ON-FARM USE OF CLINOPTILOLITE ZEOLITE WITH COMPOSTING AND AIR FILTRATION TECHNOLOGIES TO CONTROL AMMONIA EMISSIONS, ODOR, AND NITROGEN RETENTION FROM DAIRY MANURE

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Authorization to Submit Dissertation

This dissertation of Mario Emanuel de Haro Martí, submitted for the degree of Doctorate of Philosophy with a Major in Environmental Science and titled "On-Farm use of Clinoptilolite Zeolite with Composting and Air Filtration Technologies to Control Ammonia Emissions, Odor, and Nitrogen Retention from Dairy Manure," has been reviewed in final form. Permission, as indicated by the signatures and dates below, is now granted to submit final copies to the College of Graduate Studies for approval.

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ABSTRACT

The concentration of large numbers of animals in relatively small areas, high production output per animal unit, and concentration of animal excretions and air emissions are some of the staples of modern animal agriculture. Ammonia (NH_3) and odors are among the most noticeable, as well as locally and regionally problematic emissions generated by concentrated animal feeding operations (CAFO) dairy production systems.

A zeolite is a mineral comprised of crystalline, hydrated aluminosilicate of alkali and alkaline earth cations having an infinite, open three-dimensional structure. Zeolites are able to further lose or gain water reversibly and to exchange cations, ammonium (NH_4^+) and ammonia gas (NH_3) in particular, with and without crystal structure.

This dissertation presents two research projects where clinoptilolite zeolite was used to reduce NH_3 emissions, retain nitrogen in compost or the clinoptilolite itself, and reduce odors. The dissertation contains a literature review, a chapter on the “Use of clinoptilolite zeolite in composting of dairy manure to reduce ammonia emissions and retain nitrogen in the compost”. Another chapter on the “Design and testing of a zeolite filter to capture ammonia and odors from dairy Manure on-farm”. A final chapter describes “Custom made designs and developments associated with this research”.

Composting is one of the most used methods to reduce volume and weight of dairy manure while stabilizing it prior to its land application or storage. As a nutrient and waste management practice, composting reduces the volume of composted wastes between 20-60% and significantly reduces their weight, which allows the materials to be much more affordable to transport than raw wastes. Most manures, including dairy manure, don’t have the proper carbon to nitrogen ratio (C:N) for composting without the loss of nitrogen as NH_3 during the composting process. Due to the lack of enough carbon sources to balance the initial compost mix in arid and semi-arid regions, including southern Idaho (USA), amendments are used in an attempt to reduce the loss of nitrogen during the composting process. In many cases, these amendments provide uncertain results.

The objective of the study in chapter 2 was to demonstrate the effects of adding clinoptilolite zeolite to a dairy manure compost mix, specifically on ammonia emissions, compost nitrogen content and the quality of the final compost product.

The study was conducted on a commercial dairy in Southern Idaho. Manure stockpiled during the winter and piled after the corral cleaning was mixed with fresh pushed-up manure from daily operations, and with straw from bedding and old straw bales, in similar proportions for each windrow. Windrows were mixed and mechanically turned using a tractor bucket. Three replications of control and treatment windrows were made. The control consisted of the manure and straw mix as described. The treatment consisted of the same mix as the control plus the addition of 8% w/w on wet basis (15% dry basis) clinoptilolite zeolite during the initial mix. Windrows were actively composted for 145 to 157 days before screening, with five turns per windrow including the initial mix preparation.

Data were analyzed using ANOVA. Nitrate concentration in the treatment compost 702±127 mg/kg was three times higher than the control 223±127 mg/kg ($p = 0.05$). NH_4^+, showed a marked tendency to be lower in the treated windrows' initial feedstock mix. These differences from the beginning of the process indicate that clinoptilolite zeolites have an immediate impact when added to the compost mix changing the NH_4^+ and NH_3 behavior and volatilization even during the construction of the windrow. NH_3 emissions showed a significant reduction in some of the measured periods. Total cumulative NH_3 emissions were reduced by 14.4% in the clinoptilolite treated compost vs. control. The clinoptilolite treated compost had a cumulative value of 63.41 ± 7.22 mg NH_3-N/m^3 versus the control at 74.07 ± 7.22 mg NH_3-N/m^3, but such difference was not significant ($p=0.2$). An overall NH_3 emissions reduction tendency was observed on the emissions' fitted line of the treatment compared to the control, indicating that the total NH_3 emissions from the whole process would be lower in the treated windrows. Solvita® maturity test showed a significant difference ($p<0.05$) indicating a higher maturity state in treated compost, with reduction in nitrogen loss potential, higher maturity index, lower estimated NH_4^+, phytotoxicity, noxious hazard and oxygen depletion. Volume reduction, composting temperatures, and most chemical component values had no significant differences between treatment and control. No negative effects resulted from the addition of clinoptilolite to the compost mix. The project demonstrated the feasibility of using the addition of clinoptilolite zeolites into the composting process as a Best Management Practice to improve dairy manure compost quality, reduce ammonia emissions, and change the nitrogen speciation during the composting process.

The chapter 3 study demonstrated the design and operation of a zeolite filter and air stream collection from a manure pit installed on-farm at a commercial dairy. Clinoptilolite zeolites mined in Idaho were used as the filter media. The capacity of the filter to reduce NH_3 and odor emissions was tested. NH_3 emissions were reduced by 92% at three days of operation and 42% after 59 days of operation of the filter. Ammonia concentration in the pre-treatment airstream from a dairy manure collection pit was relatively high. Odor concentration reduction was 45% at six days of operation with the minimum residence time of 0.85 s. The air collection

roof-like structure and the zeolite filter were proven to be capable of operating in the harsh on-farm environment and to be adaptable to changing operative conditions within the dairy.

Finally, chapter 4 describes the design and construction of a cover used to capture the air over a flushed manure receiving pit, a zeolite filter, and a rotatory compost screen.

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A project of this magnitude and complexity can’t be possible without the collaboration, help, and participation of many individuals, institutions, and companies.

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My deep gratitude and recognition goes to all these individuals, institutions and companies. These projects were made possible thanks to all and each of them.

DEDICATION

Most than anything, I dedicate this dissertation to my family. My love and wife Mireille, who has walked with me on this path for all these years, giving me encouragement, advice, and hearing about my frustrations and crazy ideas. To my children, Marina and Marco, who have been so patient and comprehensive and at their very small age, understood and accepted that “Papi needs to finish his dissertation”. You are my life and light every day. Thank you for everything.

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TABLE OF CONTENTS

LIST OF TABLES

Tables Chapter 1

Tables Chapter 2

Tables Chapter 3

LIST OF FIGURES

Figures Chapter 1

Figures Chapter 2

Figures Chapter 3

LIST OF PICTURES

Pictures Chapter 1

Pictures Chapter 2

Pictures Chapter 3

Pictures Chapter 4

CHAPTER 1

LITERATURE REVIEW

1.1 ZEOLITES

1.1.1 Natural Zeolites

Zeolites are crystalline, hydrated aluminosilicates containing alkali and alkaline-earth metals. Their crystal framework is based on a three-dimensional network of SiO_4 tetrahedra with all four oxygens shared by adjacent tetrahedral. Zeolites have an infinite, open, three-dimensional crystal structures. The atomic ratio of O:(Si+Al) is 2. This generates a net negative charge in the structure. The alkaline cations are loosely bond within the structure and can be exchanged by other cations or molecular water. More than 48 natural zeolites' minerals have been identified and more than 150 zeolites have been synthetized (Eyde & Holmes, 2006; Virta R. , 2008).

Zeolite minerals were formed mainly by volcanic ash or other pyroclastic material fall interbedded with lacustrine sediments and saline or alkaline water by diverse processes. Other processes involve dissolution-precipitation reaction on existing zeolitic sediments. The type of volcanic material, its temperature and the way it was deposited, coupled with the characteristics of the water and lacustrine or sea bed sediments or water flowing through the formed bed, determine the type of zeolites formed and their physical and chemical characteristics. (Virta R. L., 2001; Eyde & Holmes, 2006; Flanagan, 2015).

Zeolites were identified as a new group of minerals in 1756 by Freiherr Axel Fredrick Cronstedt, a Swedish mineralogist. He named these minerals zeolites from the Greek words zein and lithos, meaning "boiling stones" because of the bubbling and vapor frothing coming from the mineral when heated with a blow pipe, losing its molecular retained water (Mumpton F. A., 1981; Mumpton F. A., 1999; Eyde & Holmes, 2006).

Some of the most important properties of zeolites include, high capacity for hydration and de-hydration through thermal processes. Low density and large void volume when dehydrated; stability of the crystal structure when dehydrated and at relatively high temperatures; high cation exchange capacity (CEC), being able to exchange cations with and without crystal structure; uniform molecular-sized channels when dehydrated, varying in size according to the type of zeolite, this allows them to serve as molecular sieves; ability to adsorb a great variety of gases and vapors; and catalytic properties.

In particular, zeolites are used commercially based on their applications related to their properties like molecular sieve, ion exchange, adsorption, and catalysis (Mumpton F. A., 1999; Eyde & Holmes, 2006). Both authors mention that zeolites own their physical and chemical properties to not only their chemical composition but particularly to their crystalline structure. For that reason, zeolite minerals from different localities may have a similar chemical composition but different crystalline structure, having different chemical and physical properties. The dimension and orientation of void spaces and the crystal shape and interconnected channels in dehydrated zeolites are important to determine their physical and chemical characteristics. Three types of channel systems have been identified: onedimensional system, a two-dimensional system, and two varieties of three-dimensional intersecting systems. Properties like adsorption and ion-exchange capacity are related to the characteristics of the channel openings in both dehydrated and hydrated zeolites. The apertures of the channels are bonded by oxygen atoms of the connected tetrahedral. The limited size of the aperture is dictated by the size of the rings, which contain 6, 8, 10, or 12 oxygen atoms. In this regard, some specific applications demand a series of trials to determine exactly how a particular zeolite (from a particular mine) will behave under the real working conditions. Extrapolating exact behavior based on the chemical composition or general crystal structure may not be very accurate in some cases. In addition to that, most natural zeolites for general industrial and agricultural applications are not 100% pure, containing some traces or percentages of other zeolites or minerals. Picture 1.1, (Mumpton F. A., 1999), shows a scanning electron micrograph of plates of clinoptilolite from Castle Creek, ID.

Clinoptilolite is the most abundant natural zeolite. Clinoptilolite and Heulandite share the same tetrahedral framework (labeled HEU). They are considered slightly different zeolites but are grouped together in the type of zeolites' frameworks. Table 1.1, adapted from (Mumpton F. A., 1984) and (International Zeolite Association, 2010), shows the general formula for the clinoptilolite series and other common zeolites. There are three types of clinoptilolite types, clinoptilolite-K, clinoptilolite-Na and clinoptilolite-Ca (International Zeolite Association, 2005). Figure 1 shows a three-dimensional schematic of clinoptilolite frameworks (Cusker & Olson, 2007). Figure 2 shows another representation of that framework, including atomic representations and relative molecule charge (Gordeszeolite, 2014).

Zeolites contain a considerable range of silicon:aluminum (Si:Al) ratios and diverse cations content. Chabazite, clinoptilolite, erionite, mordenite, and phillipsite are the only zeolite minerals with considerable commercial applications today. Erionite has very limited industrial applications as catalyst and molecular sieve due to its classification as human carcinogenic because its crystalline structure is fibrous (like asbestos for example), rendering it unusable for all the applications that may have some human or animal contact (Eyde and Holmes, 2006). All the other zeolites used industrially are considered safe for industrial and diverse consumptive uses.

1.1.2 Synthetic zeolites

Virta R. (2001; 2008) highlights that natural and synthetic zeolites rarely compete with each other. Synthetic zeolites are very pure and expensive to produce. They have well defined pore spaces that can be larger than natural zeolites' channels, allowing their application as molecular sieves involving larger molecules. Their usage as molecular sieves, detergent additives, and catalysts in many industrial processes are among their main uses. Natural zeolites, due to their impurities and variable channel size cannot compete in those fields. Synthetic zeolites are mechanically weaker that natural zeolites. Natural zeolites excel at uses were large quantities or low costs are the main advantage, or where the presence of impurities doesn't affect the desired use outcomes (Sherman, 1999).

1.1.3 Mining and occurrence of natural zeolites in the USA and the world

Natural zeolites are mined using conventional open pit mining techniques. The overburden is removed to allow access to the ore, then the ore may be blasted or stripped using front-end loaders or tractors equipped with ripper blades. The processing of the mined zeolites consists of crushing, drying, and milling the ore. The milled ore may be screened or air classified based on particle size and shipped in bags, expandable totes, or in bulk. Other processes include thermal activation of the zeolites and/or washing it with a solution to increase their ion exchange capacity (Virta R. L., 2001; Eyde & Holmes, 2006; Flanagan, 2015).

Zeolite mine production in the USA increased steadily, from 1977 to 1995. From 1996 to 2003 the industry reduced its mining production and growth. By the mid-to-late 1980's most of the major companies had withdrawn from the industry due to low production and sales, with increased imbalance between production and consumption. Those companies had based their business model as a typical mining enterprise on high volumes of production and sales of a low-cost product. The market for zeolites never achieved the necessary volume of sales to sustain that model. By the mid 1990's those companies have been replaced by several much smaller mining companies that base their business on much less mining production but increasing the value of the zeolite products offered by adding some processing or by targeted commercialization. From 2004 to 2015 the production has continued to increase at a slow but constant rate. Total reported production in 2015 was 75,100 metric tons. An example of such efforts of adding value by increased processing (offering different sizes) or targeted commercialization, is noticed by the end use of natural zeolites. In the 1980's, pet-litter applications (a bulk commodity) represented more than 50% of annual sales. Currently (2017), pet-litter applications represent a far smaller share of the market. In 2015 the major applications of natural zeolites in the USA by tonnage use in decreasing order were animal feed, water purification, and odor control. These three applications collectively accounted for more than 70% of domestic consumption. Zeolites in the USA in 2015 were mined, in order of tonnage production, in New Mexico, Idaho, Texas, California, Arizona, and Oregon (Virta R. L., 2001; Flanagan, 2015). At least nine other states have zeolite deposits that are or could be mined. Southern Idaho has several large clinoptilolite deposits, including the Bear River, Castle Rock, Chrisman Hill, and other smaller deposits (Sheppard, Gude III, & Mumpton, 1983; Altaner, Gude III, Mumpton, Sheppard, & Teague, 1993; Eyde & Holmes, 2006).

Zeolites for this study were provided by Ida-Ore Inc. This company mines zeolites from the Sheaville deposit located in the border of Idaho and Oregon. The company mines, processes and commercialize zeolite as diverse products. Sheppard et al. (1983) provided a description of the Sheaville deposit and its clinoptilolite zeolite in their Zeotrip 93 publication.

World production of zeolites has remained stable for the last three or four years, in 2015, production was in the range of 2.7 to 3.2 Mt (down from a peak of 3 to 4 Mt in the early 2000's). In early 2000's the major zeolites producing countries were China, Cuba, Japan, and USA. By 2015, China was still the leading zeolite producer (1.8 to 2.2 Mt), followed by the Republic of Korea (205,000 t), third the USA (75,100 t), Turkey (70,000 t), New Zealand, and Cuba. Around 24 other countries have zeolite mining operations (Flanagan, 2015). Eyde and Holmes (2006), mentioned the existence of zeolite deposits occurrence in 65 countries, more than half of them had some kind of zeolite production operation at that time. The major use in tonnage of zeolites around the world is for construction material and cement pozzolans. Other major uses include agricultural soil amendments, odor control and filtration applications.

1.1.4 Economic Factors affecting the use of natural zeolites

Eyde and Holmes (2006) mention that natural zeolites are still an underdeveloped market. Synthetic zeolites have a huge market worldwide and it is difficult, and arguably not appropriate, for natural zeolites to compete in those markets. Specialty products and more research with practical applications are the way natural zeolites will gain new markets and better prices. More growth is anticipated. Many other products can replace natural zeolites, so they are competitive when a very specialized zeolite product is developed or if they have a significant cost-benefit advantage (Mumpton F. A., 1981; Sherman, 1999; Eyde & Holmes, 2006; Nakhli, Delkash, Bakhshayesh, & Kazemian, 2017).

1.1.5 Uses of natural zeolites

For more than 50 years, natural zeolite minerals have been described as the industrial mineral of the future. Zeolites have many uses in several industries from construction to oil refineries, and from agriculture to human medicine. There is a great body of research that unfortunately hasn’t resulted in equal number of real-world applications. For many years, the potential application of zeolites was (and sometimes still is) oversold (Mumpton F. A., 1981; Eyde & Holmes, 2006). This has led to the appearance of companies that try to develop and sell products without proper characterization, research, or field testing, ending in most cases in failure, economic bankruptcy and a negative or exaggerated view or natural zeolites’ utilization effectiveness and possibilities. Nevertheless, many properties and possible uses of zeolites are overlooked, lack a solid body of research or practical uses’ demonstration, or are still waiting for credible research coupled with applicable and economically feasible industrial development.

It is important to note that zeolites have been used for millennia in construction. Mumpton (1999) describes the use of zeolites as dimension stone and building material since the Roman Empire in Europe and the the Zapotec Empire in Mexico. Besides such massive use of zeolitic tuff in construction, almost all cities that are near zeolitic deposits have examples of its use in structures. The use of zeolites as cement aggregate in the Roman Empire is also well documented. In the USA, zeolite tuff was used in the west in the 1800's by settlers in the construction of buildings. Other buildings have been built using zeolitic tuff in Nevada and Oregon (Eyde & Holmes, 2006). After Freiherr Axel Fredrick Cronstedt defined zeolites in 1756 very few uses were given to the mineral except for the construction as dimension stone and as a rarity for rock collectors and mineralogists. Zeolites were synthetized first in the 1930's followed by better techniques in the 1950's, but commercial use didn't pick up until 1960's as detergent additives and then the synthetic zeolites use and development exploded when their use as molecular sieves and catalysts in oil and gas processing was implemented (Sherman, 1999; Virta R. , 2008). When used as molecular sieves and catalysts, synthetic zeolites virtually displaced all natural ones in industrial applications. Natural zeolites use, especially in agriculture, have increased dramatically since the late 1950's and the 1960's when many studies and practical uses were developed in Japan. Since then, every decade has seen various sporadic resurgence in natural zeolite use research as mines change ownership and enterprises look for new markets or to recreate previous research that have some questions unanswered. In the 1980's natural zeolites research exploded, following the mining furor of that decade. By the 1990's many of the big mining companies have sold or closed their operations, and natural zeolites research receded significantly. Even though, new crops of researchers around the world are constantly attracted to the study of zeolites and their use in diverse applications. Many of the studies conducted in the 1960’s, and 70’s in many parts of the world, including Japan, the ex-Soviet Union countries, Iran, Europe and USA, are very interesting but in many cases, lacked the statistical analysis or validity to ensure its application or lacked proper technology to measure results, especially when related to agricultural uses (Mumpton F. A., 1984; Sheppard R. A., 1984; Virta R. L., 2001). Many studies based or inspired by those pioneer ones have been developed since the 2,000’s until today. Encouraged by the new, smaller mining operations and targeted market, new applications of zeolites are researched constantly and keep adding to the body of knowledge generated during the last 60 years (Nakhli, Delkash, Bakhshayesh, & Kazemian, 2017).

1.1.6 Use in manure and organic wastes management, including agricultural air emissions’ reduction

Zeolites have been used for water purification for many years, from drinking water softening and purification, to uses in fish tanks and swimming pools (Mumpton F. A., 1999; Eyde & Holmes, 2006). Uses in wastewater treatment, to control NH_3, heavy metals, and other compounds concentrations in tertiary or industrial wastewater treatments followed suit (Eyde & Holmes, 2006; Nakhli, Delkash, Bakhshayesh, & Kazemian, 2017). Zeolites were used extensively, and still are used, to reduce odor and gases’ emissions and retain moisture from pet animals as kitty litter. That use expanded through research and development to the application of zeolites to different uses in animal agriculture and crop production agriculture. Mumpton (1984; 1999), cites agricultural uses in crops and to reduce animal waste odors as early as the 1950’s.

Lefcourt and Meisinger, (2001) “Effect of adding alum to dairy slurry on ammonia volatilization and chemical composition” is one of the most cited papers regarding the reduction of NH_3 emissions from dairy manure using zeolites. The research trial included the use of fresh dairy manure slurry amended with 0.4, 1.0, 2.5, and 6.25% by weight of clinoptilolite zeolites. The addition of 6.25% and 2.5% zeolites’ treatments showed to be the most effective. Zeolites reduced emissions of NH_3 up to 50% and alum (another treatment in the trial) 60%. Soluble P was reduced ~50% at all levels of zeolites’ addition. NH_3 emissions occurred rapidly during the first 24 h in the untreated slurry, losing 65% of the total emissions in 24 h. and about 1.5% of total N a day after (96 h total trial). Total NH_3 loss from the untreated slurry was 15% of the initial slurry TKN. This study was done using fresh slurry dairy manure which has a very high moisture and nitrogen content since it has just started its process of nitrogen conversions. Meisinger et al. (2001), expanded their slurry manure study to include the effects of zeolites on NH_3 emissions reduction by dairy cow’s diet modification.

Many studies have explored the use of zeolites to stabilize organic wastes, reduce air emissions, reduce odors, retain nutrients or toxic components in all kind of wastes, from municipal solid wastes, to animal manures, to industrial and food processing wastes (Mumpton F. A., 1999; Eyde & Holmes, 2006; Flanagan, 2015; Nakhli, Delkash, Bakhshayesh, & Kazemian, 2017). Many studies have also explored the impact of adding zeolites to municipal and industrial waste water treatment plants sludges at the time of composting. Nitrogen retention as ammonium, NH_3 emission reduction, heavy metals and aromatic compounds retention in the zeolite amended compost, as opposed to losing them by leaching or plant uptake, were observed in many of those studies (Nakhli, Delkash, Bakhshayesh, & Kazemian, 2017).

Studies on animal manure handling and treatment, including composting, have concentrated on poultry and swine species for the most part. Poultry and swine manure is very high in nitrogen concentration compared with other species, especially in modern animal agriculture that tend to eliminate or reduce bedding materials with high carbon content in the housing practices common for those two species. This makes the control of nitrogen conversions and NH_3 emission reduction a paramount and challenging task. Studies on cows' manure treatment have focused on application of zeolites to corrals' surfaces and lab studies of the effects of zeolite addition to slurries or compost mixes (Sherwood, 2007; Ndegwa, Hristov, Arogo, & Sheffield, 2008).

1.1.7 Other agriculture uses of natural zeolites in crops

Zeolites have been used for many years in crop production in Japan, Cuba, and some former Soviet Union countries in Eastern Europe (Mumpton F. A., 1984). Zeolites increase the CEC of soils and because of their high pH, they buffer acidic soils. The zeolite crystal structure shields the ammonium ion from rapid consumption by nitrifying soil bacteria (Nakhli, Delkash, Bakhshayesh, & Kazemian, 2017). Zeolites can be used as carriers of fertilizers and pesticides, bacteria, and enzymes (Eyde & Holmes, 2006). Zeolites retain nitrogen, phosphorous, potassium, sodium, and other cations in their structure. This ability to retain and exchange cations and water, can be used in many agricultural applications. From applications tested in Japan by Minato Hideo and others in the 1960's (Barbarick & Pirela, 1984), to the works done in diverse countries mentioned in their review by Nakhli et al. (2017) or works by Torres Duggan et al. (2017) in Argentina, zeolites and zeolitic tuffs have been used, and are actively researched now a day, in many field crop and horticultural applications.

Zeolites have been also used to sequester heavy metals in contaminated agricultural soils (Eyde & Holmes, 2006; Nakhli, Delkash, Bakhshayesh, & Kazemian, 2017).

Sheppard (1984), noted the importance of matching the soil, crop, irrigation water and zeolite type used when zeolites are used in field crop and horticultural production, as well as when zeolites are used to conduct agricultural research. Using sodium laded zeolites can lead to sodification processes that can ruin crops (Pirela, Westfall, & Barbarick, 1984). The ability of natural zeolites to deliver and perform as expected in any agricultural use must be tested at a pilot scale before applying them to a full operation scale. In the same way, the composition, structure and performance of the zeolite mineral used must be properly described to assure repeatability and consistency.

1.1.8 Use of zeolites in animal nutrition

Zeolites have been used in animal nutrition for more than three decades, especially in Japan, Cuba, Bulgaria, and Hungary (Mumpton & Fishman, 1977; Eyde & Holmes, 2006). In the USA and Canada, feeding zeolites became more common in the last 15-20 years. Many studies have been performed in monogastric species, especially swine and poultry, and young cattle at their calves' stages. A more limited set of studies have explored the effects in several species of full grown ruminants.

Many studies related to animal nutrition explored the effects of the addition of zeolites as feed supplement on animal growth, reduction of stress due to ammonia concentrations in the air, reduction of animal excreta emissions. Other studies reported reductions in diarrhea, scours, and other metabolic disorders as well as increase in animal daily gain (ADG), feed efficiency, minimizing the effects of toxic compounds, and improving animal welfare

(Mumpton F. A., 1984; Eyde & Holmes, 2006; Hristov, et al., 2011). Again, many studies performed in the 1970-80's showed neutral or promising results in animal production parameters, but in most cases lacked statistical power to show clear differences due to the lower number of animals or short period of time in trials as seen in many cases in the Zeo-Agriculture publication (International Committee on Natural Zeolites, 1984). On the other hand, animal husbandry studies, showed results immediately (in the same publication), especially in the area of air quality, by reducing indoor ammonia concentrations, manure handling characteristics, and reduction in insects' proliferation. Some specific uses in animal production showed positive effects that were reproduced in other studies or at commercial production units. These include the reduction of diarrhea, scours, and mortality in pigs and dairy calves when zeolites were used as feeding additives. Some other studies from the 1980's and especially later ones, showed positive results in several parameters and species of animals, including increased ADG, increased feed efficiency and improved physiological responses, reduction in the effects of toxins and feed contaminants, and increments in several production parameters (Hristov, et al., 2011). In many countries, including the USA, using zeolites as feeding additives has become another common tool available for animal agriculture, even though their use has not been massively adopted by livestock producers.

1.1.9 Use of natural zeolites in aquaculture

Zeolites are used as media filter to reduce the ammonia content in water for fish farms, aquariums, and fish tanks (Mumpton & Fishman, 1977; International Committee on Natural Zeolites, 1984; Eyde & Holmes, 2006). The systems reach high removal efficiency with up to 90% NH_4^+ removal. Media can be regenerated using Na or K brines for using the same zeolites in several cycles before replacement is needed. Other systems are described in the zeo-agriculture publication (International Committee on Natural Zeolites, 1984) by Horsch and Holway, who tested the use of zeolites filters as dual exchange/biofilter media with biological regeneration of the zeolites. The scale of these systems varies from small pilot scale to full commercial fish farm operations described in the same publication.

1.1.10 Other uses of natural zeolites

Catalysis and Petroleum Refining

Natural zeolites can be used as catalysts in many refining and petrochemical industry processes but they have been displaced by synthetic zeolites in almost all those applications. Synthetic zeolites have larger channel sizes allowing for the sieve of larger molecules, are void of impurities, are more uniform and homogenous and can be manufactured specifically as a catalyst for a particular process (Mumpton F. A., 1999; Eyde & Holmes, 2006).

Desiccants

Zeolites can be used as desiccants in animal feed products, packed bacteria and enzymes in silage inoculants, and other uses where they can absorb any humidity that may compromise the product (Eyde & Holmes, 2006). Zeolites have been used as desiccants in packed air filters for vehicle breaks, moisture extractants in refrigerating systems and in food, medicine, fertilizer and pesticide applications (International Committee on Natural Zeolites, 1984; Mumpton F. A., 1999).

Dimension stone

Zeolitic tuffs have been used for thousands of years as dimension stone and building material from the Roman Empire to Central Europe, to Nevada in the USA (Mumpton F. A., 1999; Eyde & Holmes, 2006).

Gas Separation

Zeolites can be used in the separation of oxygen and nitrogen, but most of those industrial and medical uses are now taken by synthetic zeolites (Eyde & Holmes, 2006).

Medical and Personal Care Applications

Zeolites' products have been developed for medical use to stop bleeding from wounds, as a polishing agent in tooth paste, for odor and ammonia control in diapers, tampons, and human and animal waste disposal products. There are many human nutrition supplements available on the market based on natural zeolites (Mumpton F. A., 1999; Eyde & Holmes, 2006).

Nuclear Waste Treatment and Handling

Zeolites have been used to remove low level radioactive material from water streams. They have also been used for the treatment and containment of radioactive materials in places like the first atomic reactor in Arco, Idaho, the Tree Mile Island power plant site and the Chernobyl disaster. Natural zeolites are more resistant than synthetic ones to acid environments, mechanical stress, and high temperatures. Many other uses related to nuclear waste treatment around the world have been and still are studied and developed (Mumpton F. A., 1999; Eyde & Holmes, 2006; Abdel Rahman, Ibrahium, & Hung, 2011).

Removal or retention of heavy metals in water, waste water, and soils

The cation exchange capacity, physical characteristics, and cost of natural zeolites make them an excellent product for removal or retention of heavy metals (Mumpton F. A., 1999; Eyde & Holmes, 2006). Many applications of natural zeolites in purification of contaminated water, treatment of heavy metal containing wastewater and soil remediation are described by Sun, et al. (2016).

Odor Control and air purification

Zeolites, specially clinoptilolite, are very effective in removing ammonia ions. This process suppresses odors from feces and urine. Hydrated zeolites adsorb ammonia vapor, when the gas enters the zeolite pores, it bonds to or replaces crystalline water. This reduction in ammonia and the adsorption of other odorous compounds are the base for zeolites use in many air filtration systems to improve confined animal air quality in totally or partially enclosed systems, especially with air recirculation. Air purification systems based on zeolites are used in poultry and swine facilities. Air purification and odor control systems are also available for human quarters air quality improvement, ranging in sizes from the home or office to industrial working environment systems (Mumpton F. A., 1999; Eyde & Holmes, 2006).

Pozzolan and Cement

A pozzolan is a siliceous or siliceous and aluminous material that in itself possesses little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds having cementitious properties (American Concrete Institute, 2018). There are both natural and synthetic pozzolans. They can replace up to 25% of the Portland cement in concrete. Zeolitic tuffs have been used as cement additive since the Roman Empire times. Replacing up to 25% of cement with zeolite tuffs can save millions of dollars. Zeolites are also used as additives in oil and gas wells' injection and cementation mixtures (Mumpton F. A., 1999; Eyde & Holmes, 2006).

Water and Sewage Treatment

Zeolites can be used to remove ammonia and heavy metals from sewage, especially in tertiary treatments. They are also used extensively in drinking and recreational (swimming pools) water treatment facilities. These applications go from home scale water purification systems up to municipal and industrial scale plants using tons of zeolites in their reactors (Mumpton F. A., 1999; Eyde & Holmes, 2006; Flanagan, 2015).

Solar energy and Heat Exchange

Zeolites can absorb and release heat from solar radiation and can be used for air conditioning, refrigeration, and water heating applications (Mumpton F. A., 1999; Eyde & Holmes, 2006).

Use of natural zeolites in various consumer products

Natural zeolites are commercialized in a wide array of consumer products containing mostly zeolite, or as part of a mix with other compounds. These products include pet (kitty) litter (the most common use in this category), horse stable deodorants, human deodorant and desiccant powders, human nutrition additives, and other products (Mumpton F. A., 1999).

1.2 AMMONIA AND THE FATE OF NITROGEN IN MANURE MANAGEMENT

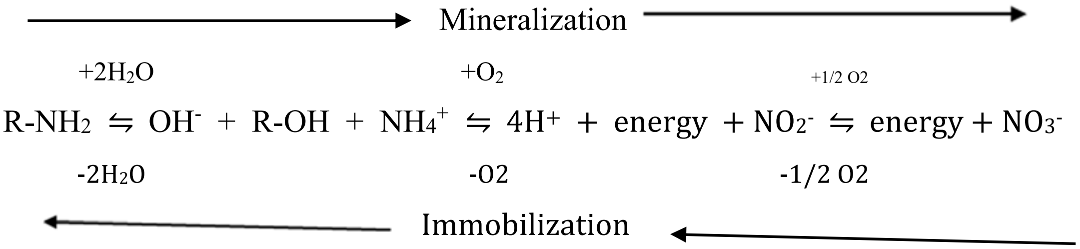
1.2.1 Nitrogen cycle

Nitrogen (N) is fundamental for plant growth and development as it is an integral part of a series of essential plant compounds. N is a major part of all amino acids, proteins, enzymes, and cellular components and functions, including nucleic acids and chlorophyll, all essential to plant function, and reproduction. Availability of N stimulates plant nutrient uptake and plant growth, greening vegetative parts and producing better fruits or tubers. N deficiency leads to chlorosis (yellowish or pale green color in leaves), stunned and weak plants, and lower protein content. If the deficiency is significative, plants reduce or stop growth, chlorotic leaves are lost, and plants mature prematurely, with less mass and vigor. When too much N is available, excessive vegetative growth is observed, plants grow bigger but weaker, tending to fall (lodging) and maturity is delayed, exposing plants to disease and insect pressure. Lower sugar content is observed in fruits and tubers, and plants tend to grow more vegetative mass, reducing crop quality. Leaching of excess N into groundwater is also a concern when N in soils exceeds plant uptake (Weil & Brady, 2017).

The nitrogen cycle is one of the most studied cycles in soils and biosphere studies, it is, arguably, one of the most complex of the primary biosphere and agricultural components due to the many forms and reactivity of N in oxidized and reduced forms. It is also very important to understand it since the transformations and translocation of N and how it moves in nature is paramount to solve many agricultural and environmental challenges (Li, et al., 2016). Representations of the N cycle can be quite simplistic as the one presented by Myrold (1997), or more complex like Figure 1.3 (Weil & Brady, 2017). Nitrogen can take several inorganic forms, the most important in agriculture studies are NO_3^-, NH_3 and NH_4^+. But it also takes other forms including N_2, N_2O, usually short lived NO_2^-, NO. Nitrogen participate in many organic processes being transformed, up taken, assimilated, and secreted by microorganisms, plants, fungi, and animals. All this adds a great layer of complexity to all the forms and reactions of N in the environment (Myrold, 1997; Weil & Brady, 2017).

Among the pathways N can take in soils, and composting, immobilization and mineralization are some of the most important. Immobilization refers to the incorporation of N into organic molecular structures that makes it mostly unavailable for plants in the short term. Mineralization is the reverse path, where organic forms of N convert to mineral forms readily available for plants, microorganisms, or prone to leaching or volatilization. Most mineralization processes are directed by enzymes inside or outside microorganisms or soils fauna.

A general formulae representation of mineralization is:



$$\xrightarrow{\qquad\qquad\text{Mineralization}\qquad\qquad}$$

$$R\text{-}NH_2 \underset{-2H_2O}{\overset{+2H_2O}{\leftrightharpoons}} OH^- + R\text{-}OH + NH_4^+ \underset{-O2}{\overset{+O_2}{\leftrightharpoons}} 4H^+ + \text{energy} + NO_2^- \underset{-1/2\ O2}{\overset{+1/2\ O2}{\leftrightharpoons}} \text{energy} + NO_3^-$$

$$\xleftarrow{\qquad\qquad\text{Immobilization}\qquad\qquad}$$

Weil and Brady (2017) mentioned that until recently, most studies of N uptake and leaching had focused on mineral N, especially NO_3. However, new studies and analytical techniques have uncovered the importance of dissolved organic nitrogen (DON) as a component of N uptake and leaching in natural and agricultural ecosystems. They mention that plants can uptake DON, especially small molecules, and it can be some of the main plant N sources in strong acidic and infertile soils, including some highly organic soils. In addition, DON has the potential to leach and it may comprise up to 30-60% of N leached from dairy farms and feed lots.

Among the mineralization processes, two are very important in manure management and the fate of N in crop soils and composting. Those are ammonia volatilization and nitrification.

Ammonia volatilization is the production of NH_3 gas from the breakdown of plant residues, animal excrements, or from fertilizers such as anhydrous ammonia or urea. NH_3 gas may diffuse into the atmosphere, resulting in a loss of valuable nitrogen and environmental impact resulting from increased N deposition from the atmosphere. Ammonia gas is in equilibrium with ammonium following the reversible reaction:

$$NH_4^+ + OH^- \leftrightharpoons H_2O + NH_3\uparrow$$

Dissolved ions Gas

Ammonia volatilization increases as the pH increases. The addition of water tends to drive the reaction to the left, raising the pH of the solution.

As NH_4^+ ions appear in the soil or compost, they are in general rapidly oxidized by bacteria and other microorganisms to first nitrites and then nitrates. Nitrification is then a two-step process, step one:

$$NH_4^+ + 1^{1/2} O_2 \xrightarrow[\text{Nitrosomonas bacteria}]{} NO_2^- + 2H^+ + H_2O + 275\text{ kJ energy}$$

Step two:

$$NO_2^- + \tfrac{1}{2} O_2 \xrightarrow[\text{Nitrobacter bacteria}]{} NO_3^- + 76\text{ kJ energy}$$

When conditions are favorable, the second reaction immediately follows the first one, reducing the concentration of toxic nitrite in soils or plants. Under anaerobic conditions, nitrifying bacteria can also produce NO and N_2O, a potent greenhouse gas (Weil & Brady, 2017).

Under conversions of N include denitrification and anammox processes that won’t be developed in this chapter since they are not so important for the processes considered in this dissertation.

1.2.2 Ammonia generation in dairy production

Dairy cattle manure has an elevated nutrient content, especially nitrogen. During the animal production cycle, the storage and treatment of manure and its application on the field as well as the fate and emissions of nitrogen (N) compounds vary greatly. Ammonia is produced as a result of natural animal and microorganisms’ processes. Agriculture is recognized as a major contributor of NH_3 emissions, contributing about 55% of global NH_3 emissions. Animal production counts for about 43% of total global emissions, counting natural and anthropogenic sources (Schlesinger & Hartley, 1992). In the USA, approximately 83% of anthropogenic ammonia emissions come from agriculture, and around 55% of that overall total comes from livestock operations (USEPA, 2015); Figure 1.4 shows the distribution of NH_3 emissions in the USA by emitting sector. Farm animals consume a considerable amount of protein and other N containing substances with their feed. This consumed N is partitioned between products such as meat, milk, eggs, and excretions such as urine, and feces. At the moment, there is no other way to produce goods with similar characteristics, cost-benefit, and nutritional value. Animal products and their by-products are an important part of human society’s development and human nutrition. Despite all the advances we have achieved in animal agriculture, the conversion of dietary N to marketable animal products is often considered inefficient, and 50 to 80% of the N consumed is excreted.

More than 50 to 60% of the excreted N is in the urine, and more than 70% of this urine N is in the form of urea-N. Organic N compounds in feces can account for up to 35% of NH_3 production (Tamminga, 1992; Arogo, Westerman, Heber, Robarge, & Classen, 2001; Hristov, et al., 2011).

> Due to the AFO production system, manure, defined as the mix of animal urine, feces, discarded feed, water from cleaning, bedding material, and other production wastes, has an augmented degradation speed, and production of NH_3 is more than the elements considered separately in other production systems (Lorimor, Powers, & Sutton, 2000; ASAE, 2005). Urea in the urine of mammals can be hydrolyzed rapidly to NH_3 and CO_2 by urease enzymes present in the feces (National Research Council, 2003). Due to the constant mix of excreted urine and feces, in the time frame from excretion, through storage, and after application, 50% to more than 70% of the N in manure can be converted to NH_3 and released to the atmosphere (Hristov, et al., 2011).

1.2.3 Environmental fate of ammonia

Once emitted to the environment, ammonia and ammonium have a half-life of days, making their direct impact a local and regional concern. Ammonia has two main fates in the atmosphere, remain as NH_3 and reach the surface as mostly dry deposition, or be converted to NH_4^+ by chemical reactions in the presence of moisture (reacting with HNO_3 or H_2SO_4 for example) and be deposited on the surface as a wet deposition. In both cases, the deposition of N rich compounds can be seen as a positive effect in agricultural lands, with the exception that farmers have no control on the location and concentration of such depositions. In all other ecosystems (forests, range lands, deserts, aquatic, cities), these depositions have a negative and sometimes very damaging effect over time, generating in many cases a nitrogen cascade effect, where the same NH_3 molecule can affect different locations or environments (National Research Council, 2003). In forests, NH_3 depositions increase not only the nutrient content but also the acidity of soils, in turn these effects negatively affect tree growth, induce nutrient leaching and soil degradation since forest ecosystems are in general in a delicate equilibrium. Nitrogen added by deposition (dry or wet) can have dramatic effects on range lands and deserts, where vegetation has naturally evolved and adapted to thrive with low or very low N inputs. When N is increased in these ecosystems, invasive species that are N hungry, tend to overcome native ones rapidly, resulting in loss of biodiversity and productivity in the long run. In aquatic environments, N deposition or water flow from affected land areas (as runoff or spring flows) promotes eutrophication processes that degrade, sometime quite dramatically, the ecosystem and impact water quality (Myrold, 1997; Li, et al., 2016; Weil & Brady, 2017). In city environments, N depositions increase the presence of weeds, and have a negative effect on structures. That N from cities, ends sooner or later washed out to water bodies or natural areas that are impacted too.

Another effect of NH_3 and NH_4^+ is their reaction with other atmospheric compounds, especially volatile organic compounds (VOC), HNO_3 and H_2SO_4 to form PM2.5 (particulate matter having an aerodynamic equivalent diameter of 2.5µm or less). PM2.5 is associated with loss of visibility, smog, formation of low level ozone, and fundamentally the increase of allergies, asthma, respiratory and cardiovascular diseases among exposed populations, with a direct impact of morbidity and death rates of such populations (National Research Council, 2003; Ogejo, Senger, & Zhang, 2010).

1.2.4 Ammonia emissions measurement

Methods to measure gas concentration can be divided into three main groups; methods dependent on chemical reactions, methods dependent on thermo-chemical reactions, and those dependent on optical absorption techniques. Chemical methods include acid scrubbers, detection tubes, electrochemical cells, passive diffusion devices, denuders, and fluorescence. Thermo-chemical methods include chemiluminescence, and gas chromatography. Optical absorption methods include spectroscopy, Fourier Transform Infrared spectroscopy (FTIR) and Ultra Violet Differential Optical Absorbance Spectroscopy (UV-DOAS), (Shah, Westerman, & Arogo, 2006; de Haro Martí, 2007).

With other research experiences using Ogawa samplers (Tate, 2002; Roadman, Scudlark, Meisinger, & Ullman, 2003; Salem, Soliman, & El-Haty, 2009) and due to its availability (USDA-ARS in Kimberly, ID loaned us the units and analyzed the pads), economy, accuracy, predictable results, and possibility to take multiple samples at the same time, the Ogawa NH_3 passive samplers (Ogawa & Co. Kobe, Japan) were used for this project. Ogawa samplers fall under the category of chemical methods with passive diffusion capture. Described by Roadman et al. (2003), the sampler consists of a solid Teflon cylinder with two open, but unconnected ends, each containing a reactive glass-fiber filter impregnated with citric acid (in this study factory ready pre-impregnated pads were used). The filter is mounted between two stainless steel screens (0.152 cm2 open area, 0.02 cm thick), situated behind a diffusion-barrier end-cap containing 25 holes (open area of 0.785 cm2, 0.6 cm thick). Figure 1.5, shows the Ogawa sampler assembly components.

1.2.5 Nitrate leaching

In addition to NH_3 emissions, one of the biggest challenges when managing manure from animal agriculture and from cropping systems' fertilization (either from synthetic fertilizers or manures) is the loss of nitrogen to the environment in the form of leaching. Even though some N is leached as dissolved organic nitrogen (Weil & Brady, 2017), the main form of N subject to leaching is NO_3^-. In contrast to NH_4^+, NO_3^- with its negative charge is not adsorbed by the negatively charged colloids present in most soils. In this way, NO_3^- tends to move downward freely with drainage water and be leached from the soil. The leaching occurs when there is an excess of NO_3 that cannot be taken by crops or when there is movement of water that flushes NO_3 down. The loss of N as leaching has three main negative implications, first, the loss of valuable nutrients. Second, the leaching of NO_3 ions stimulates acidification of soils and the co-leaching of cations such as Ca^{2+}, Mg^{2+}, and K^+. Third, the movement of NO_3 to groundwater causes serious water quality and potential health problems for humans and animals as well as impact to downstream receiving bodies of water if the groundwater surfaces (Myrold, 1997; Miner, Humenik, & Overcash, 2000; Weil & Brady, 2017). Increased NO_3 levels in bodies of water is associated with eutrophication processes as mentioned above. When NO_3 remains in groundwater and it reaches certain concentration (the NO_3 limit for groundwater for human consumption in the USA is 10 mg/l NO_3-N), impact to humans, especially children and pregnant women can be catastrophic. After being ingested in the water or by eating leafy vegetables with high NO_3 content, NO_3 changes to nitrite through metabolization and becomes extremely toxic for humans and animals. Methemoglobinemia is the decrease in the hemoglobin ability to carry oxygen to body cells due to the nitrite competency. This is known as the blue baby syndrome since hemoglobin with low oxygen tends to turn the affected individual skin blue. Small children, babies, and especially pregnant women (the unborn child) are very susceptible (Miner, Humenik, & Overcash, 2000; Weil & Brady, 2017).

1.2.6 Nutrient and manure management and nitrogen

Modern animal agriculture concentrates high numbers of single specie animals in a relatively small surface area. This concentration of animals has many economic, animal husbandry, environmental and management benefits. It also has many drawbacks, generating new challenges in each one of those areas. If those challenges are not addressed properly, some of those areas can suffer (from the economy to the management) or even have catastrophic results.

Manure, defined as the mix of animal urine, feces, discarded feed, water from cleaning, bedding material, and other production wastes, has an augmented degradation speed, and production of NH_3 is more than the elements considered separately in other production systems (Lorimor, Powers, & Sutton, 2000; ASAE, 2005). In the time frame from excretion, through storage, and after application, 50% to more than 70% of the N in manure can be converted to NH_3 and released to the atmosphere (Hristov, et al., 2011). This situation highlights one of the many challenges dairy farmers have when managing their production units. Manure is a valuable resource, even though many times it is treated and handled as a waste product of animal production, it is rich in nutrients needed in the fields to grow crops, full of energy that can be extracted, and water that can be recycled, all if managed properly. It is important to make this distinction between manure as a mere waste and manure as a formidable resource, because if not properly managed, manure can become a troublesome waste that has the potential to negatively impact the environment as well as animal and human health.

Dairy producers have a diverse array of tools, including technologies, techniques, and Best Management Practices (BMP) to use manure as a resource and to mitigate negative impacts that may arise. Some of those tools include storage of manure, solid separation, treatments like anaerobic digestion, composting, diverse field application techniques, etc. One of the main ways of using manure is by incorporating it into a comprehensive nutrient management plan, where nutrients in manure are recycled within the production system and applied to cropland for either growing animal feed that will be returned to the production unit, or other crops that will be exported outside the area. One of the components of such nutrient management is the management of N in the system. Technologies and BMP are available to reduce the loss of N as NH_3, NO_3, or other forms not discussed in this paper like N_2O. We haven't developed yet a perfect tool that will take care of everything, but we have available a set of tools that even when imperfect, can help to reduce N losses from the system. Among those tools, we count with manure application BMP and manure treatment technologies and BMP. After direct manure application, composting is the most used technique to treat and reuse dairy manure in Idaho. It makes sense that education and research efforts would be directed primarily to improve those two areas. Additional efforts should also be directed to alternative methods of treatment and recycling of the resource too, this way producers can have more options in their tool box to adjust manure management to their individual needs.

1.3 COMPOSTING

1.3.1 Composting definition, process, and ammonia losses

There are several definitions of composting, but in general and as a broad definition, it is defined as the control of the natural breakdown of organic material that produces a stable humus-rich material (Rynk, et al., 1992; Chen, de Haro Martí, Moore, & Falen, 2011). On-farm composting of manure is one BMP available to dairy producers. Composting reduces the volume of composted organic materials between 20 to 60% and weight by 30 to 60%, which allows the final product to be significantly more affordable to transport than raw wastes. Composting converts a considerable fraction of the N present in the raw manure into a more stable form, which is released slowly over a period of years and thereby not partially lost to the environment. Composting alleviates problems associated with ground and surface water contamination and also reduces odor complaints (Rynk, et al., 1992; Fabian, Richard, Kay, Allee, & Regenstein, 1993; Magdoff & Van Es, 2009). Even though, during the manure handling and composting process between 50 to 70% of the nitrogen can be lost as ammonia if not additional techniques are used to increase nitrogen retention (reducing losses as ammonia). Most of the time, manures from dairies and other livestock operations don’t have the proper carbon to nitrogen ratio (C:N) to be composted efficiently without added carbon. Since manures are richer in nitrogen (C:N ratios below 15:1) and usual bedding in Idaho consist of straw (C:N 60 to 100), a great proportion of the available nitrogen is lost as ammonia due to the lack of carbon to balance the composting process. A balanced mix for composting, maximizing the reduction of N losses as ammonia, should be between C:N of 30:1 to 40:1 (Rynk, et al., 1992; Fabian, Richard, Kay, Allee, & Regenstein, 1993; de Haro Marti, Agenbroad, & McCammon, 2014). In addition, the loss of ammonia from manures reduces the nutrient value of the manure and compost and generates local and regional pollution. This lack of carbon results in a lower grade compost that can carry high concentrations of salts, potassium, and phosphorous per mass unit of compost (Hao & Benke, 2008).

1.3.2 Compost temperature

Compost is an aerobic process that generates a temperature rise, having three distinctive temperature range periods dominated by different micro and macro organisms. At the beginning of the composting process mesophilic microorganism (working temperatures 25-45°C) dominate the compost environment. The initial mesophilic phase can last from one to 10 days approximately. The first thermophilic phase last from two days to two weeks. As temperature rises and feedstock starts to be degraded, thermophilic microorganisms (working temperatures >45°C) start to dominate, a further and defined temperature rise occurs. As the microorganisms run out of nutrients, get inhibited by the increase of temperature, NH_4, CO_2, toxins, or the lack of O_2, the thermophilic phase comes to an end. At this point, there are two possibilities, in passive and forced aerated, and in-vessel systems without turning, the compost enters its curing phase, when mesophilic microorganisms dominate again, and macro organisms may also be present (Day & Shaw, 2001). In mechanically turned windrows, the slowdown of a thermophilic phase indicates the time to turn the pile. In many cases windrows are turned before this point of temperature decline (but after three or four days at 55°C or more) to keep the process going under active thermophilic phase. At turning, feedstock is mixed again, oxygen replenished, NH_4 and CO_2 leave the compost environment and a new thermophilic cycle starts within 24-48 hours. This cycle is repeated at least five times to comply with requirements and regulations to reduce pathogens and weed seeds. Low initial C:N feedstock mixes may have difficulty reaching higher temperatures after three or four turns due to the lack of carbon. Regulations regarding temperature to be reached during composting are stablished by the USEPA Process to Further Reduce Pathogens (PFRP) (US Environmental Protection Agency (USEPA), 2003). To ensure pathogen destruction, passive and static aerated as well as in-vessel systems need to reach 55°C and maintain them for three consecutive days as a minimum. On mechanically turned windrows or piles, the regulation requires a cumulative of 15 days at 55°C. This needs to be achieved by having five cycles with at least three days of 55°C. This is required because the outer part of the windrow is exposed to atmospheric air and doesn't reach the required temperature. The action of mixing (by turning the windrow) ensures that all feedstock has the opportunity of being inside the windrow at some point and reach the desired temperature (US Environmental Protection Agency (USEPA), 2003). Inhibition or elimination of weed seeds requires reaching temperatures of 60°C (Rynk, et al., 1992).

1.3.3 Composting techniques

There are several techniques for on-farm composting including mechanically turned windrows or piles, passive aerated systems, forced aerated systems, and in-vessel composting (Rynk, et al., 1992; Rynk & Richard, 2001). I will focus exclusively on mechanically turned windrows since this is the method used almost exclusively in southern Idaho and the method used in this research. In this method, manure and any other compound to be composted, are laid in windrows usually between three to five meters wide and as long as the compost pad foot print allows (30 to 50 meters are common). The windrows are usually built by discharging manure from the back of a spreader or dump truck, one load after another. In small systems, the manure can be piled as a conical pile. Windrows are turned using a compost turner, consisting on a specialized machine that turns, aerates and beats the materials while defining the characteristic triangular or trapezoidal shape of the windrow (Picture 1.2). Another way of turning windrows is by turning them with a front-end loader or tractor bucket (Picture 1.3). In this case windrows have a triangular shape (Rynk, et al., 1992).

1.3.4 Compost stability and maturity

Compost stability is the property of avoiding or having minimum leaching (NO_3, NH_4^+) or emitting gaseous compounds (NH_3, N_2O, CH_4), to avoid damage to crops, and any significant temperature rise after the composting process is considered done and it is either stored or applied. Stability can be measured by diverse physical, chemical, and biological methods, including chemical analysis, re-heating capacity, respiration essays, and bio-essays (California Compost Quality Council, 2001; Vázquez Lima, Barrena Gómez, & Sánchez Ferrer, 2006).

Increased compost maturity means in general increased stability. Horticultural, landscaping, and many high value crops require a higher maturity compost rate than raw or extensive crops. In many cases, when compost doesn’t reach a minimum maturity rate, it ends up being used (and sometimes classified) as “dried manure” or “semi-composted manure”, which imposes certain limitations on its use (Sullivan & Miller, 2001).

One of the compost stability and maturity tests available and widespread used is the Solvita® Test. Its simplicity, accuracy, repeatability, portability, and cost makes it the test of choice for quick maturity analysis and reference. Solvita® measures the evolution of CO_2 and

NH_3 in a self-contained respiratory test with colorimetric reactions in a paddle impregnated with a reactant for each one of the mentioned gases. Reading is done by comparing the paddles' color with a printed colorimetric scale or by using an electronic color reader. Results from the test are used to determine a compost maturity index, condition of the compost, oxygen depletion, NH_3 concentration in test jar, phytotoxicity potential, noxious hazard, and N loss potential (McDonnel & Regenstein, 1997; Changa, Wang, Watson, Hoitink, & Michel Jr, 2003; Brinton & Evans, 2006; Woods End Research Laboratory, Inc., 2012).

1.4 TABLES

Table 1. 1 Representative formulae and selected physical properties of important zeolites

Zeolite	Representative Unit-cell formula	Void volume (%)	Channel Dimensions (Å)	Thermal Stability (relative)	Cation-exchange capacity (meq/g)
Analcime	$Na_{16}(Al_{16}Si_{32}O_{96})\cdot 16H_2O$	18	2.6	High	4.54
Chabazite	$(Na_2,Ca)_6(Al_{12}Si_{24}O_{72})\cdot 40H_2O$	47	3.7 x 4.2	High	3.84
Clinoptilolite (General)	$(Na_3K_3)(Al_6O_{30}O_{72})\cdot 24H_2O$	34	3.9 x 5.4	High	2.16
Clinoptilolite-K	$\vert(K,Na,Ca_{0.5},Sr_{0.5},Ba_{0.5},Mg_{0.5})_6(H_2O)_{20}\vert[Al_6Si_{30}O_{72}]$				
Clinoptilolite-Na	$\vert(Na,K,Ca_{0.5},Sr_{0.5},Ba_{0.5},Mg_{0.5})_6(H_2O)_{20}\vert[Al_6Si_{30}O_{72}]$				
Clinoptilolite-Ca	$\vert(Ca_{0.5},Na,K,Sr_{0.5},Ba_{0.5},Mg_{0.5})_6(H_2O)_{20}\vert[Al_6Si_{30}O_{72}]$				
Erionite	$(Na,Ca_{0.5},K)_9(Al_9Si_{27}O_{72})\cdot 27H_2O$	35	3.6 x 5.2	High	3.12
Faujasite	$(Na_{58})(Al_{58}Si_{134}O_{384})\cdot 240H_2O$	47	7.4	High	3.39
Ferrierite	$(Na_2Mg_2)(Al_6Si_{30}O_{72})\cdot 18H_2O$	28	4.3 x 5.5 3.4 x 4.8	High	2.33
Heulandite	$(Ca_4)(Al_8Si_{28}O_{72})\cdot 24H_2O$	39	4.0 x 5.5 4.4 x 7.2 4.1 x 4.7	Low	2.91
Laumontite	$(Ca_4)(Al_8Si_{16}O_{48})\cdot 16H_2O$	34	4.6 x 6.3	Low	4.25
Mordenite	$(Na_8)(Al_8Si_{40}O_{96})\cdot 24H_2O$	28	2.9 x 5.7 6.7 x 7.0	High	2.29
Phillipsite	$(Na,K)_5(Al_5Si_{11}O_{32})\cdot 20H_2O$	31	4.2 x 4.4 2.8 x 4.8	Medium	3.31
Linde A	$(Na_{12})(Al_{12}Si_{12}O_{48})\cdot 27H_2O$	47	4.2	High	5.48
Linde X	$(Na_{86})(Al_{86}Si_{106}O_{34})\cdot 264H_2O$	50	7.4	High	4.73

Source: Adapted from (Mumpton F. A., 1984) and (International Zeolite Association, 2010)

1.5 FIGURES

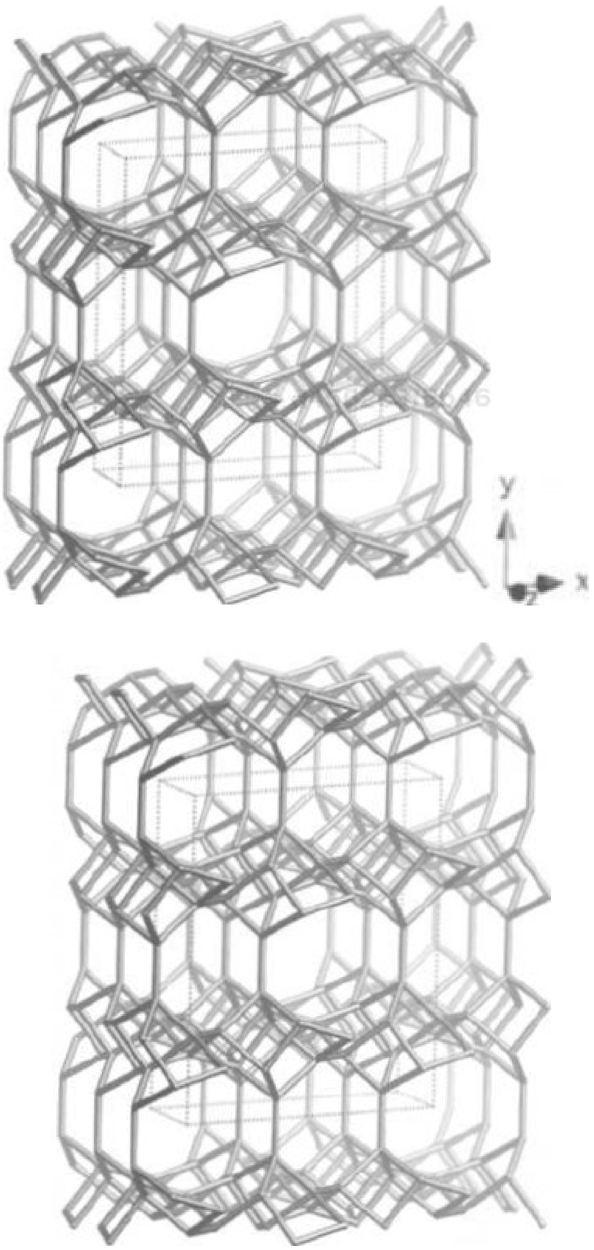


Figure 1. 1 Clinoptilolite (HEU) framework representation

Source: (Cusker & Olson, 2007).

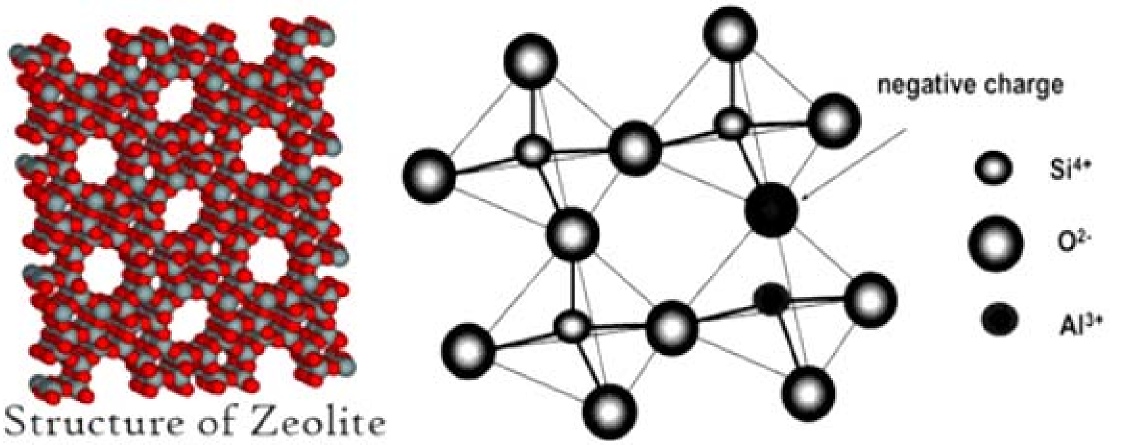


Figure 1. 2 Clinoptilolite molecule representation and relative molecule charge location

Source: (Gordeszeolite, 2014). “Another unique property of zeolites is that they are one of the few “negatively-charged” minerals found in nature. The charge is balanced by the presence of single and double-valanced atoms, such as sodium (Na+), potassium (K+), calcium (Ca+2), and magnesium (Mg+2), elsewhere in the structure”.

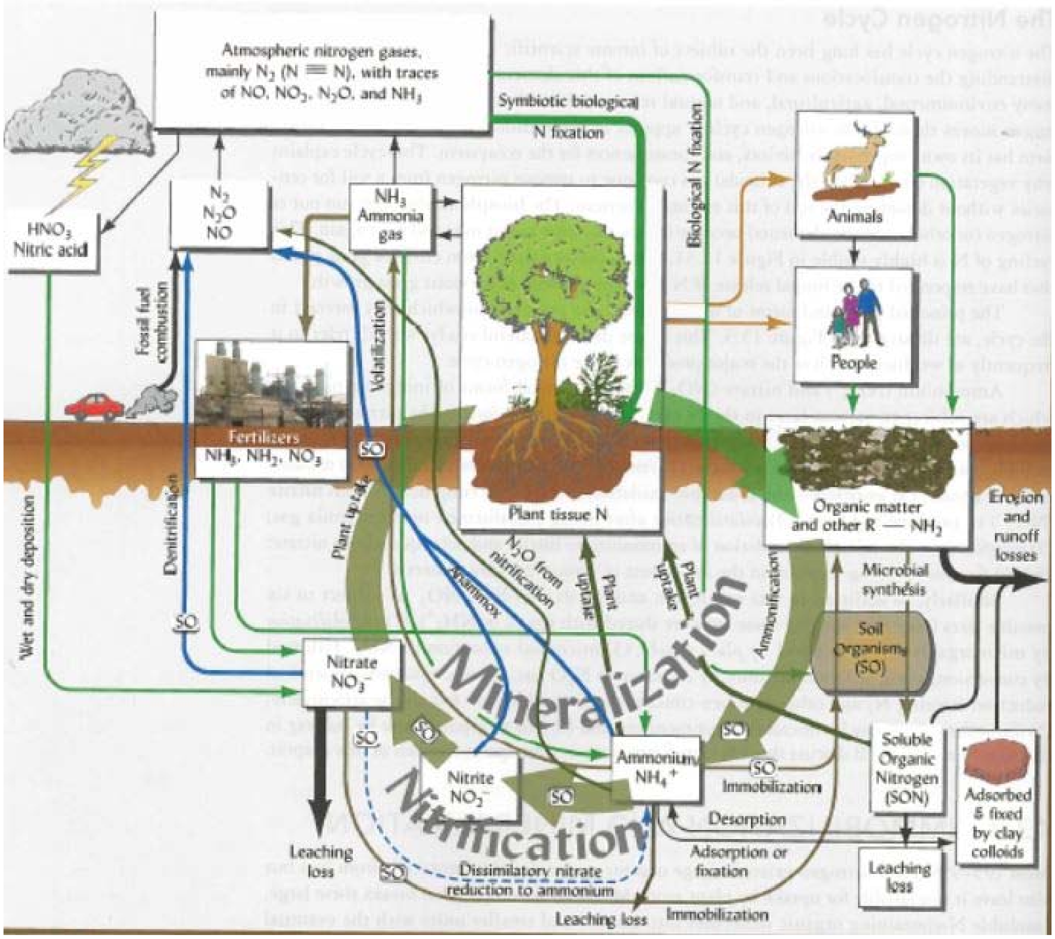


Figure 1. 3 The nitrogen cycle

Source: (Weil & Brady, 2017).

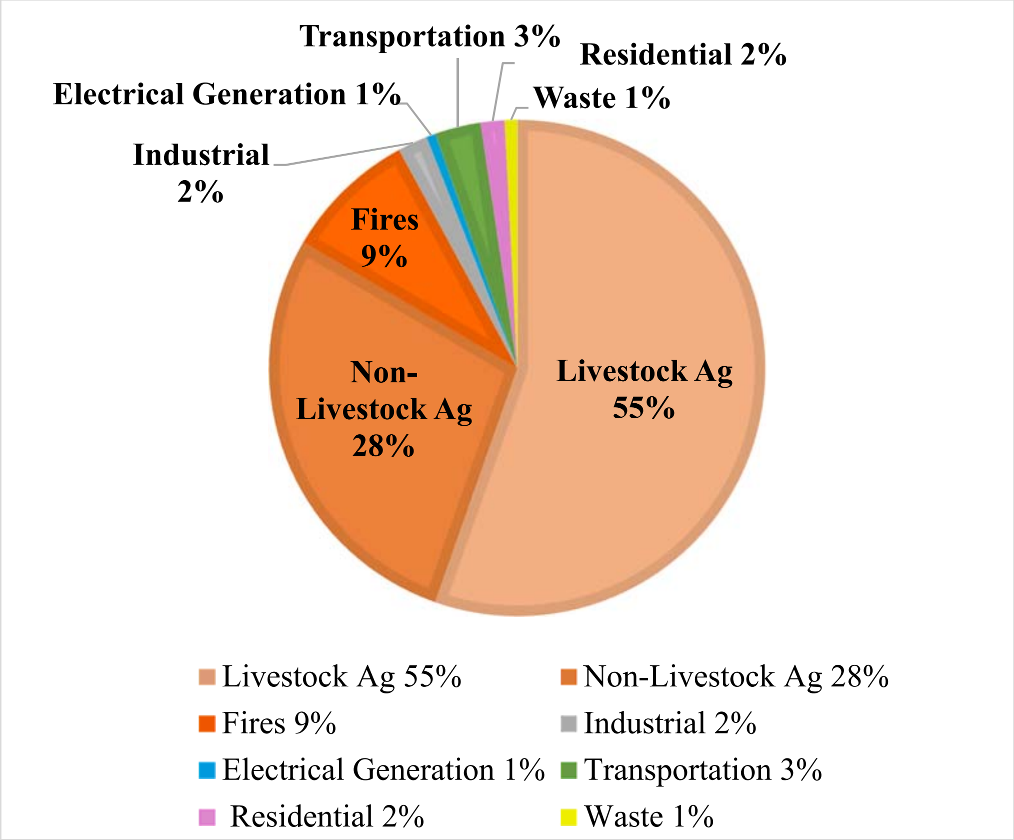


Figure 1. 4 Ammonia emissions distribution in the USA in 2011. USEPA (2015)

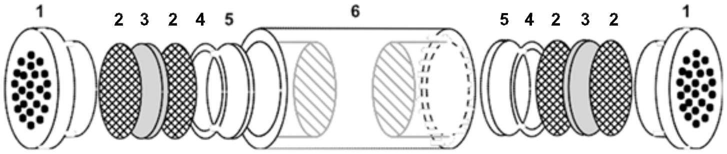


Figure 1. 5 Components of the Ogawa passive sampler

The sampler body (6) is 2 cm (outer diameter) and 3 cm (length) and has two independent cavities (1.4 cm inner diameter) each containing a diffusive-barrier end-cap (1), a reactive filter (3) between an inner and outer stainless-steel screen (2), and a retainer ring (4) over a base pad (5).

Source: (Roadman, Scudlark, Meisinger, & Ullman, 2003)

1.6 PICTURES

Picture 1. 1 Scanning electron micrograph of plates of clinoptilolite from Castle Creek, ID.

Source: (Mumpton F. A., 1999)

Picture 1. 2 Compost turner

Picture 1. 3 Windrow turning using a tractor

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CHAPTER 2

USE OF CLINOPTILOLITE ZEOLITE IN COMPOSTING OF DAIRY MANURE TO REDUCE AMMONIA EMISSIONS AND RETAIN NITROGEN IN THE COMPOST

2.1 ABSTRACT

Composting is one of the most used methods to reduce volume and weight of dairy manure while stabilizing it prior to its land application or storage. As a nutrient and waste management practice, composting reduces the volume of composted wastes between 20-60% and significantly reduces their weight, which allows the materials to be much more affordable to transport than raw wastes. Most manures, including dairy manure, don't have the proper carbon to nitrogen ratio (C:N) for composting without the loss of nitrogen as ammonia during the composting process. Due to the lack of enough carbon sources to balance the initial compost mix in arid and semi-arid regions, including southern Idaho (USA), amendments are used in an attempt to reduce the loss of nitrogen during the composting process. In many cases, these amendments provide uncertain results.

The objective of this study was to demonstrate the effects of adding clinoptilolite zeolite to a dairy manure compost mix, specifically the effects on ammonia emissions, compost nitrogen content and the quality of the final compost product.

A zeolite is a mineral comprised of crystalline, hydrated aluminosilicate of alkali and alkaline earth cations having an infinite, open three-dimensional structure. Zeolites are able to further lose or gain water reversibly and to exchange cations, ammonium (NH_4^+) and ammonia gas (NH_3) in particular, with and without crystal structure.

The study was conducted on a commercial dairy in Southern Idaho. Manure stockpiled during the winter and piled after the corral cleaning was mixed with fresh pushed-up manure from daily operations, and with straw from bedding and old straw bales, in similar proportions for each windrow. Windrows were mixed and mechanically turned using a tractor bucket. Three replications of control and treatment were made. The control consisted of the manure and straw mix as described. The treatment consisted of the same mix as the control plus the addition of 8% w/w on wet basis (15% dry basis) clinoptilolite zeolite during the initial mix. Windrows were actively composted for 145 to 157 days before screening, with five turns per windrow including the initial mix preparation.

Data were analyzed using ANOVA. Nitrate concentration in the treatment compost 702±127 mg/kg was three times higher than the control 223±127 mg/kg ($p= 0.05$). NH_4^+, showed a marked tendency to be lower in the treated windrows' initial feedstock mix. These differences from the beginning of the process indicate that clinoptilolite zeolites have an immediate impact when added to the compost mix changing the NH_4^+ and NH_3 behavior and volatilization even during the construction of the windrow. NH_3 emissions showed a significant reduction in some of the measured periods. Total cumulative ammonia emissions were reduced by 14.4% in the clinoptilolite treated compost vs. control. The clinoptilolite treated compost had a cumulative value of 63.41±7.22 mg NH_3-N/m^3 versus the control at 74.07±7.22 mg NH_3-N/m^3, but such difference was not significant ($p=0.2$). An overall NH_3

emissions reduction tendency was observed on the emissions' fitted line of the treatment compared to the control, indicating that the total NH_3 emissions from the whole process would be lower on the treated windrows. Solvita® maturity test showed a significant difference ($p<0.05$) indicating a higher maturity state on treated compost, with reduction in nitrogen loss potential, higher maturity index, lower estimated NH_4^+, phytotoxicity, noxious hazard and oxygen depletion. Volume reduction, composting temperatures, and most chemical component values had no significant differences between treatment and control. No negative effects resulted from the addition of clinoptilolite to the compost mix. The project demonstrated the feasibility of using the addition of clinoptilolite zeolites into the composting process as a Best Management Practice to improve dairy manure compost quality, reduce ammonia emissions, and change the nitrogen speciation during the composting process.

2.2 OBJECTIVES

2.2.1 The objectives of this on-farm research were:

1) To evaluate the effects of adding clinoptilolite zeolite to a dairy manure compost mix on ammonia emissions, nitrogen speciation at the end of the compost process, and nitrogen retention in the final compost
2) To evaluate the effects of adding clinoptilolite zeolite to a dairy manure compost mix on other elements commonly analyzed for nutrient management purposes, including carbon, phosphorous, potassium, sodium, iron, electroconductivity, pH.

3) To evaluate the effects of adding clinoptilolite zeolite to a dairy manure compost mix on the composting process including temperature, perceived odor, windrow turning, and compost screening

2.2.2 The main research hypotheses were:

1) Adding approximately 8% w/w on wet basis (15% on dry basis) of clinoptilolite zeolite to a dairy manure compost mix will reduce ammonia emissions, increase ammonium in the compost, and increase total nitrogen in the final compost compared to untreated compost mix.

   Null hypothesis: Adding approximately 8% w/w on wet basis (15% average on dry basis) of clinoptilolite zeolite to a dairy manure compost mix will not have an effect on ammonia emissions, ammonium content in the compost, and will not increase the total nitrogen in the final compost compared to untreated compost mix.

2) Adding approximately 8% w/w on wet basis (15% average on dry basis) of clinoptilolite zeolite to a dairy manure compost mix will not have a negative effect on the composting process. Temperatures will reach values needed to comply with the Process to Further Reduce Pathogens (PFRP), the windrows will be as easy to turn and screen as untreated windrows.

   Null hypothesis: Adding approximately 8% w/w on wet basis (15% average on dry bases) of clinoptilolite zeolite to a dairy manure compost mix will negatively impact the compost process. Temperatures will not reach PFRP, windrows will be difficult to turn and screen compared with untreated windrows.

2.3 INTRODUCTION

For more than 25 years, agriculture has been cited as the largest contributor to non-point source air pollution in the USA (National Research Council, 2003), and around the world (Chadwick, Misselbrook, & Pain, 2000). Since 1944, the number of livestock farms in the USA and worldwide has decreased dramatically, while farm size and productivity have increased considerably. For example, milk production per cow increased from 2073 kg per year in 1944 to more than 8000 kg per year in 2001. This dramatic increase in production per unit increased the unit (cow) intake and emissions, but it considerably reduced the resources used and emissions per unit of produced goods (kg of milk and beef in this case). In this regard, in the USA and most of Europe, you will need four 1944 cows to produce the amount of milk an average cow produces in 2017 (National Research Council, 2003; The World Bank, 2005). Animal Feeding Operations (AFO) and Concentrated Animal Feeding Operations (CAFO) have become the norm for commercial animal production, especially in the USA, Western Europe and many developing nations of the world. AFO are defined as agricultural enterprises where animals are kept and raised in confined situations. Animals have been, are, or will be stabled or confined and fed or maintained for a total of 45 days or more in any 12-month period, and crops, vegetation, forage growth, or post-harvest residues are not sustained in the normal growing season over any portion of the lot or facility. AFO concentrate animals, feed, manure and urine, and dead animals, such that all production operations concentrate in a small land area. Feed is brought to the animals rather than the animals grazing or otherwise seeking feed in pastures, fields, or on rangeland (USDA-NRCS, 2011; USEPA, 2016). In the USA, a CAFO is defined as an AFO that has 1000 Animal Units (AU) or more, (700 mature

Holstein dairy cows or more in the case of dairy operations), or that has been designated as a CAFO by the EPA due to a discharge (some smaller dairies), (USEPA, 2015). A high concentration of animals means increased concentrations of animal wastes. Emissions become concentrated in relatively small areas, and new handling, treatment, and disposal challenges arise.

During the animal production cycle, the storage and treatment of manure, and its application on fields, as well as the fate and emissions of nitrogen (N) compounds vary greatly. Of the many gases that may be emitted during these steps and processes, this paper will focus on ammonia (NH_3). Ammonia is produced as a result of natural animal and microorganisms' processes. Agriculture is recognized as a major contributor of NH_3 emissions, contributing about 55% of global NH_3 emissions. Animal production counts for about 43% of total global emissions, counting natural and anthropogenic sources (Schlesinger & Hartley, 1992). In the USA, approximately 83% of anthropogenic ammonia emissions come from agriculture, and around 55% of that overall total comes from livestock operations (USEPA, 2015). Figure 2.1 shows the distribution of NH_3 emissions in the USA by emitting sector. Farm animals consume a considerable amount of protein and other N-containing substances with their feed. This consumed N is partitioned between products such as meat, milk, eggs, and excretions such as urine, and feces. At the moment, there is no other way to produce goods with similar characteristics, cost-benefit, and nutritional value. Animal products and their by-products are an important part of human society's development and human nutrition.

Despite all the advances we have achieved in animal agriculture, the conversion of dietary N to marketable animal products is often considered inefficient, and 50 to 80% of the N consumed is excreted. More than 50 to 60% of the excreted N is in the urine, and more than 70% of this urine N is in the form of urea-N. Organic N compounds in feces can account for up to 35% of NH_3 production (Tamminga, 1992; Arogo, Westerman, Heber, Robarge, & Classen, 2001; Hristov, et al., 2011). Due to the AFO production system, manure, defined as the mix of animal urine, feces, discarded feed, water from cleaning, bedding material, and other production wastes, has an augmented degradation speed, and production of NH_3 is more than the elements considered separately in other production systems (Lorimor, Powers, & Sutton, 2000; ASAE, 2005). In the time frame from excretion, through storage, and after application, 50% to more than 70% of the N in manure can be converted to NH_3 and released to the atmosphere (Hristov, et al., 2011).

The environmental effects of ammonia include the addition of nitrogen (N) to sensitive ecosystems and in ecosystems where the natural supply of N is low, creating a N imbalance, and causing eutrophication in aquatic ecosystems. Arogo et al. (2001), also discuss the contribution of NH_3/NH_4^+ (ammonia and ammonium) to N imbalance and the associated emissions of nitrous oxide (N_2O), nitrogen oxide (NO), and nitrogen dioxide (NO_2). Other consequences associated with exceeding thresholds of both oxidized and reduced forms of N include the creation of particulate matter aerosols ($PM_{2.5}$), nitrate contamination of groundwater, eutrophication of water bodies, vegetation growth, and ecosystem changes due to higher concentrations of N, climatic changes associated with increasing N_2O, N saturation of forests' soils, and soil acidification via nitrification and leaching (Arogo, Westerman, Heber, Robarge, & Classen, 2001; Weil & Brady, 2017).

The dairy industry is the number one revenue commodity in Idaho. In 2017, the state ranked fourth in milk production in the nation, having more than 578,000 lactating dairy cows distributed in approximately 500 dairy operations (USDA-NASS, 2017). Considering that each cow produces approximately 67 kg of manure daily (feces and urine, not counting bedding), (Lorimor, Powers, & Sutton, 2000), in Idaho, this translates into more than 1.162 million tons of manure production per month from dairy cows alone.

On-farm composting of manure is one Best Management Practice (BMP) available to dairy producers. As a waste management practice, composting reduces the volume of composted wastes by 20 to 60% and weight by 30 to 60%, which allows the final product to be significantly more affordable to transport than raw wastes. Composting converts a considerable fraction of the N present in the raw manure into a more stable form, which is released slowly over a period of years and thereby not partially lost to the environment. Composting alleviates problems associated with ground and surface water contamination and also reduces odor complaints (Rynk, et al., 1992; Fabian, Richard, Kay, Allee, & Regenstein, 1993; Magdoff & Van Es, 2009). During the manure handling and composting process, between 50 and 70% of the nitrogen can be lost as ammonia if additional techniques are not used to increase nitrogen retention (reducing losses as ammonia). Most of the time, manures from dairies and other livestock operations don’t have the proper carbon to nitrogen ratio (C:N) to be composted efficiently without added carbon. A balanced mix for composting, maximizing the reduction of N losses as ammonia, should be between C:N of 30:1 to 40:1 (Rynk, et al., 1992; Fabian, Richard, Kay, Allee, & Regenstein, 1993; de Haro Marti, Agenbroad, & McCammon, 2014). Since manures are richer in nitrogen (C:N ratios below 15:1) and usual bedding in Idaho consist of straw (C:N 60 to 100), a great proportion of the available nitrogen is lost as ammonia due to the lack of carbon to balance the composting process. Loss of ammonia from manures reduces the nutrient value of the manure and generates local and regional pollution. Composting with insufficient carbon results in a lower grade compost that can carry high concentrations of salts, potassium, and phosphorous per mass unit of compost.

In many arid zones, including southern Idaho, there are not enough sources of carbon to balance the nitrogen present in the manure. Due to this lack of adequate carbonaceous material, additional methods to reduce the loss of ammonia during the composting process are needed. Several amendments have been evaluated in the past to achieve this reduction in nitrogen loss (Ndegwa, Hristov, Arogo, & Sheffield, 2008).

A zeolite is a mineral defined as a crystalline, hydrated aluminosilicate of alkali and alkaline earth cations having an infinite, open, three-dimensional structure. More than 40 natural zeolite minerals have been identified, but only a handful (chabazite, clinoptilolite, erionite, mordenite, and phillipsite) have current commercial applications and are abundant in nature. There are about 150 synthetic zeolites species. Natural zeolites are much cheaper than synthetic ones (Eyde & Holmes, 2006; Flanagan, 2015). Zeolites are able to lose or gain water reversibly and to exchange cations (Mumpton F. A., 1999). Natural zeolites minerals are abundant and because of their cost and characteristics are more suitable for most agricultural uses. Zeolites are mined in several western states in the USA where dairy production also concentrates. Idaho has at least three operating zeolites mines (2016) and several locations where the minerals can be mined (Sheppard, Gude III, & Mumpton, 1983; Altaner, Gude III, Mumpton, Sheppard, & Teague, 1993; Flanagan, 2015). Zeolites have excellent Cation Exchange Capacity (CEC) and great affinity to adsorb ammonia and ammonium forms of nitrogen (Mumpton F. A., 1981; Lefcourt & Meisinger, 2001). This adsorption capacity can be used to retain nitrogen from dairy manure, both during the composting process and in the final product. When mixed with manure, zeolites have been shown to retain nitrogen, thus reducing ammonia emissions and holding nitrogen in the manure or soil until it is taken up by crops. This also minimizes N leaching to subsurface waters or nutrient runoff situations (Lefcourt & Meisinger, 2001). Zeolites, in particular clinoptilolite, have been used to retain nitrogen, reduce emissions and reduce heavy metals and other contaminants mobility in swine and poultry manure, municipal sludge compost mixes, and soils amended with those materials (Weber, Barbarick, & Westfall, 1984; Mumpton F. A., 1981; Bautista, Kim, Ahn, Zhang, & Oh, 2011). A few studies evaluated the effects of clinoptilolites in beef and dairy cattle manure or composting of other production animals' manure in very small lab compost reactors (Bernal, Lopez-Real, & Scott, 1993; Giacomini, et al., 2014; Sun, et al., 2016). Studies on dairy manure composting using clinoptilolite, especially on-farm research trials, are very limited in quantity, scope and applicability.

This paper showcases an on-farm research project that explored the effects of adding natural clinoptilolite zeolite from Idaho to dairy manure at the time of composting as a tool to reduce ammonia emissions and retain nitrogen in the final composted product.

2.4 MATERIALS AND METHODS

This on-farm research and demonstration study was conducted at a 100 milking Jersey cows open lot dairy in the Magic Valley area, Southern Idaho, USA. Manure stockpiled during the winter and piled after the cleaning of the earthen corrals was mixed with fresh manure scraped from the concrete feeding alley daily, and piled up separately, and with straw from bedding and old straw bales in similar proportions for each windrow. The compost mixture was calculated using a compost spreadsheet calculator (WSU-Puyallup Compost Mixture Calculator, version 1.1. Puyallup, WA). Moisture was adjusted by adding well water to reach approximately 50% to 60% moisture on the initial mix. The squeeze test (Federal Compost Quality Assurance Organisation (FCQAO), 1993; BioCycle, 1996) was used to do the moisture adjustment in the field. Lab analysis of samples from each windrow just after construction provided the recorded moisture value for the initial mix. After that, moisture was adjusted by adding well water as needed, during the first three windrow turns. Windrows were mixed and mechanically turned using a 60 HP New Holland tractor with a front bucket (New Holland, PA).

Three replications of each, control and treatment, were made. The control consisted of the manure and straw mix as described. The treatment consisted of the same mix as the control plus the addition of 8% of zeolites by mix wet weight of compost feedstock during the initial mix (15% average on dry basis).The 8% value for the addition of zeolites on wet basis was chosen based on works by other authors that suggested additions between 6% to 10% and by the expected costs (Lefcourt & Meisinger, 2001; Meisinger, Lefcourt, Van Kessel, & Wilkerson, 2001; McDonald & Abiola, 2006). The wet weight and density of the initial mix was calculated using the bucket method (Washington State University Extension, 2017). The number of tractor buckets of mixed materials were then used to calculate the volume and the mass of the mix. Clinoptilolite zeolites were weighted and added to the treatment mix to reach the 8% w/w and then worked into the mix with the tractor before building the windrow. Pictures 2.1 to 2.7 show the sequence followed to prepare the initial mix, add clinoptilolites to treatment mixes and build and turn windrows. Clinoptilolite used in the study was mined from the Sheaville deposit at the Idaho-Oregon border, USA and provided for the study by

Ida-Ore Company (Nampa, ID). Table 2.1 shows the general formula, characteristics and analysis, provided by the company, of the clinoptilolite used in the study.

Windrows were actively composted for four months or more; following standard recommended procedures to achieve “USEPA Process to Further Reduce Pathogens (PFRP)”, (US Environmental Protection Agency (USEPA), 2003), e.g. at least five turns (including the initial mix) for mechanically turned system.

NH_3 emissions were measured using passive samplers (Ogawa & Co. Kobe, Japan), (Figure 2.2) for the first five to seven days immediately after building each windrow (called turn “0” in this study) and for similar periods of time after the consecutive two turns (collectively considered three turns for PFRP). These three “turns” that were monitored for NH_3 emissions occurred in the first 45 to 55 days of the composting process. Table 2.2 shows windrow building and turning dates, as well as the total days of composting.

Three simultaneous samples per windrow for each sampling period were collected. Each passive sampler was attached to a stake that was located in the compost mix and positioned at 52 cm from the compost surface. A 37.3 cm internal diameter and 71 cm height irrigation pipe, with a sampling surface area of 1093 cm^2 or 0.11 m^2, was located around the stake to serve as a chimney and allow emissions from the compost to be in contact with the Ogawa samplers and at the same time avoid or reduce interference from wind and surrounding gas emissions. Samplers were positioned 15 cm below the top edge of the chimney pipe using wooden stakes. Pictures 2.8 a, b, and d show the positioning of samplers on the stakes and the position of stakes into the pipes. Pipes were cut at an angle at the bottom to contact the compost windrow, and they just settled at the compost mix surface, without penetrating inside the compost mix (Figure 2.3). Pictures 2.8 c, and 2.9 show the pipes preparation and positioning on top of the compost windrow. A plastic mosquito net was fitted with elastic bands on top of the pipe to avoid interference by flies and other insects. Chimney pipes were held by surrounding their base with some compost mix material on the external part. Figure 2.3 shows the arrangement of ammonia samplers and thermometers on the windrows. NH_3 emissions per period and per turn were obtained measuring three periods of one to three days, 1) at the time of building each windrow, 2) after the first turn (turn 0 and turn 1 in Table 2.2), and 3) two periods of three or four days after the second turn. Ogawa samplers' pads were analyzed at the Kimberly, Idaho USDA-ARS research facility. Extraction was done using 5 ml of KCl 1M solution per sampler (two pads per sampler), then samples were analyzed by automated colorimetry using flow injection analysis and spectrometer, model Quick Chem 8500, ASX 520 series (Lachat Instruments, Loveland, CO). Values of mg NH_3-N/m^3 were time corrected by minutes of sampling.

Compost temperatures were recorded daily or every other day using a 91 cm (36" model) heavy duty compost thermometer with protective sleeve and guard (REOTEMP, San Diego, CA). As a secondary temperature measurement method, integrated soil temperature probes and digital temperature datalogger HOBO Pro V2 external temperature datalogger were used (part U23-003) (Onset, Cape Cod, MA). Sensor tips were located at 85 cm from the surface for the deep sensor and 45 cm for the shallow ones. I developed custom made wooden stakes with a plastic tube to contained and hold the cable and sensor tip.

Approximate windrow volume was calculated by taking measurements with a measuring tape when building each windrow and at the end of the composting process just before screening. An excel calculation table was made to calculate windrow volume. Rynk et al., (1992) windrow volume calculations were modified by using Heron's formula for irregular triangles.

After finishing the composting process, each windrow was screened using a custom-made rotatory screen designed by the author and constructed with the help of the participating dairy producer (Pictures 2.10 and 2.11). Details of the design, construction, and performance of the custom made rotatory compost screen are included in Chapter 4 of this dissertation.

Complete manure/compost nutrient lab analyses were performed for each windrow at the beginning (compost feedstock mix) and at the end of the study after compost screening. Lab analyses included dry matter (DM), pH, salts (EC), total nitrogen (TN), nitrates (NO_3-N), ammonium (NH_4-N), total carbon (TC), carbon to nitrogen ratio (C:N), phosphorous (P_2O_5), potassium (K_2O), calcium, magnesium, sulfur, zinc, iron, manganese, cooper boron, and sodium.

Compost maturity tests were performed using the SOLVITA® test (Woods End Laboratories, Mt Vernon, ME).

Statistical analyses were conducted using SAS 9.4 (SAS Institute, Cary, NC). Analyses included ANOVA (PROC MIXED) and paired t-test when applicable. All parameters were checked for normality and mixed procedure assumptions using the UNIVARIATE procedure. In this paper, results are considered significant at confidence values of $p \leq 0.05$. Results are considered as a trend at values between $p > 0.05$ and $p \leq 0.1$. p values > 0.1 are considered not significant.

2.5 RESULTS AND DISCUSSION

2.5.1 Effect of clinoptilolite addition to dairy compost mix on ammonia emissions

Cumulative ammonia emissions during the monitored periods show a difference of 14.43%, with lower emissions from the treated windrows. This difference as calculated is not significant, since the zeolite treated compost had a cumulative value of 63.41±7.22 mg NH_3-N/m^3 versus the control at 74.07±7.22 mg NH_3-N/m^3 ($P = 0.3$). Reductions were, however, significant ($p<0.05$) on turn zero (when the windrows were built) period 1, and turn 2 period 1 (Figure 2.4). Emissions in turn zero period 1 were 3.61±0.35 mg NH_3-N/m^3 for the control and 2.22±0.35 mg NH_3-N/m3 for the treatment with a difference of 1.39±0.49 mg NH_3-N/m^3 ($p<0.01$). For turn 2 period 7, emissions were 2.95±0.35 mg NH_3-N/m^3 for the control and 1.46±0.35 mg NH_3-N/m^3 for the treatment; the difference was 1.49±0.53 ($p<0.01$). Table 2.3 summarizes the average time of Ogawa samplers' exposure per period. Considering that the difference between treatment and control is significant only in period 1, that is the initial reading after building the windrow, the period that usually emits more NH_3 (Fukumoto, Osada, Hanajima, & Haga, 2003); and period 7, the one with longer exposure times, it is possible that longer exposure periods or bigger emission measurement areas may be needed to observe significant differences when using Ogawa samplers as NH_3 emissions measurement method in this type of setting. Ammonia emissions per measuring period and per turn (Figure 2.4) shows a more marked decreasing trend of ammonia emission from treated windrows than from control windrows when a fitted curve is calculated. This decreasing trend in NH_3 emissions observed in Figure 2.4 with the compost process used, that is with five cycles and approximately 150 days on average (Table 2.2), indicates that the total amount of NH_3 reduction at the end of the composting process using a compost turner (between five and 10 cycles with a total of 60 to 140 days in common composting practices in southern Idaho) will be greater than the cumulative 14.4% measured during the monitoring period. Other studies have found higher ammonia reduction values in dairy or cattle manure, but all of them have been performed in lab conditions with small compost mix volumes and the possibility to capture most or all NH_3 emitted during the researched periods (Waldrip, Todd, & Cole, 2015; Sun, et al., 2016). On-farm research of compost of other animal species manures have also found greater emission reduction, using fresher manure, or manure that contained more N at the beginning of the trials (Yun, et al., 2009; Bautista, Kim, Ahn, Zhang, & Oh, 2011).

2.5.2 Chemical composition in the initial feedstock mix windrows

Table 2.4 summarizes initial feedstock mix lab values for treatment and control windrows. The initial mix lab analysis revealed no significant differences in all parameters between control and treatment, except NH_4^+ where a tendency was observed. Many of the most stable parameters were very close to one another numerically (C:N, P_2O_5, K_2O, S, Na, etc.), indicating a good management of the on-farm feedstock formulation and mixing. Ammonium (NH_4^+) at 553.4±100 mg/kg for control and 256.77±100 mg/kg for treatment shows a tendency ($0.05<p\leq0.1$), (Figure 2.5). This difference from the beginning of the process indicates that clinoptilolite has an immediate impact in NH_4^+ when added to the compost mix, changing the NH_4^+ and NH_3 behavior and volatilization even during the construction of the windrow.

These results are coincident with observations made in dairy manure slurries, were significant NH_3 emissions reduction where observed in the first 4, 8, and 12 hours after the addition of zeolites to the slurries (Lefcourt & Meisinger, 2001; Meisinger, Lefcourt, Van Kessel, & Wilkerson, 2001). In this study, the process of building each of the 12 windrows (mixing the feedstock, adding water when needed, and building the windrow in its designated place), took between five to six hours from the point of starting the mixing process until the sample was taken. Considering the initial pH was high, 8.6±0.38 for control and 9.2±0.38 for treatment ($p > 0.3$), and the carbon to nitrogen ratio (C:N) was low, 11.73±1.14 for treatment and 12.2±1.14 for control; NH_3 emissions were expected to be relatively high (Morisaki, Kiyohiko, Nakasaki, Shoda, & Kubota, 1989; Rynk, et al., 1992; de Haro Marti, Agenbroad, & McCammon, 2014) (Rynk, et al., 1992).

2.5.3 Chemical composition changes after composting

Table 2.5 summarizes final screened compost lab values for treatment and control windrows. When comparing the final compost resulting from control and treatment windrows, the fate of nitrogen within the system surfaces as the major difference. Nitrate concentration in the treatment compost, 702±127 mg/kg was three times higher than the control, 223±127 ($p= 0.05$, Figure 2.6). Organic N (calculated) showed a tendency to be higher in the control, 14583±1321 mg/kg than in the treatment, 10503±1321 mg/kg ($p=0.09$). However, neither NH_4^+ or TN showed a significant difference between treatment and control. The standard error and standard deviation in all nitrogen compounds was quite high compared to other more stable compounds (Table 2.5). The presence of such high amount of nitrate compared to the control indicates a strong prevalence of nitrification processes (Sylvia, Fuhrmann, Hartel, &

Zuberer, 1997; Sikora & Szmidt, 2001; Weil & Brady, 2017). Values that high are desirable in high quality compost used in plant nurseries, green houses, and horticulture, and are usually obtained from feedstock with much higher carbon content than the one used in this research. The NO_3 to NH_4^+ ratio (NO_3:NH_4) in the treated windrows is also indicative of a much more stable compost than what is to be expected in a dairy compost with such low initial C:N (Sikora & Szmidt, 2001; Radovich, Nguyen, & Pant, 2011). High NO_3 concentrations in compost could generate a concern for NO_3 leaching if the compost is not managed properly during storage and at the time of application (Miner, Humenik, & Overcash, 2000; Sikora & Szmidt, 2001; Weil & Brady, 2017). Comparing the analysis of the initial feedstock mix and the final compost product within each windrow, (paired T-Test), shows a significant difference ($p= 0.03$) in the nitrate concentration in the treatment, with no significant difference in the control. NH_4^+ and TN show a tendency to decrease in the control windrows ($p= 0.10$). All other nitrogen compounds had no significant differences between initial and final status (Table 2.5). In a related beef manure compost study (McDonald & Abiola, 2006), TN concentration increased 0.13% (1300 mg/kg) at the end of the process with the addition of 5% w/w zeolites, but decreased by 0.49% (4900 mg/kg) with the addition of 9% and 17% zeolites w/w. This was a demonstration project, with no replications, lacking any statistical significance.

Clinoptilolite zeolites started the NH_4^+ adsorption process early, probably during the first hours after the feedstock mixing (Meisinger, Lefcourt, Van Kessel, & Wilkerson, 2001; Lefcourt & Meisinger, 2001). The increase in some N compounds in the treatment relative to the control (Table 2.5), coupled with the reduction of NH_3 emissions, indicate that clinoptilolite adsorbed NH_3 and helped to create conditions that produced an increase or enhancement of nitrification processes during composting in the treated windrows.

Reduction on carbon content and C:N during the composting process showed a tendency to be greater for the control windrows than for treatment windrows ($p=0.08$ for TC and 0.06 for C:N), (Figure 2.7). The final C values also have a slight tendency to be higher in the control (131.8±9.5 g/kg) than in the treatment (105.1±9.5 g/kg). This lower C content in the treated windrows may be explained by the zeolites enhancing the nitrification process, inducing retention of NH_4^+ to allow the nitrifying bacteria to consume more C and further continue with the nitrification process. There will also be a small dilution effect from the volume of the zeolites added (McDonald & Abiola, 2006). All other tested compounds showed no difference between treatment and control, including K, S, P, Ca, Mg, Na, Mn, Cu, Zn, Fe, B, and pH. Electroconductivity (EC) showed no significant difference between treatment and control in the final compost. The difference was, however, significant ($p=0.03$) when the final zeolite treated compost was compared to the initial mix (paired t-test), indicating that clinoptilolite adsorbs some of the ions responsible for EC, an effect observed by Gamze (2008) as well.

2.5.4 Windrow volume reduction

There was no significant difference in volume reduction between treatment and control. Treated windrows reduced their volume by 23.63±2.50% and control windrows by 21.42±2.50% ($p>0.5$). These volume reduction values are at the lower range of those cited in the bibliography, where values usually range from 20 to 60% (Rynk, et al., 1992; Alberta Agriculture, Food and Rural Development, 2005). This lower volume reduction can be attributed mostly to the low carbon and compostable bulking agents content in the feedstock mix (Tiquia, Richard, & Honeyman, 2000). The initial C:N was 11.73±1.14 and TC was 197.6±26.84 g/kg for the treatment windrows and 12.2±1.14 and 131.4±26.84 g/kg for the control windrows. There was no significant difference in these values in the initial feedstock mix and just a tendency ($p=0.1$) of lower C in the treatment for the final screened compost. The reduced C:N ratio and TC content in the feedstock mix is common to dairy operations in Southern Idaho due to the lack of available or easily accessible carbonous materials. The windrow turning method, using a tractor bucket, also produces less volume reduction as compared to using a windrow turner. Windrow turners break all bigger chunks and produce a more homogeneous compost. In addition, it is common to have more windrow turns using a windrow turner (six to eight or more turns are common in Southern Idaho) than using a bucket (usually five to six turns), due to the easier and faster procedure when using a compost turner. Table 2.6 summarizes the volume reduction for all windrows, size and volume at building time (initial mix), and final composted windrow size and volume before screening.

2.5.5 Solvita® compost maturity test

The Solvita® test (Woods End Research Laboratory, Inc., 2012) results (Table 2.7) show a significant difference ($p=0.007$) in the NH_3 test results between control, index 2.5±0.35 and treatment, index 5.0±0.35. Carbon Dioxide (CO_2) test results shows no significant differences between control (C) and treatment (T).

All other calculated parameters show a significant difference between control and treatment. Maturity index was 4.8±0.33 for C and 6.7±0.33 for T ($p<0.02$). Oxygen depletion was 0.022±0.002 for C and 0.009±0.002 for T ($p<0.02$). NH_4+ estimate was 1167 for C and <200 for T ($p=0.05$).

Other estimated test parameters indicate a significant difference between control and treatment results. Control windrows showed more unstable conditions, reaching the active or curing status, medium to high phytotoxicity; moderate to severe noxious hazard, and moderate to low N-loss potential. In contrast, the treatment windrows show more stable conditions, including reaching finished and curing status, no phytotoxicity or noxious hazard, and very low to no N-loss potential. Table 2.7 summarizes the results of the Solvita® test for the final compost after screening. Picture 2.12 shows that CO_2 test results weren't much different between treatment and control in the CO_2 reactive paddles color. Picture 2.13 shows the noticeable difference in reactive color changes between control and treatment in the NH_3 test results. These results, coupled with the NO_3:NH_4 ratio and much higher NO_3 values in the zeolite amended compost, indicate that the addition of clinoptilolite zeolite in this study induced not only nitrification processes, NH_4^+ retention, NH_3 emissions reduction, and lower oxygen depletion without significantly modifying the CO_2 production, but also led to compost maturity characteristics that are regularly achieved only in compost mixes with much higher carbon content and C:N ratios, usually associated with high quality composts. Bautista et al. (2011) found similar Solvita® test results composting swine manure with the addition of clinoptilolite.

2.5.6 Temperature

Figure 2.8 illustrates the average temperatures for control and treatment windrows. Figure 2.9 illustrates all windrows' temperatures. There was no significant difference between control and treatment in temperatures (Figure 2.8, p>0.6). These results differ from McDonald & Abiola (2006) where higher temperatures than the control were observed with the addition of 5% w/w zeolites, but lower temperatures were observed with the addition of 9% and 17% zeolites w/w. Villaseñor et al. (2011), also observed lower composting temperatures with the addition of higher percentages of zeolites to the mix (25% to 40%), but not at lower percentages. Other authors found no difference in temperatures between zeolite treated and non-treated compost (Giacomini, et al., 2014) or increased temperatures in the thermophilic phase and lower in the mesophilic ones (Zhang, et al., 2016).

Temperature was taken using the HOBO probes and dataloggers adapted as compost probes as described in materials and methods. After windrows' turning was initiated, some of the probes started to fail, and it was evident that the traditional method of temperature monitoring via analog compost thermometers was absolutely necessary. By the end of the trial, the rate of failure on the HOBO probes was around 60%. For this reason, the HOBO data were only used until the first, or sometimes second turn, in these analyses. After that, the analog thermometers data were used. The electronic sensor and dataloggers ended up being too fragile for the task. Many of the failures were associated with interrupted or poor connection between the sensor and the datalogger due to breakage, mostly during pulling and reintroduction operations at the time of windrow turning. This happened even when a hole was made with a metal or wooden stick in the compost mix previous to the introduction of the built stick containing the temperature sensor. All windrows show an initial struggle to reach 55ºC. This is not a common occurrence in Southern Idaho at the time of the trial initiation in June. It can be attributed to the cold well water used to reach the proper initial moisture, and the windrow turning method using a tractor bucket, which produces a less aggressive turning action as compared with a compost turner. In addition, the low initial C:N was a contributing factor in reducing the temperatures achieved and maintaining those temperatures for longer periods. This lack of temperature increase and maintenance over time due to low C:N is common in the area, but it usually becomes evident after the third turn, when windrows struggle to reach and maintain desired temperatures, once microorganisms have run out of enough carbon to keep the thermophilic phase going (Rynk, et al., 1992; Michel, Keener, Rigot, Wilkinson, & Pecchia, 2004).

2.5.7 Other observations

Odor rating at time of taking temperatures and turning windrows was lower in treated windrows. Odor rating was much lower and ammonia smell was noticeably absent in treatment windrows at the time of screening. These measures are subjective, but all four operators who participated in turning, taking temperatures and screening concurred in the assessment of lower odor ratings of treatment windrows.

There was a small difference in the amount of refuse coming out of the rotatory screen between treatment (~15%) and control (~20%) windrows. This difference can't be attributed to a treatment effect. The major parameter affecting the amount of refuse from the screen was the moisture content of the compost and the operation of the screen itself. The high amount of refuse from the screening process compared to common composting practices in the area (usually around 5% or less refuse) is related to the turning method (by tractor) that doesn't break some chunks of manure and dirt as efficiently as a compost turner. Some of the large pieces of dirt, compost, or manure were broken by the rotating action of the screen though. Moisture was the major factor in the amount of refuse obtained, higher moisture compost tended to have a cohesive behavior, forming balls that rolled out of the screen as refuse (Picture 2.14). Better mixing of the internal section of the windrow (higher moisture) and the outer part (dryer) and screen operation, by regulating the amount of compost dumped on the feeder and screen speed, helped reduce the amount of refuse.

2.5.8 Basic cost-return analysis

Table 2.8 summarizes costs and returns for the control and treatment compost under this project's conditions. Making a complete and thorough cost-return analysis is beyond the scope of this study, but a rough comparison and analysis can help to draw basic conclusions on the economic value and cost-benefit of the addition of clinoptilolite to dairy manure composting.

Calculated costs are higher than regular on-farm composting due to the experimental nature of the project. Normal on-farm composting is expected to have at least 20 to 30% lower costs than those in this research trial. This is due to economies of scale, including much longer windrows, ability to have less mixing of feedstock materials during the pre-mix, personnel more proficient with tractor, much lower monitoring costs, reduced screening and sampling times.

From Table 2.8, it can be inferred that when considering only the nutrient value of the compost, the addition of clinoptilolite, in this study, didn't generate enough retention of N in the compost to justify the costs associated with its addition. On the contrary, including the maturity and stability of the compost when clinoptilolite is added opens the possibility of using the enhanced dairy manure compost with a new set of crops as well as for landscaping. This is usually not recommended when using manure compost as it is actually produced most of the time in southern Idaho due to possible challenges with stability, maturity, and possible crop damage. In this case, a new higher end market (with higher compost prices and returns) could justify the addition of clinoptilolite.

More research needs to be done factoring long-term effects and compost-soil-crops interactions on field crops using clinoptilolite enhanced compost. Similarly, further research and economic analysis need to be done to embrace its use with confidence for the production of compost destined for high value crops or higher end uses.

2.6 CONCLUSIONS

This project demonstrated the feasibility of using the addition of clinoptilolite zeolite, a regional resource, into the composting process as an on-farm Best Management Practice to improve dairy manure compost quality and maturity, reduce ammonia emissions, and change the nitrogen speciation in the final compost product, another regional resource. Volume reduction, composting temperatures, and most chemical component values had no significant difference between treatment and control. No negative effects resulted from the addition of clinoptilolite to the compost mix. The project demonstrated that it is possible to integrate the addition of zeolites into the compost dairy operations with minimum effort, having a positive impact on the process and final product. This suggests that the use of clinoptilolite as an amendment for on-farm composting may be both viable and desirable.

Further research is needed to assess ammonia emissions for longer periods of time during the composting process, test different clinoptilolite concentrations, evaluate the effects of higher initial C:N ratios and clinoptilolite addition together, evaluate nitrate leaching potential of the final compost, evaluate the nutrient release and effects in crops of clinoptilolite amended compost, evaluate the addition of clinoptilolite earlier in the manure management chain as it relates to composting, and develop a cost-benefit analysis of clinoptilolite as amendment for dairy manure composting.

2.7 TABLES

Table 2. 1 Characteristics and description of IDA-ORE Clinoptilolite zeolite used in the study

IDA-ORE Clinoptilolite general formula: $(Na, K, Ca)_6 (Si, Al)_{36}O_{72} \bullet 20H_2O$

Cation Exchange Capacity (CEC) 147-250 meq/ 100g

Element	Report 1 %	Report 2 %
Na_2O	1.36	1.24
MgO	0.34	0.17
Al_2O_3	12.34	11.3
SiO_2	76.72	71.5
K_2O	5.08	4.55
CaO	1.5	1.22
TiO_2	0.32	0.27
Fe_2O_3	1.67	2.05
BaO	0.21	0.15

Analysis performed by The Mineral Lab, Inc.

Clinoptilolite compound selectivity

Compounds	$Cs^+ > NH_4^+ > Pb^{2+} > K^+ > Na^+ > Ca^{2+} > Mg^{2+} > Cu^{2+}\ Zn^{2+}$
Gases	CO, CO_2, SO_2, H_2S, NH_3, HcHO, Ar,O_2, N_2, H_2O ,He, H_2, Kr, Xe, CH_2OH, Freon
Major Exchangeable	Rb, Li, K, Cs, NH_4, Na, Ca, Ag, Cd, Pb, Zn, Ba, Sr, Cu, Hg, Mg, Fe, Co, Al, Or

Table 2.1 (cont.). Characteristics and description of IDA-ORE Clinoptilolite zeolite used in the study

Clinoptilolite zeolite specifications

Size used	US Std Sieve 14-40= 1.18mm to 0.416 mm
Total Surface Area	< 800 m^2/g
Specific Surface Area	1357 yd^2/oz
Average Clinoptilolite Content	87% (+/- 5%)
Specific Gravity	2.42
pH	7.29
Bulk Density	~881 kg/m^3

Table 2. 2 Compost windrows' building, turning and screening days

		NH$_3$ sampling done during these turns													
Windrow #	T or C	Built/ Turn 0	Days	Turn 1	Days	Turn 2	Days	Turn 3	Days	Turn 4	Days	Turn 5	Screened	Days	Total days
1	C	6/3	15	6/17	14	7/2	28	7/30	20	8/19	23	9/11	10/30	49	149
2	C	6/9	10	6/19	12	7/1	29	7/30	20	8/19	23	9/11	11/1	51	145
3	T	6/16	13	6/29	22	7/21	16	8/6	15	8/21			11/13	84	150
4	T	6/17	13	7/1	23	7/24	20	8/13	19	9/1			11/22	82	157
5	C	6/19	11	7/1	26	7/27	17	8/13	19	9/1			11/13	73	146
6	T	6/26	18	7/14	23	8/6	15	8/21	18	9/8			11/22	75	149

Table 2. 3 Average Ogawa samplers' exposure time in hours per period and Treatment of Control

	Turn 0			Turn 1			Turn 2	
Control	P1 C	P2 C	P3 C	P4 C	P5 C	P6 C	P7 C	P8 C
	47.8	36.9	40.5	56.7	48.7	45.2	59.4	63.8
Treatment								
	P1T	P2 T	P3 T	P4 T	P5 T	P6 T	P7 T	P8 T
	54.7	48.2	50.8	49.5	58.7	48.7	71.9	48.1
% difference on average exposure time between T or C								
	12.7	23.5	20.3	-14.7	17.0	7.3	17.3	-32.7
Average Ogawa samplers' exposure time in hours per period								
	51.3	42.5	45.7	53.1	53.7	47.0	65.6	56.0

Table 2. 4 Manure feedstock initial mix lab analysis

Variable	**Treatment or Control**	**LS Means mg/kg** unless specified	**SE**	**LS Means %**	**LS Means kg/Mg (t)**	**P**	**Significant=S Tendency=T Not Significant=N**
Solids	C	45.66%	4.45	45.66		0.29	N
Solids	T	53.30%	4.45	53.30		0.29	N
Moisture	C	54.33%	4.45	54.33		0.29	N
Moisture	T	46.70%	4.45	46.70		0.29	N
TN	C	16133	1713.02	1.61	16.13	0.13	N
TN	T	11467	1713.02	1.15	11.47	0.13	N
NH_4	C	553.40	100.13	0.05	0.55	0.10	T
NH_4	T	256.77	100.13	0.02	0.26	0.10	T
NO_3	C	19.33	4.18	0.002	0.02	0.23	N
NO_3	T	27.66	4.18	0.003	0.03	0.23	N
ON	C	15561	1659.57	1.55	15.56	0.14	N
ON	T	11182	1659.57	1.11	11.18	0.14	N
TC	C	197600	26845	19.76	197.60	0.16	N
TC	T	131400	26845	13.14	131.40	0.16	N
CN	C	12.20	1.15	0.002	12.20	0.79	N
CN	T	11.73	1.15	0.001	11.73	0.79	N
P_2O_5	C	10733	1150.85	1.07	10.73	0.32	N
P_2O_5	T	8866.67	1150.85	0.89	8.87	0.32	N
K_2O	C	27633	2654.66	2.76	27.63	0.45	N
K_2O	T	24500	2654.66	2.45	24.50	0.45	N
S	C	3600.00	436.53	0.36	3.60	0.44	N
S	T	3066.67	436.53	0.31	3.07	0.44	N
Ca	C	21800	1871.42	2.18	21.80	0.45	N
Ca	T	19567	1871.42	1.96	19.57	0.45	N
Mg	C	8933.33	563.22	0.89	8.93	0.17	N
Mg	T	7600.00	563.22	0.76	7.60	0.17	N
Na	C	5666.67	548.74	0.57	5.67	0.69	N
Na	T	5333.33	548.75	0.53	5.33	0.69	N
Zn	C	233.33	21.22	0.02	0.23	0.25	N
Zn	T	193.00	21.22	0.02	0.19	0.25	N
Mn	C	108.67	16.55	0.01	0.11	0.85	N
Mn	T	104.00	16.55	0.01	0.10	0.85	N
Cu	C	15.00	3.27	0.001	0.02	0.55	N
Cu	T	18.00	3.27	0.002	0.02	0.55	N
Fe	C	8043.67	1329.41	0.80	8.04	0.86	N
Fe	T	7701.67	1329.41	0.77	7.70	0.86	N
B	C	32.67	5.29	0.03	0.03	0.74	N
B	T	35.33	5.29	0.03	0.04	0.74	N
pH	C	8.67	0.39	8.67	8.67	0.34	N
pH	T	9.27	0.39	9.27	9.27	0.34	N
EC	C	11.63	2.09	11.63	11.63	0.37	N
EC	T	8.63	2.09	8.63	8.63	0.37	N

Table 2. 5 Final compost lab analysis

Variable	**Treatment or Control**	**LS Means mg/kg** unless specified	**SE**	**LS Means %**	**LS Means KG/Mg (t)**	**P**	**Significant=S Tendency=T Not Significant=N**
Solids	C	75.47%	2.87	75.47	75.47%	0.52	N
Solids	T	72.63%	2.87	72.63	72.63%	0.52	N
Moisture	C	24.53%	2.87	24.53	24.53%	0.52	N
Moisture	T	27.37%	2.87	27.37	27.37%	0.52	N
TN	C	14933	1379.21	1.49	14.93	0.14	N
TN	T	11300	1379.21	1.13	11.30	0.14	N
NH_4	C	128.17	94.33	0.01	0.13	0.81	N
NH_4	T	94.53	94.33	0.009	0.09	0.81	N
NO_3	C	222.67	126.89	0.02	0.22	0.05	S
NO_3	T	702.00	126.89	0.07	0.70	0.05	S
ON	C	14583	1320.76	1.46	14.58	0.09	T
ON	T	10503	1320.76	1.05	10.50	0.09	T
TC	C	131767	9484.58	13.18	131.77	0.10	T
TC	T	105100	9484.58	10.51	105.10	0.10	T
CN	C	8.90	0.30	0.0009	8.90	0.36	N
CN	T	9.33	0.30	0.0009	9.33	0.36	N
P_2O_5	C	10100	674.95	1.01	10.10	0.12	N
P_2O_5	T	8233.33	674.95	0.82	8.23	0.12	N
K_2O	C	27933	1892.38	2.79	27.93	0.88	N
K_2O	T	28367	1892.38	2.84	28.37	0.88	N
S	C	3100.00	228.52	0.31	3.10	0.17	N
S	T	2566.67	228.52	0.26	2.57	0.17	N
Ca	C	20800	1470.45	2.08	20.80	0.27	N
Ca	T	18167	1470.45	1.82	18.17	0.27	N
Mg	C	8933.33	517.47	0.89	8.93	0.18	N
Mg	T	7733.33	517.47	0.77	7.73	0.18	N
Na	C	5666.67	594.89	0.57	5.67	0.77	N
Na	T	5400.00	594.89	0.54	5.40	0.77	N
Zn	C	247.67	17.67	0.02	0.25	0.14	N
Zn	T	201.00	17.67	0.02	0.20	0.14	N
Mn	C	141.00	17.83	0.01	0.14	0.67	N
Mn	T	129.00	17.83	0.01	0.13	0.67	N
Cu	C	21.67	4.08	0.002	0.02	0.56	N
Cu	T	25.33	4.08	0.002	0.03	0.56	N
Fe	C	8946.33	700.60	0.89	8.95	0.93	N
Fe	T	8853.33	700.60	0.88	8.85	0.93	N
B	C	26.67	6.99	0.003	0.03	0.62	N
B	T	21.33	6.99	0.002	0.02	0.62	N
pH	C	9.40	0.19	9.40	9.40	0.57	N
pH	T	9.23	0.19	9.23	9.23	0.57	N
EC	C	6.50	0.61	6.50	6.5	0.21	N
EC	T	5.23	0.61	5.23	5.23	0.21	N

Table 2. 6 Windrow initial and final volume and volume reduction percentage

Windrow #	State, Initial or Final	T or C	Side A	Side B	Width	Length	Windrow volume m^3	% Reduction
1	INI	C	2.4	2.2	3.8	6.7	16.5	
1	FIN	C	2.5	2.8	4.8	5.2	14.0	15.1
2	INI	C	2.6	2.5	4	7.4	23.4	
2	FIN	C	2.5	2.6	3.4	5.5	17.8	24.1
3	INI	T	2.3	2.4	3	7.2	19.5	
3	FIN	T	2.6	2.4	3.9	4.7	14.3	26.7
4	INI	T	2.3	2.3	3.3	7.7	20.4	
4	FIN	T	2.6	2.6	3.9	4.7	15.8	22.6
5	INI	C	2.6	2.6	3.6	6.8	23.0	
5	FIN	C	2.6	2.6	3.8	5.1	17.2	25.1
6	INI	T	2.3	2.5	3.8	7.9	22.0	
6	FIN	T	2.7	2.6	4.4	5.3	17.2	21.6

Table 2. 7 Solvita® test results in the finished compost

Sample	**T or C**	**CO_2**	**NH_3**	**Maturity Index**	**Compost Condition**	**O_2 depletion**	**Phytotoxicity**	**Noxious hazard**	**pH**	**NH_4^+ Estimate (ppm)**	**N-Loss potential**
W 1	C	6.5	3.5	5.5	Curing	1.60%	Medium/Slight	Moderate/Slight	9.1	500	Moderate/Low
W 2	C	6.5	2	4.5	Active Compost	2.50%	High	Severe	9.3	1500	M/ High
W 5	C	6.5	2	4.5	Active Compost	2.50%	High	Severe	9.8	1500	M/ High
W 3	T	7	5	7	Finished Compost	0.70%	None	None	9.5	<200	V Low-None
W 4	T	7	5	7	Finished Compost	0.70%	None	None	8.9	<200	V Low-None
W 6	T	6	5	6	Curing	1.20%	None	None	9.3	<200	V Low-None

CO_2 scale varies from 1= High to 8= Low

NH_3 scale varies from 1= High to 5= Low

Table 2. 8 Basic cost-returns comparison between control and treatment compost on research windrows

Parameter	Control variable number	Control cost ($)	Control on 20 t compost per ha	Treatment variable number	Treatment cost ($)	Treatment on 20 t compost per ha
Tractor usage, hr	5.1	111.2	NA	5.2	113.6	NA
Clinoptilolite, t	0	0	NA	0.89	127.3	NA
Screen time, hr	1	20	NA	1	20	NA
Labor, hr	7	84	NA	7.2	86.4	NA
Total windrow cost		215.2	NA		347.3	NA
Cost per m^3		13.45	$269		21.71	$434
Returns						
TN	14.9 kg/t	17.56/t	298 kg/ha $351	11.3 kg/t	13.32/t	226 kg/ha $266
Readily available N	0.35 kg/t	0.41/t	7.0 kg/t $8.25	0.79 kg/ha	0.93/t	15.8 kg/ha $18.6
Compost stability	Low			High		
High end use	Unacceptable			Acceptable		

Assumptions:

All monetary values are 2015 values.

NA= Not applicable

Nitrogen cost and value based on urea ammonium nitrate (UAN) 28%.

Tractor calculated based on a 60HP SWD tractor with 1000 hr/year of use, cost= $21.8/hr.

Clinoptilolite cost $143/t. Usage= 0.89 t per 20.8 m^3 windrow, (42.8 kg/m^3).

Screen operation cost per hour $20. It does not count depreciation and replacement costs.

Labor at $12/hr.

Bulk density varies with moisture and type of compost, for simplicity in this exercise, 1 m^3 of compost = 1 metric ton.

Low compost stability has a higher risk for poor compost condition (unfinished), possible loss as ammonia, phytotoxicity, and noxious hazard.

High end use includes horticulture, floriculture, landscaping and high value crops in general.

2.8 FIGURES

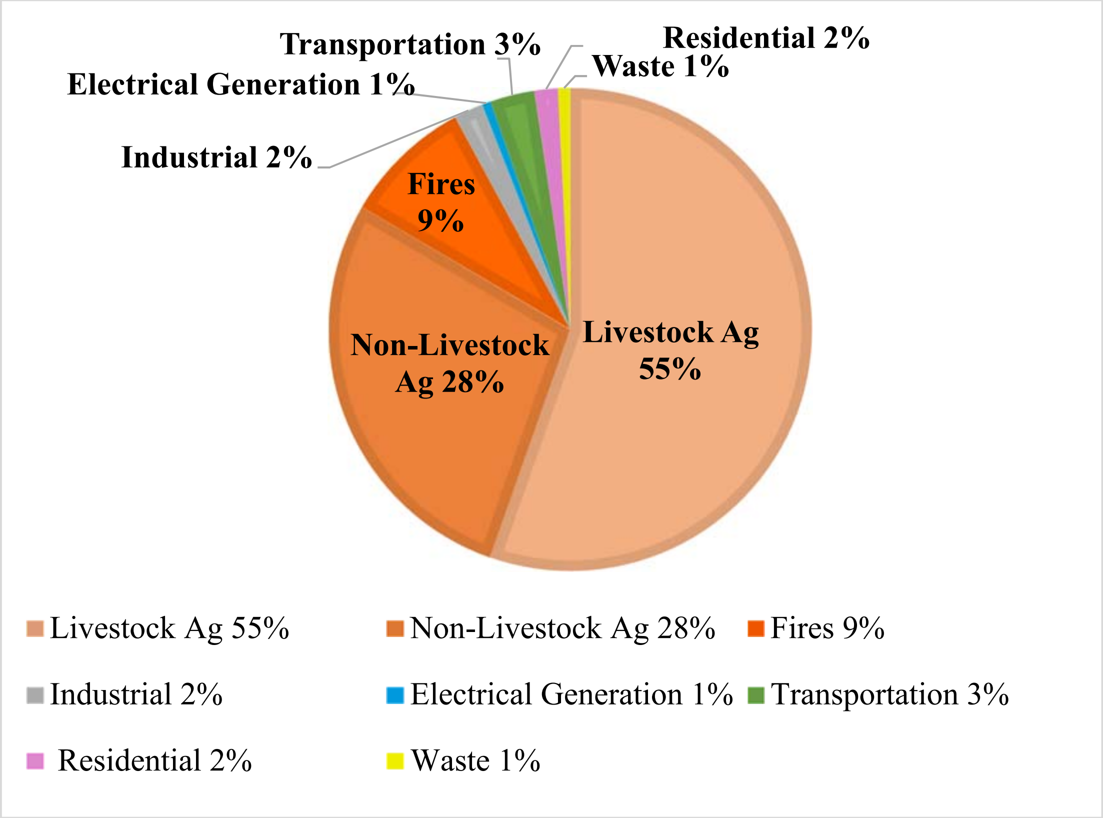

Figure 2. 1 Ammonia emissions distribution in the USA in 2011. USEPA (2015)

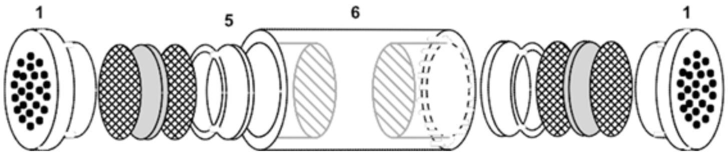

Figure 2. 2 Components of the Ogawa passive sampler

The sampler body (6) is 2 cm (outer diameter) and 3 cm (length) and has two independent cavities (1.4 cm inner diameter) each containing a diffusive-barrier end-cap (1), a reactive filter (3) between an inner and outer stainless-steel screen (2), and a retainer ring (4) over a base pad (5). Source: (Roadman, Scudlark, Meisinger, & Ullman, 2003).

Figure 2. 3 On-Farm composting with zeolites project layout

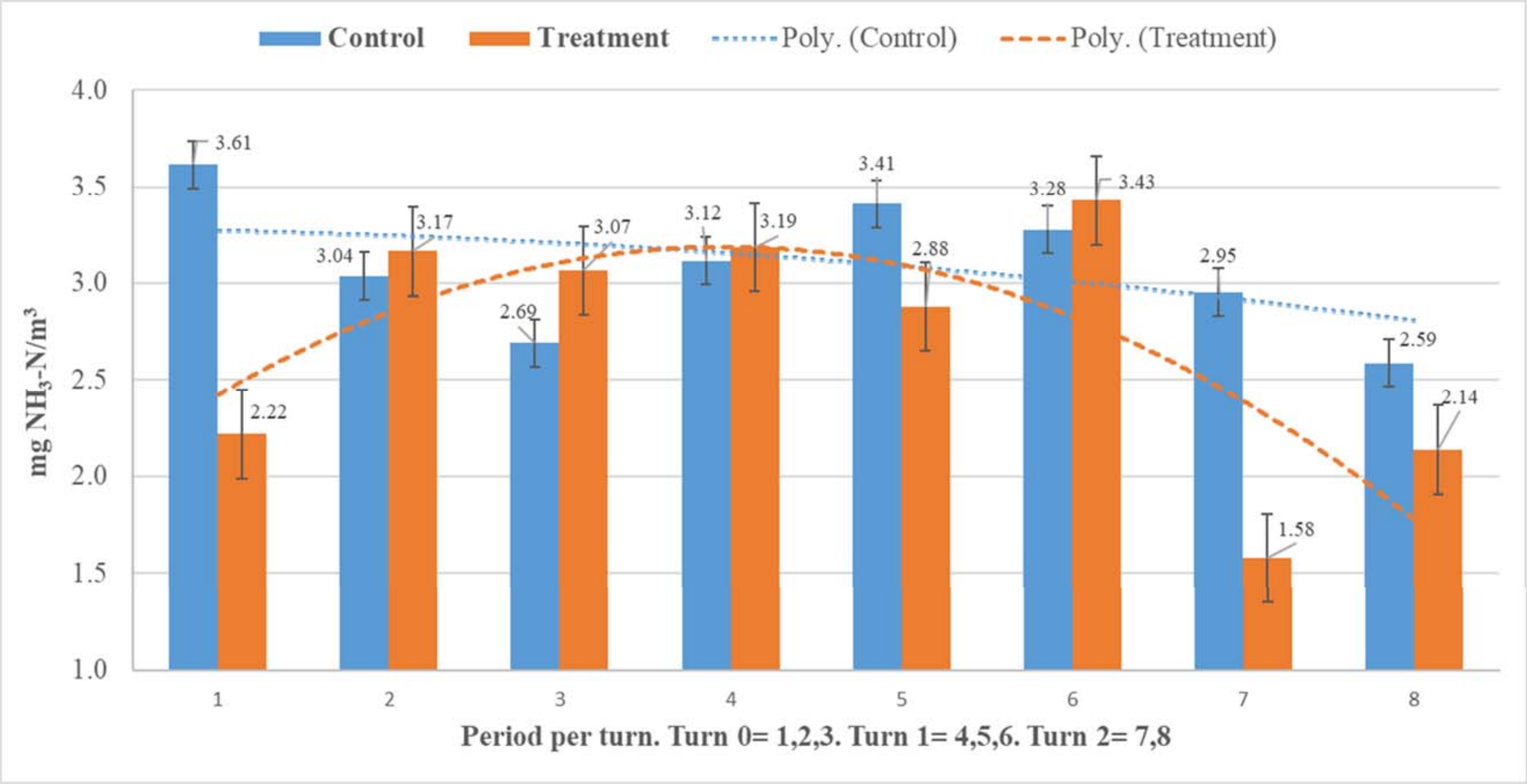

Figure 2. 4 Ammonia emissions per period and per windrow turn

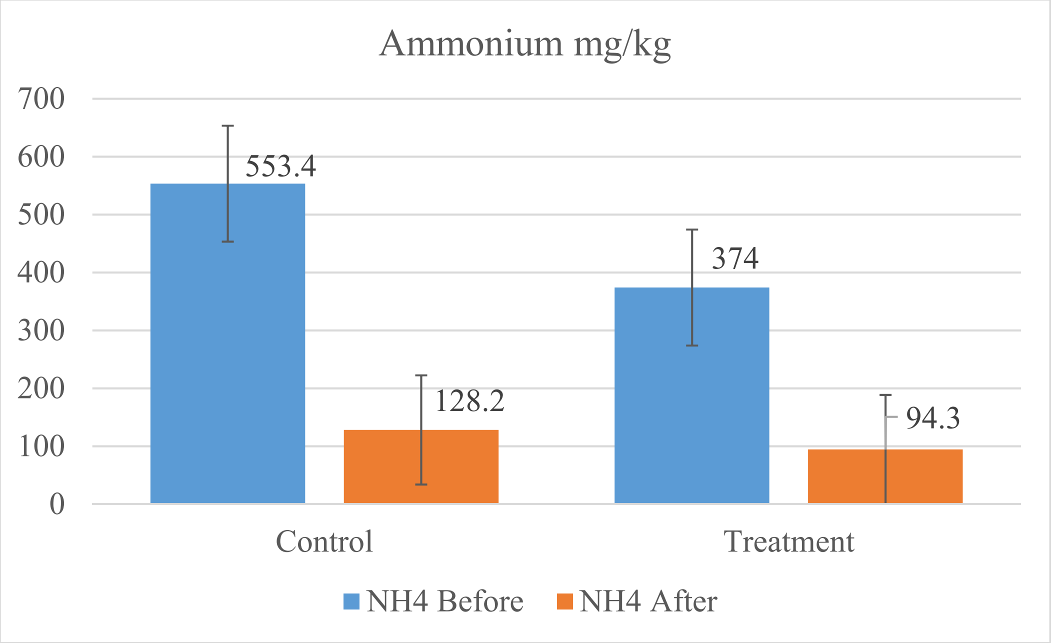

Figure 2. 5 Ammonium concentration before and after composting

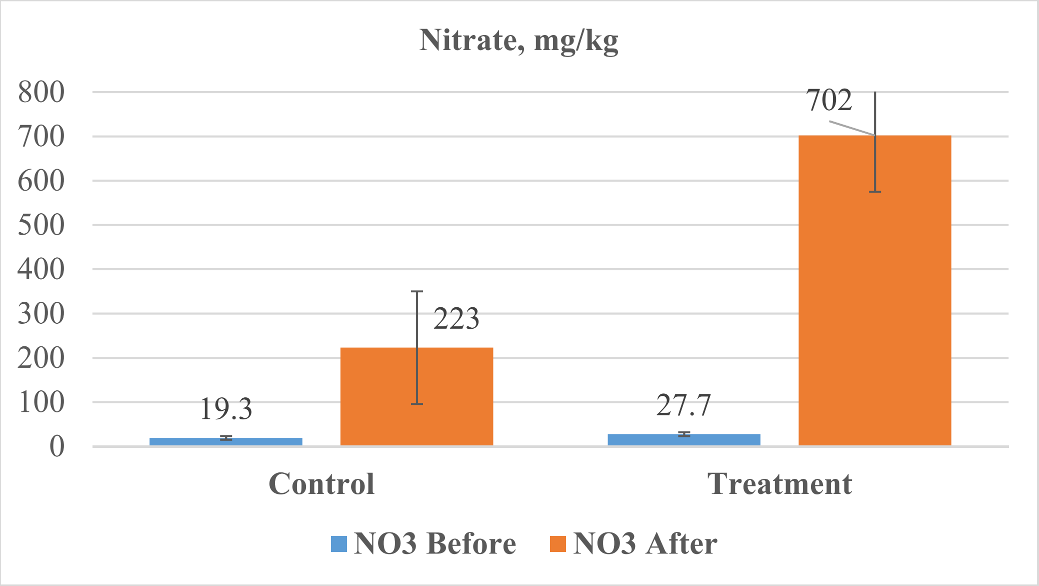

Figure 2. 6 Nitrate concentration before and after composting

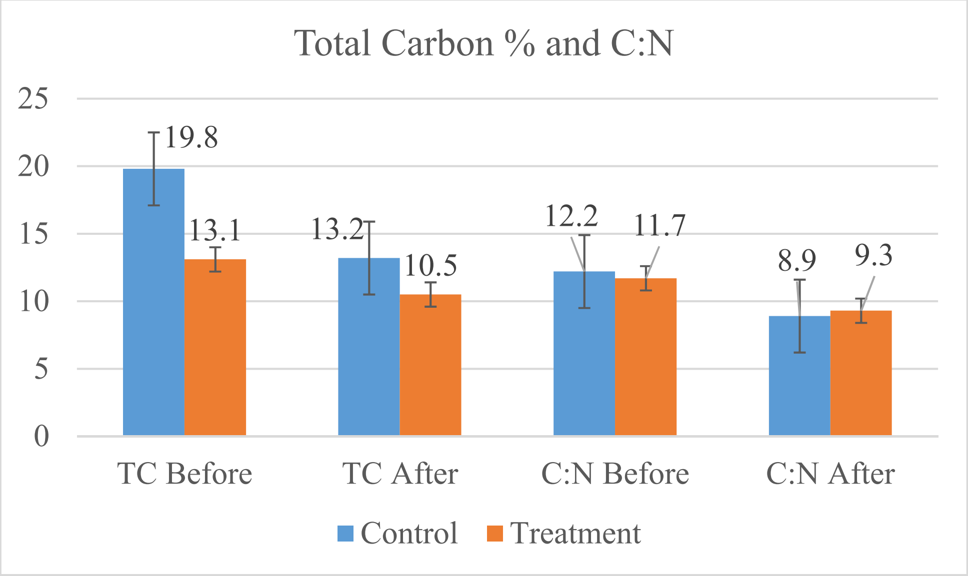

Figure 2. 7 Total Carbon concentration and C:N before and after composting

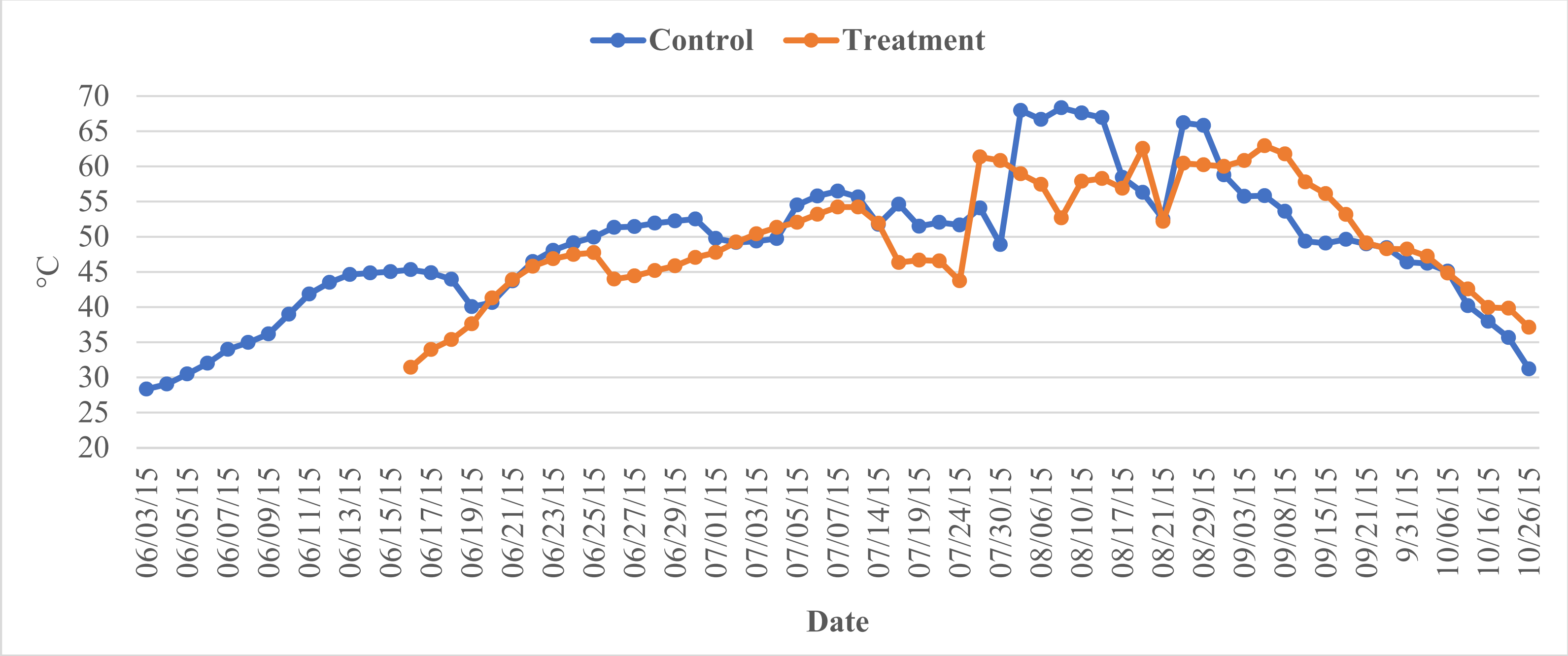

Figure 2. 8 Average compost temperature by control or treatment

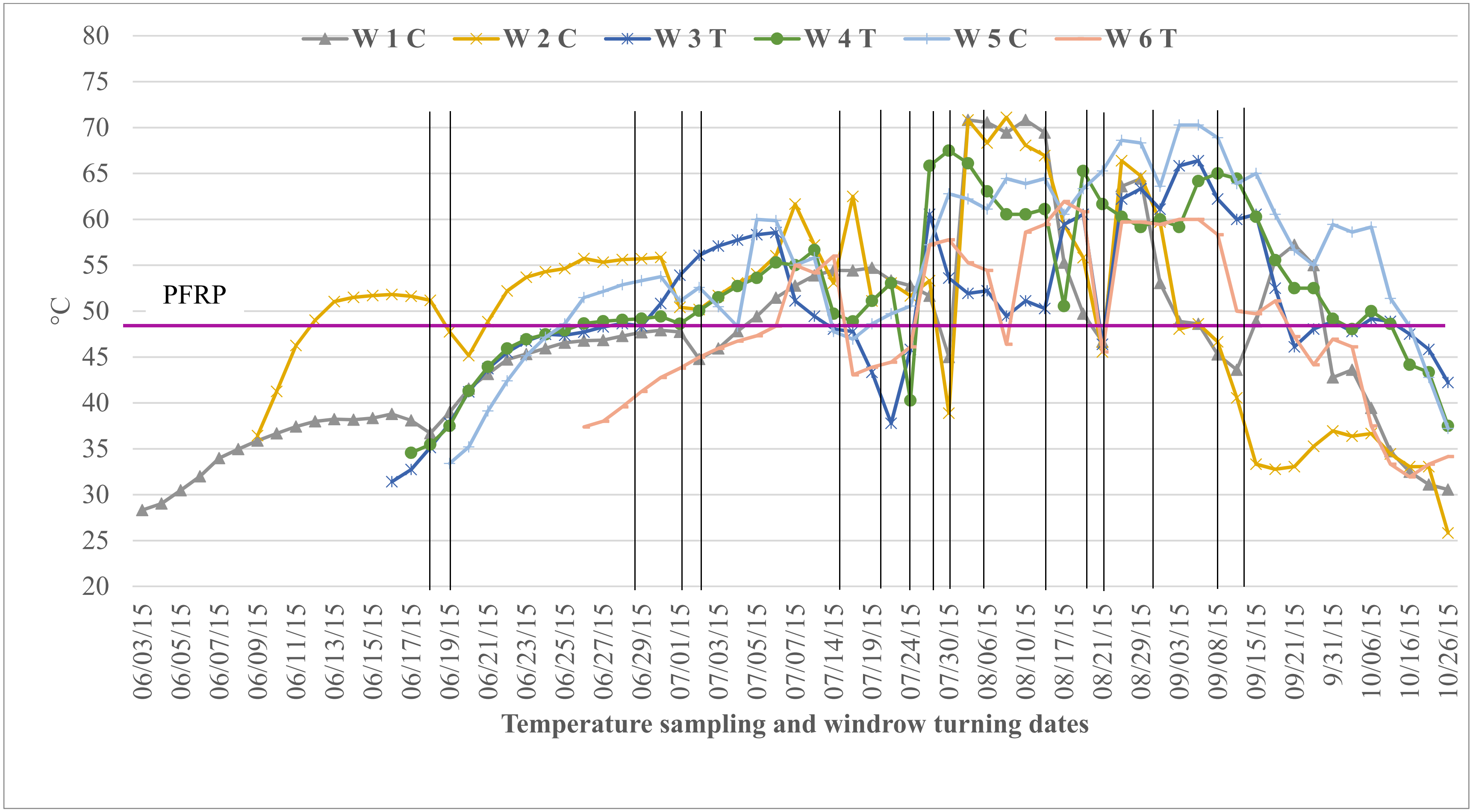

Figure 2. 9 Compost temperature and turning dates for all windrows

2.9 PICTURES

Picture 2. 1 Preparing and mixing the recipe

Picture 2. 2 Mixing the recipe

Picture 2. 3 Building a windrow

Picture 2. 4 Weighing clinoptilolite

Picture 2. 5 Preparing for clinoptilolite addition to recipe

Picture 2. 6 Ready to mix clinoptilolite into treatment mix windrow and moisture adjustment

Picture 2. 7 Windrow turning

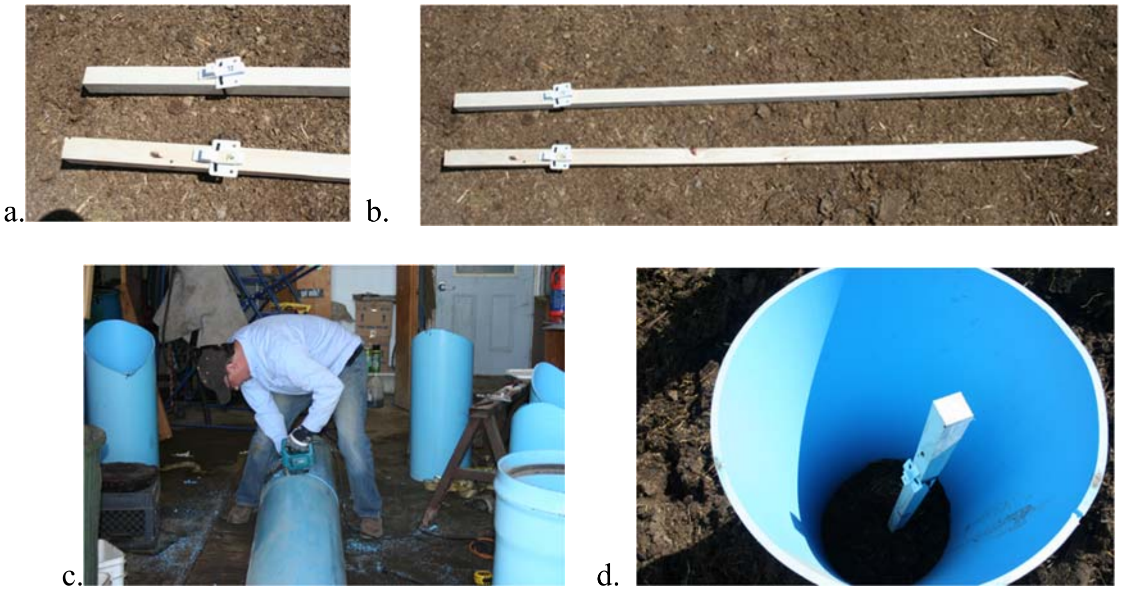

Figure 2. 8 Preparation of sampling chimney and sampler stake

a. Ogawa sampler holder position on stake. b. View of staked with sampler holders. c. Cutting the “chimneys” from irrigation pipe. c. Stake with sampler holder inside chimney pipe over compost. Pipe 37.3 cm Ø, A^2= 1093 cm^2 or 0.11 m^2, Pipe H= 71 cm, sampler at 52 cm from compost

Figure 2. 9 Pipe “chimneys” resting on top of compost

Note the mosquito net on top of pipe. Stake with sampler was inside the pipe

Figure 2. 10 Compost screening using custom made rotatory screen

Figure 2. 11 Screened compost

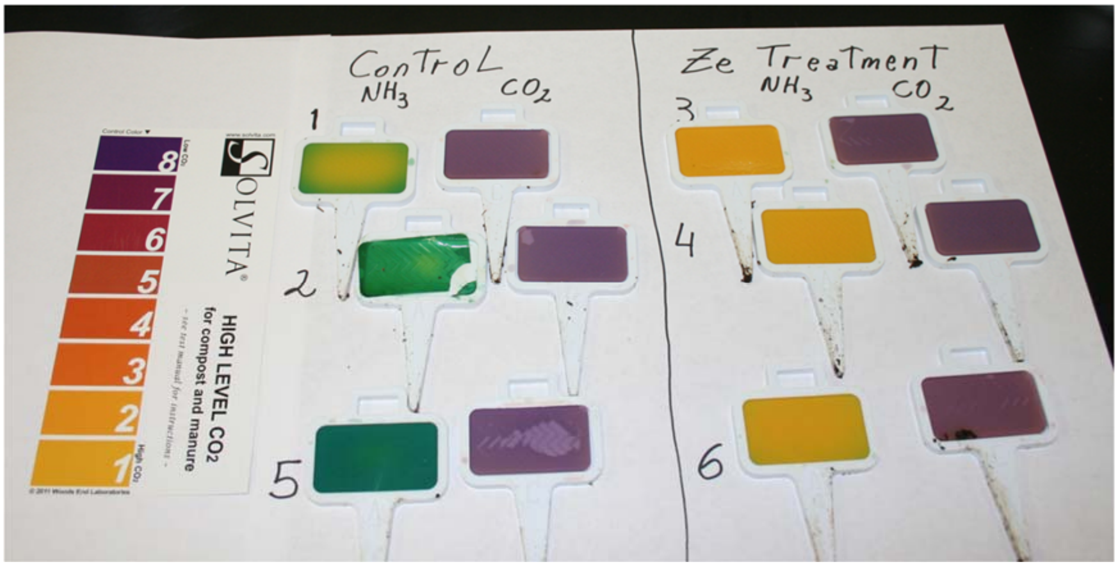

Figure 2. 12 Solvita® Test CO_2 paddle color comparison

CO_2 scale varies from 1 (Yellow)= High to 8 (Blue)= Low

In the picture both control and treatment have low CO_2 results

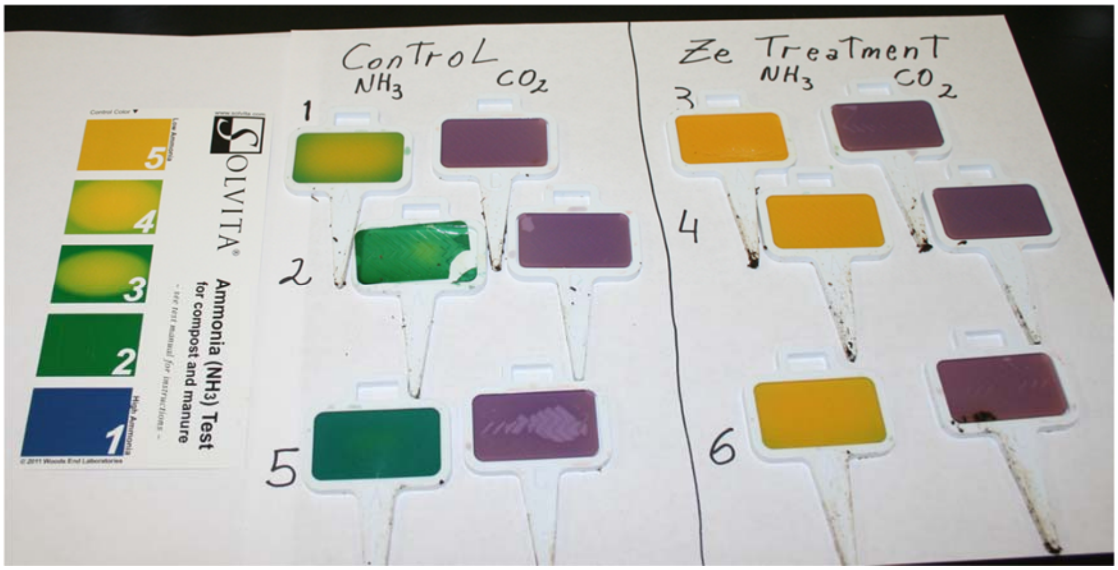

Figure 2. 13 Solvita® Test NH_3 paddle color comparison

NH_3 scale varies from 1 (Blue)= High to 5 (Yellow)= Low

In the picture, control samples (left) have much higher NH_3 than treatment samples, on the right, with lowest values on the color scale

Figure 2. 14 Refuse from screening

Note the balls like formation on the refuse

2.10. REFERENCES

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CHAPTER 3

DESIGN AND TESTING OF A ZEOLITE FILTER TO CAPTURE AMMONIA AND ODORS FROM DAIRY MANURE ON-FARM

3.1 ABSTRACT

The concentration of large numbers of animals in relatively small areas, high production output per animal unit, and concentration of animal excretions and air emissions are some of the staples of modern animal agriculture. Ammonia (NH_3) and odors are among the most noticeable, as well as locally and regionally problematic emissions generated by concentrated animal feeding operations (CAFO) dairy production systems.

A zeolite is a crystalline, hydrated aluminosilicate of alkali and alkaline earth cations having an infinite, open three-dimensional structure. Zeolites are able to lose or gain water reversibly and to exchange and retain cations, including NH_3 and ammonium.

This study demonstrated the design and operation of a zeolite filter and air stream collection from a manure pit installed on-farm at a commercial dairy. Clinoptilolite zeolites mined in Idaho were used as the filter media. The capacity of the filter to reduce NH_3 and odor emissions was tested. NH_3 emissions were reduced by 92% at three days of operation and 42% after 59 days of operation of the filter. Ammonia concentration in the pre-treatment airstream from a dairy manure collection pit was relatively high. Odor concentration reduction was 45% at six days of operation with the minimum residence time of 0.85 s. The air collection

roof-like structure and the zeolite filter were proven to be capable of operating in the harsh on-farm environment and to be adaptable to changing operative conditions within the dairy.

3.2 OBJECTIVES

3.2.1 The objectives of this on-farm research were to:

1) Design and build an on-farm pilot test filter system to capture ammonia and odor emissions from liquid or slurred dairy manure.
2) Evaluate ammonia and odor reduction using a clinoptilolite zeolite filter to treat an airstream from a liquid dairy manure aerobic pumping pit receiving flushed wastewater.

3.2.2 The main research hypotheses were:

1) Clinoptilolite zeolite will retain ammonia and reduce airstream ammonia emissions from a liquid dairy manure aerobic pumping pit receiving flushed wastewater.

   Null hypothesis: Clinoptilolite zeolite will not retain ammonia and will not reduce airstream ammonia emissions from a liquid dairy manure aerobic pumping pit receiving flushed wastewater.
2) Clinoptilolite zeolite will retain odoriferous compounds and reduce the airstream odor concentration from a liquid dairy manure aerobic pumping pit receiving flushed wastewater.

Null hypothesis: Clinoptilolite zeolite will not retain odoriferous compounds and will not reduce the airstream odor concentration from a liquid dairy manure aerobic pumping pit receiving flushed wastewater.

3.3 INTRODUCTION

One of the characteristics of modern animal production is the concentration of animals in relatively small areas. Concentrated Animal Feeding Operations (CAFO) have become the norm for commercial animal production, especially in the USA, western Europe and developing parts of the world. Increased concentration of animals means increased concentrations of animal wastes. Emissions become concentrated in relatively small areas and new handling, treatment, and disposal challenges arise.

During the animal production cycle, storage and treatment of manure and the fate and emissions of nitrogen (N) and other odorous compounds varies. Ammonia (NH_3) is produced as a result of natural animal and bacterial processes. Agriculture is recognized as a major global contributor of NH_3 emissions, contributing about 55% of global NH_3 emissions. Animal production counts for about 43% of total global emissions, counting natural and anthropogenic sources (Schlesinger & Hartley, 1992). In the USA, approximately 83% of anthropogenic ammonia emissions come from agriculture, and around 55% of that overall total comes from livestock operations (USEPA, 2015). Farm animals consume a considerable amount of protein and other N containing substances in their feed. This consumed N is partitioned between products such as meat, milk, eggs, and excretions such as urine, and feces.

The conversion of N consumed in the diet to marketable animal products is often considered inefficient, with 50 to 80% of the N consumed being excreted. More than 50 to 60% of the excreted N is in the urine, and more than 70% of this urine N is in the form of urea-N. Organic N compounds in feces can account for up to 35% of NH_3 production (Tamminga, 1992; Arogo, Westerman, Heber, Robarge, & Classen, 2001; Hristov, et al., 2011).

Due to manure handling practices within the CAFO production system, manure, defined as the mix of animal urine, feces, discarded feed, water from cleaning, bedding material, and other production wastes, has an augmented degradation speed. Production of NH_3 is thus greater than seen with the elements considered separately as in other production systems (Lorimor, Powers, & Sutton, 2000; ASAE, 2005). In the time frame from excretion through storage and application, 50% to more than 70% of the N in manure can be converted to NH_3 and released to the atmosphere (Hristov, et al., 2011).

The environmental effects of NH_3 include the addition of nitrogen (N) to sensitive ecosystems and in ecosystems where the natural supply of N is low, creating a N imbalance, and causing eutrophication in aquatic ecosystems. Arogo et al. (2001), also discuss the contribution of NH_3/NH_4^+ (ammonia and ammonium) to N imbalance and the associated emissions of nitrous oxide (N_2O), nitrogen oxide (NO), and nitrogen dioxide (NO_2), gases that can have global impact due to their greenhouse effect capabilities. Other consequences associated with exceeding thresholds of both oxidized and reduced forms of N include the creation of particulate matter aerosols ($PM_{2.5}$), nitrate contamination of groundwater, eutrophication of water bodies, vegetation growth, and ecosystem changes due to higher concentrations of N, climatic changes associated with increasing N_2O, N saturation of forest soils, and soil acidification via nitrification and leaching (Arogo, Westerman, Heber, Robarge, & Classen, 2001; Weil & Brady, 2017).

Odor generated from livestock facilities is in many cases the single most controversial issue about which producers receive complaints (Sheffield & Ndegwa, 2008). Odors from livestock farms are very complex and include a diversity of compounds. More than 160 odorous compounds have been identified in or around animal manure and from animal production facilities (O'Neil & Phillips, 1992). Odor concentration, hedonic tone and intensity varies depending on the animal species, odorous compounds present, atmospheric conditions, topography, and the sensitivity and perception of different people (Fabian-Wheeler, Hile, & Schmidt, 2012). Odors are generated at all stages of animal production, from the housing of animals to manure transport, treatment, storage, and field application. Odors can be controlled at the time odoriferous compound production, avoiding generation by, for example, diet modification (NH_3 emissions can be reduced the same way too). Odors and other gases can also be controlled after the production of the compound and before it is released to the environment (media acidification, adsorption, and other methods). Odors can be trapped and treated after being released (filtration, scrubbing). Finally, a less effective method is to mask the unwanted odoriferous compounds with other more pleasant odors (Sheffield, Ndegwa, Gamroth, & de Haro Martí, 2008).

A zeolite is a mineral defined as a crystalline, hydrated aluminosilicate of alkali and alkaline earth cations having an infinite, open, three-dimensional structure. More than 40 natural zeolite minerals have been identified, but only a handful (chabazite, clinoptilolite, erionite, mordenite, and phillipsite) have current commercial applications and are abundant in nature. There are about 150 synthetic zeolites species. Natural zeolites are much cheaper than synthetic ones (Eyde & Holmes, 2006; Flanagan, 2015). Zeolites are able to lose or gain water reversibly and to exchange cations with and without crystal structure (Mumpton F. A., 1999). Natural zeolite minerals are abundant and because of their cost and characteristics are more suitable than synthetic ones for most agricultural uses. Zeolites are mined in several western states in the USA where dairy production also concentrates. Idaho has at least three operating zeolite mines (2016) and several locations where the minerals can be mined (Sheppard, Gude III, & Mumpton, 1983; Altaner, Gude III, Mumpton, Sheppard, & Teague, 1993; Flanagan, 2015). Zeolites have excellent Cation Exchange Capacity (CEC) and great affinity to adsorb ammonia and ammonium forms of N (Mumpton F. A., 1981; Lefcourt & Meisinger, 2001). This adsorption capacity can be used to retain N from dairy manure at diverse stages, from production, transport, and treatment, to application. When mixed with manure, zeolites have shown to retain the N, reducing NH_3 emissions and holding that N in the soil until it is taken by crops, avoiding seepage to subsurface waters or nutrient runoff situations (Lefcourt & Meisinger, 2001; Nakhli, Delkash, Bakhshayesh, & Kazemian, 2017). Zeolites, clinoptilolite in particular, have been used to reduce NH_3 emissions from poultry and swine production operations (Koelliker, Miner, Hellickson, & Nakaue, 1980; Ndegwa, Hristov, Arogo, & Sheffield, 2008), as well as feedlot corrals (Sherwood, 2007; Waldrip, Todd, & Cole, 2015). Studies on dairy manure treatment using clinoptilolite that assess NH_3 and odor reductions are very limited in quantity, scope and applicability. None of the on-farm research found addresses similar situations and questions on dairies as those addressed by this study.

This paper showcases a project that explored the effects of using natural clinoptilolite zeolite as filter media to filter an air stream from a collection pit receiving liquid manure wastewaters from a dairy flush manure collection system. The project evaluated the effectiveness of the zeolites and the filter design in removing ammonia and odor.

3.4 MATERIALS AND METHODS

This on-farm research and demonstration study was conducted at a 3000 milking Holstein cows' dairy in the Magic Valley area, Idaho. Roughly half of the cows are housed in free stall facilities and the other half in open lot corrals. Both free stall and open-lot corrals handle the manure from the feeding and movement alleys hydraulically using a flush system. The flushed wastewater from all 17 corrals with a total of 14 flushing lines from feeding and connecting alleys (8 under free stalls) flushes at pre-determined intervals and is collected in a single collection and pumping pit. In addition, the pit receives liquid manure from a second dairy facility with 1800 milking Holstein dairy cows that is located 1087 meters away. This second production unit has six open lot corrals with shades that have their feeding and movement alleys scraped to a receiving flushed flume pipe that dumps into the pit. In total, the pit receives the flushing manure from 4800 cows. The manure collection pit is maintained under aerobic conditions by the constant flow of new flushed manure and mixing action of a propeller mixer that activates at the same time as the suction pump. From the collection pit, the manure is pumped to a solid separation system consisting of a set of slide separators with a roll press at the bottom, and a centrifuge. The collection pit measures 5.8 x 5.8 meters by three meters in depth (Picture 3.1). The pit was covered by a custom-made roof, designed by the author, able to withstand snow and wind loads common in the area and designed to facilitate operational and repair labors (Pictures 3.2 to 3.4). Air from the surface of the pit above wastewater and air volume covered by the roof was extracted using a centrifugal fan (Cincinnati Fan, model PB-9) with a 373 watt (1/2 HP) motor and a variable frequency drive (VFD) with three settings. The fan baseline setting operated constantly at an extraction rate of approximately 0.14 m^3/min or 5% power, based on the University of Minnesota biofilter design information (Schmidt, Jacobson, & Nicolai, 2004) guidelines, the second rate operated at 1.5 m^3/min or ~55%, and the highest rate operated at near full speed at approximately 2.7 m^3/min or 95% power, with a maximum nominal pressure of 497 Pa (2 inches water). The middle and high rates were engaged by a set of two floats that activated them when the pit received the wastewater flush flow, the system was calibrated to absorb the volume of air over the pit water surface displaced by the increased wastewater volume.

From the fan outlet, the air was conducted to the filter using a 101.6 mm PVC drainage pipe to a four way plenum made of the same pipe that distributed the airflow inside the filter (Pictures 3.5 to 3.7). The custom-made filter designed by the author consisted of a wooden box made using 1.2 m x 2.4 m pressure treated plywood sheets that covered an internal structure made using 5 x 10.1 cm pressured treated wood. External measurements of the filter box were 1.2 m wide, 1.2 m high, and 2.4 m long. The filter box rested atop 45 cm legs made of 10.1x10.1 cm wood posts. The inside of the filter was divided into two sections, one at the bottom of the filter and another one about half way from bottom to the top of the filter. Each section was composed of a movable frame with an expanded metal mesh that can hold the zeolites or other filtering material. Frames can be pulled out to vary the configuration and to change media. This disposition of two levels with movable frames allows for different configurations, including pulling the top section to be able to fill the whole filter with the media, using only the top layer for closeness to the plenum, or having two layers of media with an empty space between them. This last configuration was the one chosen for this study, totaling 2.27 m^3 of filtering media. Airflow was from the top of the filter to the bottom. The outlet was the whole bottom of the filter (Picture 3.8). Smoke tests using smoke bombs, Superior Signal, model 2B (Superior Signal, NJ) were performed to check filter sealing and air flow distribution on the outlet (Pictures 3.9 to 3.10). The empty bed residence time (EBRT), is defined as EBRT= V_f/Q, where V_f= filter bed volume and Q= air flow rate (Devinny, Deshusses, & Webster, 1999). EBRT for the filter loaded with two layers varied from 16.2 s at base airflow rate to 0.85 s at maximum fan speed. A more in-depth description of the design and construction of the pit covering structure and zeolite filter are detailed in chapter 4 of this dissertation.

Ammonia in the airstream was measured using passive samplers (Ogawa & Co. Kobe, Japan). Three simultaneous measurements were used on each side of the filter. The inlet concentration (coming directly from the pit and considered the control) was measured inside the filter inlet duct just before entering the plenum. The outlet concentration after the filter (treated airstream) was measured at the filter outlet, just below the base of the filter (Picture 3.8). Ammonia measurements were taken at three points (periods) in time. First measurement period was done at three days after turning on the filter (sampled on July 2). Then the fan was turned off and the second sample was taken on September 9 after the fan was turned back on September 6, after 64 days off (for a total of six running days between July 2 and September 9). From the second sampling period to the third sampling period the fan was run continuously (by the floats and the variable speed drive), operating the filter for 53 straight days until the sampling day on October 31. At that last sample, the filter had been operated for a total of 59 days. Two background sample periods with three samples each were taken on June 10 (Period 1 staring day -21 days) and June 20 (Period 1 -11 days) to assess the background NH_3 levels at the filter outlet. The filter outlet was open on only one side, opposite to a gravity solid separator and prevalent winds. All other three sides were covered (Pictures 3.5 and 3.7). Background samples were taken below the filter outlet, at the same locations where actual outlet NH_3 samples were taken later. The system fan was off during the background sampling period to measure only ambient and possible NH_3 diffusion in that location.

Ogawa samplers' pads were analyzed at the Kimberly, Idaho USDA-ARS research facility. Extraction was done using 5 ml of KCl 1M solution per sampler (two pads per sampler). Samples were then analyzed by automated colorimetry using flow injection analysis and spectrometer, model Quick Chem 8500, ASX 520 series (Lachat Instruments, Loveland, CO). Values of mg NH_3-N/m^3 were time corrected by minutes of sampling.

Odor samples were taken using sampling pumps, SKC Aircheck Sampler model 224-PCXR4 (Eighty Four, PA), and ten liters Tedlar sampling bags, CEL Scientific Corporation (Cerritos, CA), at six days of operation, coincident with the second NH_3 sampling on September 9. Three simultaneous odor samples were taken at each of the same locations as the NH_3 samples (filter inlet and outlet). Odor samples were shipped overnight to Purdue University Agricultural Air Quality Laboratory (Lafayette, IN) and analyzed using olfactometry (AC'SCENT International Olfactometer. St. Croix Sensory, Inc., Stillwater, MN), with Triangular Forced Choice method (20000 lpm flow, six seconds sniffing time, and five panelists). At the moment of taking the odor samples, the fan was run at maximum capacity to have the shortest residence time in the filter.

Air flow temperatures inside and outside the filter were taken using temperature probes/datalogger HOBO Pro V2 external temperature datalogger (part U23-003) (Onset, Cape Cod, MA). One of the temperature probes was located in the inlet, at the same location as the NH_3 samplers. The second temperature probe was located inside the filter in between the two internal sections holding the media. An additional temperature and relative humidity probe and datalogger HOBO Pro V2 external temperature datalogger (part U23-002) was located inside the pit roof, about one meter from the fan inlet.

Statistical analyses were done using SAS 9.4 (SAS Institute, Cary, NC). Analysis was done using ANOVA (PROC MIXED). All parameters were checked for normality and mixed procedure assumptions using the UNIVARIATE procedure.

3.5 RESULTS AND DISCUSSION

3.5.1 Ammonia emissions

Ammonia emissions reductions per day of filter operation on the three measured periods (Figure 3. 1 NH3 concentration before and after the filter, average temperature at inlet and inside filter

were:

- Period 1, reduction was 92.06% on day three of operation. NH_3 concentration was reduced from 5.287±0.04 mg NH_3-N/m^3 on the inlet airstream coming from the pit (control) to 0.421±0.04 mg NH_3-N/m^3, ($p<0.001$) on the filter outlet airstream (treatment).

- Period 2, reduction was 90.18% on day six of operation (after being off for 64 days). NH_3 concentration was reduced from 2.749±0.02 mg NH_3-N/m^3 in the inlet, to 0.270±0.02 mg NH_3-N/m^3, ($p<0.001$) on the filter outlet.
- Period 3, reduction was 42.67% on day 59 of operation. NH_3 concentration was reduced from 1.781±0.29 mg NH_3-N/m^3 in the inlet, to 1.021±0.29 mg NH_3-N/m^3, ($p=0.13$) on the filter outlet.
- Two background sample periods with three samples each were taken on June 10 (Period 1 starting day, -21 days) and June 20 (Period 1, -11 days) to assess the background NH_3 levels at the filter outlet when the system was off. Ambient concentrations were 0.428±0.01 mg NH_3-N/m^3 ($p<0.001$) and 0.477±0.009 mg NH_3-N/m^3 ($p<0.001$) respectively. The filter outlet was open on only one side, opposite to a gravity solid separator and prevailing winds, all other three sides were covered (Pictures 3.5, 3.7 and 3.8).

These values demonstrate a high effectiveness of the clinoptilolite zeolite filter for NH_3 reduction when the media was not saturated, achieving NH_3 values on the treated airstream lower than the background levels (Figure 3. 1 NH3 concentration before and after the filter, average temperature at inlet and inside filter

The 65 days between period 1 and 2 demonstrated that the filter doesn't adsorb ambient ammonia when not in use (blower off). The half-life of the filter media is estimated to be approximately 55 to 60 days at this filter size. After that period, if performance wants to be maintained at or over 50%, the media should be replaced or regenerated, or a bigger filter should be used. Neither alternative was studied in this project since the objective was to have a baseline of the clinoptilolite zeolite NH_3 and odor filtration capacities using a pilot test sized filter. Another way to increase the amount of NH_3 adsorbed in the filter would be to reduce the zeolite size in the bed (Mann, 2010). In this trial, clinoptilolite particle size was relatively large (approximately ≤ 6 cm) to prioritize airflow within the filter bed. The effect of varying media size on airflow and NH_3 retention was not studied in this trial.

Differences in NH_3 concentrations by period are noticeable and are mostly related to the differences in ambient temperature between sampling periods (Figure 3.1). A factor to consider when analyzing the efficiency and overall reduction of NH_3 control measurement on-farm in southern Idaho is the great seasonal variations in temperature and relative humidity (RH) as well as the daily variation of those two parameters within a season. Figure 3.2 shows the daily variations between temperature and RH during part of the study period. NH_3 and odor emissions are greatly dependent on ambient temperature and secondary on RH (de Haro Martí, 2007; Sheffield, Ndegwa, Gamroth, & de Haro Martí, 2008). Temperature and RH in the pit during the whole research period is not available because of a malfunction in the datalogger prompted by one of the pit foaming events. The malfunction rendered the datalogger unusable and all data in that unit was lost.

Using a small experimental air scrubber with 1635 cm^3 of zeolite per layer (up to six layers), Koelliker, et al. (1980) measured an NH_3 concentration reduction on an airstream from a chicken house with 2708 individual cages. Observed NH_3 reduction was between 45% at the beginning of the trial to 15% after 18 days of operation using the multi-layered setting in the scrubber. A perceived odor reduction was also observed but no analytical quantification was done. Koelliker study is somewhat comparable to the present trial since both were performed on-farm, although the scrubber used by Koelliker was much smaller in size and capacity. The NH_3 concentration in their study was less than half the concentration observed in the present study. Authors had issues with scrubber/filter clogging due to feathers and high air-suspended solids. In the present study suspended solids in the airstream were not an issue.

In another study performed using a lab scale biofilter with zeolites as media (von Eckstaedt, Charles, Ho, & Cord-Ruwisch, 2015), 90 to 100% reduction was achieved from a pure NH_3 gas stream up to 160 days. This concept looks promising, but besides being a combination of biologically and adsorptive driven reactions, the system requires much more management than the present design and it would be very difficult to operate during winter at on-farm locations in cold climates, as compared to the filter developed in the present study that could be operated year round with practically no maintenance between media replacement or regeneration.

3.5.2 Odor

Odor samples were taken at the same time as period 2 NH_3 samples were retrieved, that is at six days of operation. Sampling was done using the minimum residence time in the filter by setting the blower at maximum speed during odor sampling. The rationale for using this setting was to use the lower residence time to simulate the worst-case scenario on odor control when the media was still at almost full capacity.

Odor concentration (OC) difference between the inlet (control) and outlet (treatment) was significant ($p=0.001$). OC was reduced by 45% in just ~0.85 s of residence time. Threshold concentration was determined to be 22.6 ppb, determining the Odor Unit Equivalent (OUE) for these samples (St. Croix Sensory, Inc., 2005). Inlet odor concentration, measured in OUE per cubic meter, was 6640.2±252.5 OUE/m^3. Outlet (treated) was 3675.7±252.5 OUE/m^3. Table 3.1 shows the OC results as reported by the odor lab.

Hedonic Tone (HT) difference for both recognition (p=0.2) and full strength (p=0.5) was not significant. Table 3.2 summarizes the HT at recognition and full strength values reported by panelists during olfactometry.

Odor Intensity (OI) at recognition difference showed a trend (p=0.06), with 423.2±132.6 ppm in the control and 796.2±137.3 ppm in the treatment. OI difference at full strength was not significant. Table 3.3 summarizes the OI at recognition and full strength values reported by panelists during olfactometry.

Odor character shows no noticeable difference between the inlet (control) and outlet (treatment). It is important to notice that besides the low residence time of the airstream in the media, by its properties, odor from the dairy manure collection pit is quite pungent in nature. Table 3.4 summarizes the odor character at recognition and full strength reported by panelists during olfactometry.

Luo and Lindsey (2006) didn’t find significant odor reduction on trials made with a biofilter using pine bark with the addition of zeolites, filtering the air from animal rendering processes odorous airstream. A perceived odor reduction using a zeolites air scrubber in airstreams from poultry houses was noted (Koelliker, Miner, Hellickson, & Nakaue, 1980), but this study didn’t have any analytical odor measurement.

3.5.3 Zeolite filter and air collection systems field performance and adjustments

The air filter structure, ducting, sampling ports, blower and its speed regulation through the variable frequency drive (VFD) connected to floats worked as intended. No major problems arose with the system itself. Modifications to the float system and roof-like cover structure needed to be done at the beginning of the trials. In fact, these situations delayed the start of the trial several months. Initially, floats were adjusted to absorb the wastewater volume increment as the flush system flow entered the pit. After the adjustment to calculated volume displacements were done for the first time, a major change was introduced in the dairy operations. A second dairy (1800 Holstein cows) located 1087 meters away from the primary dairy pit was added to discharge its wastewater in the same pit. The frequency and volume of wastewater handled in the pit was greatly increased, needing major adjustments to the floats' system. After those adjustments were made, a new centrifuge technology was added to the wastewater solid separation treatment. Since the wastewater from the pit is pumped to the solid separation system and part is recirculated for the flush system, the addition of the centrifuge and the massive amounts of foam generated fouled the whole filter float and air capturing structure. At some point, the pressure generated by the foam blew out a plexiglass inspection window (Pictures 3.11 to 3.14). At that point all activities in the filter and capturing structure were halted until the foaming and increasingly changing wastewater volumes and characteristics were managed by the dairy. It took two to three months to have all those challenges under control and repair the capturing structure to be functional again.

The capturing structure, resembling a roof covering the collection pit (Pictures 3.2 to 3.4) also worked as intended but needed several minor modifications due to dairy operations and maintenance needs. The major points that needed changes included the surrounding seals around the main and backup pit pumps. The original design called for an almost airtight coverage of all surfaces around the pumps pipes. In one occasion, the main pump failed and maintenance personnel needed immediate access. Then, when on another occasion the backup pump also failed (with the main down at the same time), it was evident that such tight sealing wasn’t possible. Areas around the pumps’ pipes were left open and a simple cover was made using a rubber mat that could be easily flipped over the roof to access the pumps and pipes as needed (Pictures 3.15 a, b, c).

Another modification was the coverage of the plexiglass window that was blown out during the foaming events. It was replaced by a solid panel (Pictures 3.12 and 3.13). A PVC drainage system that was installed beside the dirt road to receive water flows from it, never worked as intended. After trying some minor modifications, it was cancelled due to the constant clogging and complete coverture by mud from the dirt route. Water flow from the route was re-directed passing the pit cover to the second smaller connected open pit on the side. After the wastewater volumes were stable and the foam was controlled, the capturing structure and filter worked without any operational problem.

It should be mentioned that dairy workers using the washing pad by the pit had, in general, positive comments about the pit cover. They needed to do some extra work redirecting the mud cleaned from farm machinery to the pit, since the roof like structure sealed the direct access to the pit (Pictures 3.1 before and 3.3 after). Even with that, the comments from all workers contacted were positive highlighting how the coverage of the pit by the roof-like structure had changed the intensity of odors in the washing area, making their work there easier and more enjoyable due to the significantly reduced pungent odors.

3.6 CONCLUSIONS

The zeolite filter as designed in this study, demonstrated the capacity of clinoptilolite zeolite to significantly reduce ammonia between 92% at three days of operation and 42% at 59 days of operation while receiving a relatively high ammonia concentration load in the airstream from a dairy manure collection pit. This is a media effective half-life of approximately two months. Odor concentration reduction was 45% at six days of operation with the minimum residence time (EBRT) of 0.85 s. The air collection roof-like structure and the zeolite filter proved to be capable of operating in the harsh on-farm environment and to be adaptable to changing operative conditions within the dairy. Up-sizing the filter to accommodate longer periods of high NH_3 and odor reduction could be studied in the future. In addition, future studies could also define other filter operative parameters like the effects on NH_3 reduction of using different media sizes and loads in the filter, measurement of the fertilizer value of nitrogen loaded clinoptilolite when filter is saturated, regeneration of the zeolite media as compared to reusing as nitrogen loaded amendment, and possible combination of clinoptilolite zeolite and biofiltration in a dual biofilter or as in-series system.

3.7 TABLES

Table 3. 1 Odor Concentration (OC)

Sample	T= Treatment C= Control	OU_E/m^3
1 IN	C	6989.31
2 IN	C	6015.99
3 IN	C	6915.40
1 OUT	T	3503.40
2 OUT	T	4020.25
3 OUT	T	3503.40

Table 3. 2 Hedonic Tone (HT) as reported by odor lab panelists

Hedonic Tone (HT) at recognition, ppm. Olfactometry by five panelists.						
Sample	T= Treatment C= Control B= Blank	Panelist 1	Panelist 2	Panelist 3	Panelist 4	Panelist 5
N-BUTANOL	B	-1	0	1	-1	2
1 IN	C	-1	-4	-1	-4	-5
2 IN	C	-3	-3	-1	-4	-2
3 IN	C	-3	-5	-1	-5	-3
1 OUT	T	-3	-7	-3	-5	-2
2 OUT	T	-3	-5	-1	-5	-3
3 OUT	T	-3	-4	-1	-5	-5
Hedonic Tone (HT) at full strength, ppm. Olfactometry by five panelists.						
Sample	T= Treatment C= Control B= Blank	Panelist 1	Panelist 2	Panelist 3	Panelist 4	Panelist 5
N-BUTANOL	B	-2	-3	-1	-2	1
1 IN	C	-4	-9	-3	-8	-4
2 IN	C	-3	-6	-6	-9	-4
3 IN	C	-5	-8	-3	-9	-5
1 OUT	T	-5	-9	-8	-9	-5
2 OUT	T	-5	-9	-3	-9	-4
3 OUT	T	-5	-9	-3	-9	-3

Table 3. 3 Odor Intensity (OI) as reported by odor lab panelists

<table>
<tr><td colspan="7">Odor Intensity (OI) at recognition, ppm. Olfactometry by five panelists.</td></tr>
<tr><td>Sample</td><td>T= Treatment
C= Control
B= Blank</td><td>Panelist 1</td><td>Panelist 2</td><td>Panelist 3</td><td>Panelist 4</td><td>Panelist 5</td></tr>
<tr><td>N-BUTANOL</td><td>B</td><td>250</td><td>250</td><td>433</td><td>433</td><td>250</td></tr>
<tr><td>1 IN</td><td>C</td><td>250</td><td>433</td><td>250</td><td>250</td><td>750</td></tr>
<tr><td>2 IN</td><td>C</td><td>250</td><td>433</td><td>433</td><td>433</td><td>750</td></tr>
<tr><td>3 IN</td><td>C</td><td>250</td><td>433</td><td>250</td><td>433</td><td>750</td></tr>
<tr><td>1 OUT</td><td>T</td><td>250</td><td>1299</td><td>433</td><td>750</td><td>2250</td></tr>
<tr><td>2 OUT</td><td>T</td><td>250</td><td>2250</td><td>250</td><td>433</td><td>750</td></tr>
<tr><td>3 OUT</td><td>T</td><td>250</td><td>1299</td><td>250</td><td>433</td><td>6750</td></tr>
<tr><td colspan="7">Odor Intensity (OI) at full strength, ppm. Olfactometry by five panelists.</td></tr>
<tr><td>Sample</td><td>T= Treatment
C= Control
B= Blank</td><td>Panelist 1</td><td>Panelist 2</td><td>Panelist 3</td><td>Panelist 4</td><td>Panelist 5</td></tr>
<tr><td>N-BUTANOL</td><td>B</td><td>750</td><td>6750</td><td>3897</td><td>3897</td><td>2250</td></tr>
<tr><td>1 OUT</td><td>T</td><td>750</td><td>2050</td><td>2050</td><td>2050</td><td>6750</td></tr>
<tr><td>2 OUT</td><td>T</td><td>750</td><td>11691</td><td>3897</td><td>20250</td><td>2250</td></tr>
<tr><td>3 OUT</td><td>T</td><td>750</td><td>20250</td><td>2250</td><td>20250</td><td>2250</td></tr>
<tr><td>1 IN</td><td>C</td><td>750</td><td>20250</td><td>2250</td><td>11691</td><td>2250</td></tr>
<tr><td>2 IN</td><td>C</td><td>750</td><td>6750</td><td>20250</td><td>11691</td><td>750</td></tr>
<tr><td>3 IN</td><td>C</td><td>750</td><td>11691</td><td>6750</td><td>11691</td><td>6750</td></tr>
</table>

Table 3. 4 Odor character as reported by odor lab panelists

Odor Character at recognition, ppm. Olfactometry by five panelists.

Sample	T= Treatment C= Control B= Blank	Panelist 1	Panelist 2	Panelist 3	Panelist 4	Panelist 5
N-BUTANOL (NB)	B	NB	NB	NB	NB	NB
1 IN	C	SEWER	CAT URINE	SEWER	DECAYED	DECAYED
2 IN	C	TRASH	FECES	DECAYED	FECES	FECES
3 IN	C	FART	CAT URINE	SEWER	DECAYED	FECES
1 OUT	T	FART	FECES	DECAYED	FECES	FECES
2 OUT	T	SEPTIC	FECES	DECAYED	FECES	FECES
3 OUT	T	FART	FECES	SEWER	GARBAGE	FECES

Odor Character at full strength, ppm. Olfactometry by five panelists.

Sample	T= Treatment C= Control B= Blank	Panelist 1	Panelist 2	Panelist 3	Panelist 4	Panelist 5
N-BUTANOL (NB)	B	NB	NB	NB	NB	NB
1 IN	C	SEPTIC	FECES	SEWER	DECAYED	DECAYED
2 IN	C	SEPTIC	CAT URINE	DECAYED	FECES	FECES
3 IN	C	SEPTIC	CAT URINE	SEWER	DECAYED	FECES
1 OUT	T	SEPTIC	FECES	SEWER	FECES	FECES
2 OUT	T	SEPTIC	FECES	DECAYED	FECES	FECES
3 OUT	T	SEPTIC	FECES	DECAYED	GARBAGE	FECES

3.8 FIGURES

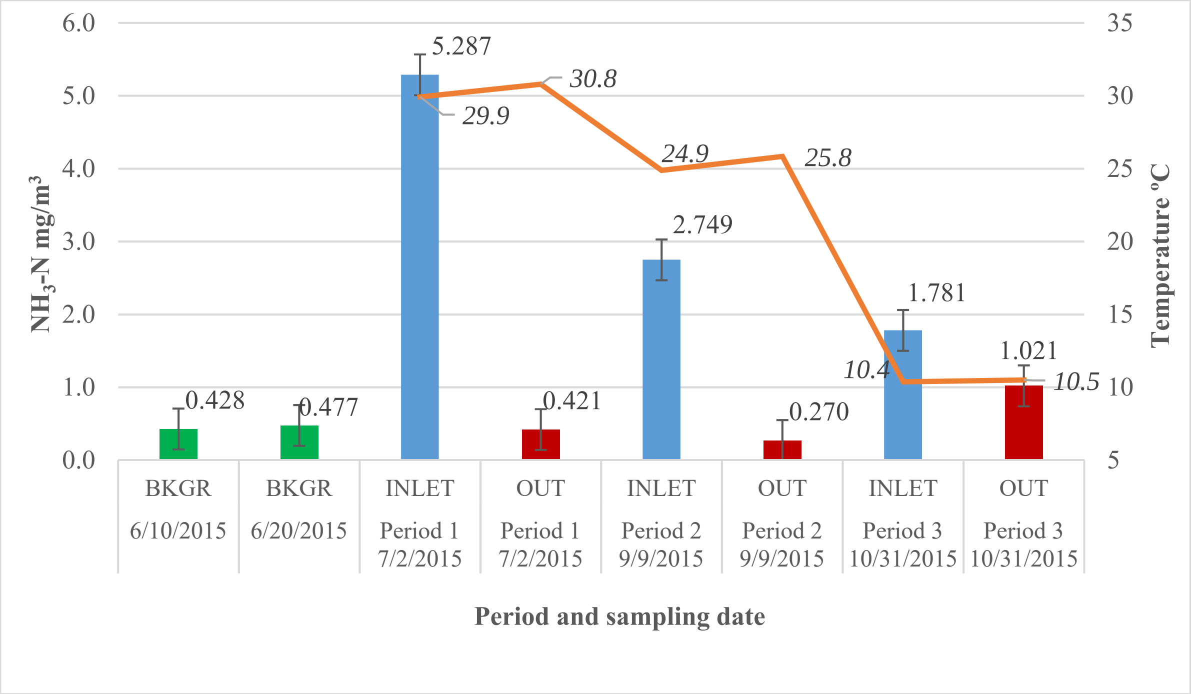

Figure 3. 1 NH$_3$ concentration before and after the filter, average temperature at inlet and inside filter

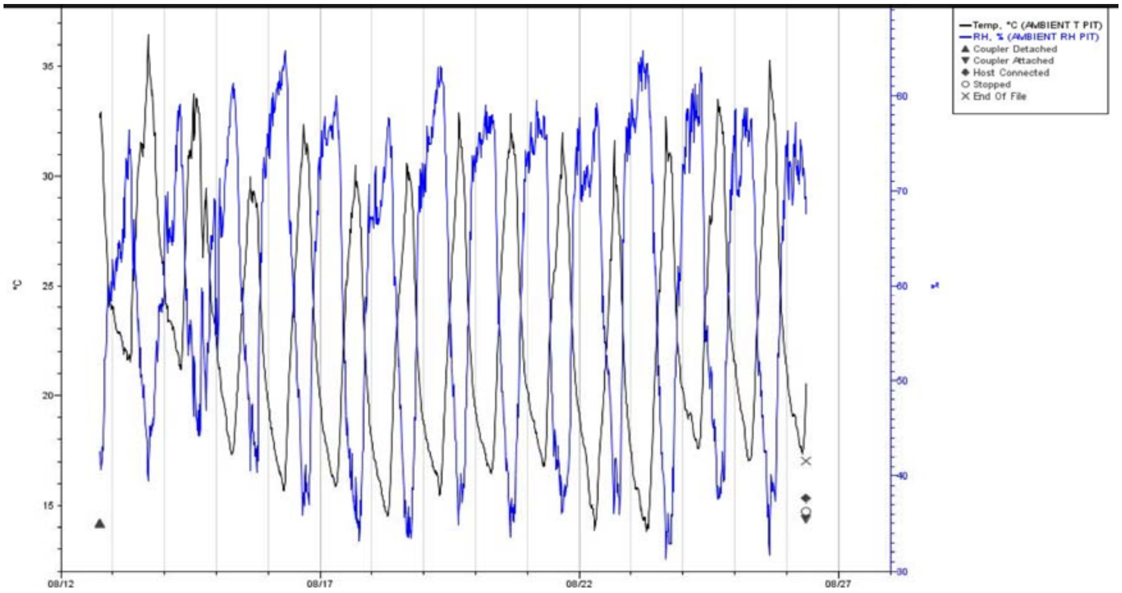

Figure 3. 2 Typical temperature and relative humidity daily variations at the dairy

3.9 PICTURES

Picture 3. 1 Dairy manure collection pit before any work on the project started

Picture 3. 2 Building the frame of the pit covering structure

Picture 3. 3 Roof like pit cover connected to the zeolite filter

Observe the gravity sand separators (left) and the machinery washing area (right) at the bottom of the picture.

Picture 3. 4 Detail of maintenance access door

Picture 3. 5 View of pipe from extraction fan to plenum

Picture 3. 6 View of plenum

Picture 3. 7 Front view of filter with connecting pipe and plenum

Picture 3. 8 Bottom and filter exhaust

Picture 3. 9 Filter smoke test

Picture 3. 10 Smoke test filter below filter outlet view

Picture 3. 11 Foaming event

Picture 3. 12 Foaming event and blown window

Observe the foam coming out around the pump pipe and motor, and the foam level line mark below the window

Picture 3. 13 Another foaming event

Observe the coverage of the machinery washing area by foam and the front of the roof like structure with the area of broken window now covered by plastic board

Picture 3. 14 Gravity separators totally covered by foam

a) First roof cut after main pump needed to be serviced

b) Cut covered by a rubber mat. This was the final solution on the main pump. Mat can be flipped over for maintenance

c) First fit around secondary pump. Eventually the roof was cut around it to allow more working space

Picture 3. 15 a, b, c Detail on different pump pipes covering

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CHAPTER 4

CUSTOM MADE DESIGNS AND DEVELOPMENTS ASSOCIATED WITH THIS RESEARCH

4.1 INTRODUCTION

Both of the research and demonstration projects “Use of clinoptilolite zeolite in composting of dairy manure to reduce ammonia emissions and retain nitrogen in the compost” and “Design and testing of a zeolite filter to capture ammonia and odors from dairy manure on-farm” were developed and conducted based on a USDA NRCS State Conservation Innovation grant from Idaho NRCS. Both projects were to research and demonstrate technologies that, when proven somewhere else, haven’t being thoroughly proven in an on-farm dairy setting. In fact, studies of these application of zeolites to dairy production and waste management were lacking or limited to lab studies with experimentation in very small volumes or mass and very controlled conditions. Another particularity of these projects is they were developed as “low budget” ones. The combination of a totally new research and the low budget available presented the interesting challenge of needing creative and adaptive solutions to deal with many of the situations and needs presented.

This combination led to the development of contraptions and techniques, unique to the research situation and that not only solved a research need, but it did so saving a considerable amount of money compared to acquiring “ready to use” solutions or “key in hand” design and construction from contracting entities. This approach of self-design and construction required extra labor that was hired with additional grants obtained by the author, taking longer time to develop and finalize the research. It also allowed for adaptation to unexpected and highly changing conditions in the on-farm setting in both projects, a positive step that allowed me to have a “trial and error” and adaptive capacity when operative conditions changed at the farm (which they did quite a lot). When contracting with third parties or acquiring ready to use packages, that option is very limited or quite expensive.

This chapter will showcase the design, construction, and basic operation of three contraptions that were fundamental to the research concretion, this include the zeolite air filter, the air capturing roof-like structure over the flushed manure pit, and the rotatory compost screen.

4.2. ZEOLITE FILTER DESIGN AND CONSTRUCTION

Some of the considerations taken when designed the filter included:

- Have the capacity to work as a test bed for diverse components and media sizes.
- Be able to change media relatively quickly when saturated or when different media needed to be tested.
- Work as a long term (eventually permanent) filter in locations with low contaminant loads.
- Be portable for both transportation and location change within the dairy, needing just any normal tractor or farm loader to lift it and load it on a regular size trailer (no special circulation permit needed).

- Be sturdy and able to resist corrosive environments common around dairy manure.
- Be self-contained and allow for measurements and minor structural changes to adapt to different research needs and farm locations. Have low construction and operation costs.

Based on the parameters mentioned above, the custom-made filter designed by the author consisted of a wooden box made using 1.2 m x 2.4 m pressure treated plywood sheets that covered an internal structure made using 5 x 10.1 cm pressured treated wood. External measurements of the filter box were 1.2 m wide, 1.2 m high, and 2.4 m long. The filter box rested atop 45 cm legs made of 10.1x10.1 cm wood posts. Pressured treated wood was used to extend the life of the filter and to make it more resistant to the corrosive environment produced by a high humidity and ammonia (NH_3) concentration in the air to be treated. The inside of the filter was divided into two sections, one at the bottom of the filter and another one about half way from bottom to the top of the filter. Each section was composed of a movable frame with an expanded metal mesh that can hold the zeolites or other filtering material. Frames can be pulled out to vary the configuration and to change media. This disposition of two levels with movable frames allows for different configurations, including pulling the top section to be able to fill the whole filter with the media, using only the top layer for closeness to the plenum, or having two layers of media with an empty space between them. This last configuration was the one chosen for this study, totaling 2.27 m^3 of filtering media. By having the possibility to vary the internal disposition and even the size of the holes in the expanded metal mesh, by adding a smaller holes' size plastic mesh on top, the filter has great flexibility to test different media size and types of media in diverse internal conditions.

The process of assembly of the filter frame, movable shelves, and enclosure is shown in pictures 4.1 to 4.3. Pictures 4.4 to 4.5 show how the filter was loaded and transported, showcasing its easy transportability capability.

The filter was designed to have a top to bottom airflow and to work under small positive pressure. From the air capturing structure over the manure pit, the air leaving the fan outlet was conducted to the filter using a 101.6 mm PVC drainage pipe to a four way plenum made of the same pipe that distributed the airflow inside the filter (Pictures 4.6 and 4.7). Below the inlet of each plenum pipe, a diffuser was located to avoid a direct hit of the airstream over the media and to redistribute airflow and pressure inside the filter (Picture 4.8). Before entering the plenum, the PVC pipe coming from the capturing structure was fitted with a double inspection port consisting of two PVC 101.6 mm diameter "T" fitted with screw caps. These two ports were used to locate measurement devices like NH_3 samplers, temperature probes, and tubing for odor measurement. More instrumentation can be accommodated as needed. Pictures 4.9 to 4.12 show the sampling port and the location of the Ogawa NH_3 samplers holders in it. In addition, the filter had holes that serve as sampling ports in the back to introduce instrumentation at different depths.

The filter was fitted with a water flow measurement device attached to the back. It allows for measurement of water flows and injection of recirculating fluids for bed regeneration. This connects to a water line on the outside and with a series of small irrigation micro-sprinklers in the inside. This feature was not used in this study, but it was included in the design for future projects. Picture 4.8 shows the water line and the micro-sprinklers inside the filter.

The outlet of the filter was the whole bottom of the unit (Pictures 4.13 and 4.14). The filter was elevated from the ground by its legs, and all but one of the long sides on that space from the ground to the bottom of the filter were closed. The open side faced a direction that put it downwind from the most common wind direction in the area. It also closed the side facing the two gravity manure separators and the side facing a smaller overflow manure pit to avoid interference of NH_3 emissions from those when measuring NH_3 at the filter outlet (Picture 4.14).

Access to the inside of the filter to fill it up or change the media, realize measurements, and service, was through two big doors (1.2 x 1.2 m each) that open a whole side on its entire length (Picture 4.6). To be able to hold the media, a holder wall consisted of a piece of plywood could be added during the filling process, and retired later for removing the media. Doors close and seal the surface through a series of hardware locks in the exterior and rubber seals in the interior. All joints and movable parts were sealed either by rubber seals or by silicone caulking, achieving a good seal with negligible to minimum leaks (tested by smoke test).

Empty bed residence time (EBRT), is defined as EBRT= V_f/Q, where V_f= filter bed volume and Q= air flow rate (Devinny, Deshusses, & Webster, 1999). EBRT for the filter coupled with the used fan and loaded with two layers varied from 16.2 s at base airflow rate to 0.85 s at maximum fan speed.

The zeolite filter worked as intended and it is ready to work in new projects. All the required design parameters were fulfilled for this research. Results on the filter and clinoptilolite media performance are included in chapter 3 of this dissertation.

4.3 DAIRY MANURE PIT COVERING AND AIR CAPTURING STRUCTURE

One of the first challenges observed when I was developing this project, was how to cover the manure pit receiving flushed wastewater from the dairy flushing system. The collection pit measures 5.8 x 5.8 meters by three meters in depth (Picture 4.15), presenting a challenge on how to cover such a big span over a pit filled with liquid manure emitting corrosive gases and located in a working dairy with multiple operating demands.

Once again, a set of design parameters and demands was determined for the pit coverage and air capture structure:

- It should be able to withstand corrosion and a humid environment from the gases and vapor rising from the pit.
- It needed to adjust to the dairy operations on the pit, including regular pit cleaning, allowing workers to catch floating debris.
- Have relatively easy access to pump motors and pipes and able to allow the extraction of the pumps and mixing propeller for maintenance.
- The covering structure should be able to withstand strong winds and snow loads common in the region.
- The structure would restrict the access from the machinery washing pad to the pit. A method to direct the wastewater and mud from washing machinery to the gravity separators on the side was needed.
- All these parameters should be achieved with a low budget.

Again, due to the characteristics of the challenge, contracting the design and construction of the pit cover was out of discussion, since the challenge of the project and the many corrections (tweaks) needed put the cost of contracting it beyond the project budget.

The roof like structure was designed by the author with the help of a certified constructor friend who donated his time, made the proper calculations, and helped erecting the skeleton (framing) part of the structure. Pictures 4.16 and 4.17 show the building of the frame. Pressure treated wood was used to build the frame and on the plywood used to cover it. The frame was anchored to the concrete pit wall using impact bolts. In the future, the structure can eventually be unbolted, disconnected from the accessory equipment and lifted as a whole. The frame, shaped as a roof, was covered by pressure treated plywood. On top of the plywood a moisture barrier was added and then it was covered with roofing tiles (Picture 4.18).

The two walls of the “A” frame were covered with plywood in some sections and clear corrugated plastic panels in others to allow for natural light entrance for inspecting the pit (Picture 4.19 and 4.21). As mentioned in chapter 3 of this dissertation, challenges arose when a manure centrifuge added after the construction of the structure generated so much foam that it blew a Plexiglas window installed to check the pit interior. After that, the window was replaced by clear corrugated plastic. On both wall sides of the “A” frame, a flipping door that flipped to rest over the roof was made to allow for inspection and cleaning of the pit (Picture 4.19).

The roof side that closed the machinery wash pad drainage to the pit was fitted with a rubber mat over the entire length of the roof and covered about 1/3 of the roof height. The rubber cover captures wastewater and mud from the concrete pad and channels it to a drain inside the gravity separator (Picture 4.20). As explained in chapter 3.5.3, an area that required several modifications was the surrounding seals around the main and backup pit pumps. The original air tight sealing was replaced and areas around the pumps' pipes were left open, with a simple cover made using a rubber mat that could be easily flipped over the roof to access the pumps and pipes as needed. This lay out allowed for much easier pump and propeller access and maintenance and for points of pressure relief and overflow in case of foaming events.

Air from the surface of the pit above the wastewater and air volume covered by the roof was extracted using a centrifugal fan (Cincinnati Fan, model PB-9) with a 373 watt (1/2 HP) motor and a variable frequency drive (VFD) with three settings (Picture 4.21). The fan baseline setting operated constantly at an extraction rate of approximately 0.14 m^3/min or 5% power, based on the University of Minnesota biofilter design information (Schmidt, Jacobson, & Nicolai, 2004) guidelines, the second rate operated at 1.5 m^3/min or ~55%, and the highest rate operated at near full speed at approximately 2.7 m^3/min or 95% power, with a maximum nominal pressure of 497 Pa (2 inches water). The middle and high rates were engaged by a set of two floats that activated them when the pit received the wastewater flush flow, the system was calibrated to absorb the volume of air over the pit water surface displaced by the increased wastewater volume.

The pit covering and air capturing structure worked as intended with minor modifications. It serves to capture air from the pit to be treated and to work on future studies testing other air treatment technologies.

4.4 COMPOST ROTATORY SCREEN

On the composting with the addition of clinoptilolite zeolite project, the need for screening the final composted product was known and many attempts were made to look for screening alternatives. A small slide screen used in a previous project wasn't big and strong enough to withstand the needed use in this project. Attempts were made to rent a commercially available compost or soil screen. No screen was available in southern Idaho that was of the needed size. Commercial compost operators and dairy producers who had compost screens either had such big units that they didn't fit in the compost pad used at the small dairy where the project was done, or they charged so much per day of operation that it was totally outside this project budget.

Once again, designing and building our own equipment was the best option. The design and working parameters for the screen were:

- It would be a rotatory screen to allow for faster screening. Rotation also allows for a mechanical action during screening that helps break down the chunks or clumps of compost.
- The screen would be able to screen compost, vermicompost, or soil.
- One of the main objectives was to develop a rotatory screen that would be cheaper to build than new small commercially available models.
- Relatively easy to replicate by farmers or researchers and to be modified to meet their needs.
- Design it to be able to build it with common and easy to find materials in an agricultural community, without the use of very specialized parts.

Regarding this last point, the design highlights the use of common materials that can be obtained at regular farm communities' shops or over the internet. The metal used is easily accessible, some parts can be (and were) recycled metal. Hydraulic pumps, hoses and actuators, as well as gears, chains, ball bearings and wheels, where similar to those used in farm machinery, tractors, or trucks. All welding was done with a regular MIG welder at the dairy farm shop by a trained welder helper. All tools and machinery used to build the rotatory screen are common to most farm shops.

The main frame was built using 10.16 cm by 10.16 cm metal beams (Picture 4.22). The screen was built using recycled tractor rims connected by 2.5 cm by 7.6 cm metal beams. The expanded metal screening element is bolted to those beams. This allows for the screening element to be changed to be able to screen to different sizes (Picture 4.23). The screen rests on top of four wheels and tires connected in pairs by a transmission rod. The screen rotates freely moved by the two tires that are connected via a transmission chain to a hydraulic motor (Pictures 4.24 and 4.25).

Below the screen, a harvesting systems consisting on "L" bars connected to rotating chains moved by a second hydraulic motor, ejects the screened compost to the side of the screen (Pictures 4.25 to 4.27). Materials not screened (refuse), leave the tubular screen at the end and are either piled out directly at the exit point or can be transported by a belt (not constructed yet) to a side of the screen (Picture 4.27 to 4.29). The screened compost that is ejected on the long side of the screen by the harvesting mechanism can either be piled up on the side (needing to be constantly removed manually due to the low profile of the screen at that point) or directed by a belt to a side pile for continuous operation.

Material moving belts for screened compost and refused materials are planned in the design, but they weren’t constructed due to lack of budget. These belts can be constructed with a metal frame and meat packing industry reused belts. Gears to move the belts can be powered by electric motors to have the option of using power from a farm if available or electric power from a portable generator to give the system total independence.

The design on the hydraulic system to move the screen and harvesting system follows the same principles of simplicity and independence of operation. Two low speed high torque hydraulic motors (Dynamic, West union, SC) and one two-way actuator with shut off (common on farm machinery and belt trucks) allows for independent speed variation on the screen and harvesting system. The actuator is the point of entrance for the hydraulic connection. The system can be connected to a small 9.7 kW (13 HP) four stroke gasoline engine, Honda GX390 (Alpharetta, GA) powering a hydraulic pump (High Performance Gear Pump; Concentric/Haldex, Itasca, IL) . The engine, pump, and 74 Lt Hydraulic fluid tank were mounted on a cart that can be connected for screen operations and then disconnected and stored in a safe place, out of inclement weather, when not in use (Pictures 4.28 and 4.29). The hydraulic fluid connection between the actuator and the pump/engine set is done via two long hydraulic hoses. This setting allows for the use of a tractor as alternative hydraulic power unit (Picture 4.27, 4.30 and 4.31), giving the user more flexibility.

The rotatory screen is fed by gravity from a feeder on one side of the structure. The feeder is top loaded and directs the compost or materials into the rotating screen via a throat like reduction where the material slides by gravity action (Pictures 4.26, 4.27 and 4.31). The feeder was designed to be able to receive dumped material from a small to medium size bucket from a tractor or skidder. In case that a bigger size bucket needs to be used (like a big tractor or front end loader), additional receiving and sliding elements can be added to the feeder. In that case, dumping operations would need to be slower since such big volumes would exceed the receiving capacity of the screen.

The whole screen structure rests on four manually actuated hydraulic jacks that can be raised or lowered independently to adjust the screen height, angle, and to level the unit in uneven ground. Jacks can be lowered until the screen chassis rests on the ground if needed (Picture 4.26, 4.27 and 4.29).

The design includes the addition of an axle with two wheels that can be put on and off on either end (front or back) of the screen structure to be able to lift the structure with a tractor bucket and chains on one side and moving it around the compost pad using those wheels. This feature wasn't built during this project due to lack of time and budget. The compost screen needs to be loaded on a trailer or truck for route transportation. The costs of making such big unit "road legal" to be directly towed on public roads were too high. The whole unit is sized to be transportable on the road, on top of a trailer or truck, without any special assistance or permit (Picture 4.32).

The compost rotatory screen worked as designed, needing minor adjustments. It has great potential for features expansion already designed but not built. Its functions of variable screen and harvesting speed coupled with the unit angle variation demonstrated it can work under diverse terrain and material to be screened conditions. No financial cost analysis was done, but an estimate on materials indicates the screen costed about half of the cheapest new units of similar screening capacity available on the market. Cost of labor to build it with in-house hired help approximately offsets the cost of transportation from the factory of similar capacity commercial screens.

4.5 PICTURES

Picture 4. 1 Filter basic frame

Picture 4. 2 Filter under construction

Observe movable shelves, covered sides, and legs

Picture 4. 3 Filter top section full enclosure and doors with locking hardware

Picture 4. 4 Loading the filter for transport

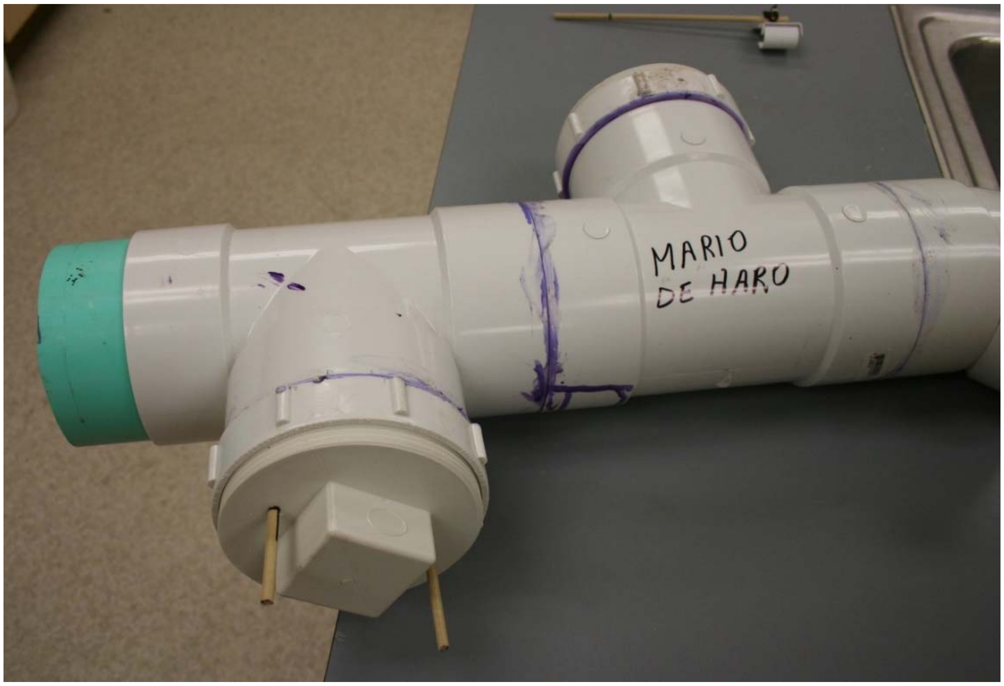
Picture 4. 5 Unloading filter at dairy

Picture 4. 6 Front view of filter and plenum

Picture 4. 7 Top view and detail of plenum

Picture 4. 8 Internal view of inlet, diffuser and watering sprinklers

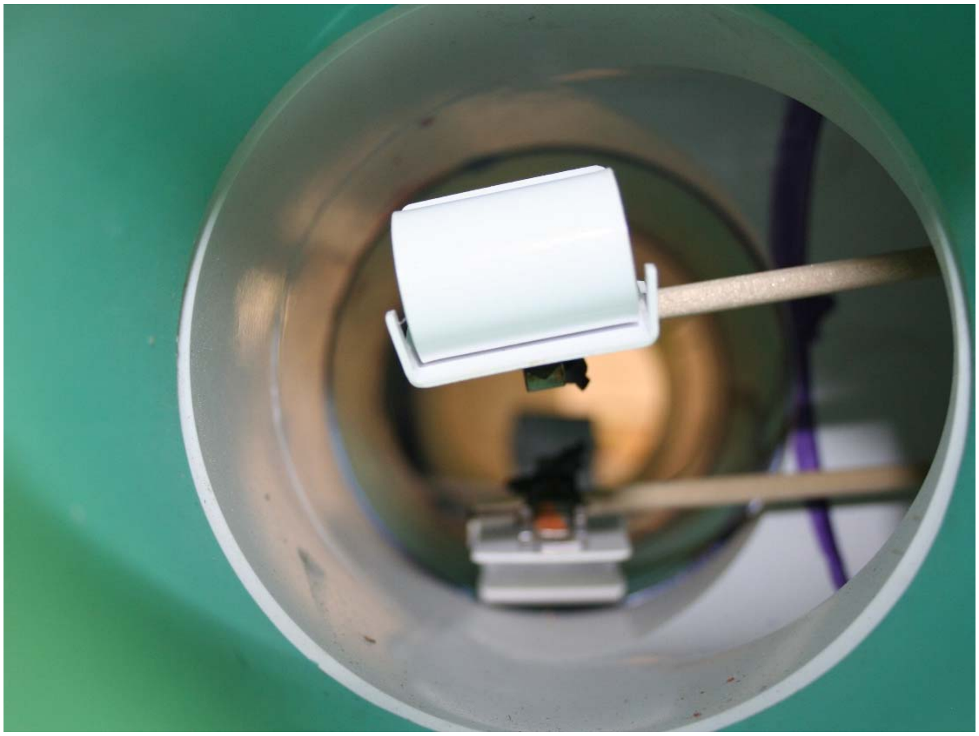
Notice the clinoptilolite at the bottom of picture. This is the upper layer



Picture 4. 9 Sampling ports and screw cap close up

Picture 4. 10 Ogawa samplers holders and sampling port insertion

a. Ogawa samplers' holders attached to sticks, b. Ogawa sampler holder and temperature probe on screw cap



Picture 4. 11 Ogawa sampler holders inside pipe

Picture 4. 12 Sampling port operation at its location

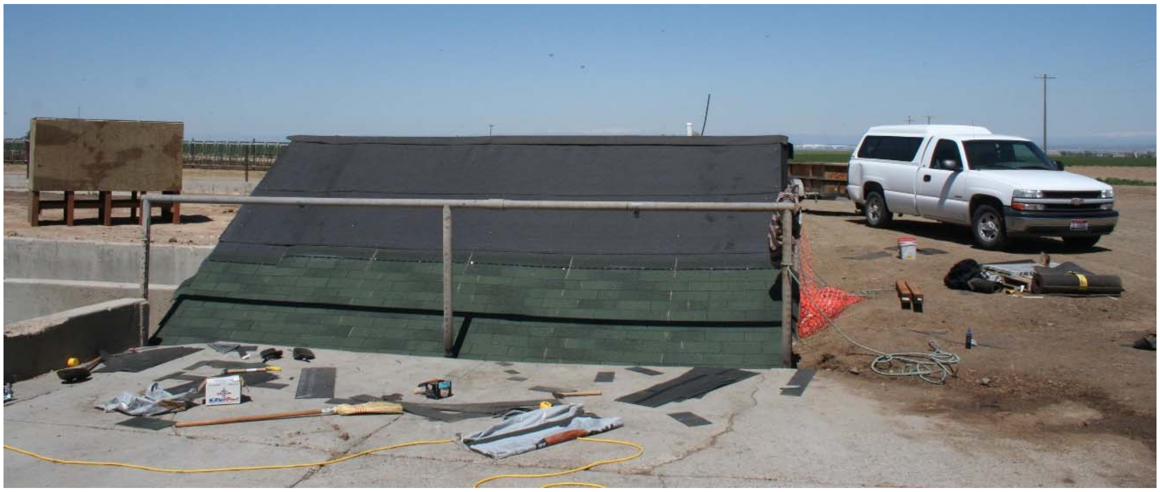
Picture 4. 13 View of bottom covered sides of filter

Picture 4. 14 View of front and air exhaust area

Picture 4. 15 Dairy manure collection pit before any work on the project started

Picture 4. 16 Building the frame of the pit covering structure

Picture 4. 17 Frame of the pit covering structure



Picture 4. 18 Pit covering structure roof-like coverage

Notice the moisture barrier and roofing tiles

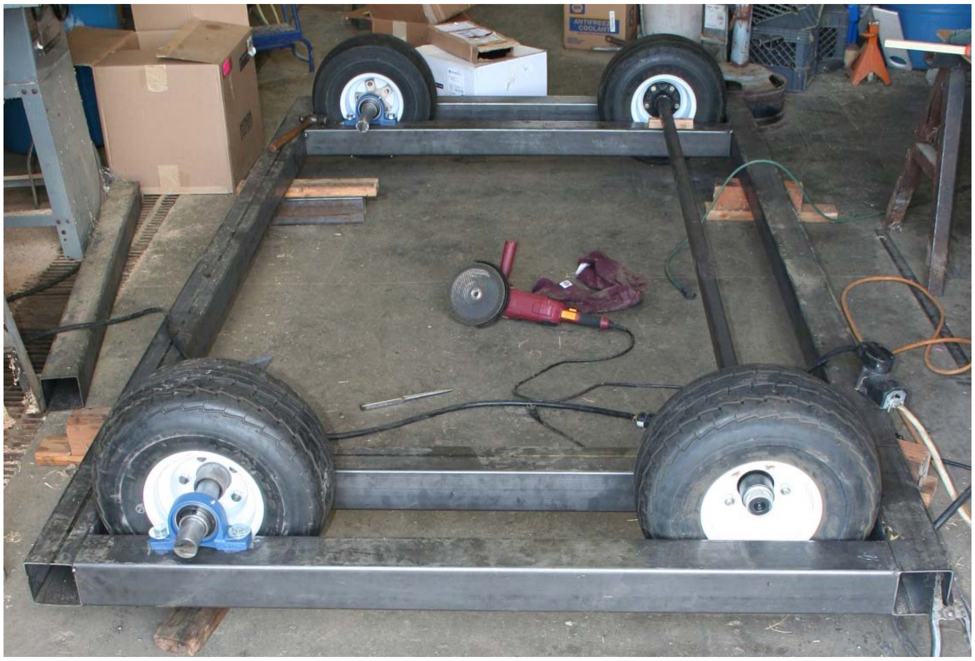
Picture 4. 19 View the "A" side, inspection door, and clear plastic coverage

Picture 4. 20 Side view of cover structure, back of filter, and washing pad

Note the rubber covering the roof to allow for washing and moving mud towards the gravity separator at left. The black pipe observed over the concrete is the water connection to the filter

Picture 4. 21 View of back of the pit cover structure

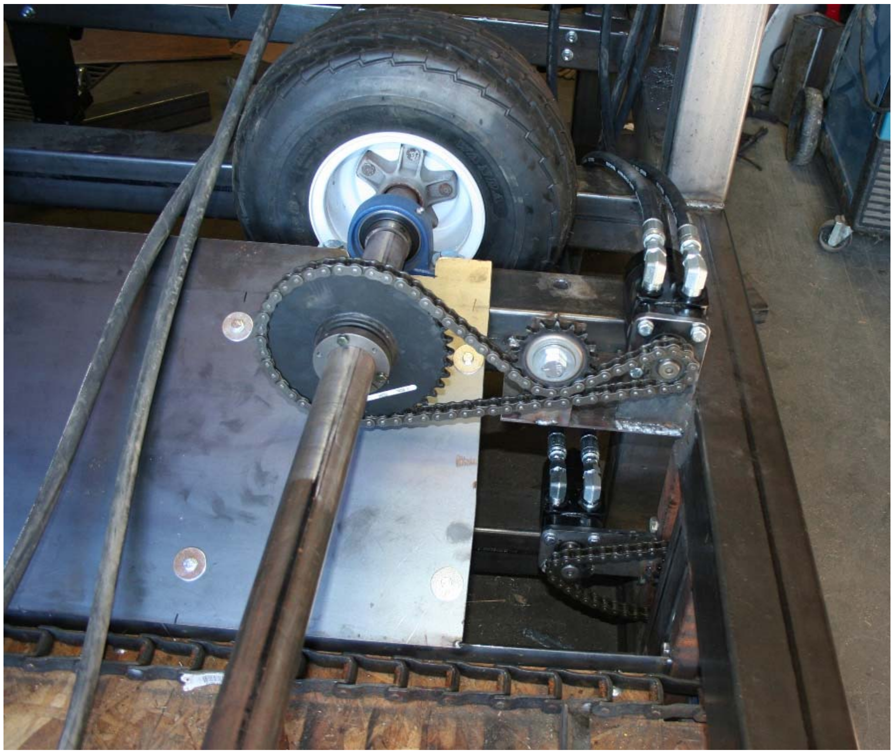
Notice the uncovered fan, connecting pipe, inspection door to the left, and clear plastic on the "A" section



Picture 4. 22 Compost screen chassis and screen holding wheels

Picture 4. 23 Screen drum

Picture 4. 24 Screen drum mounted over wheels and chassis



Picture 4. 25 Detail of gears and transmission chains for moving the screen drum and the harvesting system

Picture 4. 26 View of raised chassis and feeder throat

Picture 4. 27 View of rotatory screen powered by tractor's hydraulics

Note the screened compost on the side and the refuse at the end of drum

Picture 4. 28 Small engine, hydraulic pump and oil reservoir on a cart

Picture 4. 29 Compost screen with portable engine and pump setting

Picture 4. 30 Compost screen operating connected to a tractor

Picture 4. 31 Compost screen operating connected to an older tractor

Picture 4. 32 Compost screen loaded on a trailer for transportation