pH is important because surface pH strongly affects the gas transport through liquid-air interface, but it is very difficult to measure in praxis.

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