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Title: Zeolite Packed Biologically Active Filter (Biofilter) to Reduce Odorous Emissions from a Confined Swine Building.

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A zeolite packed biofilter was retrofitted to a confined swine feeding operation in Eastern Washington, and evaluated for its ability to reduce the malodors from fan exhaust drawn from an internal under-slat manure storage pit. Ammonia (NH_3) was used as the representative constituent of swine waste malodor due to its readily detectable exhaust air concentrations greater than 3 parts per million. Twenty-four pre-filter samples and twenty-four post-filter samples of NH_3, collected over a 10-month period using colorimetric gas detector tubes, revealed the zeolite biofilter reduced NH_3 by an average of 90%. Nitrite assays and Polymer Chain Reaction (PCR) analysis confirmed that active populations of the nitrifying bacteria *Nitrosomonas* were able to attach and grow on the surface of the zeolite. Using cotton swatch absorption method and an odor panel it was found that the zeolite biofilter improved malodors from swine barn exhaust in 70% of the trials.

Zeolite Packed Biologically Active Filter (Biofilter) to Reduce Odorous Emissions from a Confined Swine Building

by

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Andrew J. Stoeckinger, Author

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TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

LIST OF FIGURES

LIST OF TABLES

Zeolite Packed Biologically Active Filter (Biofilter) to Reduce Odorous Emissions from a Confined Swine Building

INTRODUCTION

Modern swine operations have become more intensified and increasingly mechanized as a direct result of the market driven economy that has forced farmers to maintain commercial viability. Between 1982 and 1997 the number of livestock operations in the United States decreased 51%, yet livestock production increased 10% (Gollehon et al., 2001). The number of farms in the United States peaked at 6.5 million in 1935 and has declined ever since due to the development of technologies that improves the productivity and efficiency of swine operations (NRC, 2003). One of the modern developments in swine farming is the confined animal feeding operation (CAFO), which is designed to collect waste in storage pits beneath the slatted flooring that supports the pigs. The obvious advantage of these swine operations is that they require minimal human labor for day-to-day maintenance, and increase the overall efficiency of the operation.

Despite the technological advances designed to streamline swine production, there are still instances where the management of substantial production of fecal waste from swine operations are implicated in detrimental impacts on air and water quality. Federal and state agencies have passed regulations designed to protect water resources from the impacts of swine waste; however, the regulation of gaseous emissions has proven to be more challenging. Complaints concerning the intense odors emitted from swine CAFO's pose the most serious legal threat to the livelihood of these operations. Strategies to reduce odors emitted from CAFO's can be expensive, and imposing regulatory control of odor emissions poses serious challenges for regulatory agencies, which need solid scientific information for supporting their decisions.

The inability of federal and state agencies to effectively regulate odor emissions has led citizens to take their own action through state and federal legal systems. Such legal action is supported by the Law of Common Nuisance, which states that any group or individual has the right to enjoy their property without the interference of "unreasonably obtrusive activities" of another (Miner et al., 2000; Pain, 1994). To counteract this threat, legislators in many states instituted Right to Farm Laws out of concern that odor nuisance lawsuits would become more prevalent as conflicts between local residents and farmers increased (Miner et al., 2000). Legal defense of their farming practices often leads to exorbitant legal fees that could potentially cause financial hardship for some swine farmers. Pursuit of litigious resolutions to solve odor issues has proven costly for both the complainant and defendant, and seldom ends with a mutually agreeable solution. This is due in part to the subjective nature of defining an "unreasonably obtrusive activity".

Although there are no federal air quality regulations that directly address swine odor issues, several state and local regulatory agencies have pursued strategies to abate the nuisance conflicts between residents and swine farmers. These abatement strategies are necessary because federal, state, and local entities have difficulty enforcing air quality regulations due to the lack of scientifically defensible methods for measuring odors. The only actions such agencies can take are to bring the community concerns to the attention of the farmer and perhaps offer methods to abate the problem----although there have been extreme cases where farmers were forced to relocate their livestock buildings (O'Neill, 1992; Pain, 1994). Odor abatement strategies are often most necessary where new residential subdivisions are being built within close vicinity to livestock operations. The residents of these neighborhoods are often unaccustomed to offensive livestock odors and tend to be easily irritated. Under these circumstances state and county land use agencies may have the authority to establish an appropriate separation distance prior to development, in order to allow dispersal of odor emissions (Miner et al., 2000; O'Neill, 1992).

The USDA and EPA have both instituted programs that address odorous emissions from livestock farming, but their approaches differ in response to each individual case (NRC, 2003). Both have strategies implemented by the states, but the USDA emphasizes best management practices (BMP) that can be implemented by the farmers. The EPA, on the other hand, relies on regulating air emissions through the Clean Air Act; however, very few swine operations produce pollutants in quantities that exceed Clean Air Act compliance regulations (NRC, 2003). The challenge for regulatory agencies is to acquire accurate measurements of odorous emissions that support their management decisions. Swine farmers are more likely to accept management or regulatory strategies that are supported by scientifically defensible information. Confidence in any proposed strategies may likely be met with skepticism by farmers, but lack of justification will seriously erode public confidence in such decisions.

Residents of rural regions supporting swine operations in the United States can attest to the unpleasant experience of living downwind of the putrid odors emanating from these operations. These odors not only create a nuisance by diminishing the enjoyment of one's property, they can at times be so intense they create health concerns for humans and pigs alike (Wing and Wolf, 2000). Of all the nuisance complaints due to swine odors in the United States, nearly 25% can be attributed to emissions from confined swine buildings (Bundy, 1997). These mechanically ventilated swine buildings are often equipped with negative pressure exhaust systems that essentially create a suction to draw fresh air into the building. Fresh air mixes with the volatilized gases from the manure storage pit and is released into the atmosphere. The manure storage pits beneath the floors of these buildings release ammonia (NH_3), nitrous oxide (N_2O), methane (CH_4), hydrogen sulfide (H_2S), volatile organic compounds (VOC's), and particulate matter (Asman, 1995). The complex mixture of these gases contributes to the offensive odors emitted from swine operations.

Mechanical and highly technical devices have been designed to abate swine building odors, but they often require a sizable investment and frequent maintenance. This causes many swine farm operators to be reluctant until it is deemed absolutely necessary to sacrifice the capital for implementing such devices. Therefore, there is a need for an odor abatement technology that is affordable, highly effective, and requires little or no maintenance. One promising alternative to expensive mechanical devices for odor reduction is a biologically active filter, commonly referred to as a biofilter.

The biofilter is essentially a fixed bed filter packed with moist organic or inorganic media that has a moist layer of microorganisms, called a biofilm, adhering to the media surface. A biofilter degrades odorous compounds through the process of biofiltration, which is a microbial process that occurs naturally in soils. Biofiltration is the process of biologically oxidizing gaseous compounds as they diffuse through a media supporting the growth of bacteria and other microorganisms. This process has been harnessed in biofilters by providing a bed of media for microbial attachment and then forcing gaseous emissions from a confined swine building through this media. Biofilter beds can consist of peat, compost, soil, or any media that will retain moisture and supply the nutrients necessary for bacteria growth.

Zeolite has a high affinity for adsorbing odorous compounds associated with animal waste, such as ammonia and hydrogen sulfide. It has been widely used to reduce the odors of livestock stalls and has the same structure as the "kitty litter" used for reducing odors from cat waste. The natural zeolite clinoptilolite was utilized in this study as an alternative to traditional organic biofilter media of compost, peat, and/or wood chips. Zeolite is an aluminosilicate rock that not only has a high surface area for microorganisms, but also a high cation exchange capacity for adsorbing odorous compounds. As a biofilter media, zeolite could provide the proper environment for microbial growth and its resilient silica structure may be superior to organic media prone to decomposition. The purpose of this study is to evaluate the

zeolite biofilter as an efficient method of reducing odors emitted from confined swine buildings.

LITERATURE REVIEW

Confined animal feeding operations (CAFO) have increased the automation of pig production and increased the economic opportunities for livestock producers. A CAFO is a facility where animals are confined, fed, and maintained for a period of 45 days or longer. The concentration of pigs in these buildings has intensified manure production and the odors associated with storage of swine waste. These operations can have slatted floors that allow feces to collect in storage pits underneath the living quarters of the pigs. Storing the fecal slurry in these pits for up to a year allows for partial anaerobic digestion of the fecal slurry before application to agricultural fields. To maintain a "healthy" living environment for the pigs, large ventilation fans in the walls of the pig living space are used to regulate temperature, odors, and moisture. In some designs, these buildings are equipped with manure pit ventilation fans that draw hazardous fumes from the headspace above the manure storage pit and discharge them to the outside. The manure storage pit helps prevent nutrients from leaching into surface and ground waters. However, the volatilized gas emissions drawn from the manure storage pit may pose hazards to local air quality and potentially contribute to negative impacts on regional and global environmental systems.

Environmental Impacts of Ammonia Emissions

Confined animal feeding operations (CAFO), such as the operation used to house pigs in this study, are commonly equipped with automated feeding systems and under-slat manure storage pits. Urine and feces excreted by the pigs passes through the slotted flooring into the storage pit below, and is collectively referred to as fecal slurry. The storage pits are designed to store the fecal slurry for up to twelve months. Anaerobic conditions within the manure storage pit create conditions conducive to the microbial degradation of organic matter in pig feces. The organic nitrogen in fecal slurry is converted to odorous compounds such as ammonia by a combination of

hydrolysis and mineralization, and then subsequently lost to the atmosphere by volatilization.

There are up to 331 different trace gases associated with swine manure, but ammonia is most commonly cited as the primary pollutant of concern emitted from CAFO's (Berglund and Berglund, 1988; Hartung, 1988 (b); IPCS, 1990; Miner et al., 2000; Schiffman et al., 2001; Sommer and Hutchings, 1995; Taiganides, 1992; Wathes, 1992). One such study conducted in Germany by Hartung (1988a) found that ammonia constituted up to 54% of the total emissions from pig confinement buildings throughout the country. On a global scale, it is estimated that CAFO's contribute close to 50% of the total ammonia emitted to the atmosphere each year (Aardenne et al., 2001; Galloway and Cowling, 2002; Schlesinger and Hartley, 1992). Research conducted in the Netherlands and Germany found that nearly 80% of the collective ammonia emissions from those regions were attributed to overall waste management practices in all types of livestock production, and of those emissions up to 20% could be directly attributed to emissions from CAFO's (Berglund and Hall, 1988; Hartung, 1988(a); Rom, 1993). With the increasingly concentrated nature of modern livestock operations, this poses a considerable environmental threat in regions with large-scale swine CAFO's.

Ammonia emissions from swine buildings have contributed to various environmental impacts such as soil acidification (Apsimon and Kruse-Plass, 1991; Hartung, 1991; Miner et al., 2000), acid rain (Apsimon et al., 1987; Breemen et al., 1982; Miner et al., 2000; Voorburg, 1986), and nitrogen enrichment of surface waters (Berglund and Hall, 1988; Bode, 1991; Miner et al., 2000; Tamminga, 1992; Verstegen et al., 1994). After entering the atmosphere, ammonia (NH_3) emissions will either be deposited by dry deposition or converted to ammonium (NH_4^+) by reactions with ambient aerosols in the atmosphere, such as nitric acid (HNO_3) and sulfuric acid (H_2SO_4), and returned to terrestrial surfaces by wet deposition. The ammonia emission from CAFO's can be quickly deposited on local surfaces depending on the emission concentrations, local vegetation configurations, and

relative humidity. Dry deposition of ammonia on plant surfaces can cause direct tissue damage (Geelen, 1986; Tamminga, 1992; Voorburg, 1986) and soil acidification as ammonium sulfate forms and infiltrates into the soil below (Klarenbeek and Bruins, 1988; Hartung, 1988(b); Verstegen et al., 1994). Agricultural plants are able to tolerate maximum ammonia concentrations of 100 ppb (parts per billion), whereas wild vegetation can only tolerate up to 30 to 40 ppb (Tamminga, 1992). Impacts of ammonia emissions decrease with increasing distance from the source as ammonia concentrations are dispersed into the atmosphere.

Although the direct effects of ammonia deposition usually occur within close vicinity to the confinement buildings, ammonia emissions can also have more far reaching consequences. Ammonia emissions were found to be the third highest contributor to soil acidification in regions of Eastern Europe, the Netherlands, and Scandinavia due to acid rain deposition (Apsimon and Kruse-Plass, 1991; Breemen et al., 1982; Klarenbeek and Bruins, 1988; Mannebeck and Oldenburg, 1991; Roelofs and Houdijk, 1991). Noticeable tissue damage to coniferous forests throughout areas of Eastern Europe has been attributed to ammonia deposition (Breemen et al., 1982; Roelofs and Houdijk, 1991). This is because ammonia can be transported great distances through the atmosphere by taking the form of ammonium aerosols, which are formed as ammonia mixes upwards and reacts with hydrochloric acid and sulfuric acid in the atmosphere.

Ammonia emissions from CAFO's have also been associated with nitrogen enrichment and eutrophication in aquatic systems (Klarenbeek and Bruins, 1988; Miner et al., 2000; Ogink et al., 2000; Rom, 1993; Sommer and Hutchings, 1995). Surface water impacts were of such great concern in the Netherlands that in 1990 it led to aggressive legislation toward reducing ammonia emissions from livestock production by 70% over a 15-year period (Bode, 1991; Ogink et al., 2000; Oosthoek et al., 1991). Ammonia emissions in these European regions have posed a serious environmental threat, and have lead to extensive research on potential methods for reducing ammonia emissions from CAFO's.

Human Health Issues Associated with Ammonia

Of the 331 identified gaseous compounds produced during the degradation of swine waste, ammonia is most commonly associated with CAFO's (Bruce, 1981; NRC, 2003; Verstegen et al., 1994). When this gaseous compound is found at concentrations greater than 50 ppm (parts per million) it can pose serious threats to human health. Research conducted in North Carolina by Wing and Wolf (2000) found that people exposed to the gaseous emissions from swine operations reported more frequent symptoms of burning eyes, excessive coughing, headaches, sore throat, runny nose, and diarrhea.

Ammonia is a colorless and characteristically pungent gas, and is highly soluble in water. Ammonia will remain in solution as ammonium when manure is stored in liquid form at a pH greater than 8. Thus, storing the manure in liquid form, as fecal slurry, substantially reduces ammonia volatilization and is the standard practice for many swine operations.

Ammonia is detectable to humans at concentrations greater than 10 ppm, and causes irritations to mucous membrane, such as the eyes and respiratory system, at concentrations between 70 and 100 ppm (Hurst, 1995; IPCS, 1990; NRC, 2003; Verstegen et al., 1994). The occupational exposure limit to gaseous ammonia set by the World Health Organization (WHO) and Occupational Safety and Health Association (OSHA) are from 25 ppm up to 50 ppm, and use of personal respiratory protection are recommended when conditions approach this limit (IPCS, 1990; Muir, 1977; Verstegen et al., 1994). Ammonia is only fatal to humans at concentrations greater than 2500 ppm. Serious problems with human exposure to ammonia inside confined feeding operations are very rare, but when an operator is exposed to harmful concentrations they are generally irritating enough to cause the exposed person to escape further contact. Under normal circumstances, ammonia concentrations associated with CAFO's will not exceed the 50 ppm required to pose a serious threat to the health of swine farmers or the surrounding communities. Atmospheric concentrations of ammonia measured in communities adjacent to confined feeding

operations with the most intensive manure production are still found to be lower than 0.3 ppm due to dispersal effects (IPCS, 1990; Miner et al., 2000).

By most accounts, the air quality within confined feeding operations does not violate workplace air quality standards for ammonia (Miner et al., 2000; Tamminga, 1992; Verstegen et al., 1994); however, the odors that accompany ammonia and other compounds in swine waste can have an impact on persons living near large swine operations. The most frequent complaints of people living near swine operations include burning eyes, sore throat, drowsiness and headaches (Schiffman, 1997; Wing and Wolf, 2000). In recent studies, scientists have attempted to understand the complex psychological reactions that people have when exposed to odors emitted from confined pig feeding operations (Miner et al., 2000; Schiffman et al., 1995; Schiffman et al., 1998). One such study conducted in North Carolina found people living near large swine operations suffered higher rates of mood disturbances (Wing and Wolf, 2000). The degree of emotional intensity of olfactory responses can be correlated to the history of personal experience that a subject has had with the intense odors associated with animal feeding operations. Research also suggests that even downwind exposures to malodors from animal feeding operations may induce specific physiological changes measurable in the endocrine systems of exposed persons (Miner et al., 2000). Downwind exposures to malodors have been shown to be accompanied by feelings of helplessness and depression by those exposed for significant periods of time (Miner et al., 2000; NRC, 2003; Schiffman et al., 1998).

Justification for Using Ammonia as an Odor Emission Indicator

Scientific literature concerning gaseous emissions from swine operations identify from 100 up to 331 different compounds associated with swine waste including amines, mercaptans, sulfides, organic acids, aldehydes, alchohols, esters, carbonyls and ammonia (Berglund and Hall, 1988; Miner et al., 2000; Schiffman et al., 2001). Despite the inconsistency amongst estimates of the compounds

contributing to odor, many researchers agree that ammonia is one of the primary contributors to malodors associated with swine waste (Bruce, 1981; Eikum and Storhaug, 1986; Hartung, 1988(a); Leisinger, 1988; Miner et al., 2000; NRC, 2003; Priest et al., 1994; Schiffman et al., 2001; Tamminga, 1992). Ammonia has been shown to constitute more than 54% of the total gaseous emissions from swine barns making ammonia the most prominent constituent in CAFO emissions (Hartung, 1988(b)). For this reason, the concentration of ammonia in swine barn emissions has been used as an indicator of odor intensity from swine operations (Amon et al., 1997; Hobbs et al., 2001; Kowalewsky et al., 1980; Liu et al., 1993; Miner et al., 2000; Pain et al., 1988; Ryden, 1986; Taiganides, 1992; Tamminga, 1992; Thacker and Evans, 1986; Voorburg, 1986). Ammonia is also one of the easiest compounds to detect by conventional methods, such as colorimetric detector tubes. Therefore, concentration of ammonia emissions provides a convenient and dependable indicator for measuring malodors.

Ammonia has a density less than air causing it to rise from storage pits and be easily carried away by ventilation fans (Taiganides, 1992). The use of ammonia as an indicator of odor emissions is also justifiable due to its characteristic water solubility that is quite similar to other volatile compounds associated with swine waste (Ryden, 1986). For an odor to be perceived by the olfactory senses it must first be dissolved in the mucous membranes in the nasal cavity; therefore, odorous constituents must be water soluble to reach olfactory nerves (Miner et al., 2000; NRC, 2003).

Ammonia emissions increase with increasing temperature due to increased rates of volatilization during warm weather with ambient temperatures over 20° Celsius (Anderson, 1995; Eikum and Storhaug, 1986; Miner and Hazen, 1969; NRC, 2003). Ammonia production can be correlated with increased air temperatures, ratio of surface area to volume within the manure storage pit, and ventilation rate within the swine building (NRC, 2003; Rom, 1993). Of these three factors, air temperature and ventilation rates are inclined to fluctuate significantly over seasonal and diurnal time scales. Ammonia emissions have been found to increase sharply between dawn and

midday, corresponding to, yet lagging just behind, increasing diurnal temperatures (Mannebeck and Oldenburg, 1991; Rom, 1993; Taiganides, 1992).

Microbial Oxidation of Ammonia

Common swine production facilities have slatted floors supporting the pigs with openings large enough to allow swine waste to fall into the manure storage pit. During several months of storage this fecal slurry can be digested by anaerobic and facultative microorganisms before application to agricultural fields as fertilizer.

The solid and liquid organic substrates excreted in swine feces are largely converted to microbial biomass and soluble and insoluble gaseous products by microorganisms in the waste. The anaerobic conditions found in manure storage pits are conducive to the continual conversion of organic nitrogen to NH_3 by the bacterial degradation of protein and urea in animal waste. The production of ammonia by the decomposition of organic nitrogen is referred to as ammonification. This process is essentially a fermentative process since it is an enzymatically controlled anaerobic breakdown of organic-rich material producing gases including NH_3 (ammonia).

Of the total intake of nitrogen-rich feeds consumed by growing pigs only 32% is retained as body mass while 15% is excreted as feces and 53% as urine (Tamminga, 1992). A minor portion of the N (nitrogen) in feces is excreted directly as NH_3, while the N in urine is primarily excreted as urea ($(NH_2)_2CO$) (Tamminga, 1992). The hundreds of other compounds contributing to malodors are produced through anaerobic processes such as dehydroxylation, deamination, and decarboxylation of proteins (amino acids) (Tamminga, 1992).

The metabolic efficiency of bacterial degradation processes is highly dependent on the temperature of the slurry (Hartung, 1991; Taiganides, 1992). The higher the temperature of the swine slurry, the greater the bacterial metabolism and subsequent production of NH_3; therefore, NH_3 production is strongly influenced by seasonal variations of ambient air temperature inside the swine barn (Eikum and

Storhaug, 1986; Hartung, 1991). To prevent potentially harmful gases, such as NH_3, from permeating the living space of the pigs, the headspace above the manure storage pit is commonly ventilated with exhaust fans.

As temperatures rise, volatilized NH_3 is drawn from the manure storage pit by the exhaust fans and emitted into the atmosphere. Emissions from confined swine operations are considered to be a contributing source of ammonia for eutrophication of local surface waters and acid rain. However, if these NH_3 laden emissions are forced to permeate through a highly porous substrate, such as soil, the ammonia can be oxidized to more innocuous and less odorous forms as it comes into contact with aerobic bacteria living on the surface of the substrate. This is a process that occurs naturally in unsaturated soils and could be harnessed to reduce odorous emissions from confined swine operations. The process of filtering swine waste gases through any substrate capable of supporting aerobic bacterial growth is referred to as biofiltration. Biofiltration has the potential to effectively remove many of the odorous gases associated with swine waste through microbiological oxidation, which will be discussed further in the following section. The biofiltration of NH_3 is performed by two primary species of aerobic bacteria in the process of nitrification.

Nitrification is the aerobic bacterial metabolic process that oxidizes NH_3 until it is transformed into NO_3^- (nitrate); however, NH_3 must first be absorbed to take the form of NH_4^+ (ammonium). This fact will be explored further as it pertains to the importance of maintaining high moisture content in the media used for biofiltration. This process is carried out in two separate conversions performed by two species of autotrophic nitrifying bacteria that use carbon dioxide as their carbon source. The energy for autotrophic nitrifying bacteria is derived from the oxidation of inorganic nitrogenous compounds of either NH_4^+ or NO_2^- (Schmidt and Belser, 1994).

The species *Nitrosomonas* is responsible for the initial transformation of NH_4^+ to NO_2^- (nitrite) with the following reaction:

$$NH_4^+ + 1\frac{1}{2}O_2 \rightarrow NO_2^- + 2H^+ + H_2O$$

And the bacterial species *Nitrobacter* completes the nitrification process by converting available NO_2^- to NO_3^- in the following reaction:

$$NO_2^- + \tfrac{1}{2} O_2 \rightarrow NO_3^-$$

Although there are other organisms that may be involved in the nitrification process, *Nitrosomonas* and *Nitrobacter* are the most commonly associated with swine waste and are therefore the most crucial components of biofiltration (Leisinger, 1988; Smits et al., 1995). The byproduct of these nitrification reactions are oxides including nitrogen oxide (NO), nitrous oxide (N_2O), and nitrogen dioxide (NO_2).

Nitrifying bacteria have the ability to attach themselves to surfaces in enriched cultures of adhesive slime referred to as biofilms. Under the appropriate environmental conditions these clusters of cells will grow in superimposed layers over an attachment surface. In order for biofilms to maintain metabolic synthesis the pH must remain between pH 6 and 10.2, but the optimal level for chemolithotrophic bacteria is between pH 7 and 8 (Scholtens and Demmers, 1991). The endogenous metabolic activity of these bacteria produces acidic conditions that must be neutralized by available alkaline substance in order to maintain the activity of nitrifying bacteria (Scholtens and Demmers, 1991). All of the organisms found in the biofilm require sufficient P (phosphorus) and trace metals in order to maintain metabolism of NH_3, which can be derived from the biofilter media.

Biofiltration

Biofilms of nitrifying bacteria are capable of absorbing and metabolizing the gaseous compounds commonly volatilized from swine waste. This biological capacity to oxidize odorous compounds can be exploited by providing an attachment surface for the growth of bacterial biofilms and supplying them with a steady stream of nutrient-rich gas emissions from a swine building. This process of biologically filtering odorous compounds from livestock building emissions is referred to as biofiltration.

Biofiltration is the process of filtering undesirable gases through an organic or inorganic media supporting the growth of microbiological species that are capable of oxidizing volatile organic and inorganic compounds to more innocuous byproducts such as water, carbon dioxide, mineral salts and biomass. This aerobic biological process occurs naturally in unsaturated soils and has been utilized in filtering noxious gases emitted from confined animal feeding operations (CAFO). Two common methods of biofiltration are the biofilter and the bioscrubber. Both have been proven to be an effective technology for removing ammonia, hydrogen sulfide, and other odorous compounds from CAFO emissions (Nicolai and Janni, 2000).

The bioscrubber is a form of biofiltration that entails absorbing soluble gases, such as ammonia, in a stream of water which then trickles through a fixed bed of media supporting bacteria growth. Bioscrubbers are often compared to biofilters and have been proven to be as efficient as biofilters in removing odorous compounds, but they require more maintenance and tend to be more expensive (Nielsen and Pain, 1991; Schirz, 1991; Scholtens and Demmers, 1991). The primary maintenance issue is ensuring that the bioscrubber liquid has a proper pH between 7 and 7.5, which requires checking the pH at least once every three days (Schirz, 1991). A bioscrubber is a packed bed of inorganic media that has a perpetual stream of water percolating through the media bed to ensure proper absorption of odorous compound in barn exhaust air (Schirz, 1986; Schirz, 1991). The biological mat, or biofilm, growing on the media oxidizes the absorbed odorous compounds to more innocuous substances and then re-circulates the water to capture more noxious compounds. The bioscrubber has achieved a dependable average odor reduction from approximately 80% (Schirz, 1991) up to 90% (Pain, 1994). Despite this excellent performance, the bioscrubber requires a high level of technical input to achieve and sustain the narrow pH requirements necessary for high removal rates.

The high level of maintenance necessary for most bioscrubbers is a primary reason that biofilters are considered to be more cost effective for implementing on most swine operations (Nielsen and Pain, 1991; O'Neill et al., 1992; Pain, 1994). The

annual expenses necessary for operating a standard biofilter may include increased electrical usage for operating ventilation fans under greater negative static pressure, water costs for irrigating the biofilter media, and replacement of organic biofilter media every three to five years (Schmidt et al., 2000). Irrigation is only necessary when the relative humidity of building emissions is too low to maintain proper moisture content for microbial activity. And almost any material can be used for biofiltration as long as it is highly permeable and provides the surface area necessary for microbial growth. These elements of biofiltration construction help to keep the construction and maintenance costs low in comparison to more technical filtration devices.

The primary consideration for implementing a successful biofilter is choosing a media that will provide the necessary surface area for a moist biofilm of aerobic bacteria growth. This media can be organic or inorganic in nature as long as it is able to provide the nutrients and retain sufficient moisture for the metabolic activity of bacteria and other microorganisms capable of degrading the odorous compounds associated with swine waste gases. Various biofilter media that have been utilized successfully include soil, activated carbon, peat, heather, wood chips, polystyrene, straw, and organic compost. To provide a viable ecological niche for a microbial community a biofilter media must have suitable moisture holding capacity, available nutrients for microbial metabolism, porosity for efficient airflow movement without large drops in static pressure, and optimal temperature for microbial activity (Nicolai and Janni, 2000).

Soil has performed effectively as a simple and inexpensive biofilter media in reducing odors from CAFO emissions (Eikum and Storhaug, 1986). Soil also has a longer operational life span in comparison to more organic-rich biofilter media, such as peat and compost. Efficient soil biofilter performance is dependent on the soil type and the loading rate of gaseous emissions. The relatively small pore size distribution provides excellent moisture content for microbial growth, but small pore size tends to

create high pressure drops and is prone to clogging by excessive microbial biomass (Eikum and Storhaug, 1986).

Organic materials, such as peat, provide the nutrient-rich substrate and moisture content necessary for rapid microbial colonization. Therefore, peat is a frequently used and highly effective biofilter media due to its high moisture holding capacity, nutrient content, and local availability (Lemay et al., 2000; Norén, 1986; Pain, 1994). Despite the high moisture holding capacity of peat, the constant exposure to exhaust air leads to desiccation; therefore, to maximize the performance of the peat biofilter it will need to be irrigated to maintain its moisture content.

Due to its high susceptibility to compaction and decay, peat is typically amended with media of higher porosity and decompositional resistance. A 50% peat and 50% heather mixture was used by van Geelen (1986) and Norén (1986) while Lemay et al. (2000) used ground polystyrene to prevent compaction in peat biofilters. In all three designs the ventilation air emitted by the CAFO was directed through ductwork and evenly distributed using a plenum beneath the biofilter media mixture. Experiments with peat biofilters achieved maximum odor reductions from 75% (Lemay et al., 2000) and 80% (Hartung et al., 2001; Kowalewsky, 1980).

Other organic materials used in biofilter include compost mixed with wood chips (Classen et al., 2000; Leson and Winer, 1991; Pain, 1994; Schmidt et al., 2000; Sun et al., 2000) or straw (Nicolai and Janni, 1997). The wood chips and straw provide a porous structure while the compost provides moisture holding capacity and nutrients for microbial growth. Like the peat biofilter, the compost and wood chip material is placed on slatted planks of wood, or other sturdy material, to provide a plenum for air distribution and diffusion up through the biofilter media. The yard waste compost and wood chip mixture used in the biofilter designed by Sun et al. (2000) achieved an average ammonia reduction of 75.8% by maintaining a 20 second retention time. The compost and kidney bean straw used by Nicolai and Janni (1997) reduced the odor intensity of emissions by 75%.

One of the drawbacks of many commonly used biofilters is that the organic material that they utilize is highly prone to decomposition and compaction, which creates increased resistance to airflow. Decomposition of biofilter media can be accelerated by the inorganic acids that accumulate as a byproduct of microbial oxidation of ammonia and sulfur compounds. Due to the relatively high decompositional rate of organic biofilter media they tend to require replacement every 5 to 10 years (Schmidt et al., 2000). To contend with decomposition, Leisinger (1988) recommends continually renewing the organic media in biofilters to maintain optimal pH levels and ensure a sufficient supply of inorganic nutrients for microbial growth, which adds to maintenance requirements. Organic materials also invite the burrowing activities of rodents and other pests, creating macropores and subsequent preferential flow of untreated emissions (Schmidt et al., 2000). Growth of weeds in the biofilter can also potentially contribute to restriction of airflow and should be dealt with immediately. Altering the even distribution of gas diffusion through the biofilter by compaction or macro-biological activity can lead to anaerobic zones in the biofilter bed, which could potentially contribute further to odor problems.

One of the challenges of selecting a biofilter media is maintaining an airflow that meets building ventilation requirements while simultaneously providing the most effective gas retention time in the biofilter. The gas retention time is the duration required for gas emissions to diffuse through the filter, which determines the amount of time that the emissions are in contact with the microorganisms inhabiting the biofilter media. The longer the gas retention time the greater the opportunity for biological degradation of the waste gases.

Regardless of the chosen media, the addition of a biofilter to a livestock building will inevitably increase the static pressure drop by restricting airflow. The static pressure is measured in inches of water and is dependent on the air speed through the filter and the permeability of the filter material. The permeability is dependent on the connectivity of effective pore space, which are the interstitial void spaces available for transmitting the air with minimal loss of energy. Highly

permeable biofilter materials will easily transmit emission air, whereas low permeability materials reduce the air velocity; thus, retention time tends to decrease with increasing permeability.

Nicolai and Janni (2000) reported an average static pressure drop of 0.95 inches of water across a peat biofilter that was 2.6 feet deep. Norén (1986) suggested selecting a biofilter media that is capable of maintaining a static pressure of 0.6 inches or less of water at the maximum ventilation flowrate. Again, this is a general guideline that is dependent on the permeability of the media and the fan flowrate. Retention times are based on the maximum flowrate in order to ensure effective biofiltration during maximum ventilation rates, although reaching this maximum flowrate is not common. Meeting ventilation requirements for the pigs may necessitate installing an exhaust fan with a higher maximum flowrate. However, this expense can be reduced by altering the biofilter design to include a media with high porosity and high resistance to decomposition. Such a design alteration may need to be compensated by increasing the volume of the media in order to maintain the proper gas retention time.

Zeolite Biofilter

The use of zeolite as a biofilter media offers an excellent alternative to organic media commonly used. Zeolite has served a variety of applications in the swine production industry. In the past, zeolite has been used by pig producers as a supplement in the feed to reduce intestinal disease, improve digestive efficiency, and decrease ammonia and odor in the feces before it is excreted (Miner et al., 2000).

Zeolites are hydrate aluminosilicates of alkaline earth and alkali cations with crystalline three dimensional structures (EPA, 1999; Mumpton, 1984). Their infinite, three-dimensional frameworks of SiO_4^{4-} tetrahedrals are similar to other tektosilicates such as quartz and feldspar minerals (Mumpton, 1984). Zeolites are highly hydrophilic (an affinity for polar molecules) and have the ability to gain and lose

water reversibly (Mumpton, 1984). Their extraordinary capacity for cation exchange has been effectively used as molecular sieves in oil refineries and other industrial capacities, but zeolites used in these applications are generally synthesized (Mumpton, 1984).

A natural zeolite that is commonly used for industrial purposes is clinoptilolite. It was formed naturally when very fine volcanic ash was deposited on the surface of quiescent water bodies allowing it to slowly settle to the bottom where it eventually mineralized to its current form. Natural zeolites have proven to be effective in removing odorous constituents from CAFO air emissions due to their ion exchange and adsorption characteristics (Miner, 1984). Natural zeolites, such as clinoptilolite, immobilize ammonia, hydrogen sulfide, and other odorous compounds by absorbtion and adsorbtion, due to Van der Waals nuclear attraction forces. Research conducted by Bernal and Lopez-Real (1993) determined that ammonia was adsorbed by zeolite at a rate of 14 g per kg of zeolite.

Although zeolite has not been utilized as the sole media supporting a biofilter, it has proven effective in removing NH_3 (ammonia) emitted from confined animal feeding operations (Amon et al., 1997; Koellicker, et al., 1980; Miner, 1984; Miner, 1997). Clinoptilolite was the media of choice in a packed air scrubber used to filter air emitted from a poultry confinement building. Although the retention time of the exhaust gas within the clinoptilolite air scrubber was less than one second, it was successful in removing 15% to 45% of NH_3-N from the building emissions (Koellicker, et al., 1980; Miner, 1984). Once these compounds are immobilized they can be biologically degraded by bacteria and other microorganisms attached to the zeolite in a biofilm.

Clinoptilolite has been proven to have exceptional selectivity for the ammonium ion at 2 meq/g (milli-equivalents per gram) or 3.4% by weight of NH_3 (Koellicker et al., 1980). In the absence of ammonia absorbtion by available water, it is suspected that ammonia will react with hydrous zeolite to form ammonium ions that can be easily adsorbed by the zeolite structure (Koellicker et al., 1980).

No literature to date has been found that uses zeolite as the media to support bacteria growth in a biofilter. However, there have been studies on growth of *Nitrosomonas* on highly adsorptive substrates such as vermiculite and synthetics. One such study by Underhill and Prosser (1985) demonstrated that colonization of nitrifying bacteria was greatest on ion exchange resin beads to which ammonium had adsorbed preferentially. However, similar research with clay minerals with high selectivity for ammonium found similar preferential colonization, but reduced specific growth rates (Armstrong and Prosser, 1988; Powell and Prosser, 1987). The results of these studies suggest that ammonium retained on adsorptive media would promote colonization of bacteria, but subsequent growth rates remained dependent on sufficient supply of ammonium.

Zeolite has high porosity for easy air flow, extensive surface area for biofilm attachment, high moisture holding capacity, diverse nutrient content, and very slow degradation rate; therefore, it should provide suitable physical and environmental conditions for the growth of nitrifying bacteria. The chemical analysis of clinoptilolite reveals its high phosphorus (P) and iron (Fe) content of 2,100 mg/kg and 15,800 mg/kg, respectively, which are both vital nutrients bacteria need for metabolism (McKinney, 2001). Other trace metals necessary for bacterial activity that are found in clinoptilolite include zinc, molybdenum, manganese, nickel, copper, and cobalt.

The inorganic nutrients needed for microbial growth can be provided by the clinoptilolite, fecal dust particles, and the gaseous emissions (Leisinger, 1988). Aerobic bacteria metabolism produces acidic by-products that would lower the pH around the particles of clinoptilolite, helping to release the P and other important nutrients needed for bacterial growth (McKinney, 2001). Potassium, calcium, and sodium should also help to neutralize the acidic deterioration caused by bacteria metabolism, thus prolonging the life expectancy of biofilter operation (McKinney, 2001). Unlike organic biofilter media such as compost, the clinoptilolite will not need tillage or replacement. Zeolite can be crushed to virtually any particle size; therefore, selecting a particle size of 0.5 to 1 inch in diameter will not only decrease the pressure

drop when used in a biofilter, but also discourages animal burrowing and weed growth.

Table 1. Chemical Analysis of Clinoptilolite (Potassium-calcium-sodium aluminosilicate).

Oxide	Weight Percent (%)
SiO_2	64.7
AL_2O_3	12.6
K_2O	3.3
CaO	3.3
MgO	1
Fe_2O_3	1.8
MnO	0.1
TiO_2	0.2
Na_2O	0.9

*Provided by Steelhead Specialty Minerals, Spokane, Washington.

As a biofilm grows over the pores of the clinoptilolite it may become clogged; thus, reducing its ion exchange capacity. However, the biofilm will be able to metabolize the ammonia as it diffuses through the zeolite bed (McKinney, 2001). Bacteria prefer to grow in the absence of light and presence of moisture; therefore, dryer portions of the biofilter and the surface area exposed to daylight will likely be void of substantial biofilm growth. These biologically inactive portions of the zeolite biofilter will continue to remove odors by adsorption; thus, augmenting the odor removal capacity of the biofilm.

Proper moisture content must be maintained on the zeolite biofilter in order to maintain the bacterial activity. Due to the hydrophilic nature of clinoptilolite, the suction of individual particles increases exponentially as water content decreases

(Bohn and Bohn, 1999). Therefore, to assist the microorganisms in overcoming this negative suction it is important to irrigate the bed of clinoptilolite to maintain an available moisture content of 50% to 60%; otherwise, the metabolic activity of the bacteria will decrease with decreasing supply of water (Bohn and Bohn, 1999). A great deal of the bound water in organic media is tied up within the living and dead cells making it unavailable to the bacteria, whereas the fraction of available water is much greater in inorganic media such as zeolite (Bohn and Bohn, 1999). Zeolite is able to lose and gain water reversibly without physical change in structure, thus making the water more accessible to bacteria.

Operational Requirements for Biofiltration

Three of the most important requirements for effective biofiltration are maintaining sufficient moisture content within the biofilter media, retention time of the treatment gas, and optimal temperature for microbial activity (Classen et al., 2000; Leisinger, 1988; Sun et al., 2000). As discussed above, maintaining proper moisture content is vital to sustaining microbial activity in the biofilter, so unless the humidity of the swine barn exhaust is equal to or greater than 95%, the biofilter media will gradually dry, and consequentially lead to decreased microbial activity (Bohn, 1991; Sun et al., 2000). For this reason, it is important to maintain the biofilter moisture content by either irrigation of the media or humidification of the exhaust air prior to biofiltration, especially during hot summer months. Irrigation of the biofilter is less important during winter months due to higher rates of precipitation and increased relative humidity in exhaust exiting the swine barn (Schmidt et al., 2000). Bohn and Bohn (1999) recommend maintaining 50% to 60% moisture content in all biofilter media including aluminosilicates such as zeolite. Hartung et al. (2001) found that the odor-reducing efficiency of an organic biofilter increased as the moisture content increased from 20% to 50% by weight. Another important role of moisture in

biofilters is that odorous gases must first be absorbed by water in order for the biofilm to access them for oxidation (Hartung et al., 2001; Nicolai and Janni, 2000).

Effective removal of odorous compounds associated with swine waste gases is also dependent on the gas retention time in the filter. A rough estimate of gas retention time can be calculated by dividing the empty bed volume to be occupied by the biofilter media by the maximum ventilation flow rate. The maximum ventilation rate is used for this calculation because this represents the biofilter performance during periods of least efficiency due to low gas retention time. Under normal circumstances, the actual gas retention time will be higher due to smaller average fan flowrate.

A more accurate estimate of retention time can be calculated by multiplying the effective porosity of the media, or the percent of void space, by the empty bed retention time estimate (Nicolai et al., 2002). The effective porosity is the pore space that will readily transmit airflow. Porosity is a function of the original media structure, the media structure under compaction, and moisture content. Nicolai and Janni (1998b) found that a retention time of 4 seconds was sufficient for removing odors from a swine grower building, and Zeisig (1987) found 5 seconds was necessary for reducing swine odors. Koellicker et al. (1980) used zeolite to filter up to 45% of the ammonia emission from a confined poultry building by using a retention time less than 1-second.

The empty bed design volume of the biofilter can be calculated by multiplying the desired retention time by the maximum ventilation rate of the livestock building. Using the maximum ventilation rate will result in the shortest possible retention time, and therefore designing for periods of lowest biofilter efficiency. Effective odor removal increases with increased gas retention time; however, increased retention time also increases the pressure drop across the biofilter, which can reduce ventilation efficiency (Hartung et al., 2001; Janni et al., 1996). As airflow rate increases the pressure drop in the media increases, and inversely the pressure drop decreases as porosity increases. It is important to optimize the balance between sufficient gas

retention time and efficient airflow rates in order to reduce odor emissions without compromising the health of the pigs. This is highly dependent on the effective porosity of the filter media. For instance, a media prone to compaction, such as peat will be susceptible to restricted flowrate and longer retention times. This may hinder the capability of the fan to remove potentially hazardous waste gases from the living quarters of the pigs.

Biofilter efficiency is optimized when conditions are present that will maintain a temperature range conducive to bacterial metabolic activity. The temperature range for optimal biofilter operation is between 10° C and 40° C (Li et al., 1996; Williams and Miller, 1992b) with optimal temperature being 37° C (Bohn, 1992). However, deliberate control of the media temperature is both impractical and unnecessary. The biofilter will be able to remove a substantial portion of the odorants from the exhaust air despite the decreased metabolism that occurs with decreased temperatures (Nicolai et al., 2002). Regardless, temperatures sufficient for proper biofilter operation can be maintained during colder winter months by the warm exhaust air from a heated swine building (Schmidt et al., 2000).

Subjective Odor Analysis

Odor nuisance, the public response to odors emitted by swine operations, is a function of odor offensiveness and odor intensity (Evans and Baines, 1986; Miner et al., 2000). Odor panels have proven to be a reliable method for evaluating odor offensiveness in several studies (Miner et al., 2000; Punter et al., 1986), but it is not a practical method to be used for routine monitoring of odor (Evans and Baines, 1986). The individual perception of an odor can be heavily influenced by past experiences, which provides added difficulty in deciphering a consistent measure of annoyance toward CAFO odorants.

The average human nose can detect ammonia at a minimum concentration of 1 ppm. This minimum detectable concentration is referred to as the odor threshold

concentrations (Taiganides, 1992). In fact, the human sense of smell has proven to be more sensitive than most physical-chemical field instruments for measuring odors (Berglund and Berglund, 1988). Therefore, the use of panelists is a relatively dependable method for evaluating the offensiveness of odor emitted from CAFO's.

Panelists tend to have difficulty making absolute judgments on the offensiveness of odor, so better results are achieved when they are asked to compare samples with varying degrees of offensiveness. Subjects in the research performed by Köster (1986) presented panelists with at least two odor samples and asked to identify which sample possessed the greatest degree of offensiveness. After identifying the most offensive sample, the panelists were asked to rank the odor intensity on a scale of sensory magnitude, based on the researchers desired level of description accuracy (Cain and Moskowitz, 1974; Miner et al., 2000; Williams and Schiffman, 1995). The panel should consist of at least three participants, but maximizing the number of panelists will assist in achieving a desirable level of statistical confidence (Hangartner, 1986; Taiganides, 1992). Taiganides (1992) and Williams and Schiffman et al. (1995) used 8 panelists and were able to achieve statistically significant results.

Odors can be effectively captured and transported by exposing a clean and dry cotton swatch directly to the exhaust stream from a confined animal feeding operation (Bottcher et al., 2000; Classen et al., 2000; Miner et al., 2000; Taiganides, 1992). It is recommended that each cotton swatch be exposed to the odor source between 20 minutes and 1 hour in order to obtain samples accurately reflect the source of odor (Bottcher et al., 2000; Classen et al., 2000). The exposed swatches can then be delivered in sealed glass containers for the panelists to review at their convenience. Due to the seasonal fluctuation of ammonia (NH_3) emissions from swine barns, warmer summer months with higher rates of volatilization are the preferred time to collect odor samples (Hartung, 1991).

OBJECTIVES

The objectives of this study are to evaluate the effectiveness of using the natural zeolite clinoptilolite as the media for microbial attachment within a biofilter, and determine its effectiveness in reducing malodorous gas emissions from a confined swine feeding operation.

METHODS

The zeolite biofilter used in this study was fitted to a confined feeding operation containing an under-slat manure storage pit. This confined feeding operation is a nursery-grower building, located near Moses Lake, WA, with the capacity to house up to 200 pigs weighing from 40 to 100 pounds. This building has two 16-inch fans to draw gases from the manure storage pit and one 24-inch wall fan in the pig living space for climate control. The negative static pressure 16-inch fans draw the malodorous and hazardous gases from the headspace above the manure storage pit to prevent them from diffusing up through the slatted floors and into the living quarters of the pigs above.

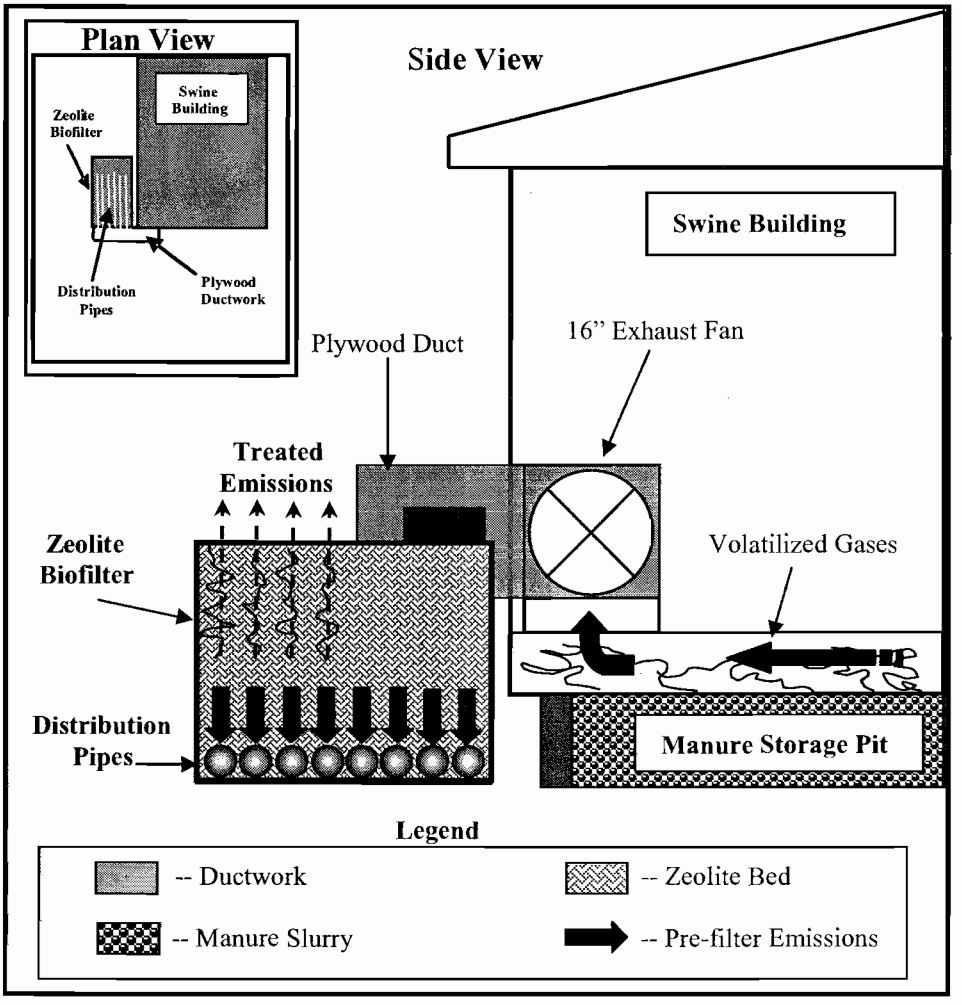
The zeolite biofilter retrofitted to this building consisted of a plywood duct system that was built on September 20, 2003. The biofilter structure was designed to capture and treat the air emitted by one of the 16-inch pit exhaust fans. The malodorous air emissions are forced through a duct system and into a distribution box. From the distribution box the emissions are forced through eight horizontally oriented perforated PVC pipes buried beneath a bed of zeolite (Figure 1).

The zeolite bed serves as a fixed film media for an active population of microorganisms capable of oxidizing odorous constituents volatilized from under-slat manure storage pits. This process of passively treating swine manure odors is referred to as biofiltration. The clinoptilolite zeolite also acts as a molecular sieve due to its cation exchange capacity of 1.3 meq/gm (milli-equivalents/gram). Zeolite has an especially high affinity for adsorbing the hydrogen sulfide (H_2S), ammonia (NH_3), and mercaptans commonly associated with swine manure odors.

Preliminary Laboratory Experiments

According to available literature, zeolite has never been utilized as the fixed film media in a biofilter. Therefore, laboratory experiments were performed at Oregon State University during February through March of 2003 to determine the

Figure 1. Diagram of Zeolite Biofilter Retrofitted to Confined Grower Building



practicability of zeolite as a biofilter media. These experiments also facilitated in determining the functional volume of the full scale biofilter by establishing the ammonia removal efficiency versus gas retention time. Ammonia removal efficiency increases with increased gas retention time, and the gas retention time is dependent on the volume of zeolite in the biofilter and the gas flowrate. In order to balance efficiency and affordability, the resultant gas retention time should provide the highest possible rate of ammonia removal with the least amount of zeolite. This was done by testing the zeolite biofilter for 2, 5, 10, 25, and 45-second gas retention times to determine the relationship between retention time and treatment efficiency, with a minimum NH_3 removal of 50%.

Samples of swine fecal slurry were collected directly from the underslat storage pits at the Oregon State University Swine Center in January, 2003. For each experiment a 500 mL Erlenmeyer flask was filled with 400 mL portions of the fecal slurry and sealed with a two-holed stopper. The sealed Erlenmeyer flasks containing the fecal slurry were ventilated with air using simple aquarium pumps with an average flowrate of 12.6 mL/sec. The air inflow was used to agitate the slurry by bubbling it through the slurry liquid, thus increasing the rate of ammonia volatilization. The exhaust air and volatilized ammonia was then pumped through the zeolite-packed columns where the concentration of ammonia was presumably reduced primarily by adsorption to the zeolite.

Ammonia is most readily volatilized when the fecal slurry has a pH of 10 or greater; therefore, sodium hydroxide (NaOH) was added to the slurry if the pH was below this level. Once measurable volatilization was achieved, the ammonia was piped through a 1.375-inch diameter polyvinyl chloride (PVC) pipe packed with ½-inch diameter clinoptilolite zeolite rock. Different lengths of PVC pipe were used to achieve gas retention times of 45, 25, 10, 5, and 2 seconds in order to determine the relationship between gas retention time and ammonia removal efficiency.

The flask exhaust air was sampled for ammonia before and after exposure to the zeolite column using Nessler reagent methods. The pre-treatment and post-

treatment air was sampled by aerating 1 liter of swine waste gases through 50 mL of 1% boric acid solution before and after the zeolite biofilter. Each 50 mL portion of boric acid used for pre- and post-filter sampling was subsequently divided into 25 mL portions to allow the gases to bubble consecutively through the first tube of boric acid solution follow immediately by the second tube. This method promotes more complete absorption of ammonia with the assumption that approximately 90% of the available ammonia will be absorbed in the first tube of boric acid and 10% in the second tube. Using independent valves, one liter of flask exhaust air was allowed to bubble solely through the pre-filter tubes of boric acid solution, which required 3 minutes. Then, the valves to the pre-filter tubes were closed to allow 1 liter of flask exhaust air to flow through the biofilter and then bubble solely through the post-filter tubes of boric acid solution, which required 6 minutes.

After exposing the samples of boric acid to 1 liter of flask exhaust air, five drops of Nessler Reagent were added to each solution to produce a yellow coloration signifying the presence of ammonium. The quantity of ammonium was then determined using a spectrophotometer at wavelengths between 400-425 nm. The percent transmittance was converted to percent ammonia using a calibration curve previously established for known concentrations of ammonia. The initial concentration of ammonia volatilized from the fecal slurry can be compared to the ammonia concentration after being filtered through the zeolite filter to calculate the reduction of ammonia by adsorption to the clinoptilolite zeolite rock.

Field Scale Experiments

The preceding laboratory experiments led to the conclusion that a 5-second gas retention time would efficiently remove an average of 53% of the ammonia volatilized from swine fecal slurry (Figure 2). Thus, the volume of the zeolite bed was designed to provide an empty bed retention time of 5 seconds. The empty bed volume for the

field scale zeolite biofilter was determined by multiplying the 1185 ft^3/min flowrate, provided by the manufacturer of the manure pit exhaust fan, by the empty bed retention time of 5 seconds (0.0833 minutes). The resultant biofilter volume was determined to be 98.7 ft^3. However, during operation the velocity of air moving through the biofilter depends on the effective porosity, or portion of total pore space available to air flow.

The effective porosity of the clinoptilolite zeolite used in the field scale biofilter was determined in experiments conducted at Oregon State University. A 2000 mL graduated cylinder was filled with approximately 1620 mL of dry 1-inch diameter zeolite. Water was then added until the zeolite rock was completely submerged to allow water to be absorbed by the zeolite. After 5 days, the excess water was drained from the graduated cylinder leaving only the water absorbed by the zeolite. Saturating the zeolite will fill the abundance of minute pore spaces within the rock so that they can be excluded from the effective porosity, since these small pores have virtually no effect on airflow. A volume of 740 mL of water was required to fill the graduated cylinder to the 1620 mL level of the saturated zeolite. The 740mL of water represents the effective pore space between the zeolite rocks. The following calculation was then used to determine the effective porosity:

$$\text{Porosity} = \frac{PoreVolume}{TotalVolume} = \left(\frac{740mL}{1620mL}\right) \times 100 = 46\%$$

Multiplying the 46% porosity by the empty bed volume of 98.7 ft^3 produced the actual void space available to air flow, calculated to be approximately 45.4 ft^3. Therefore, the empty bed gas retention time of 5 seconds will actually be closer to 2.3 seconds during operation, according to the following calculation:

$$\text{Retention Time} = \frac{98.7 ft^3 \times 0.46}{1187 ft^3/\text{min}} = 0.0382\,\text{min} = 2.3\,\text{sec}$$

Although the empty bed retention time may seem inconsequential, it was widely used in the available literature as a means of normalizing the variety of physical characteristics that accompany the abundance of potential biofilter media that have been utilized.

The biofilter used in this study was a plywood box with the dimensions 8′ x 4′ horizontal and 4 feet vertical built at ground level and located adjacent to the nursery-grower building. Emissions from the barn were directed through a 2′ x 2′ plywood duct system to a gas distribution box at the base of the biofilter. The distribution box housed the open ends of eight perforated 3″ diameter PVC pipes that distribute the emissions along the bottom of the zeolite bed. The air is then forced to diffuse upward through 3 feet of zeolite.

Measurements collected from the field site included outside ambient temperature, temperature and relative humidity of exhaust air before and after the biofilter, static pressure induced by the biofilter, and concentrations of NH_3 (ammonia) in building emissions before and after exposure to the biofilter. The temperature readings and relative humidity measurements were collected using an Omega® RH-83 digital psychrometer. Relative humidity of pre-filter gas was measured to ascertain the amount of water vapor that was supplied to the biofilter by the building exhaust gas. Static pressure was measured in inches of water using a simple U-shaped manometer of 0.01 inch diameter glass tubing. The static pressure measurements were applied to a calibrated rating curve, provided by the manufacturer of the Multifan® PH-4E40Q exhaust fan, to determine the airflow resistance created by the biofilter. Ammonia concentrations were measured using a Sensidyne® AP-1S gas detection pump and Kitagawa No. 105SD colorimetric NH_3 detector tubes. Measurements of pre-filtration NH_3 concentrations were collected via a sampling portal in the ductwork near the fan. Post-filtration measurements were collected using an inverted 5-gallon bucket. A sampling portal was drilled into the bottom of the inverted bucket to allow sampling of the exhaust air after biofiltration. The mouth of the bucket was inserted into the bed of zeolite to a depth of two inches in order to capture the post-filtration air

emissions. The sampling bucket was moved to a different location on the zeolite bed between each sampling in order to obtain a representative sampling of NH_3 emissions, and also to purge the bucket of any potential stagnant concentrations of captured NH_3 emissions.

Microbial Analysis

In order to be a biofilter there must be an active population of microorganisms living on the surface of the zeolite. Nitrite assays and PCR (Polymer Chain Reaction) analysis were used to identify the presence of nitrifying bacteria growing on the zeolite.

Samples of zeolite that had been used to filter swine manure gases for two months were collected from the 12 inches above the bottom of the bed and 12 inches below the top of the bed. These samples were immediately stored on ice upon collection until they could be analyzed in the laboratory approximately 20 hours later. In the laboratory the zeolite was placed in an Erlenmeyer flask then filled with 25 millimolar NH_3 AOB (Ammonia Oxidizing Bacteria) growth media, which is specifically formulated to support the metabolic activity and reproduction of ammonia oxidizing bacteria. These flasks, containing separate samples from the upper and lower layers of the zeolite bed, were agitated in a dark room at an incubation temperature of 30° Celsius for two weeks. The agitation serves to circulate the growth media amongst the bacteria, increase the dissolved oxygen content of the media and to cause physical detachment of the bacteria from the zeolite rocks.

After two weeks of incubation and agitation, 8 mL of liquid bacterial culture were extracted from each flask and transferred to fresh growth media without zeolite. The freshly inoculated flasks were once again agitated in the dark at 30°C for two more weeks. After the two weeks, 8mL of liquid bacterial culture was extracted and transferred into fresh AOB growth media without the zeolite. This procedure is

repeated three times for the two samples collected from the field plus a third unexposed control sample. After each two-week incubation period the samples were examined with a ThermoSpectronic® Genesys-10uv spectrophotometer at 352 and 400 nanometers before inoculation into fresh AOB growth media.

The 352 and 400 nanometer measurements collected from the spectrophotometer are used to determine the concentration of nitrite (NO_2^-) that is present in the culture. The NO_2^- measurements for each sample are normalized by dividing molar concentrations by the corresponding weight of the zeolite in the sample with the units mM/mg-zeolite. The presence of NO_2^- suggests the original AOB growth media containing 25 millimolar NH_3 has been converted by the ammonia oxidizing bacteria in the culture. This is the first indicator that a population of ammonia-oxidizing bacteria has successfully established themselves on the zeolite rocks. Data provided by the nitrite assays indicate metabolic activity of nitrifying bacteria and the layers of zeolite bed in which this activity is most prevalent.

More conclusive evidence of the presence of nitrifying bacteria on the zeolite biofilter is obtained through PCR analysis, which identifies microorganisms at the genomic level. PCR methods were used to amplify the *amoA* gene and the *16S rRNA* gene of Ammonia-Oxidizing Bacteria from genomic DNA extracted from the bacterial cultures. The *amoA* enzyme is what AOB use to oxidize ammonia; therefore, detection of the *amoA* gene would indicate that the nitrifying bacteria *Nitrosomonas* are present. The detection of the *16S rRNA* gene would suggest that these organisms belong to the grouping of Ammonia-Oxidizing Bacteria. More detailed information on the process for preparing genomic DNA samples for the PCR can be found in Appendix A.

Subjective Odor Analysis

The primary purpose of the biofilter is to reduce the odors emitted from confined pig feeding operations. A subjective analysis of the odor emitted after biofiltration helped determine the effectiveness of the zeolite biofilter to reduce the human perception of these odors. The human olfactory response is more sensitive to odor detection than man-made olfactometric instruments; therefore, a panel of eleven panelists experienced with swine odors were arranged to smell randomly selected odor samples collected before and after exposure to the biofilter. The odor samples were collected on August 24, 2004 by exposing three 7 x 7 inch cotton swatches to the pre-biofiltered air and three more to the post-biofiltered air emitted from the manure storage pits of the nursery-grower building. On August 26, 2004, each of the participants were presented with a pre- and post-biofilter odor sample and asked to identify the less offensive sample and rank its odor (refer to Appendix 2 for sample evaluation sheet). This comparison between pre- and post-biofilter odor samples was performed three times by each of the 11 participants. The participants were students and professors who have had experience around swine operations and were familiar with swine odors.

RESULTS

Preliminary Laboratory Data

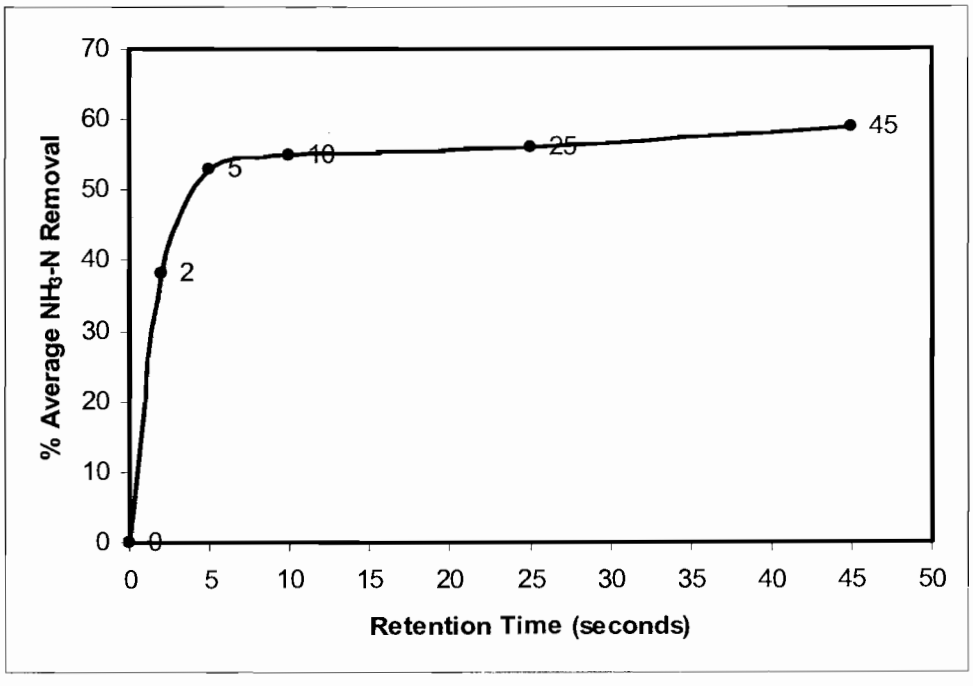
Laboratory experiments with zeolite filters were performed to verify the potential application of zeolite in the biofiltration of odorous gases volatilized from swine fecal slurry. In the laboratory experiments adsorption was the primary process by which the zeolite was able to reduce ammonia from the swine waste gases. It was assumed that a bacterial film would develop on the surface of the zeolite rocks after exposing it to the volatilized swine waste gases for three months from February through April of 2003; however, methods for confirming the presence of bacterial film were not at our disposal at the time. Therefore, the primary objectives of the laboratory experiments were to verify that the adsorption qualities inherent to clinoptilolite zeolite were capable of sufficiently filtering a majority of the ammonia volatilized from swine fecal slurry, and to determine the minimum retention time required to reduce ammonia concentrations by at least 50%. Any bacterial film that would develop on the zeolite rocks would increase the efficiency of the system to reduce odors.

Ammonium nitrogen was the primary constituent evaluated in these experiments, which can be used to determine levels of ammonia volatilized from swine waste samples. Ammonium nitrogen was measured using Nessler methods. The collected test tubes of ammonium samples were then analyzed with a spectrophotometer. The data were collected in percent transmittance from the spectrophotometer and then applied to a calibration curve to determine the approximate ammonium content measured in mg/L (milligrams per liter), which was then converted to concentration of ammonia using a calibration curve.

The zeolite filter apparatus used for these experiments were 1.5-inch diameter PVC pipes filled with an appropriate volume of zeolite, based on the desired retention time of the swine waste gases. The experimental retention times were 45, 25, 10, 5, and 2 seconds. This range of times was chosen in order to determine the gas retention

time after which there is a diminishing increase in removal efficiency. This helped to determine the shortest gas retention time necessary to remove at least 50% of the ammonia volatilized from swine fecal slurry. The retention times of 45, 25, 10, 5, and 2 seconds reduced ammonia levels by an average of 59%, 56%, 55%, 53%, and 38%, respectively. The results of these experiments, shown in Figure 2, suggest that 5 seconds is the minimum residence time that would continue to provide acceptable ammonia removal above 50%. The 5-second retention time was multiplied by the 1185 ft^3/min fan flowrate to determine the 98.7 ft^3 volume of the field-scale version of the biofilter.

Figure 2. Gas Retention Time versus Ammonia Removal Efficiency.



An important discrepancy between the laboratory and field-scale versions of the biofilters was the different diametric proportions of the zeolite used for each. The laboratory experiments were performed with ½-inch diameter clinoptilolite zeolite with an approximate bulk porosity of 40%, while the clinoptilolite zeolite used in the field-scale biofilter was 1-inch diameter with an approximate bulk porosity of 46%. For the 98.7 ft^3 design volume and the fan flowrate of 1185 ft/min, the gas retention time between the ½-inch and 1-inch diameter zeolite would be approximately 2 seconds and 2.3 seconds, respectively. Despite this relatively small difference in gas retention times between the ½-inch and 1-inch diameter zeolite, the ammonia reduction efficiencies of the field-scale zeolite biofilter outperformed that of the laboratory scale by a difference of nearly 47%.

Measurements of Ammonia Reduction

Odor reduction by the full-scale zeolite biofilter was determined by measuring NH_3 (ammonia) concentrations emitted from a confined pig feeding operation in Moses Lake, Washington during the period from October 20, 2003 through July 14, 2004. Twenty-three NH_3 samples were collected before and 23 samples collected after exposure to the zeolite biofilter on various dates during the study period. Comparison of the pre-filtration (untreated) and post-filtration (treated) NH_3 concentrations led to the determination of the percent reduction of odorous emissions. According to the data there was an average NH_3 reduction of 90% over the 10-month study period. There is convincing evidence that zeolite biofilter reduced the NH_3 concentration as measured in parts per million (two-sided p-value $< .0001$ from a paired t-test). The paired t-test shows a mean NH_3 reduction of 3.9 ppm, which corresponds to a reduction of 90.11%. A 95% confidence interval for the mean difference is 3.2 ppm to 4.5 ppm. The recorded maximum and mean NH_3 concentrations emitted from the barn during the study period were 6 ppm and 4.3 ppm, respectively.

Table 2. Statistical Evaluation of NH_3 Measurements Using Paired t-Test

Sample	n	Pre-filter Average (ppm)	Post-filter Average (ppm)	Mean Difference (%)	Standard Error	p-value
NH_3	23	4.36	0.36	90.1	0.640	0.0001

On May 21, 2004 a perforated garden hose was buried in a descending coil pattern on one half of the biofilter media to irrigate the zeolite. The remaining half of the biofilter was not irrigated; thus moisture in this half of the biofilter was provided only by water vapor from barn emissions and precipitation directly onto the exposed zeolite bed. Due to the high desert climatic conditions of Eastern Washington, irrigation was most necessary during the period from April to October with characteristically low precipitation rates, with a 7-month average of 0.39 inches/month, and increased evaporation rates, with a 7-month average pan evaporation of 6.8 inches/month. This creates a moisture deficit within the biofilter media that must be compensated by adding water to support microbial activity.

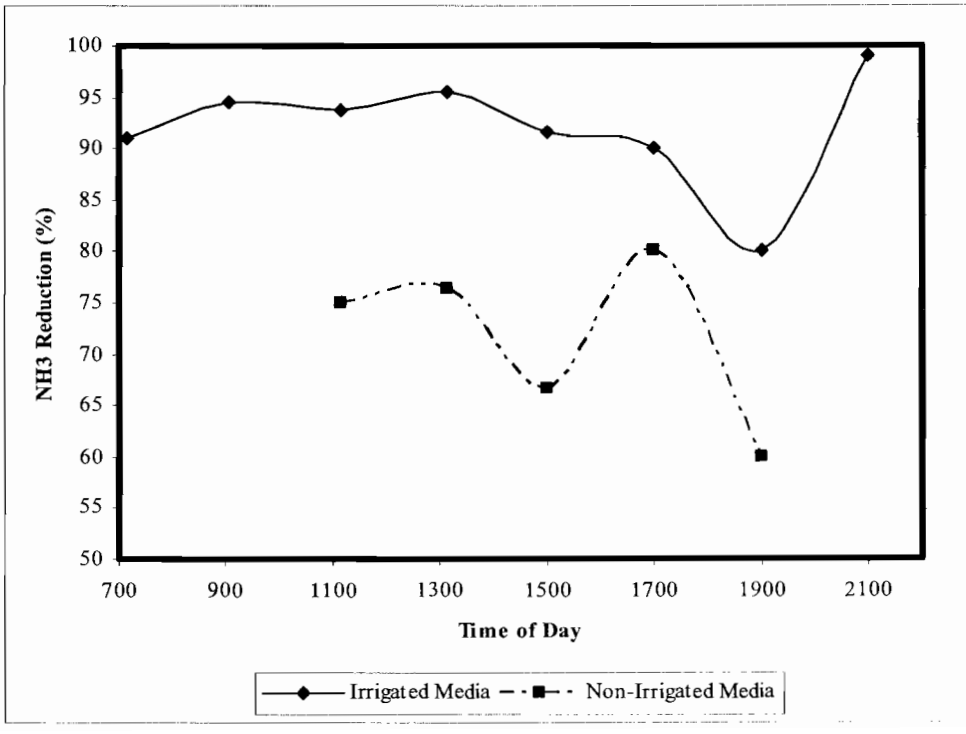
On July 14, 2004 after irrigating one half of the biofilter for 69 days, measurements of NH_3 concentrations in the exhaust gas emitted directly from the swine building and after emission from the biofilter were collected every two hours from 7 a.m. until 9 p.m. to observe the diurnal fluctuations that occur under irrigated and non-irrigated conditions. The irrigated half performed better than the non-irrigated half by removing an average of 92% of the NH_3 concentration compared to 72% of the NH_3 concentration on the non-irrigated half, shown in Figure 3. Measurements of non-irrigated NH_3 concentrations were limited to five measurements due to the limited number of colorimetric NH_3 detector tubes; however, enough measurements were collected to characterize the difference between irrigated and non-irrigated NH_3 reductions. Data presented in Figure 3 suggests that zeolite effectively filters NH_3 by adsorption, but further evidence of biological activity is necessary to

attribute removals to nitrifying bacteria. Existence of these bacteria on the surface of the zeolite qualifies this device as a biofilter.

Nitrite Assays

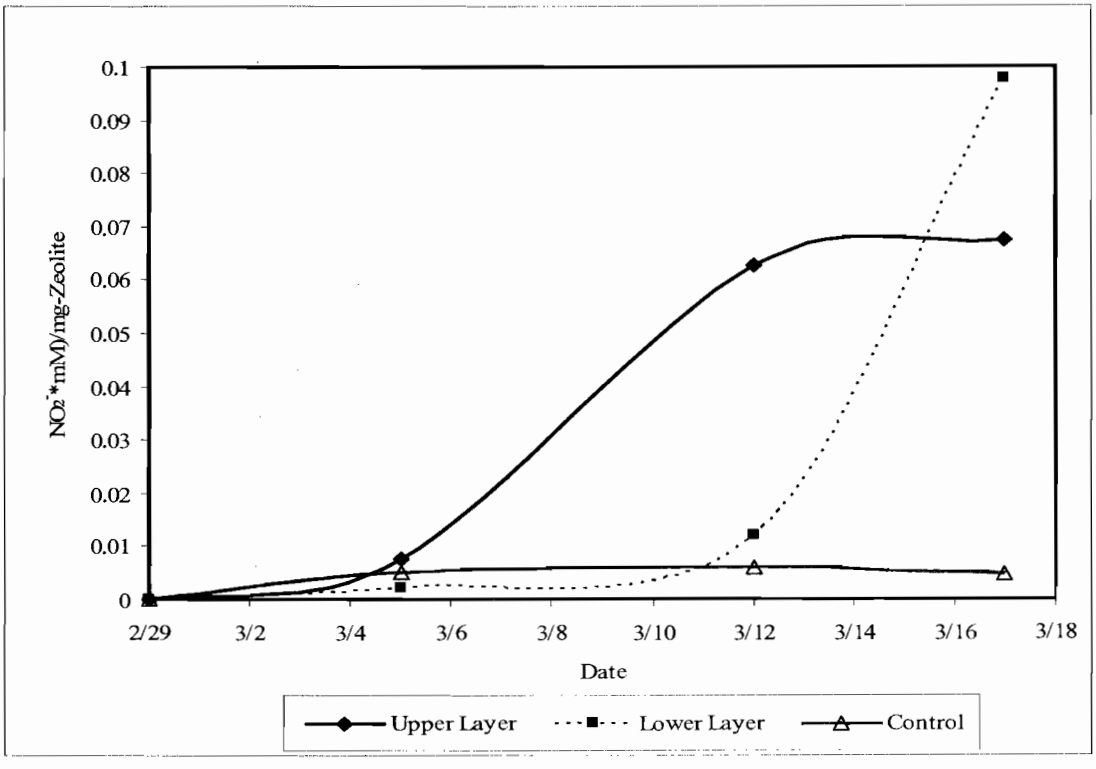
Production of NO_2^- (nitrite) gas is a positive indicator of the metabolic activity of nitrifying bacteria on the zeolite media. The bacterial activity was detected through consecutive nitrite assays performed in the laboratory. Samples of zeolite were collected from the upper and lower 12-inch layers of the zeolite bed to locate the zones of highest bacterial activity. Results from the nitrite assays also offer a crude estimate of the quantity of bacteria between relative layers of zeolite at the time of collection.

Figure 3. Diurnal Fluctuations of NH_3 Removal for Irrigated and Non-Irrigated Halves of Zeolite Biofilter on July 14, 2004.



Samples of zeolite were extracted from the biofilter on February 28, 2004 and July 14, 2004. The first set of samples collected on February 28 had been exposed to swine barn emissions for 49 days. These samples were inoculated with AOB (ammonia oxidizing bacteria) growth media and incubated at 30° Celsius for two weeks to promote the production of nitrite, which is a byproduct of bacterial metabolism. The upper layer zeolite samples had a slightly faster nitrite production rate during the first two weeks at 0.003 mM-NO_2^-/day compared to 0.001 mM-NO_2^-/day in the lower layer zeolite samples (Figure 4). The control used in this nitrite

Figure 4. Results of Nitrite Assay Performed on Zeolite Collected from Biofilter on February 28, 2004.



* Nitrite assay results are normalized by the corresponding weight of each zeolite sample, hence nitrite (NO_2^-) is measured in the units mM/mg Zeolite.

assay was sterilized clinoptilolite zeolite that was never exposed to the biofilter. The production of nitrite signifies the metabolic activity of nitrifying bacteria within the ideal conditions provided by the AOB growth media. The prompt growth response of bacteria in the upper layer suggests there were a greater number of bacteria in the upper layer of the biofilter than the lower layer at the time of collection.

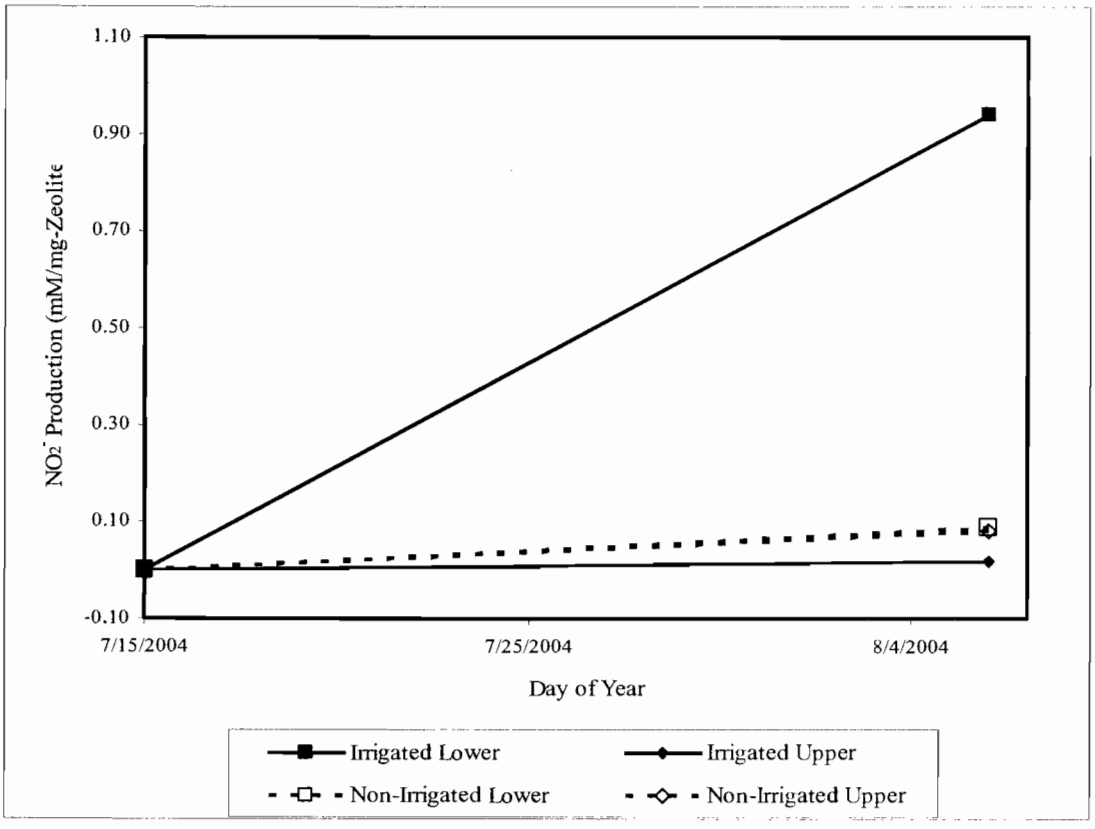
A second series of nitrite assays were conducted on zeolite samples exposed to swine barn emissions for 69 days and collected on July 14, 2004. As in the previous assay, these samples represent the upper and lower layers of the zeolite bed; however, in this instance there were two sets of samples representing the irrigated and non-irrigated halves of the biofilter. Comparison of the irrigated and non-irrigated halves provided insight on the affect moisture content has on bacterial activity and subsequent biofiltration efficiency. Half of the biofilter was irrigated to achieve 55% moisture content by wet weight, and then replenished every three days with a volume of water based on local pan evaporation estimates for each month. Therefore, the irrigated half of the biofilter was initially soaked with 180 gallons then supplemented with an average of 0.11 gal/ft3·day. The non-irrigated half received only 1.43 inches of cumulative precipitation during this period and whatever moisture derived from water vapor in the barn emissions.

The results of the second nitrite assays performed on July 14, 2004, presented in Figure 5, reveal bacterial activity on both the irrigated and non-irrigated halves of the biofilter. However, the zeolite samples extracted from the irrigated half of the biofilter experienced a nitrite production rate of 0.042 mM-NO_2^-/day compared to 0.007 mM-NO_2^-/day for the non-irrigated samples. Therefore, the nitrite production rate by nitrifying bacteria in the irrigated half of the biofilter was six times greater than that in the non-irrigated half.

Polymer Chain Reaction (PCR) Analysis

These nitrite assays do suggest the presence of nitrifying bacteria; however, more conclusive evidence of bacterial growth on the zeolite was produced through PCR (polymer chain reaction) analysis which identifies microorganisms at the genomic level. PCR analysis conducted on samples extracted from the biofilter on February 28, 2004 positively identified the presence of the bacterial species *Nitrosomonas.* The photograph of the PCR under UV (ultra-violet) light exposure is presented in Figure 6. This provides conclusive evidence that nitrifying bacteria have been able to successfully establish colonies on the zeolite media.

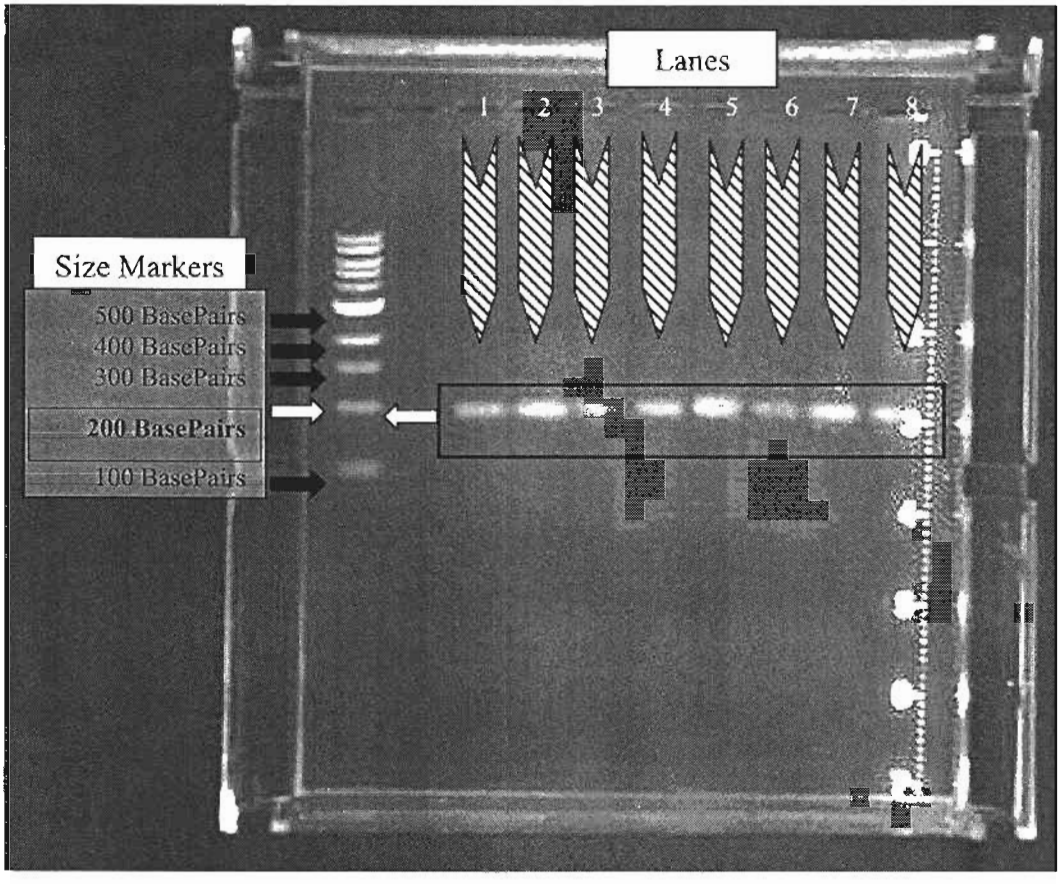
Figure 5. Results of Nitrite Assays Performed on Zeolite Collected from Biofilter on July 14, 2004.



* Nitrite assay results are normalized by the corresponding weight of each zeolite sample, hence nitrite (NO_2^-) is measured in the units mM/mg Zeolite.

Detailed information on the results of the PCR analysis is presented in Appendix A. The PCR results coupled with the nitrite assay data confirm that bacteria are able to establish active colonies on the surfaces within the zeolite biofilter.

Figure 6. Photograph of the PCR results indicating presence of *Nitrosomonas*



The *16S* and *amoA rRNA* were injected into the lanes at the top, then *Nitrosomonas* was identified when the band patterns reached the 200 BasePair (BP) size marker denoted on the left side of the photograph.

Lanes	DNA Fragment	Extraction Point from Biofilter
1&2	*16S rRNA*	Upper Layer
3&4	*16S rRNA*	Lower Layer
5&6	*amoA rRNA*	Upper Layer
7&8	*amoA rRNA*	Lower Layer

Static Pressure and Temperature Measurements

The zeolite media was also evaluated for its ability to maintain a consistent airflow rate, which is vital for proper ventilation of the swine barn. Static pressure measurements were collected for each sampling date to monitor the airflow resistance induced by the biofilter. The static pressure was measured in inches of water, using a glass tube manometer. The highest recorded measurement of static pressure of 0.57 inches-H_2O translates to the lowest airflow rate of 1345 cfm (ft^3/min), which was 45% of maximum capacity. The lowest recorded measurement of static pressure of 0.19 inches-H_2O translates to the highest airflow rate of 2599 cfm (ft^3/min), which is 88% of the maximum capacity. The maximum fan capacity at zero static pressure is 2960 cfm according to the exhaust fan manufacturer. The average static pressure over the 10-month operating period was 0.31 inches-H_2O, which is approximately 75% of maximum capacity according to the fan pressure rating curve provided by the manufacturer.

Temperature measurements of the building ventilation air emitted from the swine barn were also collected during each visit. Recall the optimal temperature range for bacterial metabolic activity is between 10° C and 40° C; therefore, these measurements provided the closest estimate of the temperature conditions in the biofilter where the bacteria are expected to reside. The lowest recorded barn emission temperature was 9° C on February 28, but the 10-month average was 20° C. Despite temperatures below optimal temperature range, the NH_3 reduction for February 28 was 99% and one of the highest NH_3 reductions recorded for the entire period of operation. Local climate records indicate a cumulative precipitation of 0.76 inches for the seven days prior to the collection of this sample.

Subjective Odor Analysis

The final stage of evaluating the performance of the zeolite biofilter entailed a subjective analysis of odor reduction by presenting odor samples to a group of 11

panelists. Samples of odor were collected by exposing three 3″× 3″ cotton swatches to pre-filtration barn exhaust and three swatches exposed to post-filtration barn exhaust. The pre-filtration swatch samples were exposed directly to the barn exhaust, via the sampling portal in the ductwork, for 26 minutes with a duct airflow rate of 2599 ft^3/min calculated using manometer readings. The post-filter swatch samples were collected with the same inverted 5-gallon sampling bucket previously utilized for collecting ammonia concentration samples. The swatches were exposed for 1060 minutes (17.7 hours) to compensate for the effects air flow dispersal over the 32 ft^2 cross-sectional area of the biofilter. The localized post-filter flowrate through the 5-gallon sampling bucket was 63.8 ft^3/min, according to the following calculations:

Post-filter Velocity = Pre-filter Flowrate ÷ Biofilter Cross-sectional Area

$$= \left(2599\ ft^3/\text{min}\right) / \left(32\ ft^2\right) = 81.22\ ft/\text{min}$$

Five-gallon Bucket Flowrate = Cross-sectional Area of Bucket × Post-filter Velocity

$$= \left(\pi(0.5\ ft)^2\right) \times \left(81.22\ ft/\text{min}\right) = 63.8\ ft^3/\text{min}$$

This careful consideration for the disparity in the pre- and post-filter flowrate was necessary to ensure that both samples were equally exposed to approximately 67,574 ft^3 of the pre- and post-filter exhaust air.

Each panelist was asked to identify the sample with the least offensive odor in three separate odor evaluation trials. Each trial consisted of one pre-filtration swatch sample paired with one post-filtration swatch sample. The panelists observed that the post-filtration sample was less offensive in 69.7% of the trials. This statement is significant within a 95% confidence interval of ± 15.7%; thus, panelists would be able to correctly identify the odor improvement created by the zeolite biofilter in 54.0% up to 85.4% of the trials.

DISCUSSION

The purpose of this study was to evaluate zeolite as an efficient biofilter media. Three performance criteria that must be met in order to establish zeolite as an effective biofilter media are: Does zeolite provide a suitable environment for bacteria growth?; Is the zeolite biofilter capable of removing up to 90% of ammonia concentrations associated with swine waste?; Does the zeolite biofilter reduce the intensity and offensiveness of odors emitted from a confined swine building, as perceived by a panel of odor evaluators?

To accomplish this evaluation a full scale zeolite biofilter was retrofitted on a swine building that supports up to 200 nursery-grower pigs weighing between 40 and 100 pounds. Evaluating the biofilter in this study entailed: (1) measuring the reduction of NH_3 (ammonia) emission from a swine building near Moses Lake, Washington; (2) nitrite assays measured with photospectrometry to detect bacterial activity on the zeolite; (3) PCR analysis to identify nitrifying bacteria growing on the zeolite, and; (4) subjective analysis to evaluate the odor reduction perceived by eleven panelists.

Eight visits to the CAFO field site in Moses Lake, Washington spanned a 10-month period from October 2003 through July 2004. During this period Eastern Washington experienced high desert weather conditions that characterized the precipitation and temperature extremes from winter to summer (Table 3). Observing the biofilter during this range of temperature and precipitation conditions assisted in evaluating the biofilter under climatic extremes that could negatively impact the bacterial activity necessary for effective biofiltration. Cold winter temperatures tend to reduce the metabolic activity of bacteria, and increased summer evaporation rates tend to deprive bacteria of vital moisture.

The capacity for bacteria attached to the biofilter media to reduce odors is improved within an optimal range of temperatures between 10° C and 40° C. The

lowest building emission temperature recorded during data collection was 9° C on February 28, 2004. Despite this low temperature the biofilter was still able to remove

Table 3. Climatic Conditions During Period of Biofilter Operation from October 2003 to July 2004.

Month	Total.Precip (inches)	Departure From Normal	Pan Evaporation (inches)	High Temp (°F)	Low Temp (°F)	Avg. Temp (°F)
Oct	0.35	-0.10	No Data	82	23	53.8
Nov	0.34	-0.81	No Data	60	13	33.4
Dec	1.35	-0.08	No Data	44	9	28.0
Jan	0.73	-0.41	No Data	52	-8	27.0
Feb	1.43	0.57	No Data	51	19	33.7
Mar	0.80	0.12	No Data	69	26	46.9
Apr	0.21	-0.26	4.74	78	34	54.6
May	1.29	0.68	6.87	82	41	59.4
Jun	0.14	-0.50	7.87	99	47	69.5
Jul	0.30	0.00	9.38	99	53	76.7

99% of the NH_3 emitted from the barn at a concentration of 5 ppm (parts per million). It was not possible in this study to distinguish the proportion of NH_3 reduction attributed to microbiological oxidation from that of physical adsorption by the zeolite. Regardless, the critical result is that the zeolite biofilter, as a so-called "black box", was able to remove an overall average of 90% of the NH_3 under sub-optimal conditions for bacterial metabolic activity.

This finding was further supported by data from nitrite assays of zeolite collected from the biofilter on February 28, 2004. The average temperature for the month of February 2004 was 33° F, with a low of 19° F. Despite these low temperatures, Figure 4 shows a higher rate of nitrite production in samples extracted from the upper layer of the zeolite bed in comparison to the lower layer. This is a reflection of higher bacterial activity in the upper layer and indirectly suggests there was a larger population of bacteria in the upper layer at the time of collection. This is

an indication that the building exhaust provides enough heat to maintain microbial activity through the winter months.

The biofilter was not irrigated at this point in the study; so, most of the moisture needed for bacterial activity was likely derived from precipitation permeating the upper layers of the exposed zeolite bed. Thus, the higher level of bacterial activity in the upper layer could also be equally attributed to the higher moisture content that derived from the 1.43 inches of precipitation recorded for February 2004. The total precipitation for the seven-day period prior to the sample collection date on February 28 was 0.73 inches. Bacterial biofilms not only require moisture for cellular growth, but they also need it to capture water soluble gases by absorbing them as they flow past. Without this absorption phase, the bacteria would not be able to access soluble gases, such as NH_3, for oxidation.

The significant nitrite production measured in the nitrite assays are a strong indication of metabolic activity of nitrifying bacteria. And evidence provided by the results of the PCR (Polymer Chain Reaction) analysis confirmed the presence of the nitrifying bacteria *Nitrosomonas*. This indicates that zeolite provides a suitable environment for the metabolic activity of nitrifying bacteria, such as *Nitrosomonas*. This also provides conclusive evidence that zeolite can indeed support bacterial growth even under winter conditions in Eastern Washington.

The odors emitted from anaerobically stored swine waste are a complex mixture of as many as 331 gaseous compounds (Schiffman et al., 2001). One of the most prominent of these compounds is NH_3; therefore, NH_3 was selected as an index for the intensity of odor emissions. Concentrations of NH_3 from the swine building used in this study were consistently above 4 ppm and quite useful as an indicator of odor.

Concentration measurements of NH_3 were collected before and after exposure to the biofilter, in order to evaluate the effectiveness of the zeolite biofilter in reducing odorous emissions. The zeolite biofilter effectively removed an average of 90% of the NH_3 emitted over the ten month study period. However, the average NH_3 removal for

the month of May dropped to 84%. The average NH_3 reduction for all prior samples collected between October 21, 2003 and February 28, 2004 was 94%. This decrease in biofilter efficiency was attributed to the onset of dry summer conditions with a corresponding increase in evaporation rates, presented in Table 3. Humidity measurements were originally collected with the notion that water vapor in building emissions would be sufficient for maintaining the moisture content of the biofilter media. According to Bohn (1991), desiccation of the biofilter media will occur when the relative humidity of the air to be treated falls below 95%. The average relative humidity of the exhaust air from the swine building was 43% over the course of the 10-month operating period, with a maximum of 88% occurring on February 28, 2004.

Relative humidity is highly prone to seasonal and diurnal fluctuations; therefore, to maintain consistent moisture content within the media it is important to provide water during periods of low precipitation and high evaporation typical of summer months. Therefore, the decision was made to irrigate one half of the biofilter using a perforated garden hose while the remaining half would continue to operate with moisture input derived only from water vapor in building emissions and precipitation intercepted by the zeolite bed. The NH_3 concentration measurements collected after installing the irrigation system revealed that the irrigated half removed an average of 92% of NH_3 emissions compared to 72% from the non-irrigated half.

Nitrite assays reflected this improvement in biofilter efficiency with irrigation. Zeolite samples extracted from the irrigated half of the biofilter experienced a nitrite production rate of 0.042 mM-NO_2^-/day compared to 0.007 mM-NO_2^-/day for the non-irrigated samples. This suggests that the nitrifying bacteria in the irrigated half of the biofilter were six times more active than those in the non-irrigated half.

The capacity of the zeolite biofilter to reduce NH_3 is also highly dependent on the gas retention time. The 5-second empty bed gas retention time of the zeolite biofilter in this study was based on the fan flowrate of 1185 ft^3/min, which was obtained via telephone conversation with a representative of the fan manufacturer. This fan flowrate was based on a 14-inch fan at static pressure of 0.2 inches-H_2O,

which is the typical pressure drop induced after the addition of a duct system. However, shortly after construction of the biofilter it was discovered that the manure storage pit exhaust fan of the swine building in this study was actually a 16-inch fan. The 16-inch fan produces a significantly higher flowrate of 2570 ft^3/min at 0.2 inches-H_2O static pressure. This difference in fan flowrate invalidated the original empty bed gas retention time of 5 seconds determined in laboratory experiments. The actual gas retention time was reduced to 2.3 seconds as a result of the higher fan flowrate. This significant discrepancy in fan flowrate might have been disastrous for biofilter efficiency were it not for the very promising ammonia reductions achieved by the zeolite biofilter, with an average removal efficiency of 90%. It appears that the zeolite biofilter was actually able to perform at more than twice the efficiency anticipated by the results from the laboratory experiments.

Another minor discrepancy was encountered between the laboratory experiments and the field-scale biofilter. The particle size of the zeolite used in the laboratory experiments was ½-inch diameter, which was significantly smaller than the 1-inch diameter zeolite supplied for the field-scale biofilter by Steelhead Specialty Minerals (Spokane, WA). This also had a drastic effect on the retention time by reducing the bulk porosity from 60% for ½-inch diameter to 50% bulk porosity for the 1-inch diameter zeolite. Therefore, the gas retention time for the experimental design based on the 1185 ft^3/min fan flowrate and ½-inch diameter zeolite was expected to be 3 seconds after accounting for the 60% effective porosity; whereas, the actual gas retention time for the 2570 ft/min fan flowrate and 1-inch diameter zeolite was 1.2 seconds with an effective porosity of 50%. Regardless of these discrepancies, the consistently high removal rates of NH_3 coupled with the positive identification of *Nitrosomonas* confirmed that zeolite is fully capable of performing as an effective biofilter media. The dimensional miscalculations encountered during the transition from the design phase to the field-scale operation of the zeolite biofilter provided the fortuitous result of further substantiating Clinoptilolite zeolite as a very promising biofilter media.

The evaluation of zeolite as a potential biofilter media was approached as a "black box" system in this study. This means that the zeolite biofilter, as a system, was provided with inputs and the outputs were observed without extensively analyzing the processes occurring inside the zeolite biofilter. An important question concerning the zeolite biofilter is how much of the NH_3 removal can be attributed to bacterial oxidation and how much to the sorption capacity of moistened zeolite. During the first month of operation, adsorption was likely the dominant NH_3 removal process over bacterial oxidation. The first measurements of NH_3 removal collected the day after installing the zeolite were as high as 99%, and since it was presumably installed deplete of any bacterial colonies this removal can be attributed to physical adsorption. Ammonia reductions during the remaining nine months of operation may have been attributed more to adsorption over biological oxidation, but there were no accessible methods for verifying this at the time.

Separating microbial processes from sorption processes is a daunting task even under the most controlled laboratory conditions, but a general estimate of the adsorption capacity of the zeolite can be made using some of the conditions observed during the course of evaluating the zeolite biofilter in this study. The average NH_3 concentration in exhaust from the swine facility in this study was 4.3 ppm (parts per million) and the average rate of exhaust was 2234 cfm (ft^3/min). The adsorption of NH_3 gas by zeolite is a physical process that is dependent on the exposed surface area throughout the bed of zeolite. The gas adsorption capacity of 2″ diameter Clinoptilolite zeolite is approximately 8% by weight according to analyses conducted by Steelhead Specialty Minerals. Therefore, the NH_3 adsorption capacity for 1.5 tons of zeolite will be approximately 108,862 grams of NH_3. Knowing that 4.3 ppm NH_3 is the equivalent to 4.3 mg/kg NH_3, the time until full adsorption capacity under constant NH_3 concentration of 4.3 ppm and fan flowrate of 2234 cfm can be calculated in the following:

$$\frac{M}{Q \cdot \rho_{air} \cdot C_{NH_3}} = \frac{108{,}862{,}160 mg}{(4.3\, mg/kg) \cdot (1.2\, kg/m^3) \cdot (63.3\, m^3/\min)} = 333{,}291 \min = 231 days$$

where,

NH_3 Adsorption Capacity for 1.5 tons of Zeolite (M) = 108,862,160 mg NH_3

Average fan flowrate (Q) = $2234\, ft^3/\text{min} = 63.3 m^3/\text{min}$

Density of exhaust air (ρ_{air}) = 1.2 kg/m^3

Emission concentration of NH_3 (C_{NH_3}) = 4.3 ppm = 4.3 mg/kg

Therefore, under controlled conditions with a constant air flowrate and NH_3 concentration the zeolite bed in this study would reach its NH_3 adsorption capacity in approximately 231 days. Since actual exhaust flowrate and NH_3 concentrations from swine operations fluctuate considerably, these ideal conditions will not exist in the field; so, actually reaching the adsorption capacity for 1.5 tons of zeolite will require a great deal more time than 231 days. During this time the bacterial biofilm will continue to grow and will be able to utilize the ammonia captured by adsorption to the zeolite. Media with similar adsorption characteristics to zeolite have been shown to promote bacterial colonization by capturing NH_3 until it is accessible to the bacteria (Armstrong and Prosser, 1988; Powell and Prosser, 1987). Reductions of NH_3 recorded after the fixed adsorption capacity of zeolite can be attributed to bacterial oxidation; however, since the bacteria will grow simultaneous to ammonia adsorption, it remains a complex task to distinguish ammonia reductions between these two processes.

The most essential result of this research is that *Nitrosomonas* was found to be capable of growing on the surface of the zeolite. And it is safe to assume that this growth will continue as long as no unforeseen circumstances arise that would prohibit such growth. The growth of *Nitrosomonas* and other aerobic microorganisms is a highly complex process dependent on environmental conditions such as temperature, pH, carbon source, moisture content, etc., and is further dependent on the even more complex nature of gas volatilization and diffusion. Estimates of specific growth rate of bacteria vary greatly depending on the substrate and bacterial species. Therefore, to perform such a count the bacteria must be grown under controlled conditions in a

laboratory and supplied with constant concentrations of ammonia and selective species of nitrifying bacteria (Saha, December 14, 2004, personal communication). Quantification of these bacteria is a task best performed with a highly technical method such as fluorescent in-situ hybridization (FISH). Understanding the rate of bacteria growth on the zeolite is an important and highly complex measurement that should be pursued, because estimating the growth of nitrifying bacteria on the surface of zeolite is an important indication of its potential as a biologically active filter.

The functional success of this zeolite biofilter is inconsequential if the average swine operation is unable to afford implementing such a device. The price of the zeolite rock is the greatest construction cost, especially when compared to organic media which can often be found on the premises of many swine operations. The advantage of zeolite over comparable organic media is that its resistance to degradation and compaction reduce maintenance costs and delay replacement costs, and the zeolite will not need to be tilled or treated for burrowing pests when larger grain sizes are used.

The initial expense for the zeolite biofilter is higher than comparable biofilters that utilize organic media; however, organic media often requires replacement every five years due to biodegradation, and they frequently need to be tilled to prevent media compaction. The silica-based structure of zeolite, on the other hand, will not degrade within the range of acidity between pH 3 and 7. This range of pH is maintained by the buffering capacity of minerals in the zeolilte, such as Calcium and Magnesium.

The cost for lumber, perforated piping, fasteners, and the 1.5 tons of zeolite rock came to a total of $1067. This comes to roughly $360 per 1000 cfm ($ft^3$/min) of exhaust capacity. This is comparable to construction costs with organic biofilter media at $150 to $250 per 1000 cfm (Nicolai et al., 2002). The longevity of the zeolite biofilter is more dependent on the durability of the construction materials. The wood materials used in this study appeared to be deteriorating relatively quickly due to the acidic and moist nature of the waste gases and fecal dust associated with the

exhaust. Therefore, materials with greater resistance to these conditions should increase the longevity of the zeolite biofilter, and perhaps the construction costs as well. A drawback to using organic media is that purchase of a more powerful exhaust fan is often required to meet the barn ventilation requirements. It appears that the stability and effective porosity of zeolite may nullify the necessity for implementing a more powerful ventilation system; therefore, this figure does not include the cost of new exhaust fans or any potential increases in electricity usage due to additional demands on the existing ventilation system.

CONCLUSIONS

This study evaluated the use of zeolite as a fixed film biofilter for the purpose of reducing odorous swine waste emissions from a confined nursery-grower building in Moses Lake, Washington. The biofilter was retrofitted to a 16-inch exhaust fan that draws odorous volatile gases from the headspace in the under-slat manure storage pit. Emissions are conducted from the barn through a plywood duct system and forced to diffuse through a vertical depth of 3 feet of zeolite before discharging to the atmosphere. The volume of the zeolite biofilter bed was initially designed to provide a minimum gas retention time of 5 seconds, but was discovered to be performing favorably at a 1.2 second retention time. The biofilter operated over a 10-month period from October 2003 through July 2004 to evaluate its performance under seasonal climatic extremes.

The evaluation of the zeolite biofilter entailed collecting measurements of pre-treatment and post-treatment concentrations of NH_3 (ammonia) to determine the percent reduction of this compound. These measurements showed average reductions of 90% NH_3 over the course of the 10-month operating period. Therefore, the zeolite was effective in reducing a significant quantity of NH_3, which is commonly associated with swine waste odors.

Samples of zeolite were collected from the biofilter on February 28, 2004 to establish whether bacteria were able to grow on the surface of zeolite. Polymer Chain Reaction (PCR) analysis was used to identify the presence of the nitrifying bacterial species *Nitrosomonas*. The presence of *Nitrosomonas* conclusively indicates that zeolite is able to support the metabolic activity of nitrifying bacteria, and thus performs as an effective biologically active filter.

Samples of zeolite were collected from the biofilter on February 28, 2004 and July 14, 2004 and returned to the laboratory for nitrite assays. These samples were inoculated in AOB (ammonia oxidizing bacteria) growth media and incubated at 30° Celsius for roughly two weeks. The samples were then measured for NO_2^- (nitrite),

which would indicate that nitrifying bacteria are converting NH_3 to NO_2^- through biological oxidation. Nitrite assays were conducted on upper and lower 12-inch layers of the biofilter in winter and summer months. The winter samples had a slightly faster nitrite production rate of 0.009 mM-NO_2^-/day compared to 0.007 mM-NO_2^-/day in the summer samples. This indicates a more active population of nitrifying bacteria inhabiting winter zeolite samples than summer samples, which may be attributed to decreased moisture content in the biofilter due to increased summer evaporation rates.

This data and conclusion is further supported by an experiment conducted to observe the effect of moisture content on biofilter performance. Half of the biofilter was irrigated while the remaining half was not. The zeolite samples extracted from the irrigated half of the biofilter experienced a nitrite production rate of 0.042 mM-NO_2^-/day compared to 0.007 mM-NO_2^-/day for the non-irrigated samples. This suggests that the nitrifying bacteria in the irrigated half of the biofilter were six times more active than those in the non-irrigated half. Therefore, providing the proper moisture content by irrigation significantly improves the conditions for increased bacterial activity. The installation of irrigation equipment also improved biofilter performance by reducing NH_3 emissions by an average of 92% compared to the non-irrigated NH_3 reduction of 72%. This data confirms that irrigation drastically improves biofilter performance; however, with an average NH_3 reduction of 72% on the non-irrigated half suggests irrigation is beneficial but not a requirement for effective biofiltration of odorous compounds.

This evaluation indicates that zeolite is an effective media for biofiltration of ventilation air exhausted from a confined swine operation. Zeolite media supports the proper conditions for growth of nitrifying bacteria and was proven effective in removing up to 90% of the odor-causing compound NH_3. And according the subjective analysis by eleven panelists, the zeolite biofilter was also successful at reducing the perceived offensiveness of odors associated with swine waste. At a cost of $360 per 1000 cfm of filter capacity, the zeolite biofilter is a potentially affordable method for reducing odors associated with confined swine buildings.

The evaluation of zeolite as a potential biofilter media in this study was approached as a "black box" system. This means that the zeolite biofilter, as a system, was provided with inputs and the outputs were observed without extensively analyzing the processes occurring inside the zeolite biofilter. Furthermore, this means there were no efforts taken to separate NH_3 removal attributed to bacterial oxidation from that due to sorption processes; so, a general estimate of the adsorption capacity of the zeolite was made using some of the conditions observed during the course of evaluating the zeolite biofilter in this study. It was calculated that the zeolite bed in this study would reach its NH_3 adsorption capacity in approximately 231 days. During this time the bacterial biofilm will continue to grow and will be able to utilize the NH_3 captured by adsorption to the zeolite.

Clinoptilolite zeolite was chosen for its ability to adsorb NH_3 and similar odorous constituents and was subsequently evaluated for its ability to perform as a biofilter. The primary performance criteria as a biofilter entailed identifying the growth of bacteria on the zeolite surface. The PCR analysis conducted in this study conclusively identified the presence of nitrifying bacteria and nitrite analyses reflected their metabolic activity; however, these methods cannot provide a reliable measure of the *in situ* growth rate of bacteria on the zeolite.

RECOMMENDATIONS

Zeolite was proven to have great potential as a biofilter media due to its adsorption characteristics and its ability to support bacterial growth. But, the lack of any bacterial colonies on the zeolite at the time of installation may hinder the biological contributions to odor removals during the first few months. The *Nitrosomonas* detected through PCR analysis would have had to be introduced to the zeolite surfaces via exhaust air; thus, *Nitrosomonas* likely required more time for colonization and growth on the zeolite compared to organic biofilter media that tend to have pre-existing bacterial colonies. Therefore, bacterial growth could be enhanced by incorporating organic media into the zeolite biofilter design. Although direct mixing of organic media with the zeolite would not be recommended, since the organic media will need to be replaced long before the zeolite. It would also be worthwhile to investigate the potential of inoculating the zeolite with active colonies of bacteria to increase the colonization and growth rate of bacteria.

Zeolite biofilter performance could also be improved by using a finer grain zeolite then that used in this study. Finer grained zeolite provides more surface area for microbial colonization, which should increase biofilter performance by having increased surface area for treating odorous exhaust. However, careful consideration should be used to ensure that the grain size will allow sufficient airflow to meet barn ventilation requirements.

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APPENDICES

APPENDIX A:

Detailed Protocol for PCR Analysis

PCR (Polymer Chain Reaction) analysis was used to amplify the *amoA* gene and the *16S rRNA* (ribosomal Ribonucleic Nucleic Acid) gene of Ammonia-Oxidizing Bacteria from genomic DNA extracted from the bacterial cultures. The *amoA* enzyme is what AOB use to oxidize ammonia; therefore, detection of the *amoA* gene would indicate that the nitrifying bacteria *Nitrosomonas* are present. The detection of the *16S rRNA* gene would suggest that these organisms belong to the grouping of Ammonia-Oxidizing Bacteria. Coupling the *amoA* gene and *16S rRNA* gene helps rule out false positives and false negatives that might occur if they were tested individually.

The PCR products were placed in an 0.8% weight by volume aragose gel, stained with Ethidium Bromide, which causes a visible fluorescence under UV (ultraviolet) light. The photo of the PCR product depicts the 100 BP Ladder® size ladder to the left which is units of KB (kilo- basepairs). These size ladder are DNA fragments cut to specific size by enzymes in the manufacturing process. When loaded onto an agarose gel it forms predictable banding patterns. The *16S rRNA* and *amoA* genes are DNA fragments that will align with a band on the size ladder; thus, the identity of the bacteria is revealed by the number of KB that form.

Genomic PCR Protocol

Upper Sample PCR Mixture

1uL Genomic DNA (1.5ug DNA as determined by spectrophotometric quantification.)
3uL NEB 10X Taq Polymerase Buffer (NEB=New England Biolabs)
0.5uL NEB Taq Polymerase Enzyme (5u/uL)
0.6uL NEB dNTPs (10mM)
1.5uL Forward Primer [16S or amoA] (10pM)
1.5uL Reverse Primer [16S or amoA] (10pM)
21.9uL Deionized Water
30uL final volume/reaction

Lower Sample PCR Mixture

3uL Genomic DNA (1.5ug DNA as determined by spectrophotometric quantification.)

3uL NEB 10X Taq Polymerase Buffer

0.5uL NEB Taq Polymerase Enzyme (5u/uL)

0.6uL NEB dNTPs (10mM)

1.5uL Forward Primer [16S or amoA] (10pM)

1.5uL Reverse Primer [16S or amoA] (10pM)

19.9uL Deionized Water

30uL final volume/reaction

PCR Cycle Conditions

Step 1: 90C 30sec

Step 2: 90C 30sec

Step 3: 50C 30sec

Step 4: 72C 60sec

Step 5: 72C 180sec

Repeat Step 2-4 30 times.

10uL of PCR product was run on an ethidium bromide stained 2% agarose gel at 70V for 2 hrs. The gel was visualized under UV light using the UVP BioDoc-It system.

APPENDIX B:

Sample Evaluation Sheet

Name_____
Date_____

Sample Set #1

1) Which sample smells better?

Sample #_____

2) Rank the smell of this sample in comparison to the worse smelling sample. (**1**= *no odor*, **2**= *faint odor*, **3**= *mildly offensive*, **4**= *strong odor*, **5**= *very strong odor*)

Odor Rank:_____

Sample Set #2

3) Which sample smells better?

Sample #_____

4) Rank the smell of this sample in comparison to the worse smelling sample. (**1**= *no odor*, **2**= *faint odor*, **3**= *mildly offensive*, **4**= *strong odor*, **5**= *very strong odor*)

Odor Rank:_____

Sample Set #3

5) Which sample smells better?

Sample #_____

6) Rank the smell of this sample in comparison to the worse smelling sample. (**1**= *no odor*, **2**= *faint odor*, **3**= *mildly offensive*, **4**= *strong odor*, **5**= *very strong odor*)

Odor Rank:_____