Ammonia transformation in a biotrickling air filter

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ABSTRACT

A simple, tubular biotrickling filter was designed for optimal removal of ammonia and odour in ventilation air from a pig house. The removal and transformation of ammonia was studied in detail by analysis and modelling of chemical gradients through the filter. Good correspondence between measurements and model was obtained by using conventional substrate and inhibition kinetics of ammonium and nitrite oxidizing bacteria. Highest rates of ammonia removal were observed in the central section of the filter. Near the air outlet and water inlet the process was ammonia limited, while high nitrous acid concentrations almost excluded any biological activity near the air inlet and water outlet. Nitrous acid inhibition also stabilized pH at 6.5-7 all through the filter. Being sensitive to both ammonia and nitrous acid the nitrite oxidation process occurred mainly in the filter sections near the air outlet / water inlet, and only 8% of the nitrite was turned into nitrate. Water supply only exceeded evaporation by 20% but modelling indicated that additional watering would have limited effect on filter efficiency. The filter was also robust to varying loading, as a 4-fold increase in ammonia inlet concentration only reduced filter efficiency from 86 to 76%.

1 INTRODUCTION

Ammonia emitted from animal facilities is a major contributor to acidification and eutrophication of terrestrial and aquatic environments (McCrory and Hobbs, 2001). Significant reductions of both ammonia and door emissions can be accomplished by use of biological trickling filters. The good results, however, are not sufficiently reproducible, and further optimization of design and operation is required for more widespread application.

Ammonia is a highly water soluble gas (62 M/atm at 20 °C) that is readily protonized to ammonium (NH_4^+) in water. In biofilters ammonia is oxidized to nitrite (NO_2^-) by ammonium oxidizing bacteria (AOB) and further to nitrate (NO_3^-) by nitrite oxidizing bacteria (NOB). The overall removal efficiency is the result of complex interactions of ammonia load, filter surface area, air and water flow, temperature, nitrifier biomasses, and inhibition kinetics. To resolve this we analyzed chemical gradients in a simple counter-current biofilter and simulated the results with a mathematical model. Long term development of nitrifier biomass and the impact of nitrification processes on the removal of organic odorants are two important aspects that will not be addressed in this paper.

2 MATERIALS AND METHODS

2.1 Tubular biotrickling filter

The first, small version of the tubular biotrickling filter optimized for studies of function is shown in Figure 1 (M. Andersen, DK Patent no. 3108_06). Contaminated air is lead into the lower end of 3 independent tubes being 5.5 meter long and with a cross-section area of 11 cm^2 each. The straight airflow gives a good gas-filter contact in relation to pressure drop and minimizes the risk of clogging. The inner surface of the tubes is covered with a thin layer of a fibrous material through which the water slowly percolates driven by gravity. The biofilm developing on the surface of the conductive layer is thus moisturized with fresh water from inside and in direct contact with the air stream outside. This almost eliminates a liquid film diffusion barrier thus promoting the removal of airborne contaminants that are not easily soluble in water. Details on NH_3 load and air and water dynamics during the experimental run are given in Table 1.

2.2 Analytical methods

Ammonia in the air was sampled in acid solution and analyzed by spectrophotometer (Bower and Holm-Hansen, 1980). Water was sampled with filter paper sticks through the sampling ports, and after dilution NO_3^- and NO_2^- was analyzed by HPLC and NH_4^+ as above. pH was determined by pH sticks. Concentrations of HNO_2 and NH_3 were calculated from pH and concentrations of NO_2^- and NH_4^+ using pKa values of 3.4 and 9.4 respectively. Evaporation was calculated from the concentration gradient of a bromide tracer added to the water supply and analyzed by HPLC.

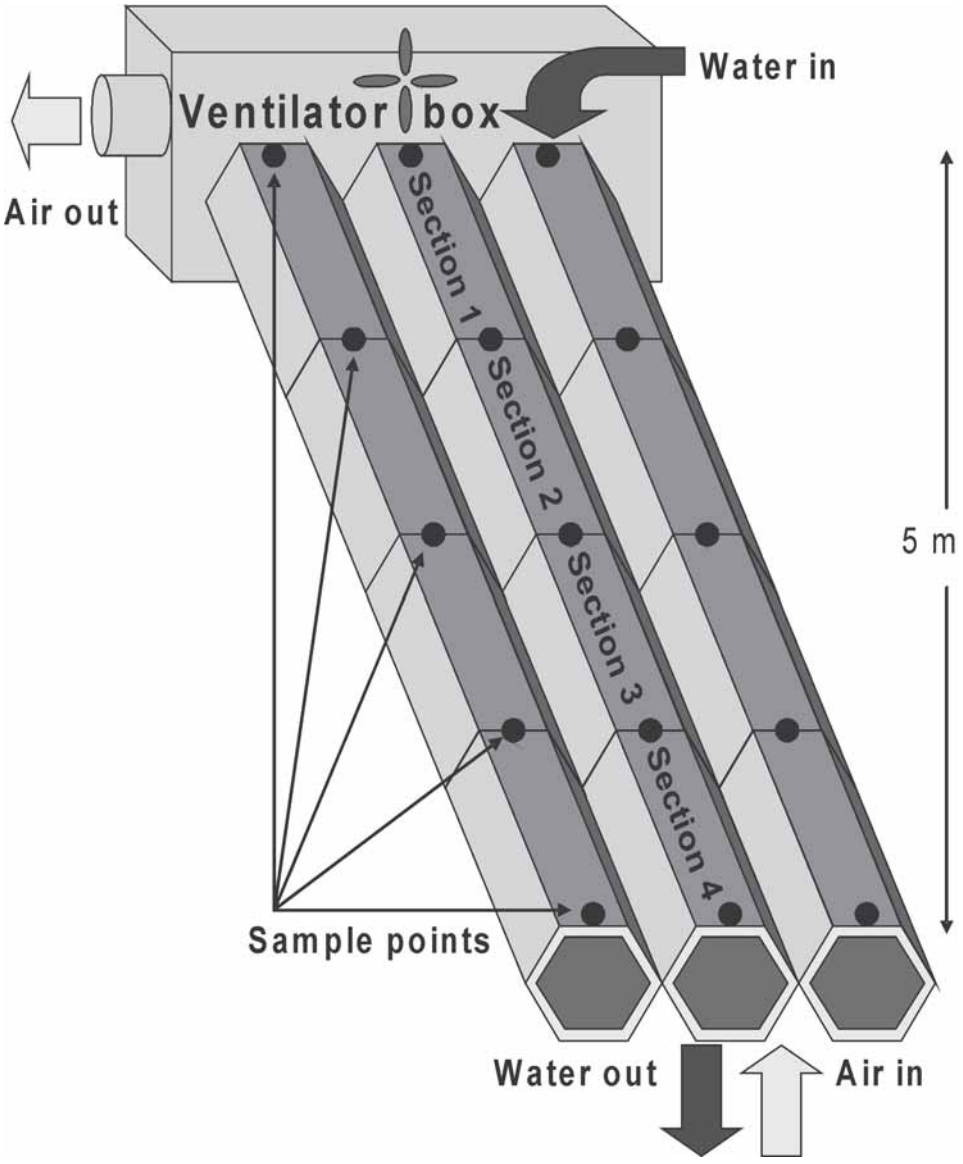

Figure 1. The experimental tubular biotrickling filter. The 5 sample points divide the filter in 4 sections of equal length.

Table 1.
Parameters of the model and the experimental filter. Values apply to one filter tube. The terms AOB and NOB stands for ammonium and nitrite oxidizing bacteria, respectively.

Parameter	Value
Inlet NH_3 concentration	8.6 ppm
Airflow	19400 L/h
Water flow	63 mL/h
Air volume per section	4.65 L
Water volume per section	23 mL
Evaporation, section 3	23 mL/h
Evaporation, section 4	30 mL/h
Air/water mass transfer coefficient per section	5 mL/s
Substrate limitation factors	C/(C+Km)
NH_3 inhibition factor for AOB	$e^{(-C/Ki)}$
Other inhibition factors	$1/(1+(Ci/Ki)^2)$
Km of NH_3 for AOB	786 μM
Km of HNO_2 for NOB	114 μM
Ki of NH_3 for AOB	2000 μM
Ki of NH_3 for NOB	168 μM
Ki of HNO_2 for AOB & NOB	1.14 μM
AOB capacity	50 x NH_3 load
NOB capacity	20 x NH_3 load
Model iteration frequency	100/s
Model runtime	20 h

2.3 Model

The mathematical model was programmed in JAVA and followed in most aspects a new, more general biofilter model (Nielsen *et al*., in preparation). The model filter was divided in 4 sections according to Figure 1 with fully mixed air and water phases and fixed biomass. In each iteration the changes of gaseous NH_3, total NH_4^+, total NO_2^-, and total NO_3^- were calculated from air/water NH_3 mass transfer, nitrification rates and water and air transport between sections. Subsequently the pH was calculated by solving a charge balance equation using a two-step Newton-Raphson approximation as described by Volcke *et al.* (2005). Inlet ammonia concentrations, air and water flow and evaporation were set to observed values in the experimental filter (Table 1). Compared to NH_3 the concentration of organic compounds in the ventilation air was an order of magnitude lower and transformations of organics were ignored in the present model version. Model parameters, kinetic equations, and initial values are

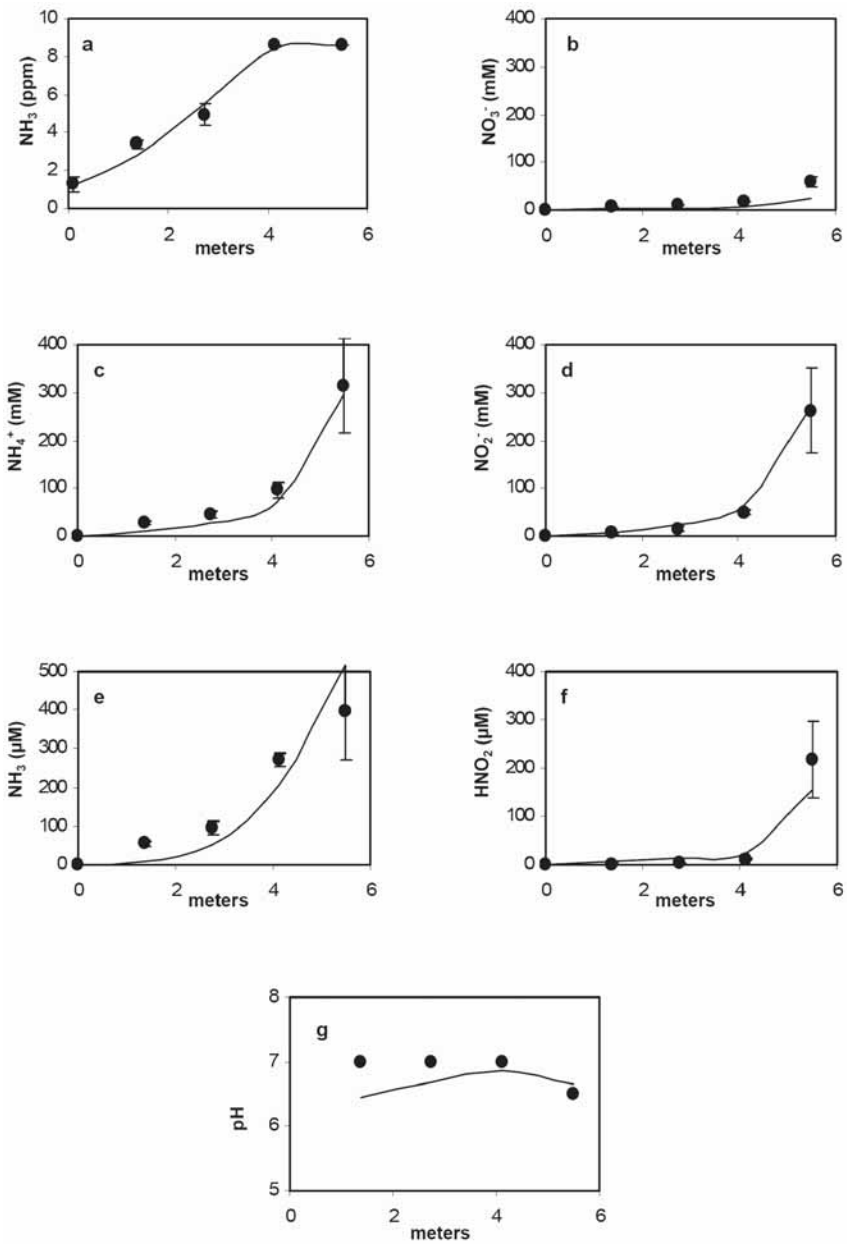

Figure 2. Concentration gradients from the water inlet at the top of the filter to the air inlet at the bottom showing NH_3 in the air (a) and NO_3^-, NH_4^+, NO_2^-, HNO_2, NH_3, and pH in the water (b-g). Lines are model simulation results and symbols are measured averages with standard errors (n=3).

listed in Table 1. Many different kinetic constants are found in the literature, but the general patterns of the model output were quite robust to variations in kinetic constants. The chosen values were mainly derived from Anthonisen *et al.* (1976). Notice that the uncharged species NH_3 and HNO_2 and not NH_4^+ and NO_2^- were considered the real species for substrate uptake and inhibition of nitrifiers (Anthonisen *et al.*, 1976). Chemical equilibrium constants for the inorganic nitrogen and carbon species at 20 °C were obtained from table values.

3 RESULTS

3.1 Chemical gradients

Of the water supplied 86% evaporated in the two lower sections (Table 1). Good correspondence between measured and modelled chemical gradients was obtained after proper adjustment of ammonium oxidation capacity and the results are shown together in Figure 2. Ammonia content of the air declined throughout the filter to an outlet concentration of 1 ppm corresponding to 85% overall removal. Most of the removal, 78%, occurred in the two central sections while the upper and lower section only accounted for 21 and 1% respectively. Concentrations of NO_2^- and NH_4^+ increased down the filter with final steep increases up to about 300 mM in the evaporation zone (Figure 2c-d). Concentrations of NO_3^- were much lower and both measured and simulated data showed that virtually all nitrite oxidation occurred in the upper two sections (Figure 2b). The discrepancy between simulated and measured NO_3^- concentrations could be ascribed to under estimation of the nitrite oxidation capacity. Despite the absence of any chemical buffer or pH regulation, the pH values remained between 6.5 and 7 (Figure 2g). By comparison with the Km and Ki values the concentrations of free NH_3 and HNO_2 indicated strong substrate limitation of AOB in the upper sections and strong HNO_2 inhibition of both AOB and NOB in the lower section (Figure 2e-f, Table 1).

4 DISCUSSION

There are many ways to examine the regulation of ammonia transformations in a biological airfilter, and some interesting points can actually be derived without running any models or experiments.

One point is that if the maximum capacity of the ammonium oxidizer biomass exceeds the NH_3 load, the process will have to be restricted accordingly by NH_3 limitation and/or inhibitors. As long as the overall NH_3 removal efficiency is good, a high inhibitor level is therefore not an indicator of a critical filter situation but rather

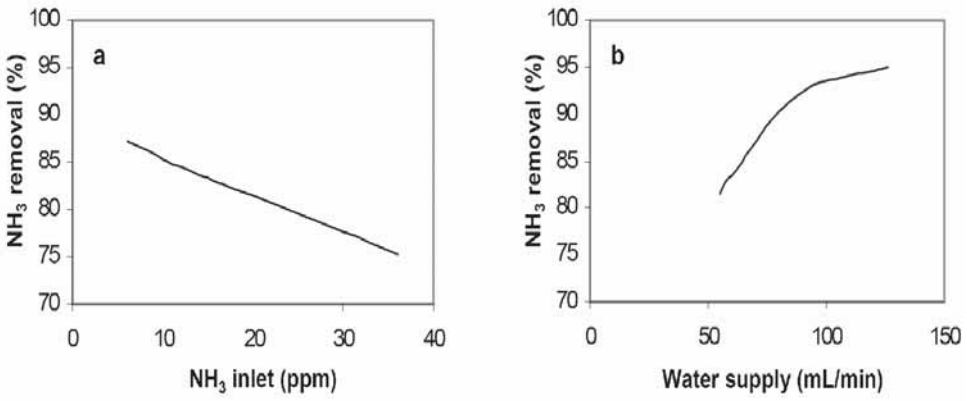

Figure 3. Modelled NH_3 removal efficiency as a function of inlet NH_3 concentration (a) and water supply (b). All other parameters are as shown in Table 1.

an indicator of excess nitrifier biomass. In the present case the maximum capacity in the model was set to 50 times the NH_3 load, and therefore the kinetics somehow had to reduce ammonium oxidation to less than 2% of the capacity. The results showed that this was accomplished mainly by HNO_2 inhibition in the lower half of the filter with concentrations up to 170 times the inhibition constant, and by NH_3 limitation in the upper end of the filter with concentrations 15-80 times lower than the Km value (Figure 2e-f, Table 1). The point that inhibitor level and substrate limitation is essentially determined by the biomass/loading ratio has other perhaps counter-intuitive implications; including that inhibitor level must decrease significantly with higher NH_3 loading but not with enhanced watering. Model perturbations indeed showed that a 6 times increase in NH_3 inlet concentration only reduced filter efficiency from 86 to 76% (Figure 3a).

Another general point is that in time only half of the NH_3 taken up in a biofilter will be oxidized, while the other half will remain in solution as NH_4^+ (Smet *et al.*, 2000). This is simply because NH_4^+ in reality is the only cation available to balance the produced anions NO_2^- and NO_3^- when concentrations are up in tens to hundreds of mM N. The measurements confirmed this by perfect charge balances, i.e. 310 mM NH_4^+ versus 320 mM $NO_2^- + NO_3^-$ in the outlet (Figure 2). Another way to address the general point of half-way nitrification is to consider pH: If the nitrifiers tried to generate just 1 mM $NO_2^- + NO_3^-$ more in excess of NH_4^+ the anion excess would have to be balanced by H^+, thus implying a pH drop to around 3 which would stop the bacteria long before. In the present filter with significant NO_2^- accumulation, the immediate effect of lowering pH was the protonization of NO_2^- to form the highly inhibitory HNO_2. In that way kinetics of HNO_2 inhibition of ammonium oxidation served as a

biological pH buffer ensuring that pH nowhere dropped below 6.5, despite the continuous uptake of a strong base, NH_3, and conversion to a moderately strong acid, HNO_2 (Figure 2). In other filters with well-established nitrite oxidation and therefore accumulation of NO_3^- in place of NO_2^- pH may drop below 5, as the HNO_2 block is not operating (L.B. Guldberg, unpublished).

In biological airfilters there must be some water run off removing the generated nitrogen salts. Not only in order to sustain NH_3 removal but also to avoid emission of the detrimental gasses NO and N_2O as observed in poorly watered biofilters (Trimborn *et al.*, 2003). The cost of handling the wastewater, however, makes it relevant to consider how the run off can be minimized. Of the 63 ml supplied every hour to each filter tube 53 ml evaporated in the lower part of the filter and only 10 ml drained off. This means that microorganisms in the upper half of the filter were blessed with more than 6 times the flow of water that eventually was discharged wastewater. The lowest section essentially served as a waste condenser with poor biological conditions due to nitrous acid accumulation. Osmotic stress might have been another important limiting factor at these high salinities (Smet *et al.*, 2000). Model perturbations (Figure 3b) showed that the overall removal efficiency would only increased from 85% to 95% following a doubling of the water supply to 126 mL/h and thereby the generation of about 7 times more wastewater ((63 mL + 10 mL)/10mL). On the other hand a reduction of the water supply by 16% to 53 mL or less would leave no wastewater and the filter would stop working. The major ambition with the modelling studies partly presented here is actually to develop better algorithms for optimization of water supply and biomass management in response to varying ammonia and door loading, air flow, temperature, humidity, etc.

5 ACKNOWLEDGEMENTS

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