RESEARCH REPORT
ENVIRONMENT

Title: The Development of a Biofilter System for Ammonia and VOCRemoval from Swine Operations **– NPB #01-086**

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ABSTRACT:
Biofilters have been used to degrade a wide range of air pollutants including odorous compounds such as H_2S and ammonia. Design procedures for biofilters in agricultural processes have been developed, but lack critical eliminates, such as the kinetics of oxidation required for accurate reactor sizing. Reaction kinetics is critical to accurately cost and size biofilters for the desired outlet concentration. Thus, a mobile, skid mounted biofilter was designed and built to determine the kinetics of ammonia oxidation at a modern 2400 sow farrow-to-wean unit. The biofilter system consisted of a variable speed blower, packed bed humidifier, and two reactors (4 ft x 4 ft with a packing volume of 12.5 ft^3 per reactor) configured in parallel. Prescreened, composted yard waste was used since compost contains a large number of active microorganisms, is relatively inexpensive, and easily available. Ammonia emissions (0-12 ppmv) from the swine facility (and 0-25 ppmv in simulated stream) were transported downward across packing in the reactors and spray nozzles at the top each reactor were used to add moisture to the packing. Ammonia conversion ranged between 25 to 95 % depending on the residence time and inlet NH_3 concentration. Using first order kinetics, the measured ammonia degradation rate ranged from 0.06 to 0.8 (mg NH_3/m^3/sec) for volumetric loading rates ranging from 0.05 to 0.25 mg/m^3/sec. Residence time distribution (RTD) analysis was also performed to determine the effect of scale-up on axial dispersion and deviation from plug flow. RTD analyses suggest that non-ideal reactor design equations may be required to predict reactor size for desired ammonia conversions. A reactor design method (i.e., sizing calculation) has been presented based on the kinetics of ammonia oxidation (i.e., how fast the reactor removes ammonia). For example, assuming a volumetric flowrate of 13 m^3/s, NH_3 conversion of 95% (C_{NH3in}=25 ppmV), and a first order rate constant of 0.08 1/s, a reactor volume of 487 m^3 and residence time of 37.5 sec is required. The size of the reactor will change, depending on the characteristics of the swine facility. Pressure drops across the bed should be 0.25 in H_2O or less in order to utilize in-house fans. This will probably limit the height of the reactor to 1 m or less. The mass of compost required can be estimated from its bulk density. Moisture content must be maintained between 40-60% in the biofilter to maintain biological activity. Additional research is required to develop inexpensive methods of emission humidification, online moisture analysis, and water addition.

III. INTRODUCTION

Recent measurements indicate that ammonia levels can exceed 25 ppm (~17.4 mg/m^3) in swine houses. Ammonia emission rates between 22-1298 mg/animal/hr for sows, weaners and finishers were reported (Groot Koerkamp et al., 1998). Based on ammonia emission rates from poultry houses, one U.S. EPA study indicated a factor of 0.179 kg/animal/year (http://www.epa.ohio.gov/dapc/general/amm_ani.pdf or http://www.epa.gov/ttn/chief/efdocs/ammonia.pdf). Based on this factor alone (0.179 kg/animal/year), local state regulatory agencies indicate that there may be ammonia emissions from large poultry farms such that current exemptions would no longer apply (http://www.epa.ohio.gov/dapc/general/ammonia.html). Since emission rates from swine operations are similar to poultry (Groot Koerkamp et al., 1998), swine operators may be impacted by future regulations on ammonia emissions.

Compost-based biofilters are one of the most cost effective treatment technologies for low concentration air pollutants, compared to traditional technologies such as thermal and catalytic oxidation (O'Neil 1992, Bohn 1992). Recent cost analysis performed for the petroleum and agricultural industries indicates that biobased systems are more economical than conventional technology (Leson and Smith 1997; O'Neil 1992; Nicolai and Janni 1998).

In a biofilter, pollutants are collected and passed through a reactor containing a packing (e.g., compost) seeded with a microbial biofilm. In addition to compost, other amendments (e.g., wood chips) are added to reduce pressure drop and/or a solid phase buffer. As the emissions pass through the biofilter, the air pollutants are transported from the gas phase to the stationary water/biofilm on the compost matrix and degraded to CO_2 and H_2O by the microorganisms in the biofilm. If the air pollutants are inorganic in nature (e.g., NH_3), lithotrophic bacteria will develop that consume the inorganic compound as an energy source (e.g., nitrifying bacteria that convert $NH_3 + O_2 + H^+ \rightarrow NH_4NO_3$ salts, equation not balanced).

Advantages of compost biofilters include:

- Low energy cost and oxidation to inert compounds
- Continuous degradation without the use of chemicals or high temperatures
- Diverse microbial community capable of mixed substrate degradation
- More cost effective than adsorption, catalytic oxidation and incineration
- Higher degradation rates compared to soil and peat
- Waste material is re-used (e.g., solid waste can be composted and used in biofilters)
- Large surface area and thin biofilm reduces mass transfer resistance and thus the reactor is applicable towards poorly water-soluble compounds such as dimethyl disulfide or H_2S.
- Reduced water consumption.

LITERATURE REVIEW

Compost biofilters have been used to degrade a wide range of air pollutants, such as benzene, toluene, ethanol, MEK, styrene, and hexane (Bohn, 1992; Ottengraf, 1986; Cox, 1993; Morales, 1994; Kastner 1996 and 1999). Biofilters have also been used to remove odorous compounds such as H_2S and ammonia (Tang et. al., 1996; Leson and Winer, 1991; Yang and Allen, 1994; Prokop and Bohn, 1985; Chung and Huang, 1998; Weckhuysen et. al., 1994; Smet et al., 2000). Recently, compost based reactors were shown to remove NH_3 at high rates (14.6 mg NH_3/m^3/hr) and inlet concentrations (> 70 mg/m^3; Smet et al., 2000). Ammonia oxidation probably occurred due to the presence of

nitrifying bacteria in finished compost, since inoculation of these bacteria was not required. Ammonia toxicity was not observed even at inlet concentrations as high as 550 mg/m^3 (~790 ppm). However, inhibition was eventually observed due to NH_4NO_3 build-up.

Given the advantages of biofilters, multiple large-scale units have been installed and operated for several years in industrial applications (Special Biofiltration Issue: Environmental Progress (18) 1999; Devinny et al. 1999). However, most ammonia biofiltration projects have focused on small bench-scale units and no research has been conducted on actual waste streams in the United States. Design procedures for biofilters in agricultural processes have been developed, but lack critical eliminates (Phillips et al., 1995; Scotford et al., 1996). These design procedures did not measure ammonia degradation kinetics critical to accurate sizing. Thus, although biofilters have been successfully used for odor and volatile organic compound control for 20 years or more, no design data are available applicable to swine operations. Little data are available on ammonia and VOC degradation kinetics in swine operations, scale-up effects on conversion, effect of ammonia cycling on conversion, reactor longevity, pressure-drop versus time, water requirements, and feasibility of using compost as the catalyst for NH_3 degradation. This information is critical to accurately cost and size biofilters for the desired outlet concentration.

IV. OBJECTIVES

1. Install and operate a pilot scale biofilter at a swine operation to treat ammonia and VOC emissions.
2. Determine the degradation rate of the air pollutants and the residence times required for 90, 95 and 99% removal.
3. Obtain kinetic data on the degradation of ammonia and VOCs in the air emissions.
4. Use the kinetic data to develop rate laws for use in reactor design equations to predict packing volume and reactor size required at full scale.
5. Provide a preliminary design and cost for a full-scale biofilter system.
6. Quantify the composition and concentration of air pollutants from the swine operation, with ammonia as the main compound of interest.
7. Evaluate the potential of an electronic nose as a real time sensor.

V. MATERIALS AND METHODS

Many biofilters designed for agricultural processes have ignored the kinetics of oxidation of the air pollutant and proposed packing material based on pressure drop requirements and cost alone. Ignoring degradation kinetics of the target air pollutant can lead potential errors upon scale-up. Thus, a range of media were chosen and tested at the bench scale to determine both pressure drop and if the packing material was capable of degrading ammonia. These tests were designed to define a packing material for the field trial and determine the kinetics of ammonia degradation for modeling of the process.

Biofilter Media Description (Bench Scale):

Four different media types were used in this study: 1) rice hulls/hen manure compost, composted in a 2:1 hulls to manure volume ratio, 2) peat moss, 3) pine bark, and 4) yard waste. The different media were sieved to determine particle size distribution. Bark contained small to mid size nuggets having the highest media particle sizes. Yard waste and peat media contained small particles with yard waste containing some large particles. Rice hulls particles were evenly distributed with the majority in the mid range. The initial weight and height of the media were determined before start-up.

Before use, the biofilter media were analyzed for bulk density, pH, nitrate and ammonium concentration and for moisture content. Except for rice hulls, which were recently composted, other media had a low pH (below 7.0). Also, the relatively high nitrate and ammonium concentration of rice hulls was attributed to the presence of composted hen manure. Moisture content was adjusted to approximately 55 %, which is in the desirable range (40-60 %) for biofilter media.

Pilot Scale Biofilter:

A mobile, skid mounted biofilter was used to determine biofilter feasibility (Fig. 1). The biofilter system consisted of a packed-bed humidifier and two reactors, each constructed of fiber-reinforced plastic. The two reactors were 4 ft in diameter and 4 ft in height. A variable speed blower, 10-100 SCFM, was used to draw air from one the exhaust fans at the swine facility. The slip-stream consisted of flexible corrugated PVC pipe connected to the intake (suction side) of the blower. Gas sample ports were installed along the reactor to determine concentration profile for kinetic analysis. The reactors had a packing volume of approximately 12.5 ft^3 per reactor or 25 ft^3 total with a support matrix (plastic plenum – Fig.2) for air distribution (for upward flow). In our study, air was passed downward across the reactor bed. Moisture was added via spray nozzles in each reactor and on-line monitoring system of flow, pressure drop, and temperature was used.

Figure 1. Pilot scale biofilter system configured for in-series flow (humidifier, and Reactors right to left).

Pilot Scale Biofilter Media:

The media for the mobile biofilter was 4:1 yardwaste compost/plastic bulking agent or yardwaste compost alone. The yardwaste compost was screened to remove all particles greater than one inch. The compost was produced by the University's physical plant from organic debris (mostly woody) collected from the campus. The material is transported to the BREC and stored. Approximately every 6 months a tubgrinder grinds the material. The ground material is then placed in 360 ft windrows. The windrows are turned periodically. Eventually the material is deemed finished (9-12 months). The material we started with for this project had been screened with a 2-inch screen.

Analysis:

Pilot Scale Ammonia:

Ammonia concentration was measured using coloring tubes (RAE Systems, Model #100-05, Sunnyvale, CA) and an ammonia sensor (Polytron 2, DRAGER, Germany). The Polytron 2 was factory calibrated and the calibration was checked in our lab using a gas standard generator (Kin-Tek, LaMarque TX). Inlet NH_3 concentration was varied (0-100 ppmv) for various runs in the bench scale studies and the pilot scale system (0-25 ppmv). Ammonia concentration was measured at the inlet, outlet, and the three ports along each column in the bench scale studies. Similarly, ammonia concentrations were analyzed at the inlet, along the three sample ports and the outlet of each reactor in the pilot scale studies.

Electronic Nose:

A handheld electronic nose designed by Cyrano Sciences (Cynose-320). The Cyrano Science unit contains a 32-sensor chip that generates a unique digital signal, dependent on the air pollutant composition and concentration. Statistical software is included with the unit for principal component and signal analysis, and PC interfacing. Acquired data is downloadable via an RS-232 and USB port.

Pilot Scale Kinetics:

Swine Facility

RAE ammonia tubes (Model #100-05) were used to determine the NH_3 concentration (ppmv) of the exhaust from the hog farm (inlet) compared to the concentration of ammonia in the air exiting the biofilter from both reactors. The tube was placed directly in the flow and a 100 ml sample was taken over a minute. The concentration was estimated from the tube by observing how far up the tube the media changed from purple to beige, which corresponded to a scale of 1-30 ppmv.

After a sample was taken from all three locations the airflow was increased by turning the fan up to the next predetermined location. While the concentration equilibrated for 15 minutes, airflow measurements were taken with a TSI air velocity meter (Model # 8355). The flow-meter gave digital readings for air velocity, volumetric flowrate, and air temperature on an average basis. The readings were taken at two points, one before the split to the reactors and one on the line to the second reactor. Therefore, total flow and the flow to reactor two were measured, and flow to reactor one was calculated.

Simulated NH_3 Stream

During a majority of the kinetic analysis at the swine facility, inlet NH_3 concentrations ranged from 0-10 ppmv. In order to test the effect of increasing NH_3 concentrations on removal efficiencies it was decided to bring the unit back to UGA and set-up a simulated NH_3 stream. A separate source of NH_3 (off gas from a tank of liquid NH_3) was fed into the air stream. Ammonia was injected before the humidifier and after the blower (note the humidifier was not operated to prevent removal of ammonia in this unit operation). The inlet and outlet concentrations from the biofilter were analyzed to determine the fractional removal efficiency of ammonia. The flow rate from a tank the liquid ammonia was controlled by a Dwyer flow meter with a range of 0-1 L/min. The flow meter was set for 0.2 L/min to give an approximate concentration of 25 ppmV at the inlet. However, periodic oscillations in the inlet concentrations were observed due to temperature fluctuations during the day.

Draeger Polytron 2 transmitters with ammonia sensors monitored the inlet and outlet concentrations. A Campbell Scientific 21X data logger collected the data from the three transmitters. The data logger received a 4-20 mA signal averaged over 60 seconds and was recorded every 5 minutes. The data was collected daily using Campbell Scientific computer software.

Ammonia RAE tubes were used daily at the inlet and outlets to manually check the concentration and the calibration of the Polytrons. The tubes had a range of
0 – 30 ppmv, and a sample volume of 100 mL. Other parameters monitored daily were temperature and relative humidity at the inlet and outlets. They were observed using an Omega Digital Humidity Meter, Model RH30-C. The airflow through the reactors was measured using a TSI VelociCalc, Model 8355. Also, once a week the RAE tubes were used to take a profile of the reactors to monitor the removal over the column.

Pilot Scale Moisture Analysis:
Moisture content of the media was determined occasionally by a gravimetric method and adjustments made accordingly. However, it was difficult to blend water uniformly with the media without removing the media from the column. The pressure drop across each column was also determined as function of flow rate. Finally, relative humidity and temperature were measured at each port when conducting kinetic studies using a digital humidity meter probe (Model RH30-C, OMEGA Engineering, Stanford, CT). The initial moisture content of the composted yard waste used in the pilot scale biofilter was approximately 35-40% (wet weight, g/g). On a periodic basis water was added via the spray nozzles in each reactor to first raise the moisture content to 50-60% and then maintain the moisture content in this range.

Packing Material – Pilot Scale Biofilter
Based on bench scale results and other research conducted within our group the following decisions were made regarding the packing material for the pilot scale biofilter system. A compost-based material was used since compost contains a large number of active microorganisms; it is relatively inexpensive and easily available. The compost was pre-screened to exclude fine particle sized material that can cause pressure drop problems. Recently finished compost that was processed using a windrow composting operation was chosen. The compost was amended with an inert packing material (e.g., plastic saddles) to increase porosity, minimize pressure drop and minimize compaction and channeling (Fig. 2). Another reactor received an organic amendment (compost alone) in order to compare the effect of the different amendment types (Fig. 2). Although less expensive, organic amendments are anticipated to degrade with time causing compaction, increased pressure drops and channeling. The media was not inoculated (e.g., with activated sludge) before or after start-up. The reactors were packed to a height of 2.83 ft, resulting in approximately a 35.6 ft^3 active reactor volume.

A

B

C **D**

Fig 2: Packing material used in pilot scale biofiltration of ammonia: A – plastic plenum, B and C – compost mixed with inert plastic saddles (Reactor 2) and D – compost only (Reactor 1).

Pulse Tracer Analysis:

A hydrocarbon tracer analysis was completed on the biofilter on June 18th and 19th, 2002. One liter of 1% CH_4 (10,000 parts per million) methane was injected in the 4" PVC pipe using a calibrated syringe just in front of the biofilter. Using a Thermo Environmental 680 Hydrocarbon Vapor Meter connected to a port after the biofilter, the air was sampled and recorded every second until the concentration had dropped to zero again. This was repeated four times at predetermined flow rates repeated at the end of July, using two liters of 1%, 10,000 ppmV methane.

VI. RESULTS

Kinetics of Ammonia Removal (Objectives 1-6)

An important objective in reactor design is to determine a rate law that can be substituted into a design equation to estimate the reactor volume or catalyst mass required for the desired conversion. It was initially assumed that the biofilter acted as a plug flow reactor and first order kinetics applied (equation 1), since the inlet ammonia concentrations were low (0-5 ppmv at the Swine Facility; 0-25 ppmv during simulation studies at UGA). Removal efficiencies ($[Cg_{in}-Cg_{out}]/Cg_{in}$) for reactors treating a simulated ammonia stream ranged from 70 to 100% conversion for inlet flow rates of 16-30 ft^3/min (70-133 sec residence) and ammonia inlets from 8-25 ppmv (Figs. 3 and 4). Removal efficiencies were much lower at lower inlet concentrations (0-5 ppmv at the Swine Facility) and residence times (Table 1).

The design equation for a tubular or plug flow reactor was used to calculate a rate constant and reaction order, assuming a homogeneous system, constant reactor volume (V), constant pressure, constant temperature, and O_2 in excess. The integral method was used to determine the rate constant, k and the reaction order, n (again n was assumed to be 1). The form of the rate law was assumed (e.g., 1st order – Equation 1), substituted into the design equation (Equation 2), integrated and solved for k, assuming a constant flow rate (Equation 3). If after changing the mass flow rate, F_A by changing the inlet flow rate, Q or the inlet concentration, C_{Ao}, k remains constant, then the form of the rate law is correct and k and n are known (over the range of conditions tested – Smith 1981).

$$-r_A = kC_A \quad \textbf{(1)}$$

$$\frac{dF_A}{dV} = -r_A \quad \textbf{(2)}$$

$$k = \frac{Q}{V}\ln\left(\frac{C_{Ao}}{C_A}\right) \quad \textbf{(3)}$$

Where, $-r_A$ is the ammonia degradation rate, k is the first order rate constant, F_A is mass rate of ammonia, V the reactor volume, Q the volumetric flow rate, C_{A0} is the inlet gas phase concentration, and C_A is the outlet concentration. There are two ways to analyze equation 3 to determine k. The rate constant k can be calculated at each point (i.e., fractional conversion) or a plot of V/Q versus $\ln(C_{A0}/C_A)$ can be made with the slope equal to k. The value in the first method is that if a systematic change occurs in k, this suggests the first order assumption may be incorrect. The systematic increase in k (first order) with fractional conversion for data sets from both reactors does suggest that a first order overall model may not be valid (Fig. 5). However, assuming a zero order rate law (i.e., $-r_A$ = k) gave a larger variation in the rate constant, suggesting that the reaction order at these concentrations was first order (Fig. 5). Thus, the first order rate constant was 0.08±0.03 1/sec and 0.051±0.03 1/sec for reactor 1 and 2 respectively. In addition, analysis of data at higher inlet NH_3 concentrations again indicated that the overall rate of NH_3 was first order; the second order rate constant increased linearly with NH_3 concentration compared to relatively constant value if first order was assumed (Fig. 6). The average first order rate constant was 0.038 1/sec and 0.011 1/sec for reactor 1 and 2 respectively (Table 2); similar in value to the previous results (Table 1), but lower than the values based on analysis performed at the swine facility and lower inlet concentrations.

Assuming an overall first order reaction, the NH_3 reaction rate (mg consumed/m^3 of packing/s) was calculated over a range of inlet concentrations (Equation 1) for kinetic analysis performed both at the swine facility and the simulated experiment. In general the reaction rate was higher in reactor 1 (compost only) compared to the reactor with compost and saddles (reactor 2) – see Fig. 7. This may have been due to the, on average, lower moisture content in reactor 2 (see Table 3).

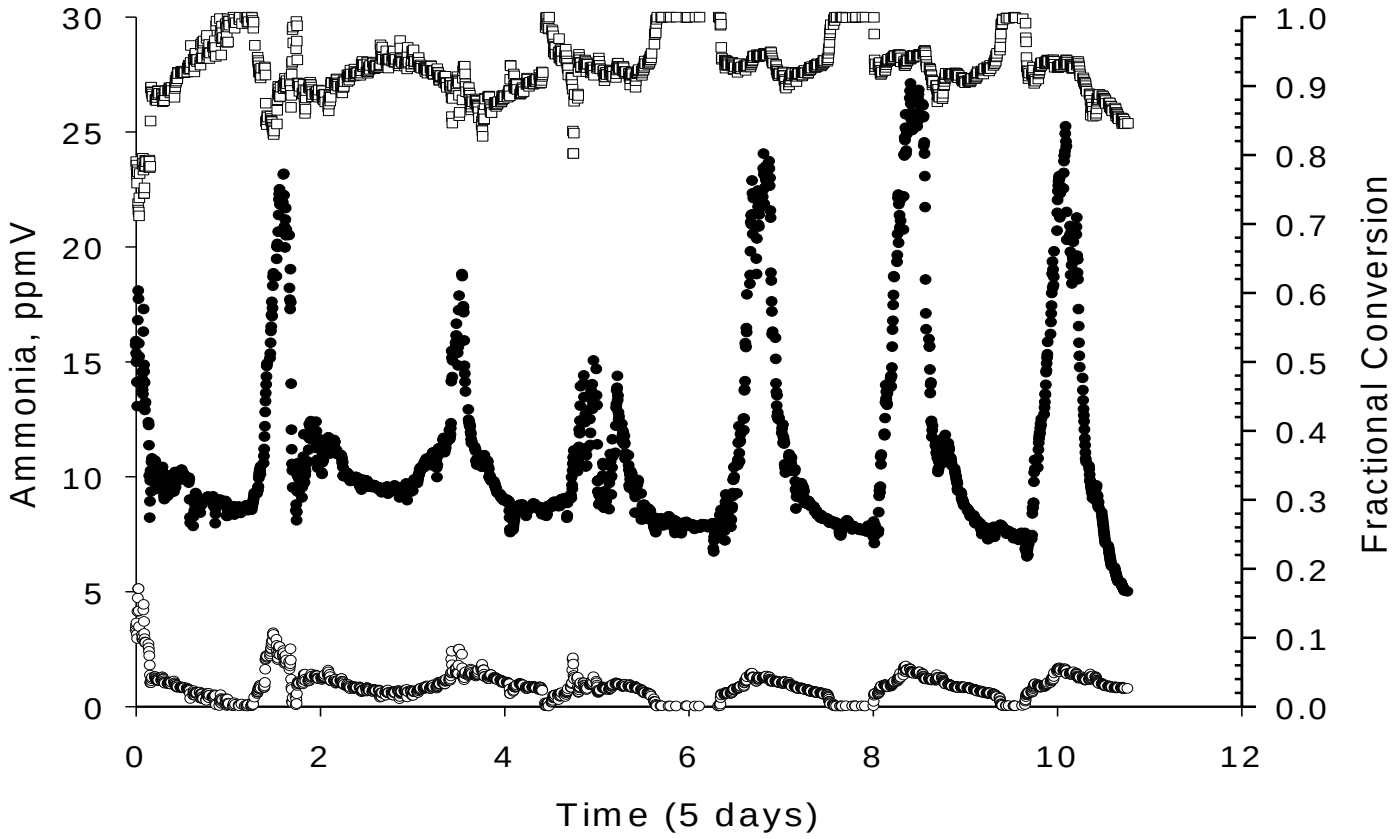


Fig. 3: Ammonia removal efficiency in a biofilter packed with compost only at a residence time of 70.5 seconds (Q=0.014 m^3/s). ●, inlet NH_3; ○, outlet NH_3, and fractional conversion, □.

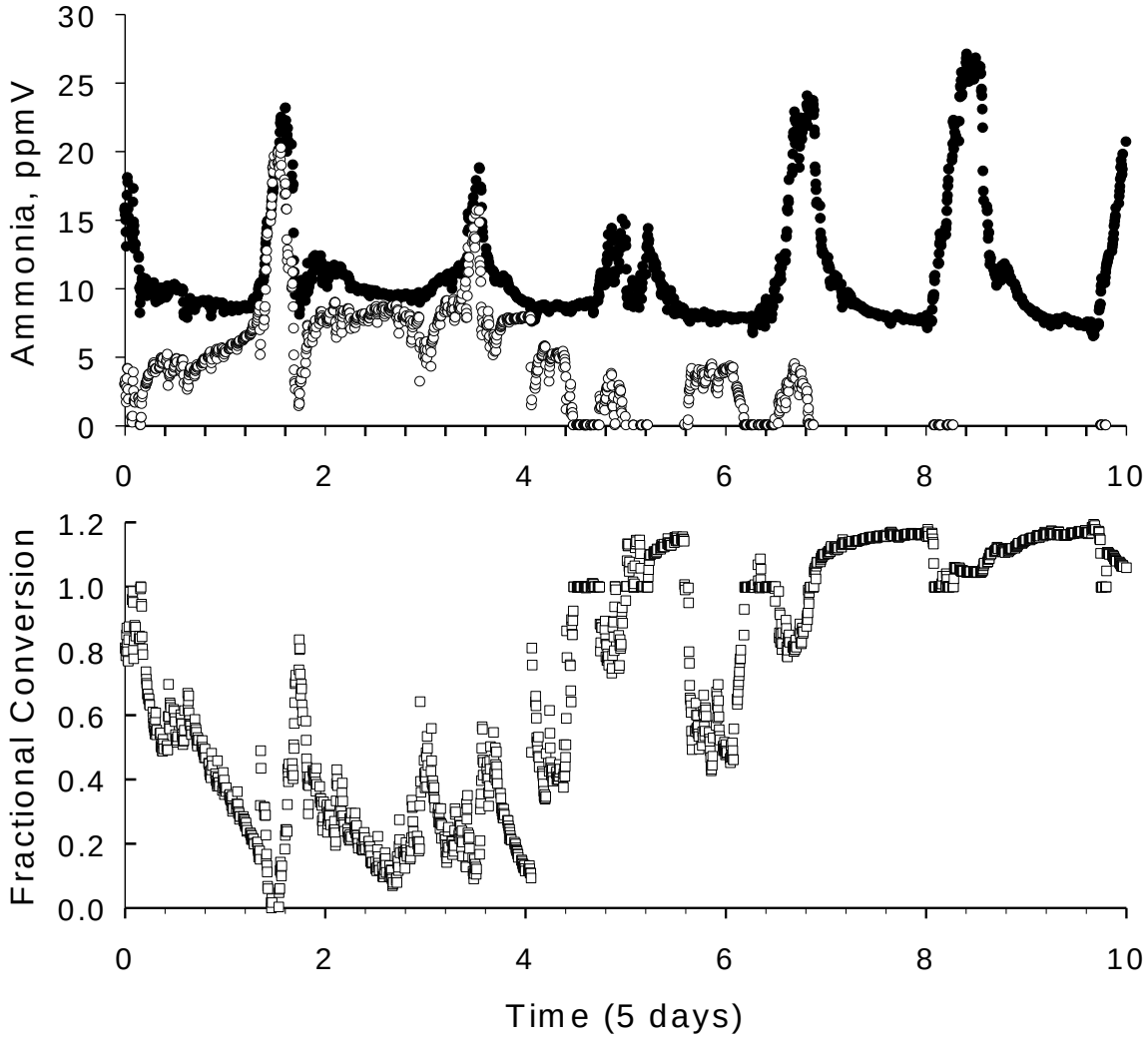


Fig. 4: Ammonia removal efficiency in a biofilter packed with compost and plastic saddles at a residence time of 133.5 seconds (Q=0.008 m^3/s). ●, inlet NH_3; ○, outlet NH_3, and fractional conversion, □

Table 1: Kinetic analysis of a biofilter treating low inlet concentrations of ammonia at a Swine facility.

Experiment	Reactor #1				Reactor #2			
	Inlet NH_3, ppmv	Outlet NH_3, ppmv	Residence Time, sec	k, 1/sec	Inlet NH_3, ppmv	Outlet NH_3, ppmv	Residence Time, sec	k, 1/sec
1	5	2	21.866	0.050	5	3.5	17.74	0.023
2	6	1.5	13.467	0.112	6	2	15.11	0.092
3	4.5	2	17.80223	0.051	4.5	3	15.82	0.026
4	5.5	1	16.123	0.093	5.5	2	14.99	0.084
5	5	2	14.93894	0.073	5	3	14.05	0.049
6	5	1	13.394	0.104	5	3	13.39	0.052
7	5	2	14.33737	0.077	5	3.5	14.05	0.029
8	5	1	12.947	0.107	5	3	12.75	0.054
Mean±sdev				0.083±0.02				0.051±0.03

Table 2: Kinetic analysis of a biofilter treating high inlet concentrations of ammonia in simulated stream.

Time, day	Range	Reactor #1			Reactor #2			
	Inlet NH_3, ppmv	Outlet NH_3, ppmv	Residence Time, sec	k, 1/sec	Inlet NH_3, ppmv	Outlet NH_3, ppmv	Residence Time, sec	k, 1/sec
1	8		70.5		8		133.5	
5	20				20			
Mean±sdev				0.038±0.013				0.011±0.016

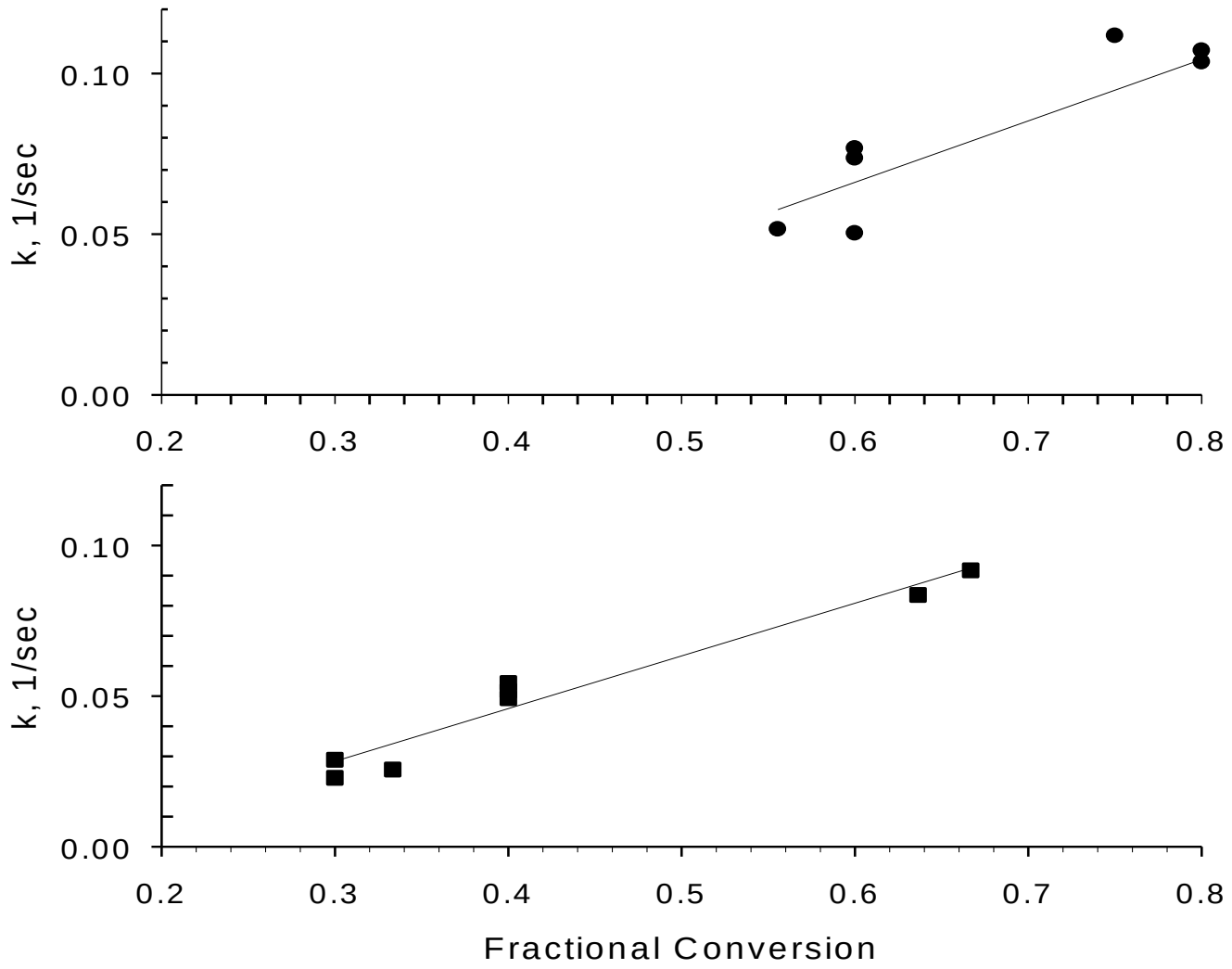


Fig. 5: First order rate constant for ammonia degradation in a compost-based biofilter treating emissions from a Swine Facility (NH_3 inlets ranging from 5 to 6 ppmv). ●, reactor 1 and ■, reactor 2 with plastic saddles.

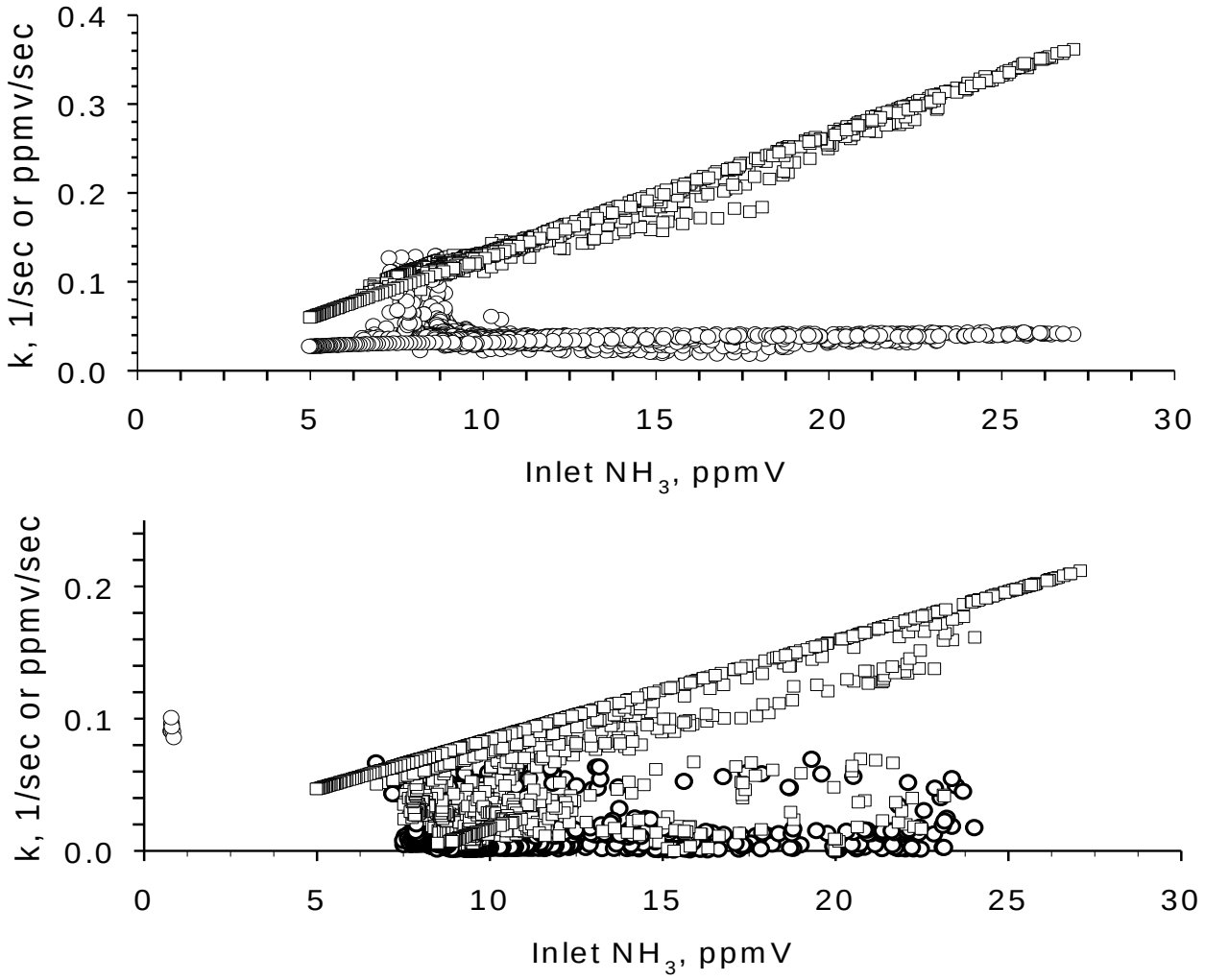


Fig. 6: Comparison of first (○) and second order (□) rate constants for ammonia degradation as a function of inlet NH_3 levels in a compost based biofilter treating simulated NH_3 emissions. Reactor 1 (top) and reactor 2 (bottom) with plastic

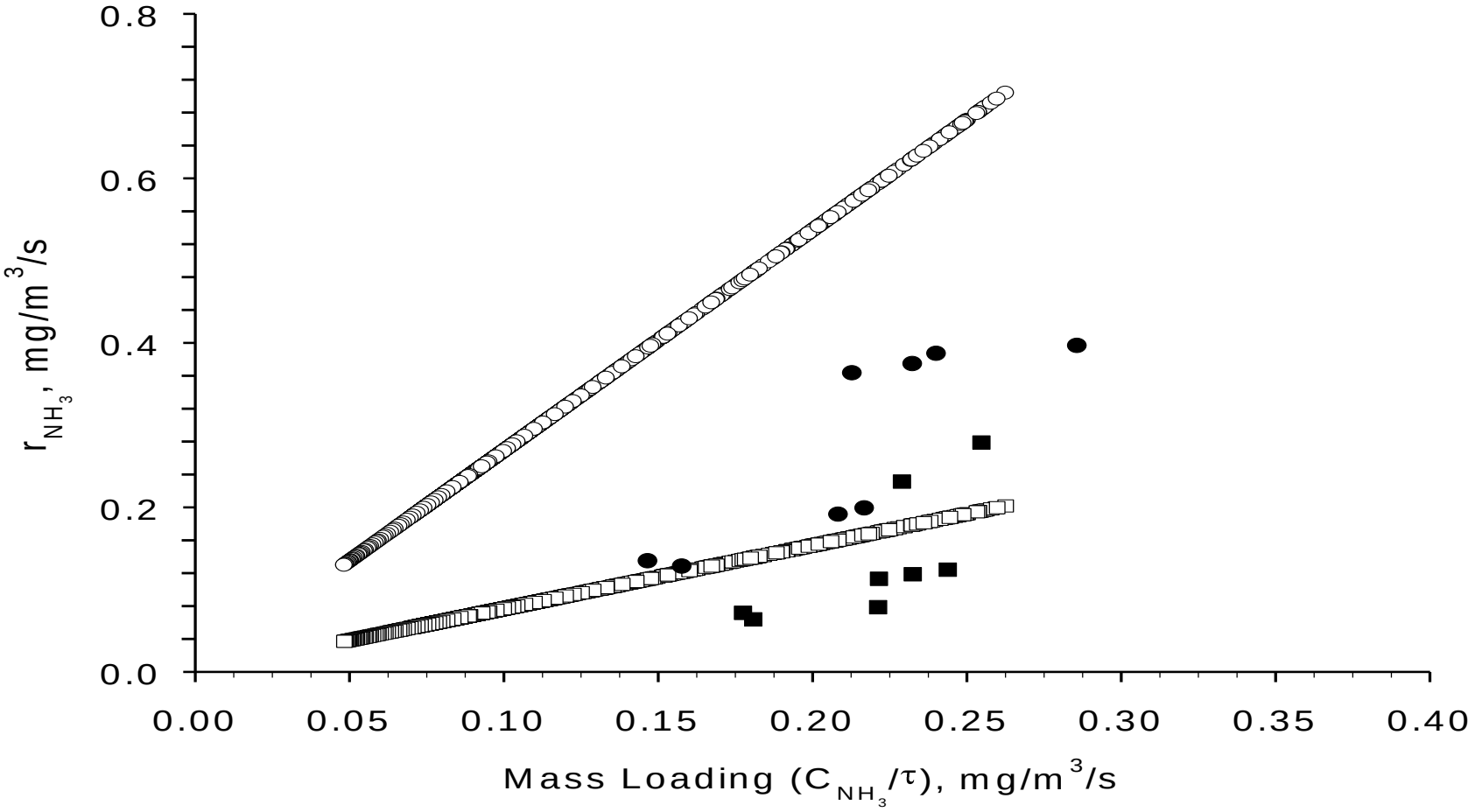


Fig. 7: Estimation of the overall degradation rate of ammonia (mg/m^3/s) as a function of the inlet mass loading of ammonia based on the first order rate constant derived from each kinetic experiment. ○, simulated study compost only; ●,swine facility study compost only (reactor 2); □, simulated study compost plus saddle; ■, swine facility with compost plus saddles.

Effect of Moisture Content

One of the primary difficulties in operating the biofilter was to maintain adequate moisture content for microorganism survival or activity and thus ammonia degradation. Due to the high flow rates, low inlet relative humidity, and the non-uniform distribution of the spray nozzles, the moisture content of the packing material fluctuated significantly (Tables 3 and 4). It is apparent from Tables 3 and 4, and Fig. 8 that the moisture content declined with depth in the direction of air flow (downward across the bed), although moisture was added at the top via spray nozzles. Investigation of the spray pattern indicated that the water stream was not significantly uniform to provide contact with the entire packing, thus resulting in preferential wetting. In addition, comparison of the profiles of ammonia concentration along the length of packing with moisture contents at different depths, demonstrate the effect of low moisture content on removal efficiency. If the moisture content was above 30-40%, ammonia was oxidized in the reactor (Fig. 8, top), but declines in moisture content significantly reduced removal efficiency (Fig. 8, bottom). For example, overall ammonia removal efficiency only reached 30% when the moisture content was at or below 30%, compared to 80% when the moisture content in 50% or more of the bed was above 50% moisture content (Fig. 8). It also clear from these data that ammonia removal rates could be increased if moisture control is maintained; e.g., based on the ammonia profile and moisture content analysis only approximately 20-50% of the packing was utilized (Fig. 8).

Table 3: Change in moisture content as a function of position within reactor 1 (compost only) with a total packing depth of 0.861 m.

		Moisture Content										
Position, m / Date	1/23/02	2/13	2/21	3/7	3/19	4/5	6/1	6/25	7/8	7/11	7/22	8/8
0.10 – top		13	45	9.2	7.0	16.45	25.8	36.5	28	14	26.4	6.2
0.405 – middle		18	12.5	10.3	8.0	9.28	56.0	54.7	49	50.7	8.7	17.3
0.71 - bottom		47	48	41.5	14.4	10.84	62.2	59.1	58	58.3	34.7	41.9
Mean		26	35.27	20.3	9.8	12.19	48	50.1	45	41	23.3	21.8
Mean, over entire period												30.24

Table 4: Change in moisture content as a function of position within reactor 2 (compost with plastic saddles) with a total packing depth of 0.861 m.

		Moisture Content										
Position, m/ Date	1/23/02	2/13/02	2/21	3/7	3/19	4/5	6/1	6/25	7/8	7/11	7/22	8/8
0.10 – top		15	33	8	14.5	38.64	14.9	37.7	20.6	9.4	27.8	9.7
0.405 – middle		37	18.5	10.6	8.8	17.75	30.8	30.9	28.9	32	6.5	14.5
0.71 - bottom		57	51.7	36.5	11.7	14.65	50.7	39.2	54.4	49.8	13.2	39
Mean		36.33	34.4	18.36	11.67	23.68	32.13	35.93	34.63	30.4	15.83	21.1
Mean, over entire period												26.7

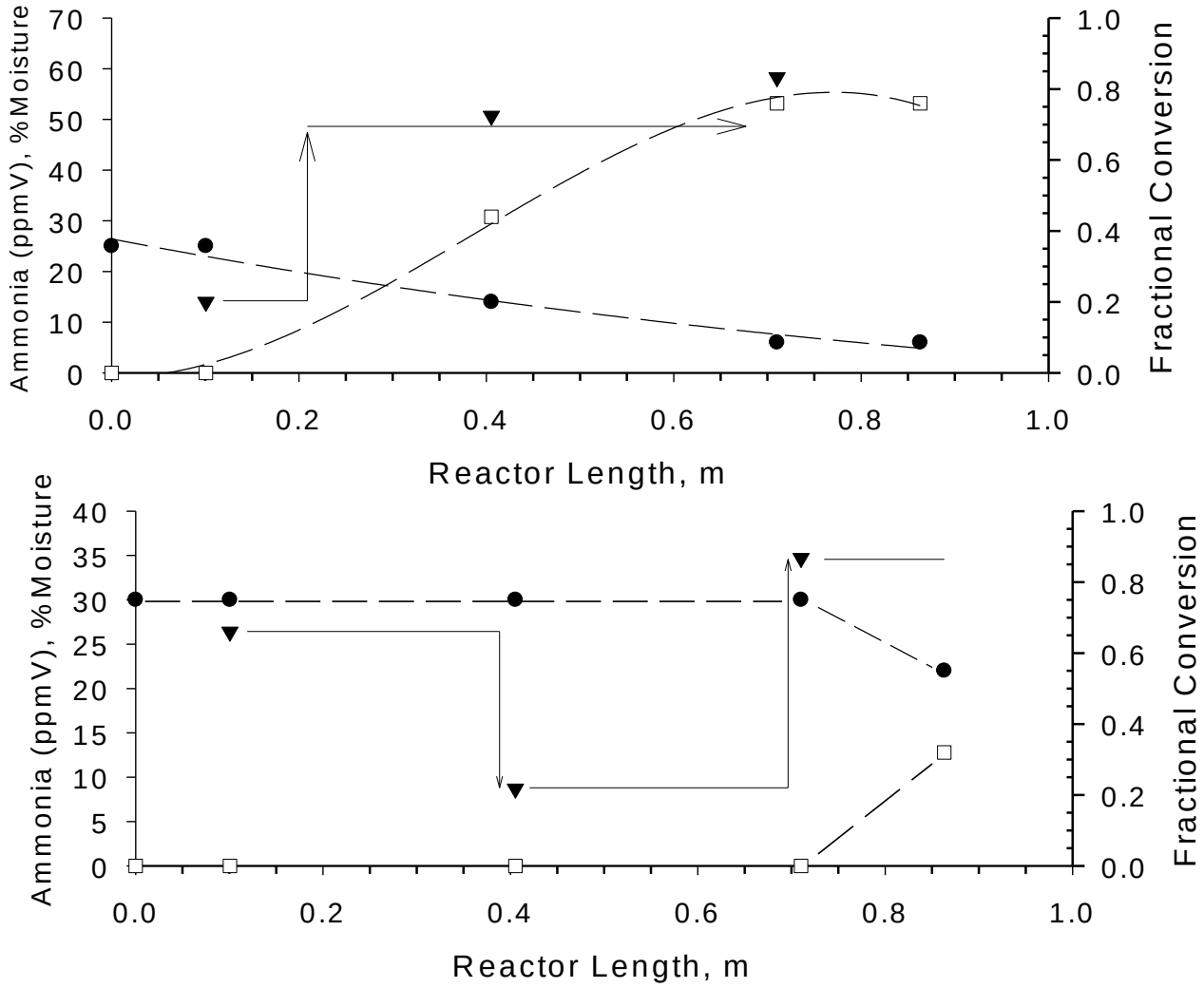


Fig. 8: Effect of moisture content (▼) on the profile of ammonia removal (concentration, ●; fractional conversion, □) along the length of the reactor at two different times (Top – 7/11 through 7/15/02 and Bottom -7/22/02) in the reactor with compost only.

Non-Ideal Reactor Design

Residence Time Distributions

Compost based biofilters are packed-bed reactors typically assumed to be of the plug flow type. However, as reactors are scaled-up, height to diameter ratios decrease significantly (to reduce pressure drop, packing heights are typically limited to 3-5 ft), which may cause channeling and bypassing of the media. Wetting and drying cycles may also cause preferential path formation and channeling as well; all of which would reduce the effective reactor volume and reduce predicted conversion efficiencies. In order to evaluate the potential of non-ideal flow patterns in the reactors and their consequence on conversion, a tracer analysis test was performed. Methane, a relatively inert, poorly water-soluble compound was used as the tracer. Methane was used since little would dissolve into the moisture or be consumed in the reactor during the short duration of the pulse analysis (in most compost there are few bacteria, i.e., methanotrophs, present that are capable of degrading methane, especially if the reactor media has not been pre-exposed to methane). In addition, use of methane as the tracer allowed continuous monitoring of the outlet stream for presence of the tracer using a hydrocarbon tester. The resultant shape of the outlet tracer concentration versus time curve would be indicative of channeling or extensive dispersion within the reactor indicating deviation from ideal plug flow.

Methane pulse tracer analysis indicated that flow through the compost beds deviated from plug flow, however distinct channeling was not observed (i.e., that is a bimodal distribution in the concentration versus time curve was not observed). A typical tracer analysis is shown in Figure 9 (CH_4 recovery ranged from 65-100.3%). The residence time distribution (RTD) analysis was subsequently developed from the tracer data and application of equation 3 (the data were numerically integrated to obtain the RTD). The true mean residence time (t_m) was calculated using the tracer data and equation 4.

$$E(t) = \frac{C(t)}{\int_0^\infty C(t)\,dt} \qquad \textbf{(3)}$$

$$t_m = \int_o^\infty tE(t)\,dt \qquad \textbf{(4)}$$

The RTD studies were also used to estimate dispersion within the packed bed reactors (i.e., deviation from plug flow). The vessel dispersion number (or $1/P_e$, where P_e is the Peclet number) was calculated from the tracer analysis, E(t), t_m and equation 5 (second moment about the mean or variance – Fogler 1986).

$$\sigma^2 = \int_o^\infty (t - t_m)^2 E(t)\,dt \qquad (5)$$

The vessel dispersion number was calculated from the variance and equation 6 by trail and error numerical solution (Fogler 1986).

$$\sigma^2 = t_m^2 \left(\frac{2}{P_e} - \frac{2}{P_e^2} \left(1 - e^{-P_e} \right) \right) \qquad (6)$$

Vessel dispersion has reported ranges of $1/P_e < 0.025$ (small), $0.025 < 1/P_e < 0.2$ (intermediate), and $1/P_e > 0.2$ (large – Fogler 1986). The Peclet number is equal to the linear velocity (U) times the packing length (L) divided by the effective dispersion coefficient (D_e).

In our experiments, the vessel dispersion number ranged from 0.03 to 0.08, indicating that deviation from plug flow was in the intermediate range. In addition, it appeared that as the height to diameter or width of the reactor was decreased, dispersion increased; e.g., there was less dispersion in the bench scale reactors with a H/D ratio of 6/1 compared to the pilot scale reactors at a H/D less than 1 (Fig. 10). These data suggest that scale-up to treat larger volumetric flow rates will result in significant deviations from ideal plug flow that must be accounted for in the design equations; i.e., the packing volume required for 95% or greater ammonia conversion could be significantly larger than that predicted using first order kinetics alone. For example, a typical biofilter treating 100,000 to 125,000 ft^3/min has dimensions of 3 ft H x 40ft W x 100 ft L or a H/W ratio of 0.075, which could result in significant dispersion. This could result in under estimating the packing volume required to treat the ammonia emissions due to the reduction in the effective reactor volume relative to ideal conditions.

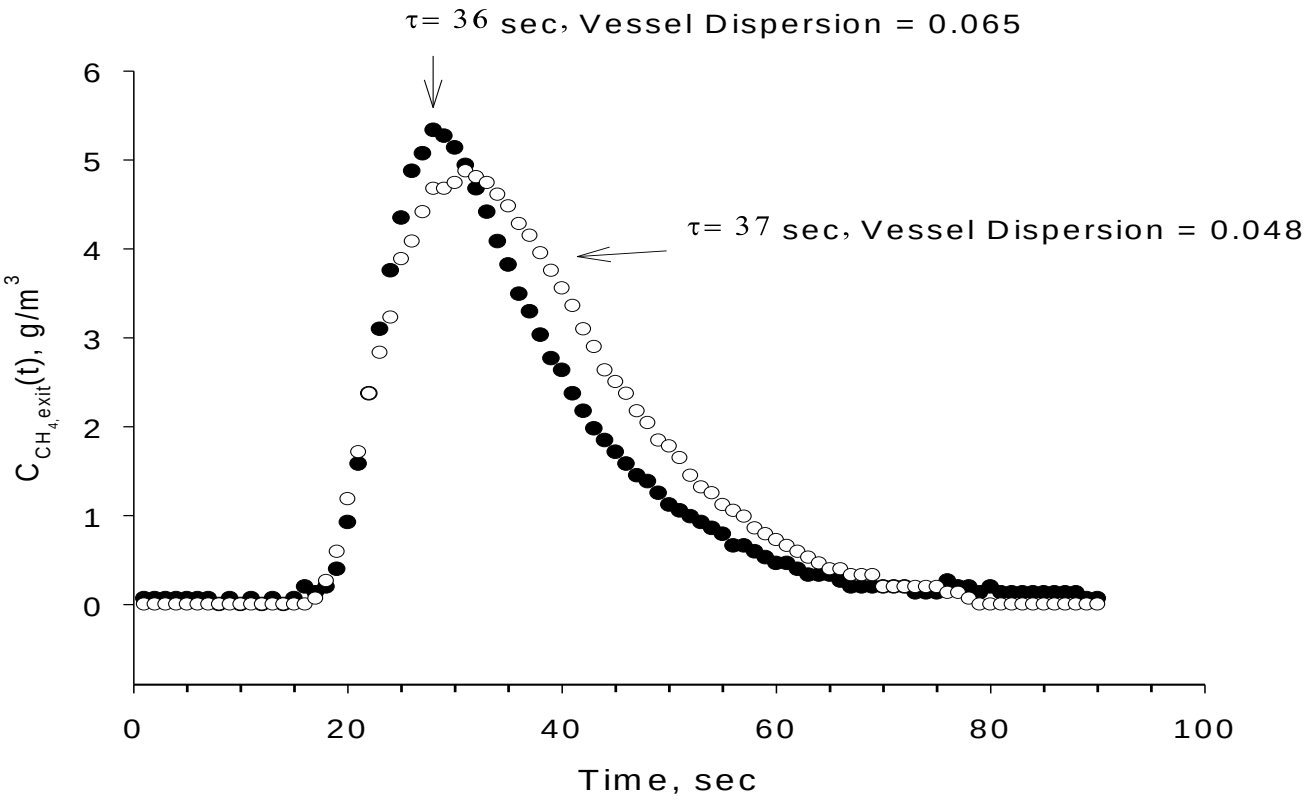


Fig. 9: Pulse tracer analysis of biofilter reactors (H/D = 0.7) used to treat ammonia emissions. Top: the true mean residence time and the vessel dispersion number are reported for each reactor with compost only ●, and reactor 2, with saddles, ○. Bottom: RTD analysis for bench scale reactors at H/D ratio of 6/1.

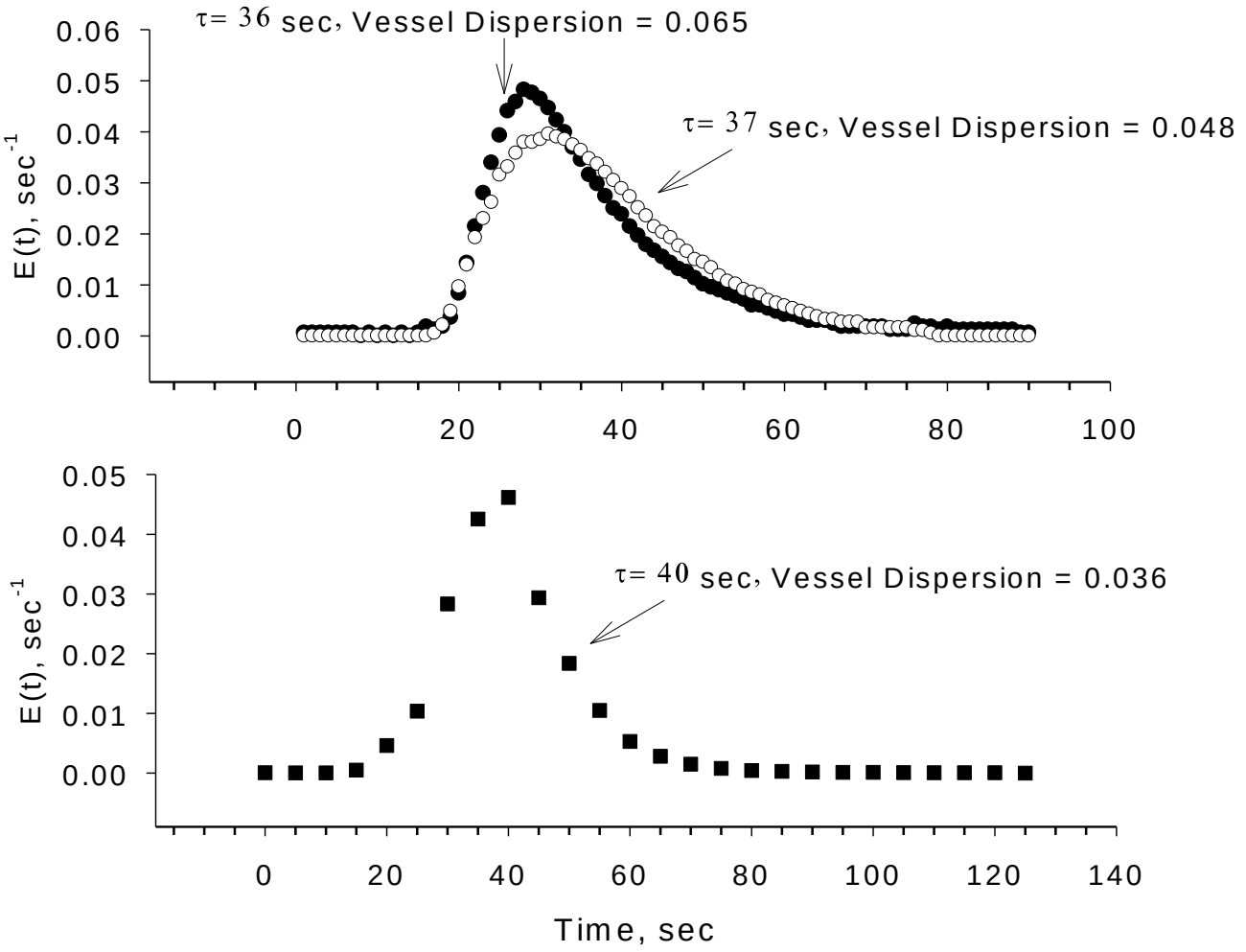


Fig. 10: Residence time distribution analysis of biofilter reactors (H/D = 0.7) used to treat ammonia emissions and the resultant residence time distribution. Top: the true mean residence time and the vessel dispersion number are reported for each reactor with compost only ●, and reactor 2, with saddles, ○. Bottom: RTD analysis for bench scale reactors at H/D ratio of 6/1.

Sizing the Reactor

As noted by Lesson and Winer (1991), biofilter design should be based on bench or pilot scale kinetic data. Thus, once the rate law ($-r_A$=f[rate constant, C_A, temperature]) has been determined it can be inserted into the design equation and solved for the reactor volume (equation 7), given the inlet conditions and required removal efficiency or X ($X=[C_{Ain}-C_{Aout}]/C_{Ain}$). Equation 7 assumes that Q is constant and that r_A depends on only one species. The presence of multiple VOCs would require separate kinetic data. Depending on the operating kinetic region(s) the volume required for the desired conversion will vary with the order and flow rate.

$$V = Q \int_{C_{Ao}}^{C_A} \frac{dC_A}{-r_A} \qquad \textbf{(7)}$$

Sample calculations follow in which the reactor design approach is used to size a biofilter to remove ammonia from a hypothetical swine facility stream of 40 m^3/s and 5 ppmv ammonia (3.3 mg/m^3, T= 25°C, C_{Ao}), and 6 m^3/s and 25 ppmv (16.5 mg/m^3). The ventilation flowrate was estimated from Nicoli and Janni (1998) based on the maximum and minimum ventilation rates (i.e., summer and winter) for a sow gestation building and a deep pit system. Inlet NH_3 concentrations were based on our measured concentration during the summer and projected maximum values to occur during winter months. Calculations were made assuming a 99% conversion is required resulting in an outlet NH_3 concentration (C_A) of 0.033 mg/m^3 and 0.165 g/m^3 respectively. Since the kinetics of ammonia appeared to be first order to 25 ppmV NH_3, a first order rate law was assumed and a rate constant of 0.08 1/s was used (Table 1), resulting in a rate law of $-r_A = 0.08\ C_A$. The rate law was inserted into equation 7 and then integrated resulting in equation 8, which was used to determine the reactor volume required for the two defined conditions (assuming ideal plug flow). Using this approach, reactor (i.e., packing) volumes of 345 to 2300 m^3 were calculated (Table 5).

$$V = \frac{Q}{k} \ln\left(\frac{C_{Ao}}{C_A}\right) \qquad \textbf{(8)}$$

Once the reactor volume required for conversion has been determined, the mass of catalyst (e.g., compost) can be determined from the bulk density or reactor packing density. Compost bulk density has been reported to range from 0.18 to 0.30 g/cm^3 (45.6 to 63 wt % water) and packing densities of 0.5 to 0.7 g/cm^3 have been reported (Kastner et al., 1999; Yang and Allen 1994). We measured a bulk density of 637 kg/m^3 (53% moisture), which was used to estimate the mass of media required for each condition (Table 5). Compost bulk density has been reported to range from 180 to 300 kg/m^3 (45.6 to 63 wt % water) and packing densities of 500 to 700 kg/m^3 have been reported (Kastner et al., 1999; Yang and Allen 1994).

Table 5**:** Predicted packing volumes and mass required for 99% removal of ammonia using first order kinetics. A bulk density of 637 kg/m^3 (53% moisture) was assumed.

Flow Rate Q, m^3/s	C_{Ao}, mg/m^3	X	k, 1/s	V, m^3	Mass, tons
6	16.5	0.99	0.08	345.3878	242.5176
13	10	0.99	0.08	748.3402	525.4549
40	3.3	0.99	0.08	2302.585	1616.784

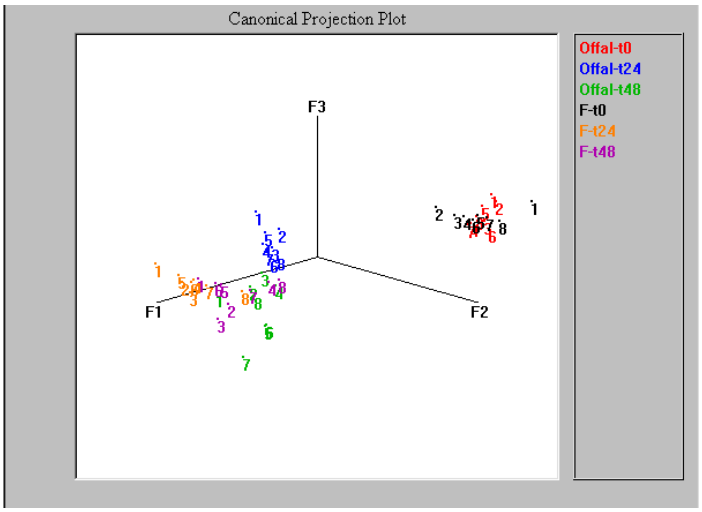
Dimensioning the Reactor

Once the reactor volume has been calculated based on the kinetics of the reaction (and the required conversion and volumetric flowrate), the height and cross sectional area must be specified. The height and cross sectional area of the reactor will be a function of the pressure drop at the required flow rate and should be based on a pressure drop per unit height versus linear velocity curve for the packing of interest. A pressure drop ranging from 100-150 Pa was measured over a linear velocity of 0.04 to 0.14 m/s for the pilot scale biofilter, and higher pressure drops were measured for the bench scale studies with smaller particle sizes (Fig. 12). Nicoli and Janni (2000) measured pressure drops ranging from 20-1000 Pa/m for linear velocities of 0.002 to 0.167 m/s; a pressure drop of 0.20 in H_2O (50 Pa) across the biofilter allowed operation of the ventilation system. Using an allowed $\triangle P/L$ of 50 Pa/m (packing height = 1 m), a maximum linear velocity of 0.025 m/s was defined (Fig. 12), which requires a reactor of 1600 m^2 ($Q = 40$ m^3 s^{-1}; $V = 2300$ m^3; $A_c = Q/U$).

Electronic Nose (Objective 7)

An electronic nose (EO) was tested on rendering emissions (a screening method) to determine if the EO could be used to detect odor concentration and breakthrough in the biofilter process. Samples (offal, feathers, and blood) were collected from a local poultry processing plant in Athens, Georgia, and all incubation studies were begun within one hour of collection. When longer time was required to setup the experiment, the samples were refrigerated at 4°C until needed. Two treatments (15 and 35°C) of incubations were conducted. Each sample (offal, feathers, and blood) was replicated three times. Bottles were placed in a shaker incubator where the temperatures were maintained at the constant value chosen. Sampling was done periodically for a total period of 72 hours. The orange cap of the reactor was removed and an **electronic nose analyzer** (Cynose-320, Cyrano Sciences Inc.) was placed into the neck of the reactor. Sample was drawn for 15 seconds and the lid was replaced on the reactor while the Cynose-320 completed measurement by purging the sensors. The process was repeated for a total of four samples from each reactor.

The electronic nose was not very consistent in distinguishing between samples. It was good at identifying the presence or absences of hydrogen sulfide, but was not effective at differentiating between concentrations. The preliminary results show that the nose can tell some difference between T_0 (initial) samples and T_{24} (24-hour), but it was not as effective at identifying the difference between T_{24} and T_{48} samples as illustrated by the canonical projection of on the 35°C runs (Figure 11).



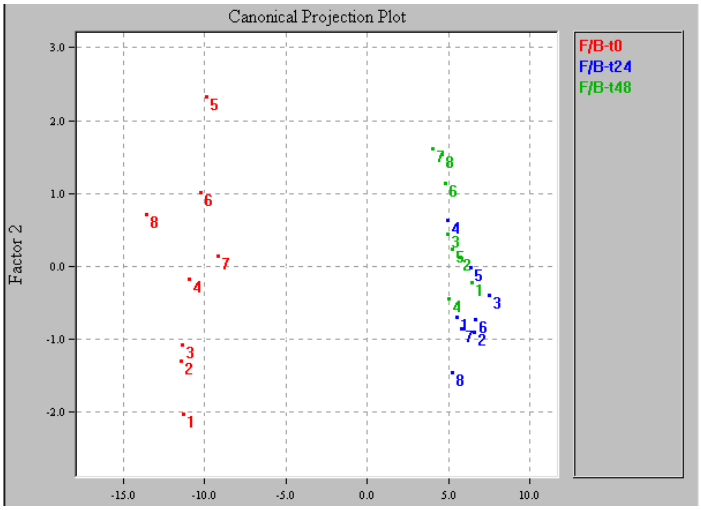


Figure 11. Electronic nose identification using clustering of response sensor. Data collected during incubation of offal at 35°C.

VII. DISCUSSION

Kinetics:

The degradation of ammonia in a pilot scale biofilter has been demonstrated and followed first order kinetics up to an inlet ammonia concentration of 25 ppmV (~17 mg/m^3); that is the removal rate increased with increasing ammonia concentration. The first order rate constant for the process ranged from 0.01 to 0.08 1/s. Using first order kinetics the overall removal rate was calculated to increase linearly with inlet NH_3 concentration and range from 0.04 to 0.8 (mg consumed/m^3 packing/s) for mass loading ranging from 0.05 to 0.25 (mg/m^3/s). Our results compare favorable to Smet et. al., 2000 who measured removal rates of 0.3-2 mg/m^3/s at higher loading rates (0.6-2.6 mg/m^3/s – due to treating higher inlet concentrations, 70-550 mg/m^3) in bench scale reactors.

These data suggest that the compost based biofilter system can handle much higher concentrations of ammonia, if required. Again, similar to our results, Smet et al., reported instantaneous ammonia removal using composted material (not greater than 2 months old), without inoculation of ammonia oxidizing bacteria. These data indicate the value in using composted material as the packing media to minimize start-up time and increase the capacity of ammonia oxidation. It is highly unlikely that using bark, wood chips, or heather alone would have resulted in significant ammonia removal (or a long lag time would be required), given the limited microbial populations in these media. For example, Nicolai and Janni (2001) reported a reduction in ammonia removal if the percentage of compost decreased below 30% in a biofilter system treating ammonia.

Effect of Moisture:

Our results also indicate that the overall NH_3 removal rate could be increased and clearly better maintained if the moisture content is controlled between 45-60% (by weight), potentially reducing the reactor size and mass of compost required to remove the ammonia at a defined conversion. The primary problem with our system was the spray pattern and that fact that we did not pre-humidify the air inlet (this was done to make sure the NH_3 removal was solely due to the biofilter). Prehumidifying the air and using a more uniform distribution pattern for the water in the reactors (e.g., soaker hoses installed throughout the reactor), could significantly improve moisture control. The negative effect on the reduction in ammonia removal efficiency has been previously observed (Nicoli and Janni, 2001; Hartung et al., 2001); both references suggest moisture contents should be maintained above 40% (40-50%). Interestingly, Nicoli and Janni, 2001 observed that reduced moisture content has less of an impact on media composed of higher ratios of compost to wood chips. This may be due to the higher moisture holding capacity of compost. It is clear that future research is required to develop inexpensive methods to prehumidify the air, and monitor and control bed moisture content.

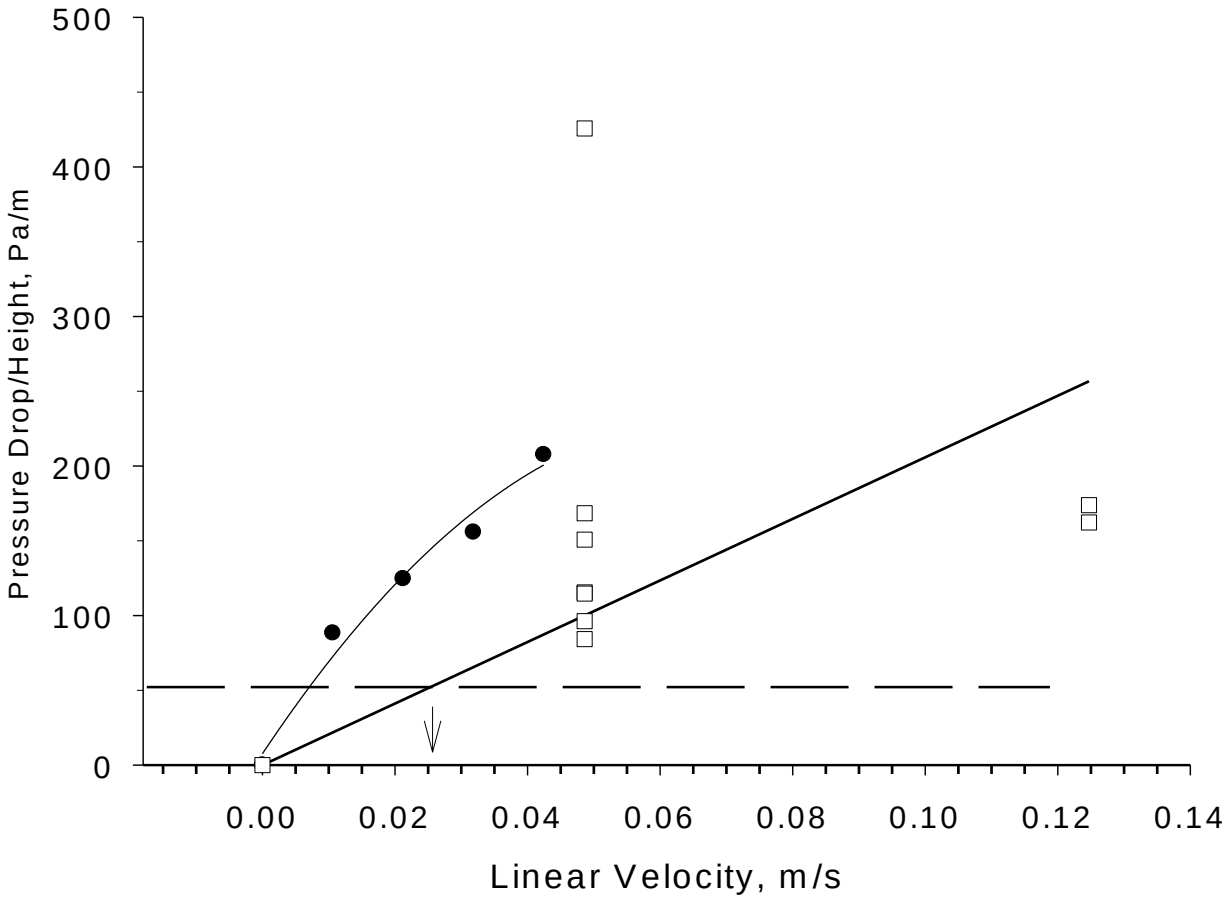


Fig. 12: Pressure drop as a function of linear velocity for the bench scale (●) and pilot scale biofilter (□).

Reactor Design:

Once degradation kinetics has been measured (i.e., the reaction order and constant determined) for the packing media of choice (finished compost is suggested), the reactor volume required for a defined conversion of ammonia can be designed. A general outline of the design procedure follows:

1. Choose the media:
    - Recently composted material should be used (0-2 months)
    - Particle size should range 2-3 < d < 25.4 mm
    - Wood chips or other relatively inert media with particle sizes greater than 20 mm should be added to reduce pressure drop
    - The percentage of amendments to reduce pressure drop should be based on a △P/L (pressure drop per length) versus linear velocity study.
2. Determine the kinetics of degradation with the active media of choice (i.e., a composted material) as outlined in this report.
    - Is the overall reaction, first, zero or intermediate order?
    - Kinetics can be determined with bench or pilot scale systems, but must be of the packed-bed type.
    - Determine the rate constant for the process!
3. Use the rate law and plug flow design equation (see below) to calculate the required reactor volume (i.e., volume of active packing). Data required are:
    - Maximum inlet NH_3 concentration at the Swine facility
    - Maximum volumetric flow rate
    - Required conversion of ammonia to define the outlet concentration

$$V = Q \int_{C_{Ao}}^{C_A} \frac{dC_A}{-r_A}$$

4. Calculate the mass of active compost required from the bulk density of the compost.
5. Mix the active compost with an inexpensive bulking agent such as wood chips at different ratios and perform a △P/L versus linear velocity study. Defining the maximum allowable pressure drop across the biofilter and height of packing, choose the ratio that gives the highest linear velocity and minimizes the pressure drop. Nicoli and Janni, 2001 suggest a minimum thirty percent (% w/w) compost to wood chip ratio.
6. Calculate the mass of wood chips or other amendments required based on the bulk density of the amendments and steps 4 and 5.
7. Calculate the surface area of reactor using the linear velocity obtained in step 5 and the entering volumetric flow rate (A_c = Q/U; Q is the volumetric flow rate and U is the linear velocity).

In the above design procedure it was assumed that flow through the reactor is of the plug-flow type. However, our data indicate that reducing the height to diameter or length ratio will increase longitudinal dispersion, potentially reducing the predicted conversion using the ideal reactor design equations. Until a formalized method is developed to predict the Peclet number (or vessel dispersion number) from the reactor height to length ratio and porosity of the media, a correction factor should be added to the ideal the reactor volume calculated from the plug flow design equation (potentially 10-20%, but this number needs further validation).

Electronic Nose

Advances in electronic nose (EO) technology have led to the production of relatively low-cost, hand held units (~$8,000, with anticipated cost reduction as volume increases). Advantages of the electronic nose are low cost (e.g., relative to gas chromatography methods), rapid results, and selective response to changes in mixture composition. The EO can potentially be used not only to monitor reactor efficiency but to also provide a basis for real-time control. Since electronic noses can be trained to detect changes in complex mixtures, it was our theory that EO's could be used to continuously monitor reactor effluent and signal a response when the outlet composition changes (e.g., breakthrough of odor), indicating an onset in catalytic decay in the biofilter. The initial screening of the EO suggests that at this time (i.e., the current state of the technology) the electronic nose is not capable of being used as an online monitor of volatile organic compound concentration in the inlet and outlet streams of the biofilter. It may be possible to detect odor breakthrough in the biofilter system using the EO, however further research is required to determine the detection limits of the EO and the cost must be reduced significantly for use in agricultural applications.

Summary: Key Points

- Compost based biofilters have been shown to be a viable method of ammonia removal from swine facilities.

- A reactor design method (i.e., sizing calculation) has been presented based on the kinetics of ammonia oxidation (i.e., how fast the reactor removes ammonia).

    - For example, assuming a volumetric flowrate of 13 m^3/s, NH_3 conversion of 95% (C_{NH3in}=25 ppmV), and a first order rate constant of 0.08 1/s, a reactor volume of 487 m^3 and residence time of 37.5 sec is required.

    - The size of the reactor will change, depending on the characteristics of the swine facility.

    - Pressure drops across the bed should 0.25 in H_2O or less in order to utilize in-house fans.

        - This will probably limit the height of the reactor to 1 m or less

- The mass of compost required can be estimated from its bulk density

- Additional research is required to develop a formalized method to predicate deviations from ideal conditions and correction factors for reactor volume (i.e., size) at full scale.

- Moisture content must be maintained between 40-60% in the biofilter to maintain biological activity (i.e., high removal efficiency).

- Additional research is required to develop inexpensive methods of emission humidification, online moisture analysis, and water addition.

    - Recycling of water from sludge dewatering operations could potentially be used for water addition, but should not contain nitrates or nitrites that could inhibit ammonia oxidation.

    - Methods used to measure soil moisture content (time domain reflectometry or TDR) can't be used for compost-based biofilter because of the high porosity of the packing.

    - It may be possible combine a wet scrubber (e.g., a spray column) with the biofilter for partial ammonia removal and air humidification.

        - This would remove particulate matter from the air stream, which carries odor-causing compounds and can clog pores in the biofilter media and thus increase pressure drop across the bed (i.e., reactor).

- Real time ammonia detection and odor analysis

    - The Draegor Polytron ammonia sensor worked well for short duration's (5 days – 1 week), however periodic drift and spikes in output signals were a problem.

        - It was successfully calibrated using a certified gas standard generator

        - The unit was capable of detecting ammonia up to 100 ppmv and could acquire data in real time for subsequent downloading

        - However, the sensor could not read ammonia levels if the air stream of interest was introduced directly at the sensor.

        - This required that the sensor be located in a small isolated chamber to which a slip-stream of the air emissions was directed. This significantly increased the response time of the detector.

        - Thus, the Polytron unit was not feasible as a continuous in-line ammonia detector.

- The electronic nose is not currently capable of being used to analyze for odor concentration or to differentiate different odor patterns. The cost of the unit's also currently limit their use. However, the EO may have potential in determining odor breakthrough in the biofilter (and at other locations) with further research, and as costs come down (e.g., mass production of sensor chips) could be used as real time sensors for agricultural applications.

VIII. LAY INTERPRETATION

Compost-based biofilters are one of the most cost effective treatment technologies for low concentration air pollutants, compared to traditional technologies such as thermal and catalytic oxidation. Recent cost analysis performed for the petroleum and agricultural industries indicates that biobased systems are more economical than conventional technology. In the biofilter, air pollutants are collected and passed through a reactor containing a packing (e.g., compost) seeded with a microbial biofilm (composted material is pre-inoculated with a diverse microbial community capable of degraded a wide range of air pollutants). In addition to compost, other amendments (e.g., wood chips) are added to reduce pressure drop and/or a solid phase buffer. As the emissions pass through the biofilter, the air pollutants are transported from the gas phase to the stationary water/biofilm on the compost matrix and degraded to CO_2 and H_2O by the microorganisms in the biofilm. If the air pollutants are inorganic in nature (e.g., NH_3), lithotrophic bacteria present in the compost will consume the inorganic compound as an energy source (e.g., nitrifying bacteria that convert $NH_3 + O_2 + H^+ \rightarrow NH_4NO_3$ salts, equation not balanced).

Advantages of compost biofilters include:

- Low energy cost and oxidation to inert compounds
- Continuous degradation without the use of chemicals or high temperatures
- Diverse microbial community capable of mixed substrate degradation
- More cost effective than adsorption, catalytic oxidation and incineration
- Higher degradation rates compared to soil and peat
- Waste material is re-used (e.g., solid waste can be composted and used in biofilters)
- Large surface area and thin biofilm reduces mass transfer resistance and thus the reactor is applicable towards poorly water-soluble compounds such as dimethyl disulfide or H_2S.
- Reduced water consumption.

In this project, a mobile, skid mounted biofilter was designed and built to determine the kinetics of ammonia oxidation (determine how fast ammonia would be degraded) at a

modern 2400 sow farrow-to-wean unit. The biofilter system consisted of a variable speed blower, packed bed humidifier, and two reactors (4 ft x 4 ft with a packing volume of 12.5 ft^3 per reactor) configured in parallel. Prescreened, composted yard waste was used since compost contains a large number of active microorganisms, is relatively inexpensive, and easily available. Ammonia emissions (0-12 ppmv) from the swine facility (and 0-25 ppmv in a simulated stream) were transported downward across packing in the reactors and spray nozzles at the top each reactor were used to add moisture to the packing. Ammonia removal efficiency approached 95 % depending on the residence time and inlet NH_3 concentration. A reactor design method (i.e., sizing calculation) has been developed based on the kinetics of ammonia oxidation (i.e., how fast the reactor removes ammonia). For example, assuming a volumetric flow-rate of 13 m^3/s, a required ammonia conversion of 95% (C_{NH3in}=25 ppmV), and a first order rate constant of 0.08 1/s, a reactor volume of 487 m^3 and residence time of 37.5 sec is required. The size of the reactor will change, depending on the characteristics of the swine facility. Pressure drops across the bed should be 0.25 in H_2O or less in order to utilize in-house fans. This will probably limit the height of the reactor to 1 m or less. The mass of compost required can be estimated from its bulk density. Moisture content must be maintained between 40-60% in the biofilter to maintain biological activity. Additional research is required to develop inexpensive methods of emission humidification, online moisture analysis, and water addition and accurately predicting reactor size at full scale.

Major Impacts:

- Engineering design data has been developed that can be used to 1) determine the feasibility of using compost based reactors to remove ammonia from CAFO's, 2) scale the process (i.e., estimate the reactor size and mass required for high ammonia conversion for a full scale farm), and 3) cost analysis.

- Presentations:

    1. Crompton BJ (Undergraduate Research), JR Kastner. January 2003. Applying Biofiltration on an Industrial Scale to Treat Air Pollutants. *Institute of Biological Engineering* Annual Symposium, Athens GA. (Oral Presentation).

    2. Crompton BJ (Undergraduate Research), JR Kastner. January 2003. Applying Biofiltration on an Industrial Scale to Treat Air Pollutants. *Institute of Biological Engineering* Annual Symposium, Athens GA, Poster: Awarded 2nd Prize in Graduate Student Competition.

    3. James R. Kastner, K.C. Das, Crompton BJ**.** Kinetics of Ammonia Oxidation in a Pilot Scale Biofilter. Air Pollution 2003, Raleigh, NC October 11-14. Oral presentation to be presented.

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