Global sensitivity analysis of a process-based model for ammonia emissions from manure storage and treatment structures

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Abstract

The development of process-based models to estimate ammonia emissions from animal feeding operations (AFOs) is sought to replace costly and time-consuming direct measurements. Critical to process-based model development is conducting sensitivity analysis to determine the input parameters and their interactions that contribute most to the variance of the model output. Global and relative sensitivity analyses were applied to a process-based model for predicting ammonia emissions from the surface of anaerobic lagoons for treating and storing manure. The objectives were to compare global sensitivity analysis (GSA) to relative (local) sensitivity analysis (RSA) on a process-based model for ammonia emissions. Based on the first-order coefficient, both GSA and RSA showed the model input parameters in order of importance in process model for ammonia emissions from lagoon surfaces were: (i) pH, (ii) lagoon liquid temperature, (iii) wind speed above the lagoon surface, and (iv) the concentration of ammoniacal nitrogen in the lagoon. The GSA revealed that interactions between model parameters accounted for over two-thirds of the model variance, a result that cannot be achieved using traditional RSA. Also, the GSA showed that parameter interactions involving liquid pH had more impact on the model output variance than the single parameters: (i) temperature, (ii) wind speed, or (iii) total ammoniacal nitrogen. This study demonstrates that GSA provides a more complete analysis of model input parameters and their interactions on the model output compared to RSA. A comprehensive tutorial regarding the application of GSA to a process model is presented.

1. Introduction

Ammonia (NH\textsubscript{3}) is emitted to the atmosphere from different sources including synthetic fertilizers, biomass burning, fossil fuel combustion, and animal manure (Krupa, 2003). Atmospheric NH\textsubscript{3} plays a role in the acidification and eutrophication of ecosystems (Erisman and Schaap, 2004; Krupa, 2003). Damage to vegetation foliage has been observed closer to NH\textsubscript{3} emission sources, possibly due to NH\textsubscript{3} deposition (Krupa, 2003). While the chemical processes involving NH\textsubscript{3} in the atmosphere are complex, it is known that it reacts with sulfuric and nitric acids to produce ammonium sulfate and ammonium nitrate, which are considered secondary particulate matter (Erisman and Schaap, 2004; Seinfeld and Pandis, 1998). Particulate matter can cause health concerns and degradation of visibility in the atmosphere (US EPA, 2009). This paper focuses on NH\textsubscript{3} emissions from animal feeding operations (AFOs) where the major sources of NH\textsubscript{3} include (i) animal housing, (ii) manure collection, (iii) treatment and storage structures, and (iv) land application of manure (Reidy et al., 2009).

Knowledge of the quantities of gases emitted from AFOs is needed to make better decisions on the development of optimum and cost-effective best management practices or mitigation strategies to control the emissions. In this regard, the National Research Council (NRC, 2003) recommended that direct measurements of emissions be combined with the development of process-based models for estimation of emissions from AFOs. Process-based models can be used in lieu of direct measurements to estimate gaseous emissions from AFOs because they are: (i) amenable for use in locations where site characteristics may present physical challenges to performing direct measurements, (ii) cost effective, and (iii) flexible to use (Arogo et al., 2003; NRC, 2003).

Models for estimating NH\textsubscript{3} emissions from lagoons and outdoor manure storage facilities have been developed (Aneja et al., 2001; Liang et al., 2002; Pinder et al., 2004; Berthiaume et al., 2005,
The generalized equation used in the process-based model for surface emission of NH₃ is:

\[ M_f = A \times K_f (C_L - C_a) \]  

(1)

where, \( M_f \) is the mass release rate of NH₃, kg s⁻¹; \( A \) is the surface area of exposed to the atmosphere, m²; \( K_f \) is the mass transfer coefficient of NH₃ from liquid to air, m s⁻¹; \( C_L \) is the concentration of NH₃ in the liquid, kg m⁻³; and \( C_a \) is the concentration of NH₃ in the air, kg m⁻³. The input parameters to this equation are easily measured or obtained at the site of the manure storage or treatment structure and include: (i) liquid temperature, (ii) air temperature, (iii) liquid pH, (iv) total ammoniacal nitrogen concentration of the manure in storage, \( C_{TAN} \), (v) surface area of manure stored, and (vi) atmospheric pressure.

Critical to process-based model development is conducting sensitivity analysis (SA) to determine the parameters that contribute most to the variance of the model output. Sensitivity analysis helps identify significant model parameters and their interactions and/or insignificant ones that could be removed and not affect model output (Saltelli et al., 2000). Thus, when used correctly, SA can help minimize the number of measurements needed at an AFO to effectively predict NH₃ emissions. Two types of SA can be performed: (i) local sensitivity analysis (LSA) and (ii) global sensitivity analysis (GSA) (Saltelli et al., 1999; Campolongo and Saltelli, 1997). Local sensitivity analysis can be further divided into absolute and relative sensitivity analysis (RSA). Currently, RSA is the more popular SA method used for NH₃ emission models from manure treatment and storage structures (Aneja et al., 2001; Liang et al., 2002; Misselbrook et al., 2004; Bajwa et al., 2006; Berthiaume et al., 2007). In RSA, the response of the model output is obtained by varying one input parameter at a time over a defined range, while holding the others fixed at their mean values as described by Eq. (2):

\[ S_f = \frac{\Delta Y / \bar{Y}}{\Delta x / \bar{x}} \]  

(2)

where, \( S_f \) is the relative sensitivity index; \( \Delta Y \) is the change in the model output; \( \bar{Y} \) is the mean of the model output; \( \Delta x \) is the change in input parameter over the range being considered; and \( \bar{x} \) is the mean value of the input parameter being varied (Liang et al., 2002; Arogo et al., 1999; Zerihun et al., 1996).

The quantity of NH₃ volatilized from liquid manure depends on (i) animal diets, (ii) liquid pH and temperature, and (iii) environmental factors such as air temperature and relative humidity (Ndegwa et al., 2008). Using the RSA approach, Aneja et al. (2001) considered pH, surface liquid temperature, wind speed, and lagoon \( C_{TAN} \) concentration in their model and concluded that NH₃ emissions from lagoons was most sensitive to liquid temperature. The authors noted that pH and wind speed were more sensitive in some cases. Liang et al. (2002) applied RSA to their model and showed model output was sensitive to (in order of importance) pH, liquid temperature, and wind speed. Bajwa et al. (2006) reported that lagoon temperature, pH, \( C_{TAN} \), and wind speed had significant effects on NH₃ flux but quantitative measures were not given. Berthiaume et al. (2007) used RSA to show that nitrogen fluxes from outdoor manure storage were sensitive to amount of proteins in feed, pH of the manure in storage, and air velocity above the manure surface. The use of RSA to identify pertinent model parameters in the approaches above has excluded potential interactions of model parameters, which are known to exist. The RSA approach also does not explore the entire input space of parameter values. The RSA method, although widely used, is (i) limited to a given point in space, (ii) cannot consider the entire ranges of input parameter values, and (iii) does not explore interactions between parameters.

The GSA method uses Monte Carlo simulations to calculate model outputs based on inputs generated over the entire range of possible parameter values. The sensitivity of a model input is then evaluated using a variance-based analysis method described by Saltelli et al. (2000). In the variance-based method, the sensitivity analysis is estimated using the contribution of each input variable, \( X_i \), to the total variance, \( V(Y) \) of the output \( Y \). To calculate the sensitivity indices for each input variable, \( X_i \), the decomposition property of the total variance is utilized as shown in Eq. (3). The decomposition consists of all first-, second-, and higher-order variances for each variable. The main advantage of GSA over the partial derivative-based RSA is that it allows the influence and interaction of model input parameters over their entire input range on the model output (Saltelli et al., 2008).

\[ V(Y) = \sum_i V_i + \sum_{i<j} V_{ij} + \sum_{i<j<m} V_{ij,m} + \ldots \]  

(3)

The objectives of this study were to (i) conduct a GSA on a process-based model for NH₃ emissions from liquid manure storage and treatment surfaces and (ii) compare the use of GSA and RSA on predicting important model input parameters. Significant to this work is that the GSA will provide a measure of the impact of model parameter interactions (e.g., temperature and pH) on the variance of the model output. Despite the fact that a considerable amount of literature has been published in recent years on the methods of GSA, the implementation of GSA can be difficult. So, a simplified tutorial for effective implementation of GSA has been included in this study. Although the tutorial is based on the NH₃ emissions model, it provides a step-by-step guide for analyzing any model using GSA.

2. Procedure

2.1. Model equations for NH₃ emissions

The process of NH₃ volatilization from liquid manure surfaces is generally described by Eq. (1) based on the two-film theory proposed by Whitman (1923). The two-film theory assumes that a stagnant fluid layer comprised of two films is formed at the interface of the two fluids in contact. The two stagnant films provide resistance to the transfer of matter between the two fluids. The pertinent equations used in the model for NH₃ volatilization in this study are presented in Table 1 were developed by Zhang et al. (2005) and briefly described below.

2.1.1. Overall mass transfer coefficient (\( k_L \))

The over all mass transfer coefficient (\( k_L \)) was calculated using the resistance to the transfer of NH₃ by the stagnant gas and liquid layers, \( k_G \) and \( k_L \), respectively, and Henry’s constant, \( H \). The stagnant gas layer resistance (\( k_G \)) is a function of the: (i) wind velocity 8 m above the liquid surface (\( U_b \)), (ii) diffusivity of NH₃ in air (\( D_{air,NH_3} \)), and (iii) diffusivity of water vapor in air (\( D_{air,H_2O} \)). The stagnant layer liquid resistance (\( k_L \)) is a function of the: (i) \( U_b \), (ii) diffusivity of NH₃ in water (\( D_{H_2O,NH_3} \)), and (iii) diffusivity of oxygen in water (\( D_{H_2O,O_2} \)). Henry’s constant (\( H \)) is expressed as a function of the liquid temperature (\( T_{liquid} \)).

2.1.2. Concentration of NH₃ in the liquid (\( C_L \)) and NH₃ in air (\( C_a \))

The concentration of NH₃ in the liquid (\( C_L \)) is expressed as a fraction, \( F \), of total ammonium nitrogen (\( C_{TAN} \)) in solution. The fraction, \( F \), is a function of the liquid pH. The concentration of NH₃ in the air (\( C_a \)) is the measured ambient NH₃ concentration. The background ambient ammonia concentration in the Southeastern United States where data used in this study were derived have been...
reported to range from 0 to 20 μg m⁻³ (Harper et al., 2004a,b).

Given the presence of mass transfer boundary layers, the value of $C_a$ was varied, and the GSA was repeated. No differences in the final results were observed (data not shown), so, $C_a$ was assumed to be zero in this study.

2.1.3. Surface area ($A$)

The surface area ($A$) of the liquid containment depends on the geometry of the structure. For lagoons, it is a function of the bottom length (BL) and bottom width (BW), the side slope (Z), the depth of liquid above minimum treatment volume ($d$) and the volume of accumulated sludge (MWPS, 1993). Thus, the surface area of the lagoon was calculated by the following relationship.

$$A = (BL + 2Zd) \times (BW + 2Zd)$$ (4)

2.2. Input parameters

The input parameters to the model were: (i) ambient air temperature ($T_{air}$), (ii) lagoon TAN concentration ($C_{TAN}$), (iii) lagoon liquid pH (pH), (iv) wind velocity 8 m above the lagoon surface ($U_8$), (v) atmospheric pressure ($P$), (vi) lagoon bottom width (BW), (vii) lagoon bottom length (BL), (viii) lagoon side slope (Z), and (ix) the depth of liquid above the minimum treatment volume and sludge volume ($d$). The hourly average weather data for the years 2001–2008 were obtained from State Climate Office of North Carolina (personal communication, state weather office, Raleigh North Carolina) and were used to determine the range of air temperature, wind speeds, and atmospheric pressure to use in the model. The ranges of values of the input parameters are in Table 2.

2.3. Global sensitivity analysis

Global sensitivity analysis was performed according to published methods and protocols (Saltelli et al., 2008, 2004) to assess the importance and investigate interactions of model input parameters. Briefly, the sensitivity coefficient, $S_x$, of a parameter $x$ in GSA is calculated as follows:

$$S_x = \frac{\sqrt{\langle (E(y|x) - \langle E(y|x) \rangle)^2 \rangle}}{\sqrt{\langle E(y|x)^2 \rangle}}$$ (5)

where $V_y$ is the variance of the model output, $y$, over $N$ Monte Carlo simulations. The numerator is the variance of the expected value of $y$ given a constant $x$. For the analysis to be independent of the value of $x$, the above relationship was taken over all values of $x$ and averaged. Similarly, the second-order sensitivity index which describes interaction of two model parameters on the model output was calculated using Eq (6).

$$S_{xy} = \frac{V(E(y|x,z)) - V(E(y|x)) - V(E(y|z))}{V_y}$$ (6)

Finally, the total effect index of a model parameter is described as the summation of all sensitivity indices containing the model parameter of interest. This includes the first-order sensitivity coefficient and all multi-dimensional sensitivity indices (e.g., second-, third-, fourth-order terms, etc.) containing the parameter. Obtaining an accurate representation of the $V(E(y|x))$ term over all values of $x$ is not trivial.

The "sample" and "re-sample" matrices approach to GSA was used to calculate the first- and second-order sensitivity coefficients for the model parameters: (i) $T_{liquid}$, (ii) $C_{TAN}$, (iii) pH, (iv) $U_8$, and (v) $P$. These were also calculated for the lagoon geometry-related parameters: (vi) BW, (vii) BL, (viii) Z, and (ix) $d$. The model

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Units</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia emission rate</td>
<td>$M_A$</td>
<td>kg s⁻¹</td>
<td>$M_A = A \times \tilde{K}(C_1 - C_a)$</td>
</tr>
<tr>
<td>Overall mass transfer coefficient</td>
<td>$K_t$</td>
<td>m s⁻¹</td>
<td>$\frac{1}{K_t} = \frac{1}{K_1} + \frac{1}{K_2} \frac{1}{\eta R_C}$</td>
</tr>
<tr>
<td>Henry’s constant</td>
<td>$H$</td>
<td>–</td>
<td>$2.395 \times 10^6 \left(\frac{C_1 - C_a}{T_{liquid} + 273.15}\right)$</td>
</tr>
<tr>
<td>Mass transfer coefficient in the gas phase</td>
<td>$k_g$</td>
<td>m s⁻¹</td>
<td>$(5.167 \times 10^{-5} + 1.955 \times 10^{-5}U_8 \frac{T_{liquid}}{\eta R_C})^{-0.67}$</td>
</tr>
<tr>
<td>Mass transfer coefficient in the liquid phase</td>
<td>$k_L$</td>
<td>m s⁻¹</td>
<td>$(1.676 \times 10^{-5} + 2.369U_8 \frac{T_{liquid}}{\eta R_C})^{-0.57}$</td>
</tr>
<tr>
<td>Dissociation constant for ammonia</td>
<td>$K_d$</td>
<td>–</td>
<td>$K_d = \frac{282}{T_{air} + 273}$</td>
</tr>
<tr>
<td>Fraction of free ammonia</td>
<td>$F$</td>
<td>–</td>
<td>$F = \frac{1}{\frac{2532}{T_{air} + 273} - 0.002}$</td>
</tr>
<tr>
<td>Diffusivity of ammonia in air</td>
<td>$D_{NH_3}$</td>
<td>m² s⁻¹</td>
<td>$3.068 \times 10^{-4}T_{air}^{-0.38}$</td>
</tr>
<tr>
<td>Diffusivity of NH₃ in water</td>
<td>$D_{H_3O+}$</td>
<td>m² s⁻¹</td>
<td>$7.602 \times 10^{-30}T_{liquid}$</td>
</tr>
<tr>
<td>Diffusivity of water vapor in air</td>
<td>$D_{H_2O}$</td>
<td>m² s⁻¹</td>
<td>$3.003 \times 10^{-4}T_{air}^{-0.38}$</td>
</tr>
<tr>
<td>Diffusivity of oxygen in water</td>
<td>$D_{O_2}$</td>
<td>m² s⁻¹</td>
<td>$6.145 \times 10^{-30}T_{liquid}$</td>
</tr>
<tr>
<td>Temperature of the air</td>
<td>$T_{air}$</td>
<td>°C</td>
<td>$T_{air} = 2.9 \frac{T_{air} - 273}{T_{air} + 273}$</td>
</tr>
</tbody>
</table>

$C_{TAN(aq)}$ – Total ammonium (NH₃ + NH₄⁺) nitrogen in the manure storage; $C_{NH_4(aq)}$ – Concentration of NH₄⁺ in the atmosphere or air above the liquid in storage.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid temperature ($T_{liquid}$), °C</td>
<td>5–35</td>
</tr>
<tr>
<td>TAN ($C_{TAN}$), kg m⁻³</td>
<td>0–0.6</td>
</tr>
<tr>
<td>Ambient ammonia concentration ($C_a$), kg m⁻³</td>
<td>0–2.0 × 10⁻⁵</td>
</tr>
<tr>
<td>Lagoon pH</td>
<td>6.5–8.5</td>
</tr>
<tr>
<td>Wind speed ($U_8$), m s⁻¹</td>
<td>0–15</td>
</tr>
<tr>
<td>Atmospheric pressure ($P$), atm</td>
<td>0.876–1.025</td>
</tr>
<tr>
<td>Bottom width (BW), m</td>
<td>15–120</td>
</tr>
<tr>
<td>Bottom length (BL), m</td>
<td>15–120</td>
</tr>
<tr>
<td>Side slope (Z)</td>
<td>1.5–3</td>
</tr>
<tr>
<td>Depth above minimum treatment volume ($d$), m</td>
<td>0–5.8</td>
</tr>
</tbody>
</table>

Table 1

Pertinent equations used in the storage emissions model.

Table 2

Input parameters.
parameters examined are not all independent. For example: pH is a function of $T_{\text{liquid}}$, $P$ is a function of $T_{\text{air}}$, and the available fraction of $C_{\text{TAN}}$ that can be volatilized is a function of pH. In GSA, for non-independent input parameters (e.g., pH), the first-order sensitivity coefficient represents the amount of (output) variance caused by pH changes only. The variance from the temperature dependence of pH shows up in the second-order coefficient that contains both pH and $T_{\text{liquid}}$. This is the significant strength of GSA over RSA (Saltelli et al., 2008, 2004). Relative sensitivity analysis can only assess the unconditional means and variances are calculated from these data as shown.

The GSA was performed for the three cases involving the calculation of: (i) total NH$_3$ emission rates ($M_A$) with the lagoon surface area calculated by Eq. (4); (ii) the NH$_3$ emissions flux ($J_A$), and (iii) $M_A$ with a specified surface area. In case (i), sensitivity coefficients were calculated for all lagoon geometry-related parameters; however, in case (iii), these were all lumped together as a single total surface area ($A_{\text{total}}$) parameter. This method allowed for the direct calculation of first- and second-order sensitivity indices for each of the model input parameter listed in Table 2. Sample calculations are presented in Figs. 1–4 to serve as a tutorial for applying GSA using the “sample” and “re-sample” matrices approach. We found this method the most effective for performing a GSA on the NH$_3$ emissions model of this research; however, this method will apply for any model.

The first step of the GSA procedure is shown in Fig. 1. Two matrices, $M_1$ (the “sample” matrix) and $M_2$ (the “re-sample” matrix), are created. Each column of these matrices is dedicated to a model parameter. The number of rows of these matrices corresponds to the number of simulations performed ($N$). For the NH$_3$ emissions simulations $N$ was set to 100,000. The elements of each column in $M_1$ and $M_2$ are filled in with uniformly distributed values generated randomly within the upper- and lower-limits (Table 2) of that parameter. We also tested normally distributed random values and found no change in the results (data not shown). Each row of both matrices is used to simulate the model. The resulting NH$_3$ emission rates ($M_A$) were stored in the output vectors $Y_1$ and $Y_2$. The estimated unconditional means ($\hat{E}_{Y_1}$ and $\hat{E}_{Y_2}$) of $M_A$ values from $Y_1$ and $Y_1$ were calculated and used in the calculation of the estimated unconditional variances ($\hat{V}_{Y_1}$ and $\hat{V}_{Y_2}$) shown in Fig. 1.

An example for the use of these unconditional means and variances of the “sample” and “re-sample” matrices to calculate a first-order sensitivity coefficient is shown in Fig. 2 for the model parameter, $T_{\text{liquid}}$. First, a new matrix ($P$) was created from $M_1$ and $M_2$. The $P$ matrix contains the values from the “sample” matrix for the model parameter for which the first-order SA is being performed. All other columns in $P$ were taken from the “re-sample” matrix. The rows of this new matrix $P$ were then used as model inputs, the model was simulated $N$ times, and the results were stored in a new vector, $Y_P$. The vectors $Y_1$ and $Y_2$ were then used to calculate the variable $U_P$, shown in Fig. 2. Then, $U_P$, $\hat{E}_{Y_1}$, $\hat{E}_{Y_2}$, and $\hat{V}_{Y_1}$ were used to calculate the first-order sensitivity coefficient, shown in Fig. 2 for $T_{\text{liquid}}$ ($S_{T_1}$).

An example for the calculation of the second-order (i.e., interaction) sensitivity coefficient between $T_{\text{liquid}}$ and pH for the NH$_3$ emissions model is given in Fig. 3. Here, another new matrix $Q$ was created and contains parameter values from the “sample” matrix ($M_1$) for model parameters being used to calculate a second-order sensitivity coefficient. All other columns of $Q$ contain values from the “re-sample” matrix ($M_2$). Rows of this new matrix $Q$ were taken from the “sample” matrix ($M_2$). Rows of this new matrix $Q$ were taken from the “re-sample” matrix ($M_2$), and the vectors $Y_1$ and $Y_2$ were used to calculate $U_Q$ shown in Fig. 2. Finally, the second-order sensitivity coefficient was calculated from $U_Q$, $\hat{E}_{Y_1}$, $\hat{E}_{Y_2}$, and $\hat{V}_{Y_1}$, and the first-order sensitivity coefficients of the parameters being considered for the second-order calculation. Calculation of the second-order sensitivity coefficient for $T_{\text{liquid}}$ and pH ($S_{T_1}^p$) from the “sample” and “re-sample” matrices is shown in Fig. 3.

1. Create two matrices with random values over the range of each variable.

![Table 1](image)

**Table 1.** Creation of the “sample” and “re-sample” matrices for global sensitivity analysis based on limits of input parameters and calculation of model outputs. The estimated unconditional means and variances are calculated from these data as shown.
The final calculation of the GSA is that of the total effect index. Conceptually, the total effect index can be thought of as the sum of the first-order and all second- and higher-order sensitivity coefficients containing a parameter of interest. An example computed for \( T_{\text{liquid}} \) in the NH\(_3\) emissions model is presented in Fig. 4. Here, a new matrix \( R \) is created. This matrix contains values from the “re-sample” matrix \( (M_2) \) for the parameter of interest. All other parameters contain values from the “sample” matrix \( (M_1) \). Model simulations with the rows of \( R \) produce outputs that are stored in the \( Y_R \) vector. Again, the \( UR \) variable is calculated from \( Y_1 \) and \( Y_R \), and the total effect index is calculated from \( UR, EY_1 \), and \( VY_1 \). The total effect index for \( T_{\text{liquid}} \) \((ST_{\text{TL}})\) is calculated from the “sample” and “re-sample” matrices in Fig. 4.

For the calculations in this study, a total of 100,000 simulations \((N = 100,000)\) were used. The first-order sensitivity coefficients were calculated for all model parameters. Then, second-order sensitivity coefficients were calculated for all combinations of model parameters. Finally, the total effect index was calculated for every model parameter using these methods. The complete analysis was repeated 20 times, and results were averaged. The standard deviations of SA results were calculated. All GSA are reported as the average of these 20 replicates \((\pm 1 \text{ standard deviation})\).

As shown in Eq. (1), the model implies a direct correlation between the rate of NH\(_3\) emission and the surface area of the lagoon. We have interests in determining (i) whether the geometry of the lagoon is important in determining NH\(_3\) emission rates and (ii) which lagoon liquid and environmental parameters are important in determining NH\(_3\) emissions per unit surface area. To assess these, we performed the GSA twice. In the first set of simulations, the model output was set to be the total NH\(_3\) mass release rate, \( M_A \). This allowed investigation of lagoon geometry. In the second set of simulations, the model output was set to be the NH\(_3\) emissions flux, \( M_A \).

**Fig. 2.** Creation of the \( P \) matrix from \( M_1 \) and \( M_2 \) and calculation of the first-order sensitivity coefficient. This example is based on the \( T_{\text{liquid}} \).

**Fig. 3.** Creation of the \( Q \) matrix from \( M_1 \) and \( M_2 \), using the \( T_{\text{liquid}} \) as an example. This enables calculation of the second-order interaction coefficient between \( T_{\text{liquid}} \) and \( pH \) as shown. These calculations are repeated for all possible variable interactions. This method is also used to calculate higher-order interactions between three or more variables.
2.4. Relative sensitivity analysis

The RSA was performed using the following parameters: (i) liquid temperature ($T_{\text{liquid}}$), (ii) TAN concentration ($C_{\text{TAN}}$), (iii) pH of the lagoon, and (iv) The wind speed 8 m above the surface ($U_8$). The relative sensitivity values were calculated using Eq. (7) described by Zerihun et al. (1996).

$$S_r = \frac{\Delta f_A}{\Delta X}$$

where, $S_r$ is the relative sensitivity coefficient; $f_A$ is the NH3 emissions flux; $\Delta f_A$ is the change in NH3 emissions flux; $X$ is the mean value of the input parameter; and $\Delta X$ is the change in the input parameter over the range being considered.

The RSA result represents the percent change in NH3 flux per unit percent change in the input parameter over the range being considered. For each input parameter, the relative sensitivity was calculated for specified ranges while keeping all other parameters constant at their mean values. The range of input parameter values are presented in Table 2 and the mean values of the input factors used were: $T_{\text{liquid}} = 20$ °C, (ii) $C_{\text{TAN}} = 0.456$ kg m$^{-3}$, (iii) pH = 7.8, and (iv) $U_8 = 3.6$ m s$^{-1}$. The RSA considers only the first-order components of model input parameters.

3. Results

3.1. Global sensitivity analysis

The GSA results are listed in Table 3. The summation of all first- and higher-order sensitivity coefficients is equal to 1 by definition (Saltelli et al., 2008, 2004). For case (I), only the atmospheric pressure ($P$) and the side slope ($Z$) returned first-order sensitivity coefficients of zero. These two parameters have first-order coefficients of zero for all three cases. As expected, the lagoon geometry first-order coefficients were zero for cases (II) and (III). The summation of the first-order coefficients related to lagoon geometry is 0.0373 in case (I). When all lagoon geometry parameters were lumped into the $A_{\text{total}}$ parameter (case (III)), the first-order coefficient was 0.0385. The pH returned the highest first-order sensitivity coefficient, followed by (in order) $T_{\text{liquid}}$, $U_8$, and $C_{\text{TAN}}$ for all three cases. The summation of the first-order coefficients were 0.355, 0.447, and 0.367 for cases (I), (II), and (III), respectively. This means that 35.5%, 44.7%, and 36.7% of the variance of the model output can be explained by individual model parameters for these cases.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Case I: Sensitivity Coefficient ($S_i$ or $S_j$) for $M_A$</th>
<th>Case II: Sensitivity Coefficient ($S_i$ or $S_j$) for $M_A$</th>
<th>Case III: Sensitivity Coefficient ($S_i$ or $S_j$) for $M_A$ (Total Area)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{\text{liquid}}$</td>
<td>0.0693</td>
<td>0.0940</td>
<td>0.0719</td>
</tr>
<tr>
<td>$U_8$</td>
<td>0.0590</td>
<td>0.0876</td>
<td>0.0634</td>
</tr>
<tr>
<td>$C_{\text{TAN}}$</td>
<td>0.0418</td>
<td>0.0563</td>
<td>0.0440</td>
</tr>
<tr>
<td>pH</td>
<td>0.0219</td>
<td>0.0219</td>
<td>0.0227</td>
</tr>
<tr>
<td>$C_{\text{TAN}}$</td>
<td>0.0196</td>
<td>0.0309</td>
<td>0.0233</td>
</tr>
<tr>
<td>$T_{\text{liquid}}$</td>
<td>0.0200</td>
<td>0.0200</td>
<td>0.0200</td>
</tr>
<tr>
<td>$A_{\text{total}}$</td>
<td>0.0355</td>
<td>0.447</td>
<td>0.367</td>
</tr>
</tbody>
</table>

Table 3

First- and second-order sensitivity coefficients of model parameters calculated using a global sensitivity analysis.

This analysis assumed total ammoniacal nitrogen content of the air ($C_{\text{air}}$) of 0 mg L$^{-1}$.

* A total of 45 s-order coefficients were calculated for each column. Only those coefficients with a value greater than 0.01 in any simulation are reported here. All other second-order coefficients are close to zero.
cases. The remaining variance must be explained by parameter interactions.

The first-order influence of each model parameter is illustrated in Fig. 5. Here, the results of stochastic model simulations \((N = 100,000)\) were plotted against the input values of each model parameter, individually. Parameters with a higher first-order sensitivity coefficient have higher-ordered data sets, with larger values of the model output corresponding with higher values of the model parameter itself. This is a simple method to visualize the impact of the calculated first-order sensitivity coefficients. Second-order coefficients are presented in Table 3. Only those with a value greater than 0.01 (in at least one case) are listed in Table 3. The interaction of \(T_{\text{liquid}}\) with \(pH\) produced the highest second-order sensitivity coefficient in all three cases. This reveals a possibly significant interaction between these two model parameters. The model parameter \(pH\) also showed an elevated interaction with \(U_8\) in all three cases. Over 37% of model output variance could be explained by second-order model parameter interactions for all three cases. Over 37% of model output variance could be explained by second-order model parameter interactions for all three cases (with >45% for case (III)). This leaves 18% (over 26% for case (I)) attributed to higher-order interactions of model parameters. These are interactions of three or more parameters.

The total effect index defined as the summation of all first- and higher-order sensitivity measures that contain a particular model parameter are presented in Table 4. Because higher-order sensitivity measures count for multiple model parameters when calculating the total effect index, the summation of all total effect indices is greater than one, when higher-order indices are non-zero. As shown in Table 4, pH is the most sensitive model parameter followed by \(T_{\text{liquid}}\) and \(U_8\). The total effect indices for these parameters are greater than that of \(A_{\text{Total}}\). This suggests that liquid and environmental parameters have more influence in determining total \(\text{NH}_3\) emissions from a lagoon than the surface area of the lagoon. Of course, this is only true for the range of area values considered by this study.

### 3.2. Relative sensitivity analysis

The RSA results are presented in Fig. 6. In general, the sensitivity of the model output increased with increasing absolute values of the relative sensitivity index. The relative sensitivities ranged from 15.3 to 17.9, 0.3 to 2.7, and 0.75 to 1.54 for \(pH\), \(T_{\text{liquid}}\), and \(U_8\) respectively (Fig. 6a,b,c). The relative sensitivity for \(C_{\text{TAN}}\) was constant at a value of 1.0 (Fig. 6d). The constant sensitivity index for \(C_{\text{TAN}}\) implies that \(\text{NH}_3\) emission is directly proportional to the \(C_{\text{TAN}}\) concentration (constant slope). The order of importance of model parameters as predicted by RSA are: (i) \(pH\), (ii) \(T_{\text{liquid}}\), (iii) \(U_8\) and (iv) \(C_{\text{TAN}}\). RSA showed that \(C_{\text{TAN}}\) may be an important parameter compared to \(T_{\text{liquid}}\) and \(U_8\) at temperatures below 10°C and wind velocity below 3 m s\(^{-1}\).
4. Discussion

A comparison of results for GSA (Tables 3 and 4) and RSA (Fig. 6) reveal the same order of importance of the parameters used in the model as: (i) pH, (ii) $T_{\text{liquid}}$, (iii) $U_8$, and (iv) $C_{\text{TAN}}$. Additionally, GSA shows that the second-order coefficients can be more important than some first-order coefficients, an aspect not captured by RSA. In our case, GSA shows the interaction between pH and $T_{\text{liquid}}$ was more important than $T_{\text{liquid}}$ alone (Table 3). This also confirms the dependence of pH on $T_{\text{liquid}}$. The GSA also suggests that attention should be paid to the interaction between pH and $U_8$, rather than $U_8$ alone. Previous studies using RSA have reported mixed results on what was the most sensitive model input parameter for ammonia emissions from lagoons. It is suspected that parameter interactions may account for the significant model output variance that has led to conflicting results obtained from the previous studies that used RSA only.

The GSA approach shows that about two-thirds of the model output variance is determined by second- and higher-order model parameter interactions. This effect would be missed by the commonly used RSA methods. Thus, first-order sensitivity coefficients, like those returned from local sensitivity analyses, inadequately represents model output variation with changes in inputs. The first- and second-order measures of sensitivity of model parameters $P$ and $Z$ were zero. This provides considerable evidence that the atmospheric pressure ($P$) and the lagoon side slope ($Z$) parameters are insignificant compared to other model parameters. From the total effect indices using GSA, it is apparent that the model is not dominated by a single parameter as suggested by RSA, where the sensitivity index for pH was an order of magnitude higher than other parameters. For both GSA and RSA, the pH of the system was found to be the most influential model parameter on the prediction of NH$_3$ volatilization. Secondly, GSA shows that the factors that impact the interaction between the lagoon liquid pH and temperature are of importance compared to liquid temperature alone. Methods that could possibly control a temperature and wind velocity interaction should then be considered.

The $C_{\text{TAN}}$ was the least sensitive model parameter compared to $T_{\text{liquid}}$, pH, and $U_8$. The total effect index of $C_{\text{TAN}}$ was approximately 46% of the value for pH. Global sensitivity analysis results suggest that even for high values of $C_{\text{TAN}}$, the $M_A$ of $A$ is controllable through the manipulation of other system parameters, particularly pH. However, it is most likely a combination of system parameters (e.g., $T_{\text{liquid}}$ and pH) that may be used to manipulate the system or explain system variance, as the summation of the higher-order sensitivity measures is greater than that for the first-order coefficients. Although RSA predicted similar ranking of input parameters based on the first-order sensitivity coefficients, the fatal limitation of RSA (and all derivative-based sensitivity analysis methods) is in cases where the input parameters are uncertain and have unknown linearity (Saltelli et al., 2008). In this study, the wind velocity and temperature are examples of parameters which may not be certain. The derivative-based methods provide information valid only at the base point for which they are computed and are only good for linear systems where extrapolation from the points of computation is possible (Saltelli et al., 2008).

Ammonia emissions can be mitigated by (i) the changing the nitrogen content in animal diets, (ii) implementation of processes that use biological principles to convert ammonia to other nitrogen forms that are non-volatile, (iii) chemical processes that react with ammonia to produce non-volatile forms, and (iv) physical methods that bind ammonia (Ndewa et al., 2008). Thus, if one was to choose from the several strategies to control ammonia emissions, sensitivity analysis results could be used to target technologies that manage input parameters the model output is most sensitive. Our results suggest that the management of the liquid pH is of the utmost importance compared to $C_{\text{TAN}}$. Also, significant reductions in ammonia emissions will be observed with implementation of technologies that can control both pH and $T_{\text{liquid}}$. 

Fig. 6. Relative sensitivity analysis for the effect of pH, $T_{\text{liquid}}$, wind speed ($U_8$), and total ammonia concentration ($C_{\text{TAN}}$) on the ammonia emissions from a lagoon estimated by the model.
5. Conclusions

SA allows identification of significant model parameters and elimination of model parameters that have little impact on model output variance. Further, calculation of higher-order coefficients identifies critical model parameter interactions. When applied to the estimation of ammonia emissions from lagoons, sensitivity analysis can minimize the number of measurements needed to estimate ammonia emissions/inventory from animal feeding operations. Currently, RSA is the most commonly used method for process-based models. We have demonstrated that:

(i) GSA provides a complete understanding of model input parameters and their interactions on the model output variance compared to RSA,
(ii) some higher-order coefficients (parameter interactions) calculated using GSA, may contribute more to model output variance than some individual parameters, and
(iii) although GSA and RSA ranked model parameters with the same order of importance for the case presented here, only GSA accounted for 100% of the model output variance.

Thus, GSA is much more ideal for the development of process-based models and design of emissions control and mitigation strategies.

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