MEASUREMENT AND MODELLING OF AMMONIA EMISSIONS AT WASTE TREATMENT LAGOON-ATMOSPHERIC INTERFACE

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Abstract. Global emissions of ammonia are approximately 75 Tg N/yr (1 Tg = 10^{12}g). The major global source is excreta from domestic animals (~ 32 Tg N $^{-1}$yr^{-1}). Waste storage and treatment lagoons are used to treat the excreta of hogs in North Carolina (NC). Proteins and nitrogen rich compounds in the lagoon are converted to ammonia, through a series of biological and chemical transformations. The process of ammonia emission has been investigated using two different model approaches: (1) Coupled Mass Transfer with Chemical Reaction Model (Model I), and (2) Mass Transport without Chemical Reaction Model (Model II). A sensitivity analysis is performed with the models, and the model results are compared with ammonia emission experiments at a swine waste storage and treatment lagoon in NC using a dynamic emission flux chamber.

Results of model predictions of emission flux indicate an exponential increase in ammonia flux with increasing lagoon temperature and pH, a linear increase with increasing lagoon total ammoniacal nitrogen (TAN), and a secondary degree increase with the increasing wind speed. In addition, the fluxes predicted by Model I are consistently larger than fluxes predicted by Model II. Experimental values of flux agreed well with model predictions, with the experimental values lying in different positions between the two model predictions under different physical and chemical conditions. Further, when compared to diurnal and seasonal experimental flux values, Model I corroborates the results in calm meteorological conditions (wind speed U10 = 1.5 m s^{-1}). However, the observed results are better predicted by Model II during unstable conditions, when wind speeds are higher than 2.0 m s^{-1} and physical transfer process functions dominate.

Keywords: ammonia, emission, mass transfer, modelling, swine waste storage and treatment system

1. Introduction

Ammonia is increasing in importance in the rural atmosphere over the eastern United States (Aneja *et al.*, 2001, 2000; Asman *et al.*, 1998; Paerl, 1997). Gaseous ammonia is closely linked to the presence of ammonium in the atmosphere, which in turn acts as a neutralizing agent in the atmosphere (Warneck, 1999). Ammonium salts remain a major component of inorganic atmospheric aerosols and thus NH_X (NH_X = ammonia + ammonium) plays a major role in the physical and chemical process of the atmospheric nitrogen cycle. Ammonia also substantially influences the transport and removal of airborne oxidants as a reactant that is more biolo-

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gically active than oxidized nitrogen species in coastal and estuarine ecosystems (Paerl, 1997). The spatial scale of a particular NH_3 source contribution to atmospheric nitrogen input is controlled partly by the conversion rate of ammonia to ammonium. Due to the short residence time of NH_3 in the atmosphere, (less than 5 days), low source height and relatively high deposition velocity, its distribution may be limited to the near surrounding. However, ammonium aerosols, with atmospheric lifetimes of the order of 10 days (Warneck, 1999), can travel and deposit at larger distances.

The major global sources of ammonia include volatilization losses from fertilizers, emission from soils, biomass burning, and domestic animal waste (Bouwman *et al.*, 1997). The process of bacterial decomposition of urea to NH_3 and CO_2 is the predominant source and may be responsible for $40 \sim 90\%$ of the total atmospheric ammonia input. Aneja *et al.*, (2000) provided a preliminary nitrogen emission inventory for North Carolina revealing that a dominant contributor is livestock farming. The investigation reported that swine operations contribute $\sim 20\%$ towards North Carolina's nitrogen emissions inventory and comprise $\sim 47\%$ of total ammonia emissions in the state. North Carolina has experienced intense growth in its hog industry during the last decade. More than 90% of the state's hog population resides in the Coastal Plain region of the state where there exists a greater potential to directly impact coastal estuaries. In swine operations, the animal waste is stored in anaerobic lagoons, where enzyme-mediated nitrogen transformation processes convert tri-methyl amine into ammonia.

During the past decade, collaborative research has been performed to more accurately quantify the atmospheric ammonia flux from the gas-liquid interface (Aneja, 2000 – North Carolina waste storage and treatment lagoon; Asman, 1998 – North Sea; Olesen and Sommer, 1993 – Slurry). The progress of ammonia research, process description and affecting factors for ammonia emission have been reviewed by Asman *et al.* (1998). Olesen and Sommer (1993) have modelled ammonia volatilization processes from stored slurry and considered the effects of wind speed and surface cover on ammonia fluxes. The desorption model for ammonia emission by Koelliker and Minor (1973) for anaerobic lagoons used a two-film theory with an overall mass transfer coefficient given by Halsam *et al.* (l924), which is dependent on wind velocity and temperature. A limitation of this model is that the model leads to zero flux during calm conditions (i.e. zero wind speed). Other modelling, such as the earlier work reviewed by Asman *et al.* (1998), takes only an upper limit value of the assumed downward ammonia flux into consideration, based on the assumption of zero concentration of dissolved NH_3/NH_4^+ (NH_x) in the liquid. To improve the estimation of ammonia flux, Asman *et al.* (1994) used data of seawater composition with respect to dissolved ammonium and other species as well as additional meteorological data to calculate the net flux between the air and sea. The theoretical basis of the analysis was that diffusive resistance at the gas-phase side controls ammonia exchange. It may be, however, invalid to apply this heavily meteorologically involved model to the heterogeneous topography surrounding lagoons unless instantaneous measurements of meteorological parameters are available.

In this paper, a Coupled Mass Transfer and chemical reaction model (Model I) based on the concept of simultaneous mass transfer and equilibrium chemical reactions at the gas-liquid interface was used. The intensively applied mass transport model without chemical reaction (Model II) is also used for comparison to the newly developed model. An analytical investigation has been conducted to determine atmospheric ammonia emissions from swine waste storage and treatment lagoons. From this study, experimental results were utilized (Aneja *et al.*, 2000) to evaluate the models' accuracy in calculating lagoon ammonia emissions.

2. Experimental and Calculation Methodology

2.1. SAMPLING AND MEASUREMENT

NH_3 flux measurements were made at a 'farrow to finish' commercial hog operation in Sampson County, North Carolina (Aneja *et al.*, 2000). The waste from the hog sheds (urine and faeces) was flushed out with recycled lagoon water and discharged into the lagoon from the top ('top-loading'). The lagoon is an anaerobic system with sloped sides that reach a maximum depth of about 4 m at the center. The detailed sampling and precise measuring procedures have been described in earlier published works (Aneja *et al.*, 2000). To determine the concentration of total nitrogen (aqueous ammonia, ammonium, and nitrates) in the slurry, lagoon water samples were taken once every day during the flux sampling periods. Samples were analyzed for Total Kjeldahl Nitrogen (TKN) using a digestion procedure, which converts all organic and reduced nitrogen in the lagoon samples to NH_4^+. The NH_4^+ concentration in the sample was determined by colorimetry.

Ammonia flux was measured using a dynamic flow through chamber system (Aneja *et al.*, 2000), consisting of a fluorinated ethylene propylene (FEP) Teflon-lined open bottom cylinder inserted into a floating platform. When the platform and chamber were placed on the lagoon, the chamber penetrated the lagoon surface to a depth of $\sim$ 4 cm forming a seal between the lagoon surface and the air within the chamber. The placement of the chamber on the lagoon surface was performed in a statistically random manner. Compressed zero-grade air was pumped through the chamber at a known flow rate and the air in the chamber was continuously stirred by a motor driven Teflon impeller. Once the chamber reached steady state conditions, samples were drawn through Teflon tubes to a Measurement Technologies 1000N stainless steel NH_3 converter which transformed the N_T ($N_T = NH_3 + R\text{-}NH_2 + NO + NO_2$) constituents of the sampled air into nitric oxide (NO) at $\sim$ 825 °C. The sample flow from the NH_3 converter was routed to an Advanced Pollution Instruments (API) Model 200 chemiluminescence based NO monitor where the N_T concentration (in ppbv) was determined. Part of the flow from the chamber was bypassed directly to the API, which measured NO_X ($NO_X = NO + NO_2$) via a molybdenum converter heated to ~ 325°. The API then determined the NH_3 concentration in surface lagoon air by subtracting the NO_x signal from the NT signal ($NH_3 = N_T - NO_X$). All analytical instruments and data acquisition systems were housed in a temperature controlled mobile laboratory (modified Ford Aerostar van).

The measuring period began on August 1, 1997, and ended on May 27, 1998, during which time four seasons were sampled to determine the annual trend. Generally, lagoon water temperature was monitored continuously with a temperature probe (Fascinating Electronics, Deer Island, Oregon) immersed 15 cm below the lagoon water surface. The lagoon pH was monitored simultaneously using a double junction submersible electrode (Cole Parmer, Venon Hills, Illinois) which was placed ~ 48 cm from the chamber and adjacent to the temperature probe. Some measurements of temperature and pH were recorded manually.

3. Mass Transport Models

Two models, based on the quiescent thin film concept (Danckwerts, 1970), are considered. In both models a gas phase film extends upward from the air-liquid interface to the well-mixed air region, and a liquid phase film extends downward from the same interface to the well-mixed liquid region of the lagoon. In both models, the film thickness of a given phase was defined as the ratio of the ammonia diffusion coefficient for that phase to the mass transfer coefficient of ammonia as experimentally determined by Mackay and Yeun (1983) for the same phase.

3.1. MODEL I: MASS TRANSFER WITH CHEMICAL REACTIONS

This model explicitly takes into account molecular diffusion and chemical reactions. In the liquid film, only ammonia's reversible reaction in water is considered, and pH is assumed constant. Based on these assumptions, a theoretical result of Olander (1960) is used to define the ammonia flux (J_i) in the liquid phase at the air-liquid interface,

$$J_i = \left(\frac{D_c}{t_L}\right)(C_L - C_{Li})\left(1 + \frac{D_A}{D_c}K_{rL}\right). \tag{1}$$

Where A denotes ammonium $[NH_4^+]$ and C = $[NH_3]$; D_A and D_c are the diffusivities of ammonium and ammonia in the liquid phase, respectively. t_L is the thickness of the liquid film. C_{Li} and C_L are ammonia concentrations at interface and in the bulk of liquid phase, respectively. K_{rL} is the overall effective equilibrium constant and is given by, $K_{rL} = \frac{K_{NH_4^+}}{[H^+]}$, in which $K_{NH_4^+}$ is the dissociation constant for the equilibrium equation of ammonium in the liquid.

For the gas phase film, the primary reactions of ammonia with sulfuric acid (H_2SO_4), nitric acid (HNO_3), hydrochloric acid (HCl), water, and the hydroxyl radical (OH) are considered (Finlayson-Pitts and Pitts, 1986; Warneck, 1999). In the gas film, these five compounds are assumed to have constant concentrations, giving an effective first order reaction for ammonia, with first order reaction rate constant of ammonia in the gas phase, k_{ra}, being inferred as follows

$$k_{ra} = [NH_3] \times \{k_1[HSO_4] + k_2[HNO_3] + k_3[HCl] + k_4[H_2O] + k_5[OH]\} \quad (2)$$

The following equation describes the transport of ammonia in the gas phase:

$$D_a \left(\frac{d^2C(z)}{dz^2} \right) = k_{ra} \times C(z) \quad (3)$$

where, C(z) is the ammonia concentration at the height of z in a gas film of thickness t_a. D_a is the molecular diffusion coefficient of ammonia in the gas phase. The boundary conditions are

$$z = 0; C(0) = C_{ai} \quad (4a)$$

$$z = t_a; C(t_a) = C_a \quad (4b)$$

The solution to the mass transport equation results in ammonia flux to the atmosphere being expressed in terms of film thickness, gas phase ammonia diffusion coefficient, the effective first order rate constant, and the concentrations at the film boundaries.

Assuming the gas phase and liquid phase ammonia concentrations at the air-liquid interface are in equilibrium and related by Henry's law constant (H), Equation (1) can be combined with a gas phase interfacial expression for flux based on the solution to Equation (3). The result is an expression for the flux of ammonia from the lagoon water to the troposphere.

3.2. MODEL II: MASS TRANSPORT WITHOUT CHEMICAL REACTIONS

Without chemical reactions, ammonia flux to the atmosphere (J_{IIa}) is given by the expression

$$J_{IIa} = -K(C_a - HC_L); \quad (5)$$

where K is the overall mass transfer coefficient, $(H/k_L + 1/k_a)^{-1}$ (Sherwood *et al.*, 1975). The parameters k_L and k_a are the mass transfer coefficients for an inert gas in liquid and air phases respectively (Mackay and Yeun, 1983), and H is Henry's law constant. C_a is the concentration of ammonia at the top of the gas phase film, and C_L is the concentration at the bottom of the liquid film, having the same meaning as in Model I.

4. Results and Discussions

The two models developed above reveal that the calculated ammonia flux depends on temperature, pH, and total ammoniacal nitrogen ([TAN]) content of the lagoon, and wind speed. Model simulations show that as long as the lagoon surface temperature remains constant, an increase of air temperature (T_a) from 5 to 40 °C indicates a corresponding decrease of ammonia flux of less than 0.1% for both the models. The variation of ambient ammonia concentrations of 1 to 100 ppmv provides a flux change within the same scale, i.e. $\sim$ 0.1%. Therefore, the average ambient air temperature (10 °C) and ammonia concentrations (10 ppmv), measured at a swine farm in Sampson County (McCulloch *et al.*, 1999), are used for the model calculations.

Sensitivity analysis was performed on both models using a range of lagoon temperature, pH, TAN and wind speed. The results are discussed below.

4.1. EFFECTS OF LAGOON TEMPERATURE ON AMMONIA FLUX

The lagoon temperature plays a significant role in estimating ammonia flux (Figure 1a). Effects of lagoon temperature include molecular diffusion coefficients in both phases and concentration controls through variations of Henry's Law constant and dissociation constant. Throughout the measurement campaign, the lagoon temperature (T_L) varied in the range of 0 to 37.7 °C. Variation of T_L in the models increases the ammonia flux values exponentially for the given constant values of wind speed (0.89 m s^{-1}), TAN (293 mg l^{-1}) and pH (7.6). The exponentially increasing tendency indicates the combined influence of the factors involved. By increasing the temperature from 2.5 to 37.5 °C, the corresponding ammonia flux values increases from 89.1 μg NH_3-N m^{-2} min^{-1} to 5320.6 μg NH_3 –N m^{-2} min^{-1} for coupled mass transfer with chemical reaction model (model I), and from 57.9 μg NH_3-N m^{-2} min^{-1} to 1508.4 μg NH_3-N m^{-2} min^{-1} for the mass transport without chemical reaction model (model II), respectively.

4.2. EFFECT OF LAGOON pH ON AMMONIA FLUX

Lagoon pH, which controls the chemical equilibrium of NH_3-NH_4^+ system in the aqueous phase, was varied in the models from 6.0 to 8.2. The measured pH values lie between 6.8 and 8.1. The results display an increasing trend in the NH_3 flux with increases in the pH by both the models (Figure 1b). Increase of ammonia flux with respect to pH is exponential for both models. Observations indicate that the flux values are small at pH values of 7.0 or below, while the flux values are considerably high at pH above 7.5, which indicates that the ammonia flux is sensitive to pH values.

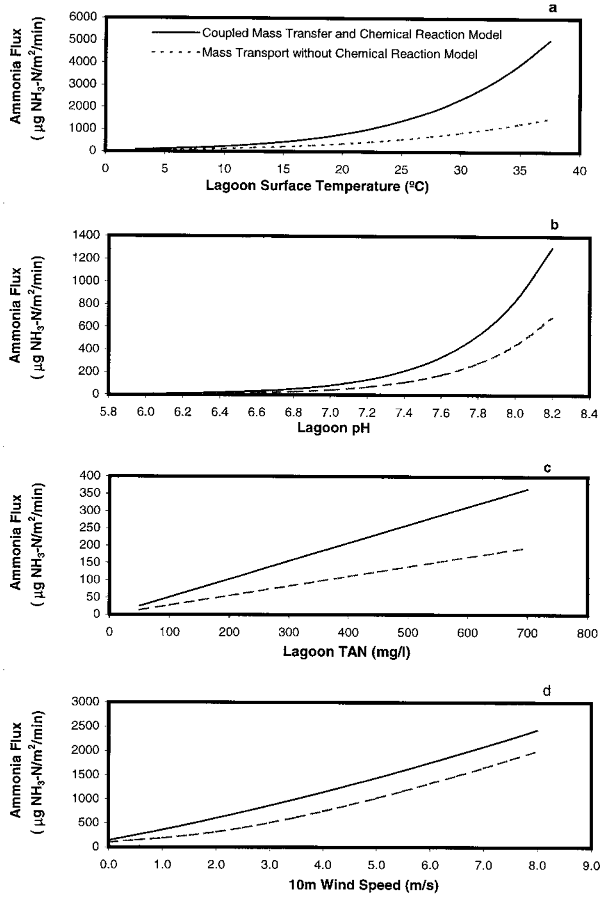

Figure 1. Sensitivity Analysis of Simulated Ammonia Emission with respect to a) Lagoon surface temperature; b) Lagoon pH; c) Lagoon TAN; d) Wind speed. Unit of ammonia emissions are μg NH_3-N/m^2/min. The standard conditions, if not being varied, are as following: 10m Wind Speed: 0.89m/s; pH: 7.6; Air Temperature: 10 °C; Lagoon Surface Temperature: 12.8 °C; Ambient Ammonia Concentration: 10 ppbv. The solid line (—) is the analysis based on Mass Transfer with Chemical Reaction Model; the dashed line (----) is the analysis based on Mass transport without Chemical Reaction Model.

4.3. EFFECT OF LAGOON TAN

The waste from the hog sheds (urine and faeces) was flushed out with recycled lagoon water, and discharged into the lagoon from the top ('top-loading'). In the anaerobic environment the enzyme-mediated transformation (hydrolysis) initially takes place for higher molecular mass compounds, suitable for use as sources of energy and cell carbon. The compounds produced are then converted to other identifiable products of lower molecular mass, which are further converted to simpler end products, principally methane and carbon dioxide. The amines in the solution are converted to ammonia. The Total Ammoniacal Nitrogen (TAN) was varied in the models from 50 to 700 mg l^{-1} with constant values of lagoon temperature (12.77 °C), wind speed (1.44 m s^{-1}) and pH (7.6) (Figure 1c). Since the experimental data of different TAN are not available from the measurement campaign, no comparison was made between the theoretical calculations and the measurements.

4.4. EFFECT OF WIND SPEED ON THE MASS TRANSPORT COEFFICIENTS

Since the air film thickness is a laminar sub-layer, it is affected by meteorological and environmental parameters such as wind speed, stability, cloud cover, etc., and therefore the meteorological parameters may also affect the ammonia emission. Previous studies have determined the mass transport coefficients, and different relationships were given as functions of Reynolds numbers (*Re*), frictional velocity (U_*), Schmidt numbers (*Sc*) or temperature (*T*) (Mackay and Yeun, 1983). The formulas given by Mackay and Yeun provide a more realistic estimations at zero wind speed, which is not the case for other studies. Therefore, the Mackay-Yeun relationships were used to obtain the mass transfer coefficients and the film thickness in both the models. The contribution of related physical and chemical factors such as wind speed, lagoon temperature, and Henry's Law constant may be expected to influence the mass transfer coefficients and therefore the ammonia flux. Modelling calculations (Figure 1-d) showed that, keeping constant values of air temperature, TAN and pH, wind speed variation from 0.5 m s^{-1} to 7.0 m s^{-1} provides a flux change from 98 μg NH_3-N m^{-2} min^{-1} to 2001 μg NH_3-N m^{-2} min^{-1} for the mass transport model and a change from 138 μg NH_3-N m^{-2} min^{-1} to 2429 μg NH_3-N m^{-2} min^{-1} for the coupled mass transfer with chemical reaction model.

4.5. VALIDATION OF THE MODEL

Measurements of lagoon and meteorological parameters were taken near the anaerobic lagoon (Aneja *et al.*, 2000; McCulloch *et al.*, 1998). The Total Ammoniacal Nitrogen values were not available for the Sampson County lagoon site; therefore an average value of 85% of Total Kjeldahl Nitrogen (TKN) was taken for the calculation purpose based on Filhage (1998) recommendations. The wind speed varied between 1.52 and 4.0 m s^{-1} during the measurement period. Figures 2(a)–(c) present comparisons of relationships between plots of NH_3 flux values versus lagoon temperature for the two models and the in-situ measurements under different meteorological parameters. At a wind speed of 1.67 m/s (Figure 2a) the measured values appear to fall closer to the coupled mass transfer and chemical reaction model (i.e. chemical reaction sensitive case) than the mass transport without chemical reaction model. All the measurements used in this graph were made during the nighttime in which the strongly stable meteorological conditions reduced the turbulence relative to more unstable conditions during the day.

As wind speeds were increased in the model simulations to 2.3 and 3.9 m s^{-1} (Figures 2b and 2c), most of the experimental data were found to drop from Model

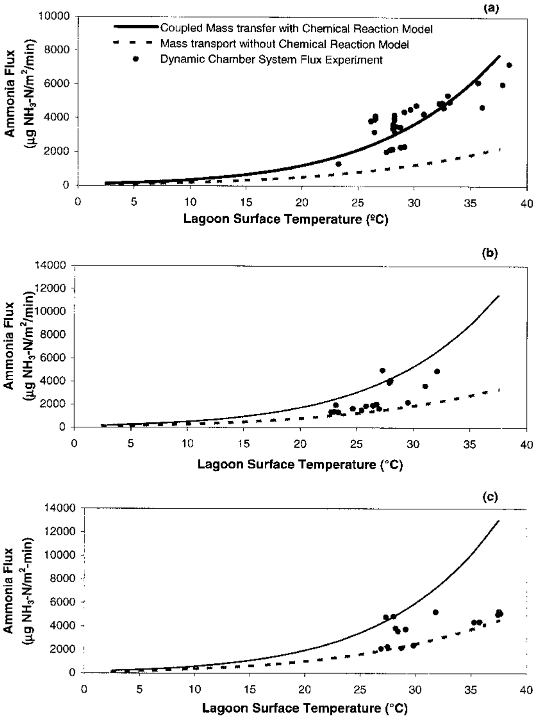

Figure 2. Comparison of Ammonia Emission Results Based on Modelling Predictions and the Dynamic Chamber System Flux Experiments. 10m Wind Speeds: (a) 1.67 ± 0.15m s^{-1}; (b) 2.30 ± 0.10 m s^{-1}; (c) 3.90 ± 0.15 m s^{-1}. Other parameters for all three graphs: TAN: 640 ± 10 mg l^{-1}, pH: 7.6 ± 0.1, 2 m Air Temperature: 10 ± 5 °C, Ambient ammonia concentration: 10 ppbv. Lagoon Temperature varies from 2.5 to 37.5 °C, which covered the possible range of measured data. Unit of ammonia emission flux is μg NH_3-N m^{-2} min^{-1}.

I predictions and lie between the two predicted values, with wind speeds increasing up to 4.0 m s^{-1} (Figures 2b, c). A possible interpretation of this tendency is that Model I is much more applicable in the case of calm meteorological conditions (i.e., lower wind speed and nighttime stability) since the chemical reactions contributed considerably to the total ammonia transport. However, under unstable conditions and higher wind speeds, the physical transfer will dominate the transport process and thus model II (only mass transfer considered) is applicable. Underestimations of Model II were observed in both stable and unstable conditions (Figure 2a, b, c). The transferability of the two models under extremely unstable condition can be explained mathematically. By replacing the Olander's equation of liquid phase with the general diffusion equation provided by Taylor's approximation, Model II can be obtained from Model I given equal emissions in two directions, the same boundary conditions, and Henry's Law at the interface.

Figures 3 and 4 provided the comparisons of NH_3 flux modelling calculations and experimental results for diurnal and seasonal variations, respectively. The di-

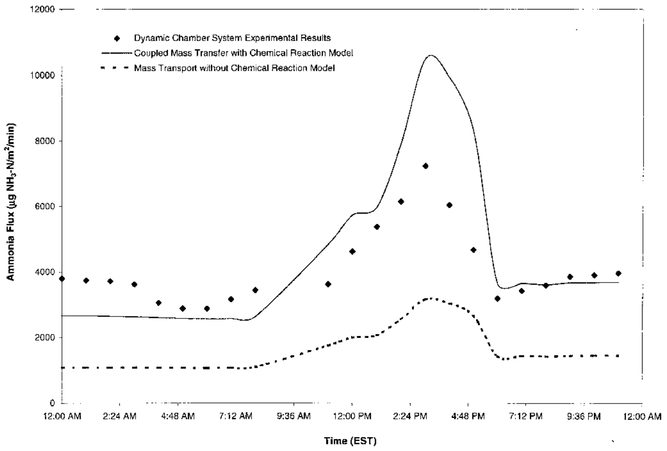

Figure 3. The Diurnal Variation Comparisons of Ammonia Emissions based on Model Results and Dynamic Chamber System Flux Experiments (Date: August 11, 1997).

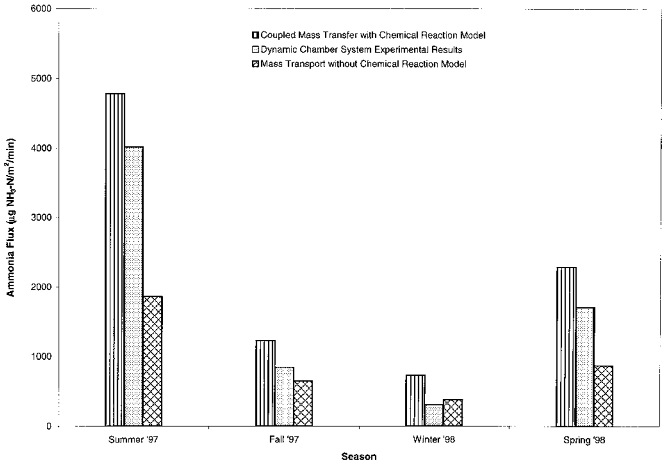

Figure 4. Seasonal Variation Comparisons of Ammonia Emissions between Modelling Results and Dynamic Chamber System Experiments.

urnal ammonia emission profile (Figure 3) displays a pronounced afternoon peak, which appears to be related to lagoon temperature and meteorological conditions. The emission curve remained flat before sunrise, began to increase after sunrise, and achieved the maximum emission between 2:00 PM and 4:00 PM, coinciding with maximum temperature and instability of the surface boundary layer. Compared to Model II, Model I matched the experiment results more closely, especially during stable conditions. The experimental values fell towards the Model II during peak emissions when the physical mass transfer mechanism is assumed to dominate.

Figure 4 shows a seasonal average comparison between the mass balance experimental results and the modelling calculations on the basis of the measurements taken during August 1997 and May 1998 (Aneja *et al.*, 2000). The average wind speed used is from McCulloch *et al.* (1999). The spring and summer were found to emit larger amounts of ammonia into the atmosphere than that in the fall and winter. Higher spring and summer emissions can be explained by higher lagoon temperatures, even though pH values were lower during this period, validating that the model is more sensitive to lagoon temperature than to other factors. Figure 4 also confirmed the applicability of the two models in different conditions. The experimental results are better represented by Model I during average temperatures when the chemical reactions are most active. The mass transport model without chemical reactions more closely matched the experimental results in lower average temperature conditions in which chemical reactions are limited and the pure physical transport processes dominate.

5. Conclusions

The Coupled Mass Transfer with Chemical Reaction Model simulations corroborate the experimental results and validate the application to the ammonia emission calculation. The chemical reactions of ammonia in the gas and liquid phases are responsible for the increase in ammonia emissions.

Due to the relatively constant values of other controlling factors, lagoon temperature is the most sensitive factor affecting ammonia flux. In some cases, wind speed and lagoon pH are also significant variables in predicting ammonia emissions. The predictions of Model I are in good agreement with experimental results under stable meteorological conditions, where chemical reactions contribute to the total emission. In unstable conditions where mass transfer dominates the emission process, the mass transport without chemical reaction model offers better results.

It will be interesting to further explore the factors affecting the physical mass transfer. Cloud ceiling, humidity, and other meteorological and fluid dynamical parameters may act as substantial forces influencing the emission process. Further consideration should also be given to the potential application of this model to the ammonia flux calculation on a larger scale water body, for example, the open sea. The concentration of TAN will be much lower in natural environments so that the interface exchange could decrease significantly. In this case the flux will be more sensitive to the atmospheric ammonia concentrations, which is almost negligible in the present case of waste storage and treatment lagoon.

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