

**ZEOLITE AS NATURAL FEED ADDITIVES TO REDUCE
ENVIRONMENTAL IMPACTS OF SWINE MANURE**

Jagannath Tiwari

Department of Bioresource Engineering

McGill University, Montreal

October 2007

**A thesis submitted to McGill University in partial fulfilment of the
requirements of the degree of Master of Science**

©Jagannath Tiwari, 2007

ABSTRACT

The intensification of swine farming in recent year has resulted in excessive manure applications in some areas affecting both the terrestrial and aquatic ecosystems. The source reduction of manure nutrients by using zeolite (clinoptilolite) as a feed additive in the ration of hogs is envisaged as one of the possible solutions to reduce the excessive applications of manure nutrients in land. In this context, an experimental feed trial was performed to test the effect on the manure physico-chemical properties and the growth performance of hogs of supplementing grower hog rations with a 4% zeolite (90%+ clinoptilolite).

The zeolite ration tested, namely R2, R3 and R4, contained 4% zeolite (90%+ clinoptilolite) and either 100, 90 or 90% crude protein (CP) and 100, 90 or 85 % energy, respectively. These rations were tested against a control ration, R1, with no zeolite and 100% CP and energy.

The first experiment consisted in feeding each ration to three hogs and collecting their manure to analyze the physico-chemical characteristics. Also, 2% and 4% zeolite was added to fresh manure, to measure its viscosity. The zeolite rations did increase the total solids (TS) content of the manure. Rations R3 and R4 produced manures which flowed better and emitted less odours after aging for 67 days, as compared to the control ration R1. Ration R2 produced less odours than the control ration R1, although the results were not significantly different ($P>0.05$). Thus, supplementing hog rations with zeolite can have some positive impact on the physico-chemical properties of the manure.

The second experiment consisted in testing the effect on hog performance of adding 4% zeolite (90%+ clinoptilolite) to their ration, while also lowering the ration crude protein and energy content. A batch of 192 hogs were split into two groups, one housed in a room and fed the control ration R1, and the second in another identical room and fed two of the zeolite

rations, namely rations R2 and R3. The experiment was repeated while changing the treatment assignment per room, and using rations R3 and R4. Although the zeolite and all of its crude protein (CP) and energy levels had no significant impact on hog performance, some differences were observed with ration R3 during the 12 week growth period. This indicates that more research is needed to adjust the ration with hog growth stage. The heavy metal content of the carcasses was not significantly affected ($P>0.05$) by zeolite supplementation.

RESUMÉ

Depuis 20ans, on observe l'intensification des entreprises porcines et la concentration régionale de la production de fumier. Cette concentration a engendré des problèmes de qualité d'eau et de sol, ainsi que de contamination de l'air par les odeurs. Comme solution, la zéolite pourrait être ajoutée à la ration des porcs pour améliorer l'ingestion des nutriments et réduire l'effet de concentration des fumiers. Dans ce contexte, deux essais furent réalisés pour mesurer l'impact d'ajouter de la zéolite dans les rations pour porcs à l'engraissement : le premier visait les propriétés physico-chimiques des fumiers, et ; le second visait la productivité porcine. La zéolite expérimentale contenait plus de 90% de clinoptilolite et fut utilisée à un taux de 4%.

Les rations testées, R2, R3 and R4, contenaient 4% de zeolite (90%+ clinoptilolite) et soit 100%, 90% ou 90% de protéine brute et 100%, 90% or 85% d'énergie respectivement. Ces rations furent testées conjointement avec une ration témoin contenant 100% de protéine brute et d'énergie mais sans zéolite.

Pendant le premier essai, on alimentait chaque ration à trois porcs et on prélevait leurs fumiers pour analyser leurs propriétés physico-chimiques. Aussi, 2% et 4% de zeolite était ajouté à du fumier frais pour mesurer la viscosité du fumier. L'alimentation de la zéolite a augmenté le taux de siccité des fumiers, sans toute fois avoir un impact sur leur viscosité. Les rations R3 et R4 ont produit des fumiers qui coulaient mieux et qui dégageaient moins d'odeur après 67 jours de stockage, comparativement à la ration témoin R1. La ration R2 a produit un fumier dégageant moins d'odeur que la ration R1, mais sans toute fois donner des résultats significatifs ($P>0.05$). Donc, l'ajout de zéolite dans les rations pour porcs à l'engraissement peut avoir un impact positif sur les propriétés physico-chimiques des fumiers produits.

Le second essai consistait à ajouter de la zéolite dans la ration pour porcs à l'engraissement et à mesurer l'impact sur leur performance animale.

Un groupe de 192 porcs fut divisé en deux, dont un fut logé dans une salle et alimenté de deux rations avec zéolite, soit R2 et R3, et l'autre fut logé dans une autre salle et alimenté de la ration témoin. L'essai fut répété mais en renversant le traitement par salle et en utilisant les rations avec zéolite R3 et R4. Quoique la zéolite et les différents taux de protéine brute et d'énergie n'aient pas eu d'effet significatif sur la productivité animale, quelques différences intéressantes furent observées avec la ration R3, au cours des 12 semaines d'alimentation. Par conséquent, il est recommandé de continuer la recherche et de mieux ajuster le taux de protéine brute et d'énergie en fonction du stade de croissance des porcs. Le taux de métaux lourds des carcasses n'a pas été affecté de façon significative, par l'ajout de zéolite dans la ration ($P>0.05$).

ACKNOWLEDGEMENT

First of all, I would like to express a sincere gratitude to my supervisor, Prof. Dr. Suzelle F. Barrington, Department of Bioresource Engineering, McGill University, for her intellectual guidance, wisdom, encouragement and full cooperation throughout the graduate studies. I would like to extend sincere thanks to my co-supervisor, Prof. Dr. Xin Zhao, Department of Animal Science, McGill University, for his valuable comments on this study.

My deepest gratitude goes to Mr. Bijaya K. Adhikari, a doctorate student, Department of Bioresource Engineering, for his encouraging academic and social advice throughout the study period.

I would like to express my sincere thanks to Dr. M. Ngadi and Mr. A. Adedeji, Department of Bioresource Engineering, for lending the equipments and guidance during the experiments.

I would like to say thank you to Dr. G. Dodds and Mr. S. Leung, Department of Bioresource Engineering, for their comments on the thesis and valuable information, respectively.

It would be my pleasure to mention Mr. Denis Hatcher, for his help during experimental phase which is highly appreciated.

I am proud and honored to my parents, brothers, relatives and friends for their continued support to fulfill my academic career.

Finally, I am grateful to my wife Gyanu Tiwari, who constantly inspired and supported me throughout my study period, and at the same time, she took care of our lovely sons Aayush and Binayek Tiwari who's cheerful and smiling faces were always encouraging factor for successful completion of this study.

AUTHORSHIP AND MANUSCRIPT

This thesis is written in manuscript-based format. The contributions of authors are: 1) first author carried out experiment and writing of manuscripts, 2) second author supervised in technical correction of the work and manuscripts, 3) third author provided analytical advice and technical information.

The authorship of the papers is as follows:

First paper (CHAPTER THREE): J. Tiwari, S. Barrington and X. Zhao. This paper will be presented to the Journal of Microporous and Mesoporous Materials.

Second paper (CHAPTER FOUR): J. Tiwari, S. Barrington and X. Zhao. This paper will be presented to the Journal of Animal Science.

TABLE OF CONTENTS

ABSTRACT	ii
RESUMÉ	iv
ACKNOWLEDGEMENT	vi
AUTHORSHIP AND MANUSCRIPT	vii
TABLE OF CONTENTS	viii
LIST OF TABLES	xi
LIST OF FIGURES	xii
LIST OF APPENDICES	xiii
ABBREVIATIONS	xiv
CHAPTER ONE	
GENERAL INTRODUCTION	1
1.1 Problem statement	1
1.2 Objectives	4
1.3 Scope	4
1.4 Thesis layout	5
1.5 References	6
CHAPTER TWO	
LITERATURE REVIEW	9
2.1 Swine manure production	9
2.2 Manure nutrients and environmental issues	9
2.3 Feed additives	11
2.3.1 Phytase	11
2.3.2 Zeolite	11

<i>Structure and properties of zeolite</i>	12
<i>Types of zeolite</i>	13
<i>Clinoptilolite</i>	14
2.4 Effect of zeolite (clinoptilolite) on swine performance	14
2.4.1 Effect on feed intake and feed conversion	14
2.4.2 Effect on body weight gain	16
2.5 Effect of zeolite (clinoptilolite) on carcass quality and heavy metal concentration	18
2.6 Effect of diet manipulation on manure characteristics	19
2.7 Conclusion	20
2.8 References	22
CONNECTING STATEMENT TO CHAPTER THREE	39
CHAPTER THREE	
EFFECT ON MANURE CHARACTERISTICS OF SUPPLEMENTING GROWER HOG RATION WITH CLINOPTILOLITE	40
ABSTRACT	40
3.1 Introduction	41
3.2 Methods and materials	43
3.2.1 Experimental materials	43
3.2.2 Methods	44
3.2.3 Analytical method	47
3.2.4 Statistical analysis	48
3.3 Results and discussion	48
3.3.1 Effect of zeolite on nutrient content	48
3.3.2 Effect of zeolite on manure flow and viscosity	49
3.3.3 Odour	51

3.4 Conclusions	52
3.5 Acknowledgement	53
3.6 References	54
CONNECTING STATEMENT TO CHAPTER FOUR	66
CHAPTER FOUR	
EFFECT OF CLINOPTILOLITE DIET SUPPLEMENTATION	
AND LOWER CRUDE PROTEIN AND ENERGY LEVELS ON	
GROWER HOG PERFORMANCE	67
ABSTRACT	67
4.1 Introduction	68
4.2 Materials and methods	70
4.2.1 Experimental ration	70
4.2.2 The experimental hogs	70
4.2.3 The experimental rooms	71
4.2.4 Methodology	71
4.2.5 Statistical analysis	72
4.3 Results and discussion	73
4.3.1 Body weight and body weight gain	73
4.3.2 Feed intake and feed conversion	73
4.3.3 Carcass quality and heavy metal contamination	74
4.4 Conclusions	74
4.5 Acknowledgements	75
4.6 References	76
CHAPTER FIVE	
GENERAL CONCLUSION	90

LIST OF TABLES

CHAPTER TWO

Table 2.1 General physical properties of zeolite	30
Table 2.2 Zeolite (clinoptilolite) tests as feed additives at different supplement levels in swine, cattle, chicken, lamb, and rat's mice and rat's diets	31

CHAPTER THREE

Table 3.1 Composition of feed supplied to hogs during the test	62
Table 3.2 Bulk composition of experimental zeolite by percent weight	63
Table 3.3 Characteristics of the raw and aged manure	64
Table 3.4 Manure odour level at different feed rations	65

CHAPTER FOUR

Table 4.1 Experimental feed composition for 100% crude protein and energy	80
Table 4.2 Bulk composition of experimental zeolite by % weight	81
Table 4.3a Least square mean (LSM) values for body weight	82
Table 4.3b Least square mean (LSM) values for body weight gain	83
Table 4.3c Least square mean (LSM) values for feed intake	84
Table 4.3d Least square mean (LSM) values for feed conversion	85
Table 4.4 Effect of control and zeolite rations on carcass quality	86
Table 4.5a Effect of control and zeolite rations on heavy metals concentration in hog's liver tissue	87
Table 4.5b Effect of control and zeolite rations on heavy metal concentration in hog's kidney	88
Table 4.5c Effect of control and zeolite rations on heavy metal concentration in hog's muscle tissue	89

LIST OF FIGURES

CHAPTER TWO

Fig 2.1 Molecular sieve of zeolite Type A & Type X	12
--	----

CHAPTER THREE

Fig 3.1 Experimental set-up to compare hog manure flow characteristics	58
--	----

Fig 3.2a Velocity as a function of total solids (TS) obtained with manures from the four experimental rations, exposed to a 1.8m hydraulic head flowing though a 9mm inside diameter rubber tube	59
--	----

Fig 3.2b Friction coefficient as a function of manure total solids (TS) for the samples obtained from each four rations, and flowing through a 9mm inside diameter rubber tube exposed to a 1.8m hydraulic head	59
--	----

Fig 3.3a Effect of manure zeolite content (0, 2 and 4%) and TS (10%) on shear viscous properties	60
---	----

Fig 3.3b Effect of manure zeolite content (0, 2 and 4%) and TS (8%) on shear viscous properties	60
--	----

Fig 3.3c Effect of manure zeolite content (0, 2 and 4%) and TS (6%) on shear viscous properties	61
--	----

Fig 3.3d Effect of manure zeolite content (0, 2 and 4%) and TS (4%) on shear viscous properties	61
--	----

APPENDICES

APPENDIX A

Amendment to animal use protocol by McGill University Animal Care Committee	93
--	----

APPENDIX B

Animal Use Protocol – Research by McGill University	94
---	----

APPENDIX C

Permission by Canadian Food Inspection Agency for Temporary Feed Registration	96
--	----

APPENDIX D

Certification of Animal Training for Species Other Than Laboratory Rodent/Rabbit by McGill University Animal Care Committee	98
---	----

APPENDIX E

Workplace Hazardous Materials Information System (W.H.M.I.S) Training Certificate by McGill University Environmental Health and Safety	99
--	----

APPENDIX F

Signed waiver form	100
--------------------	-----

ABBREVIATIONS

AB	Alberta
Al	Aluminum
Al ₂ O ₃	Aluminum oxide
ANOVA	Analysis of variance
As	Arsenic
AU	Animal units
AU/km ²	Animal units per square kilometre
°C	Degree centigrade (temperature scale)
C	Carbon
Ca	Calcium
Ca ⁺⁺	Calcium ion
CaO	Calcium oxide
CaCO ₃	Calcium carbonate
Cd	Cadmium
CEC	Cation exchange capacity
Cl	Chlorine
Cmol ⁺ /kg	Centimoles of charge per kilogram
Co	Cobalt
contd.	Continued
CP(s)	Crude protein(s)
Cr	Chromium
CRD	Completely randomized design
Cu	Copper

D	Inside diameter of rubber tube
dm	dry matter
Eq.	Equation
EU	European Union
f	Friction factor
Fe	Iron
Fe ₂ O ₃	Ferric oxide (iron oxide)
g	Gravitational constant
g/kg	Gram per kilogram
GLM	General linear model
gm	Gram
h	Hour
HCl	Hydrochloric acid
h_L	Hydraulic manure head
HNO ₃	Nitric acid
H ₂ O	Water
H ₂ S	Hydrogen sulphide
H ₂ SO ₄	Sulphuric acid
H ₂ O ₂	Hydrogen peroxide
ICP	Inductively coupled plasma
IEC	Ion exchange capacity
IU/kg	International units per kilogram
K	Potassium, or rheological consistency coefficient
K ⁺	Potassium ion

Kcal	Kilocalorie
Kcal/kg	Kilocalorie per kilogram
kg	Kilogram
kg/ha	Kilogram per hectare
kg/kg	Kilogram per kilogram
kg/m ³	Kilogram per cubic metre
km ²	Square kilometre
K ₂ O	Potassium oxide
L	Length of rubber tube plus funnel neck or litre
L/s/hog	Litre per second per hog
LSM	Least square mean
m	Metre
m ³	Cubic metre
mg/kg	Milligram per kilogram
mg/l	Milligram per litre
m ² /hog	Square metre per hog
ml	Millilitre
mm	Millimetre
m/s	Metre per second
m/s ²	Metre per second square
M	Mole
Mcal/kg	Mega calorie per kilogram
ME	Metabolic energy
Mg	Magnesium

MgO	Magnesium oxide
MJ/kg	Megajoule per kilogram
Mn	Manganese
Mo	Molybdenum
n	Rheological behaviour index
η_{app}	Apparent viscosity
N	Nitrogen
Na	Sodium
Na^{+}	Sodium ion
Na_2O	Sodium oxide
NaOH	Sodium hydroxide
NH_3	Ammonia
NH_4^{+}	Ammonium ion
Ni	Nickel
nm	nano metre
O_2	Oxygen
pH	Acid and base measurement units
ppm	Parts per million
P	Phosphorus or Probability
Pa	Pascal
Pa-s	Pascal second
Pb	Lead
s	Second
s^{-1}	Per second, units of shear rate

S	Sulphur
Se	Selenium
SE	Standard error
Si	Silicon
Si/Al	Ratio of silicon and aluminum
SiO ₂	Silicon dioxide
SiO ₄	Ortho silicate (Silicate powder)
t	Time
TC	Total carbon
TiO ₂	Titanium dioxide (Titania)
TK	Total potassium
TKN	Total Kjeldahl nitrogen
TN	Total nitrogen
TP	Total phosphorus
TS	Total solids
UK	United Kingdom
USA	United States of America
v	Velocity of manure flow
V	Volume of manure
VOCs	Volatile organic compounds
VSD	Very small for detection
XR	X-ray
Zn	Zinc

CHAPTER ONE

GENERAL INTRODUCTION

1.1 Problem statement

The swine industry is a growing sector in Canadian agriculture. In recent years, due to intensification of farming systems, the number of swine farms has decreased from 16,780 in 2000 to 12,560 in 2006. However, the average number of swine per farm has increased from 790 to 1,160 over the same period (Statistics Canada, 2007). The Canadian Census of Agriculture reported about 14 million heads of swine in 2001, 37% more than that were reported in 1991; however, the cattle heads were increased by 20% during the same period (Beaulieu and Bedard, 2001). A similar scenario was reported in European Union (EU) countries where the intensive swine farming rate has been reported to be greater than the cattle farming since 1980 (Burton and Turner, 2003; Vidal, 2000) resulting in a greater number of swine at specific locations.

From 1991 to 2001, Canadian livestock increased from 1.2 to 1.4 animal units (AU)/km² including an increase in swine from 0.7 to 0.74 AU/km² (Beaulieu and Bedard, 2001). A 40% increase in swine manure in 20 years resulted in a 15 million tons of manure production in 2001 (Hofmann and Beaulieu, 2001). The contribution of swine manure to a total livestock manure production was relatively low (about 10%) (Hofmann and Beaulieu, 2001); however, the concentration of nutrient-rich manure in a localized area resulted in a negative effect to the natural ecosystems. In the past, manure has been used as a fertilizer to sustain crop production so that the livestock farming and crop productions were sustainable and the nutrients were in balance (Leung, 2004). However, due to the recent trends of intensive livestock farming, the manure production has exceeded the crop's nutrient requirement at farm level and in some cases, at the regional level (Leung, 2004).

Due to greater livestock density at specific locations, more land base is required for environmentally safe disposal of excess manure (Beaulieu et al., 2001). The regions with greater livestock densities included the Fraser Valley and Greater Vancouver Regional Districts in British Columbia with 365 and 183 AU/km² respectively; Lethbridge and Ponoka Counties in Alberta with 143 and 72 AU/km² respectively; Waterloo Regional Municipality, Perth, Wellington and Oxford Counties in Ontario with 125, 87, 84 and 78 AU/km² respectively; and Desjardins, Le Haute-Yamaska and Acton Counties in Quebec with 118, 94 and 92 AU/km² respectively (Beaulieu and Bedard, 2001; Chambers et al., 2001). The problem started due to the excessive land application of manure for nitrogen (N) supplement with N loss allowance, resulting in a tendency to accumulate phosphorus (P), potassium (K) and other elements not subjected to losses by volatilization. This caused a nutrient imbalance in the soil (Lindley et al., 1988) and ultimately accelerated the pollution of surface, subsurface and ground water bodies.

Excessive application of manure in specific regions of different provinces in the country increased soil nutrient concentrations such as P and N, resulting in the contamination of downstream water bodies (AAFC, 1998). There has been growing concern in Quebec over agricultural effluents due to high levels of nutrients they bear. For example, P levels were reported as ranging from 0.01 to 1.17 mg/l in agricultural land drainage waters (Jamieson et al., 2003), exceeding the Quebec river water quality standard of 0.03 mg/l (Beauchemin et al., 1998). Agricultural activities, such as intensive livestock farming, are at least in part, responsible for excess nutrients in freshwater bodies (Bolinder et al., 2000). These excess nutrients result in substantial additional aquatic plant growth, including a sudden rapid growth (bloom) of cyanobacteria, which upon decomposition deplete the water's oxygen supply, leading to fish kills and other adverse environmental consequences (Falconer and Humpage, 2005).

This issue can be addressed in one of the following options:

- a manure solid-liquid separation, reduces the odour and volume, and makes it easier to handle and transport to the manure-deficitary (intensive cropping) regions of the country (Møller et al., 2000; Zhang and Lei, 1998). This process removes the organic solid from liquid manure or slurry, and offers a potential benefit of nutrient-rich organic solid production, odour reduction in subsequent liquid manure storage tanks (or pits) and anaerobic lagoons; and ultimately reduces liquid manure treatment processes and costs (Møller et al., 2000; Zhang and Westerman, 1997). During the separation process, removal of manure particles (<0.25mm diameter) helps to reduce the N and P content of liquid manure and effectively control odour generation (Møller et al., 2000; Zhang and Lei, 1998) due to the presence of organic nutrients (N and P) and odour-producing compounds (carbohydrate, protein and fat) in the fine particles (Møller et al., 2000; Zhang and Westerman, 1997).
- improvement of a nutrient (N, P, and K) digestibility through a diet manipulation so that the manure nutrients are reduced at the production source (Honeyman, 1993; Sutton et al., 1999). Because the growing swine uses only 30 to 35% of the N and P they ingest, the remainder goes to waste in manure (Jongbloed and Lenis, 1998). Diet manipulation has the potential to reduce both the excess N and P in swine manure, and the negative effects of odour and other gaseous emissions, from the swine waste (Cromwell et al., 1998; Sutton et al., 1999; Jongbloed and Lenis, 1998). Sutton et al. (1999) also commented upon the potential for odorous compound reductions in swine manure through a diet modification and reported on ammonia (NH₃) emission reductions of 28 to 79%.

Source reduction of manure nutrients due to feed additives in swine diets is expected to change a manure characteristic so that the environmental impact due to excessive manure application could be minimized. Manure physical characteristics influence the handling, transportation, pumping and

application of manure in the field (Landry et al., 2004). Manure odour, generated from swine production facility, is another issue that causes a nuisance and air pollution to the surrounding environments (Lin, 2006). Intensification of a swine farming results in a larger quantity of manure accumulation into a relatively small geographical pocket area that increases the intensity and duration of odour release (Lin, 2006).

However, with the diet modification process, the swine performance and meat quality needs to be improved so that farmers would easily adopt this technology for an excess manure nutrient management. In this study, zeolite was tested as a possible additive to traditional feed and analyzed for its impact on swine performance, carcass quality, heavy metal concentrations and manure characteristics.

1.2 Objectives

The overall objective of this research was to investigate zeolite as a swine feed additive and also, as a possible technology to reduce adverse environmental effects resulting from excess nutrients present in the manure. The specific objectives of the study were to:

- (i) observe the effect of clinoptilolite, as a grower hog feed additive, on manure quality {total solids (TS), total nitrogen (TN), total phosphorus (TP), total potassium (TK), total carbon (TC), viscosity and odour};
- (ii) conduct an experimental feed trial to test the effect of clinoptilolite as a feed additive coupled with lower crude protein (CP) and energy, on a grower hog feed conversion, weight gain and carcass quality.

1.3 Scope

The experimental feed trial was conducted on 24 female hogs, with an average initial body weight of 30 (\pm 2) kg, randomly assigned to one of the four groups housed in a single pen inside the grower room. When the hogs

reached a mean weight of 60 (\pm 5) kg, 12 hogs were randomly selected and transferred into individual stainless steel metabolic cages for 8 days, with the data collected for 5 days after 3 days of acclimatization. The second test was conducted on 192 crossbred hogs ($\frac{1}{2}$ Duroc, $\frac{1}{4}$ Landrace and $\frac{1}{4}$ Yorkshire) with an average body weight of 23.9 (\pm 1.0) kg and tested for 14 weeks. The zeolite used in the feed trial was supplied by KMI, a mine in Nevada, USA. Both the tests were conducted at the swine complex of Macdonald Campus, McGill University.

1.4 Thesis layout

Chapter 1 presents general introduction, including a problem statement, objectives of the study, scope and thesis layout. Chapter 2 presents a general literature review covering the topics of swine manure production; manure nutrients and environmental issues; feed additives; effect of zeolite (clinoptilolite) on swine performance (i.e., feed intake and feed conversion, and body weight gain), carcass quality and manure characteristics; and conclusion. Chapter 3 is a paper presenting the effect on manure characteristics of supplementing grower hog rations with clinoptilolite. Chapter 4 is a second paper presenting the effect of clinoptilolite diet supplementation and lower CP and energy levels on grower hog performance. Chapter 5 presents a general conclusion, and appendices are attached at the end of the thesis. Figures and tables are presented in a sequence at the end of each chapter. The literature cited for a given chapter is presented at the end of each chapter.

1.5 References

- Agriculture and Agri-Food Canada (AAFC). 1998. Research strategy for hog manure management in Canada. Cat. no. A42-77/1998E. Ottawa: Department of Supply and Services Canada. Available at <http://dsp-psd.pwgsc.gc.ca/Collection/A42-77-1998E.pdf> (accessed February 2007).
- Beauchemin, S., R.R. Simard, and D. Cluis. 1998. Forms and concentration of phosphorus in drainage water of twenty-seven tile-drained soils. *Journal of Environmental Quality*. 27:721-728.
- Beaulieu, M.S., and F. Bedard. 2001. A geographic profile of Canadian livestock. Research paper. Cat. no. 21-601-MIE-no. 062. Agriculture Division. Jean Talon Building, Twelfth floor, Ottawa, ON. K1A OT6.
- Beaulieu, M.S., F. Bedard, and P. Lanciault. 2001. Distribution and concentration of Canadian livestock. Agriculture and rural working paper series. Working paper no. 47. Cat. no. 21-601-MIE01047. Statistics Canada Agriculture Division. Jean Talon Building, Twelfth floor, Tunney's Pasture, Ottawa, ON. K1A OT6.
- Bolinder, M.A., R.R. Simard, S. Beauchemin, and K.B. MacDonald. 2000. Risk of water contamination by phosphorus. *Canadian Journal of Soil Science*. 80(1):153-163.
- Burton, C.H., and C. Turner. 2003. Manure management: Treatment strategies for sustainable agriculture. Second edition. Silsoe Research Institute. Silsoe, UK. p. 9.
- Chambers, P.A., M. Guy, E.S. Roberts, M.N. Charlton, R. Kent, C. Gagnon, G. Grove, and N. Foster. 2001. Nutrients and their impact on the Canadian environment. Agriculture and Agri-Food Canada, Environment Canada, Fisheries and Oceans Canada, Health Canada and Natural Resources Canada. p. 241.
- Cromwell, G.L., L.W. Turner, J.L. Taraba, R.S. Gates, M.D. Lindemann, S.L. Traylor, W.A. Dozier, and H.J. Monegue. 1998. Manipulation of swine diets to reduce odours and harmful gaseous emissions from manure.

Final report. p. 12. Available at
<http://www.porkboard.org/environment/Research/researchReports/1997PDF/97-1791-Cromwell-U%20of%20KY.pdf> (accessed 15 March 2007).

- Falconer, I.R., and A.R. Humpage. 2005. Health risk assessment of cyanobacterial (blue-green algal) toxins in drinking water. *International Journal of Environmental Research and Public Health*. 2(1):43-50.
- Hofmann, N., and M.S. Beaulieu. 2001. A geographical profile of manure production in Canada. Agriculture and rural working paper series. Working paper no. 077. Cat. no. 21-601-MIE. Statistics Canada Agriculture Division. Jean Talon Building, Twelfth floor, Ottawa, ON. K1A 0T6.
- Honeyman, M.S. 1993. Environment-friendly swine feed formulation to reduce nitrogen and phosphorus excretion. *American Journal of Alternative Agriculture*. 8(3):128-132.
- Jamieson, A., C.A. Madramootoo, and P. Enright. 2003. Phosphorus losses in surface and subsurface runoff from a snowmelt event on an agricultural field in Quebec. *Canadian Biosystems Engineering*. 45.
- Jongbloed, A.W., and N.P. Lenis. 1998. Environmental concerns about animal manure. *Journal of Animal Science*. 76:2641-2648.
- Landry, H., C. Lague, and M. Roberge. 2004. Physical and rheological properties of manure products. *Transactions of the American Society of Agricultural and Biological Engineers*. 20(3):277-288.
- Leung, S. 2004. The effect of clinoptilolite properties and supplementation levels on swine performance. A M. Sc. thesis submitted to McGill University, Montreal, Quebec, Canada.
- Lin, X.J. 2006. Simulation of odour dispersion around natural windbreaks. A Ph. D. thesis submitted to McGill University, Montreal, Quebec, Canada.
- Lindley, J.A., D.W. Johnston, and C.J. Clanton. 1988. Effect of handling and

storage systems on manure value. *Applied Engineering in Agriculture*. 4:246-252.

Møller, H.B., I. Lund, and S.G. Sommer. 2000. Solid-liquid separation of livestock slurry: efficiency and cost. *Bioresource Technology*. 74:223-229.

Statistics Canada. 2007. Statistics Canada Agriculture Division. Cat. no. 23-010-XIE. Hog statistics. Ottawa: Statistics Canada, ON. K1A 0T6. 6(1):32-35. Available at <http://www.statcan.ca/english/freepub/23-010-XIE/23-010-XIE2007001.pdf> (accessed March 2007).

Sutton, A.L., K.B. Kephart, M.W.A. Verstegen, T.T. Canh, and P.J. Hobbs. 1999. Potential for reduction of odorous compounds in swine manure through diet modification. *Journal of Animal Science*. 77:430-439.

Vidal, C. 2000. Twenty years of agriculture in Europe—ever larger holdings but different economic situations, *Statistics in focus, agriculture and fisheries*, Theme 5 – 9/2000, Eurostat, Luxembourg.

Zhang, R.H., and F. Lei. 1998. Chemical treatment of animal manure for solid-liquid separation. *Transactions of American Society of Agricultural Engineers*. 41(4):1103-1108.

Zhang, R.H., and P.W. Westerman. 1997. Solid-liquid separation of annual manure for odour control and nutrient management. *American Society of Agricultural Engineers*. 13(3):385-393.

CHAPTER TWO

LITERATURE REVIEW

2.1 Swine manure production

The swine industry is a growing and dynamic sector in Canadian agriculture. Due to intensification of swine farming in recent years, the number of swine farms reported in the Canadian Census of Agriculture, decreased from 16,780 in 2000 to 12,560 in 2006. However, the average number of swine per farm increased from 790 to 1,160 in the same period (Statistics Canada, 2007). A similar scenario was reported in the European Union (EU) countries, where the intensive swine farming rate was found to be higher than cattle farming since 1980 (Burton and Turner, 2003; Vidal, 2000).

Canadian livestock produced an estimated 178 million tons of manure in 2001 to which swine contributed about 10% (Hofmann and Beaulieu, 2001). Due to intensification of farming systems, the higher livestock density regions in Canada, for example, Fraser Valley and Greater Vancouver Regional Districts in British Columbia; Lethbridge and Ponoka Counties in Alberta; Waterloo Regional Municipality, Perth, Wellington and Oxford Counties in Ontario; and Desjardins, Le Haute-Yamaska and Acton counties in Quebec do not have an adequate land base to use all the manure in an environmentally acceptable manner (AAFC, 1998; Beaulieu and Bedard, 2001; Chambers et al., 2001).

2.2 Manure nutrients and environmental issues

The amount of nutrients in animal manure mainly depended on the feed ration (protein and fiber content) and its digestibility (Lindley et al., 1988). According to Smith et al. (2000), the quality and quantity of excreta produced by hogs depended on animal size, feed type, water inputs, and housing environment. Repeated excessive land application of manure for nitrogen (N)

supplement with N loss allowance, tends to accumulate phosphorus (P), potassium (K) and other elements not subjected to loss by volatilization, causing nutrient imbalance in the soil (Lindley et al., 1988).

Nutrient loss from agricultural land, especially P, has been a growing concern in Quebec (Jamieson et al., 2003) where total phosphorus (TP) concentrations ranged from 0.01 to 1.17 mg/l (Beauchemin et al., 1998). Many sites, in Quebec, exceeded the Quebec river water quality standard of 0.03 mg/l TP in 1994-95 (Beauchemin et al., 1998; AAFC, 1998). A manure nutrient application rate greater than crop nutrient uptake rate results in accumulation of nutrients in the soil. The excess nutrients in soil ultimately reach lakes, rivers and ground water through surface runoff, subsurface drainage or leakage, resulting in an additional aquatic plant growth, which on decomposition depletes water's oxygen supply and causes the death of fish (Falconer and Humpage, 2005). Intensive livestock farming (Bolinder et al., 2000) and repeated excess N-based fertilizer application accelerates the increase of nutrient concentrations in Quebec waterways.

Problems associated with livestock waste depend on the nature of the waste, concerns of the farmer, distance to neighbours, vulnerability of the surrounding environment and current legislation (McCrory and Hobbs, 2001). According to Woestyne and Verstraete (1995), the practice of proven methods such as biogas (methane) production, anaerobic and/or aerobic purification, and solid separation is limited due to the higher cost and expertise requirements to operate the systems effectively. According to McCrory and Hobbs (2001), intensive swine farming has intensified the release of offensive odours and ammonia (NH₃) volatilization.

The use of feed additives has a positive impact on manure handling, and also, has the potential to reduce the leakage of manure nutrients and the spread of pathogenic bacteria to watercourses (McCrory and Hobbs, 2001).

2.3 Feed additives

The use of feed additives for diet manipulation reduces N and P content in swine manure and minimized the negative effects of odour and other gaseous emissions from swine waste (Cromwell et al., 1998; Sutton et al., 1999; Jongbloed and Lenis, 1998). Literature reviews suggest that one of the reasons for excess nutrient accumulation in swine manure is poor N, P and K digestibility of typical swine diets. Grower hogs use only 30 to 35% of ingested N and P (present in the natural feed) and the remaining portion goes to waste in the manure (Jongbloed and Lenis, 1998). Sutton et al. (1999) reported 28 to 79% NH₃ emissions reduction in swine manure through diet modification. Phytase, zeolite (clinoptilolite), yucca extract, modified carbohydrates (inulin) are the commonly used feed additives for diet manipulation to reduce nutrients in swine manure (Cromwell et al., 1998).

2.3.1 Phytase

Phytase, a specialized enzyme often present in feed components of plant origin acts as a catalyst to break down the undigestible phytic acid (phytate) in grains and oil seeds, thus liberating digestible P and calcium (Ca) for the swine. Adding phytase to hogs diets increased availability of phytate P in a corn-soy diet by 15 to 45%, and increased trace mineral absorption and amino acid digestibility, thus reducing P in the diet, which ultimately reduced P in the manure (McMullen and Holden, 2001). The amount of reduction in P depended on diet type, inclusion rate of phytase, degree of replacement of inorganic P, and dietary P relative to animal needs (McMullen and Holden, 2001). Genetically altered hog produced phytase for better feed digestion and excreted 60% less P in their manure (Forsberg et al., 2003).

2.3.2 Zeolite

Zeolites are crystalline, hydrated aluminosilicates of alkali and alkaline earth cations that possess three-dimensional structures with interconnecting

channels and large pores, capable of trapping molecules of proper dimensions (Mumpton, 2006). Each zeolite has its own unique chemical composition, crystalline structure (similar to honeycomb) and therefore, possesses its own set of adsorption properties. Water moves freely in and out of the pores, however the zeolite framework remains rigid. Exchangeable cations maintain electrical neutrality within the structure. Depending on the crystalline structure and chemical composition, zeolite has many applications such as assisting plant growth and acting as an excellent filtration media (ZeoponiX, 2000). Physical and chemical properties of zeolite, such as ion exchange capacity (IEC), catalysis and adsorption provide a wide application in industrial and agricultural sectors (Mumpton, 2006).

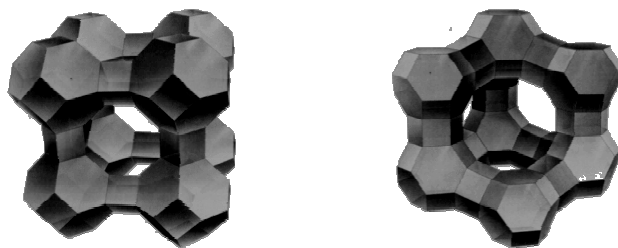


Fig 2.1: Molecular sieve of zeolite Type A & Type X (Mumpton and Fishman, 1977).

Structure and properties of zeolite

Zeolite consists of SiO_2 (68.3%), Al_2O_3 (12.3%), Fe_2O_3 (0.1%), CaO (4.3%), MgO (1.1%), K_2O (1.0%) and Na_2O (0.3%). Zeolite has well-defined structures containing aluminum (Al), silicon (Si), and oxygen (O_2) in their regular framework and possesses voids with cations (+ ions) and water (Emfema, 2005). The Si and Al atoms are tetrahedrally coordinated with each other through the shared oxygen atoms and these tetrahedrons are basic building blocks for various zeolite structures, such as zeolites Type A and Type X (Fig 2.1). Zeolites, due to the presence of alumina, exhibit a

negatively charged framework counter-balanced by positive cations, resulting in a strong electrostatic field on the internal surface. These cations can be exchanged to fine-tune the pore size or the adsorption characteristics. For example, sodium (Na) form of zeolite A has a pore opening of 0.4 nm, but if Na^+ is exchanged with the larger K^+ then the pore opening is reduced to 0.3 nm (0.3 nm molecular sieve). On ion exchange with calcium (Ca), one Ca^{++} replaces two Na^+ . Thus, the pore opening increases to approximately 0.5 nm (Mumpton, 2006). General physical properties of zeolites are presented in Table 2.1.

As a feed additive zeolite has demonstrated a potential to reduce N and P in manure and minimize the negative effects of odour and other gaseous emissions such as NH_3 , and hydrogen sulphide (H_2S) (Cromwell et al., 1998). As a manure treatment additive, it is efficient in controlling NH_3 and effective in adsorbing volatile organic compounds (VOCs) and odour (Cai et al., 2007). Zeolite increases flowability of feed and it has the ability to retain ammonium ions (NH_4^+) and NH_3 gas in the digestive system. According to Emfema (2005), zeolite allowed better performance of intestinal microflora, eliminated NH_3 odour and contributed to a healthier environment for animals and humans. It also improved feces consistency, and reduced diarrhea, and bound mycotoxins and aflatoxins, in feed and digestive system (Emfema, 2005). Depending on the physical and chemical properties, there are many types of zeolites available.

Types of zeolite

There are about fifty naturally occurring zeolite species recognized, each with a unique structure (Mumpton, 2006). The pore size in commercially available zeolite ranges from approximately 0.3-0.8 nm (Zeoponix, 2000). Clinoptilolite is a most widely used natural zeolite in animal studies due to its structural stability under high temperatures and acidic conditions.

Clinoptilolite

Clinoptilolite, a species of zeolite, has widespread applications in agriculture due to its high affinity for NH_4^+ and K^+ ions. It has wide geographic distribution and abundance in nature with high grade and large size deposits (Sheppard, 1984). It is the most commonly occurring natural zeolite in volcanic minerals (Sheppard, 1984; Bernal and Lopez-Real, 1993), and is made of hydrated alumino-silicate, with infinite three-dimensional framework of silicon-oxygen (SiO_4) tetrahedra (Emfema, 2005). Clinoptilolite has a relatively open structure with a total pore volume of approximately 35% (Godelitsas and Armbruster, 2003), and chemical formula $(\text{Na}_4\text{K}_4)(\text{Al}_8\text{Si}_4\text{O}_{96}) \cdot 24\text{H}_2\text{O}$ (Mumpton, 2006). It has been further characterized by having a Si/Al ratio greater than 4 (Perraki and Ourfanoudaki, 2004). According to Mumpton (2006), the unit-cell formula of clinoptilolite is reported as $(\text{Na}, \text{K})_2 \cdot \text{Al}_2\text{O}_3 \cdot 10\text{SiO}_2 \cdot 6\text{H}_2\text{O}$ and the cations (Na^+ and K^+) in parenthesis are the exchangeable cations, which vary depending on the immediate environment. Exchangeable cations maintain electrical neutrality within the structure.

Clinoptilolite can be used as a feed additive due to its stable behaviour at high temperature and low pH (Shurson et al., 1984). The strong relationship between NH_3 emission and pH of manure resulted in a decrease of NH_3 emissions at low pH (Cromwell et al., 1998). Clinoptilolite can be used as a natural feed additive to reduce manure nutrient content because of its molecular sieving properties, high cation exchange capacity (CEC), adsorption and high affinity for NH_4^+ and potassium (K^+) ions (Mumpton, 2006).

2.4 Effect of zeolite (clinoptilolite) on swine performance

2.4.1 Effect on feed intake and feed conversion

Zeolite (clinoptilolite) in swine diet improved feeding efficiency (Pond et al., 1988; Coffey and Pilkington, 1989; and Yannakopoulos et al., 2000) as well as digestibility of crude protein (CP) and nitrogen-free extracts (Han et

al., 1976). Feed use efficiency in hogs depended on age, weight and feeding conditions (Vrzgula and Bartko, 1984; Nestorov, 1984). In case of laying hens, dietary use of zeolite resulted in a better-feed efficiency and egg productivity in comparison to the use of control feed (Elliot and Edwards, 1991; Olver, 1997). Mumpton (2006) compared dietary use of natural zeolite with control diets for poultry, swine and ruminants; and suggested that efficient use of nutrients in animal production could be due to the integral mechanism of ion-exchange and adsorption properties of the zeolite used.

Zeolite (clinoptilolite) at 2% supplement level by weight in a hog diet increased daily feed intake (Pond et al., 1988; Coffey and Pilkington, 1989; Yannakopoulos et al., 2000); however, it also reduced the number of piglets with splay-legs, and with swelling and reddening of vulva (Papaioannou et al., 2002). Supplementation of 3-5% clinoptilolite-rich tuff into the diets of young chickens, hogs and beef cattle decreased feed consumption (Tsitsishvili et al., 1977). According to Pond and Lee (1984), zeolite (60% clinoptilolite) at 5% level in weanling hog's diet controlled diarrhea; however, when it was mixed with ammonium carbonate at 4% by weight and fed to the hogs, it decreased weight gain. Also, zeolite (40 to 60% clinoptilolite) at a 5% level in a grower hog's diet corrected the diarrhea and produced firmer feces after 6 hours of treatment, and treated hogs gained weight twice as fast as compared to non treated hogs (Nestorov, 1984; Vrzgula and Bartko, 1984). Zeolite (85% clinoptilolite) at 0.5% level in hog's diet improved metabolic energy use; however, it did not affect weight gain to feed intake ratio (Shurson et al., 1984). Zeolite (85% clinoptilolite) at 2.5%, 5% and 7.5% levels in hog's diet reduced odourous p-cresol in feces; however, this increased in urine, and also there was low energy absorption due to the increase in urinary energy loss (Shurson et al., 1984). Zeolite A (95% clinoptilolite) at 2.5%, 5% and 7.5% levels by weight in diet showed linear decrease of mineral (Ca, Fe, Mg, Na and P) retention in the hog's stomach; and resulted in the increase of N, and of urinary and fecal excretion of Ca, Fe, K, Mg, Na and P. Zeolite (77% clinoptilolite) at a 5% level in hog's diet showed feed conversion of 0.15

kg/kg of body weight gain (Barrington and El Moueddeb, 1995); however, clinoptilolite (85%) at same supplement level showed no effect on hog performance and metabolic energy utilization (Shurson et al., 1984). Castro and Elias (1978) reported a 12% increase in feed efficiency of hogs fed with 7.5% zeolite supplemented diet in comparison to control diets. Among the treatment levels of 0%, 5% and 10% zeolite (95% clinoptilolite), the 10% level showed better feed conversion (Cool and Willard, 1982) (Table 2.2).

Zeolite (clinoptilolite) added to the diet of hogs at lower CP and energy levels resulted in better results when compared to higher CP and energy levels for feed intake and feed conversion. A 15.2% CP in the hog's diet resulted in better feed intake rates (Pond et al., 1988); however, a 16% CP didn't show any such effects (Pond and Yen, 1982). Similarly, Nestorov (1984) reported an increase in weight gain to feed conversion ratio in hogs with a CP of 14.6% and 2.9 Mcal/kg energy in diets in comparison to higher CP and energy levels (Table 2.2).

Thus the literature tends to suggest that use of clinoptilolite as a feed additive in hog's diet results in positive effects on feed intake and feed conversion rate; however, there are reports of negative results depending on the % clinoptilolite in zeolite, supplemental level of clinoptilolite by weight in rations as well as CP and energy levels in the feed.

2.4.2 Effect on body weight gain

Zeolite (clinoptilolite), as feed additives in hog's diet, increased body weight and weight gain rate due to its ion exchange capacity (IEC), adsorption and related molecular sieving properties (Pond et al., 1988; Coffey and Pilkington, 1989; Yannakopoulos et al., 2000), and showed positive results on fat or muscle in comparison to the control diet (Pond et al., 1988; Hagedorn et al., 1990; Kovar et al., 1990). The effectiveness of zeolite in hog's growth increase depended on zeolite species, properties and supplement level (% zeolite by weight) used in the diet (Mumpton, 2006).

Clinoptilolite at a 2% supplement level by weight in diet increased litter size, gave higher piglet weight at a birth and higher piglet weight gain during lactation (Kyriakis et al., 2002; Papaioannou et al., 2002); however, it decreased liver and kidney weights (Pond et al., 1988). Pond and Lee (1984) reported increases in weight gain due to addition of clinoptilolite (70%) at a 3% level in young growing hog's diet however, the research report of Poulsen and Oksbjerg (1995) showed the increase of N excretion in feces, higher feed intake to body weight gain ratio, and decrease of daily weight gain at the same supplement level. Clinoptilolite (85% or 92%) at 5% level in hog's diet showed no toxic effects on grower hogs; however, it showed a decrease in daily weight gain in comparison to other compositions of clinoptilolite with traditional feed (Pond and Yen, 1982; Pond and Lee, 1984). In comparison to a regular diet, the clinoptilolite at 5% and 10% levels by weight in hog's diet resulted in a weight gain of 27% (Kondo and Wagai, 1968) and 8% (Nestorov, 1984) respectively; however, Pond and Yen (1982) at the same clinoptilolite levels found no effect on body weight gain, feed intake, and weight gain to feed intake ratio. According to Ma et al. (1984), a 5% clinoptilolite level resulted in less weight gain in comparison to 0% and 2.5% levels in sow's diet and also, the supplementation of 2.5% and 5% clinoptilolite in pregnant sow's diet decreased ovulation rate by 1.0 and 2.2 ova, respectively; however it did not affect embryo-survival rate significantly (Table 2.2).

Tests of clinoptilolite (60%) and synthetic zeolite A at 3% supplement level by weight in male lamb's diet resulted in weight increase due to addition of clinoptilolite, but a decrease with zeolite A (Pond and Lee, 1984). According to Pond and Lee (1984), clinoptilolite (60% and 72%) at 3% and 5% levels in female rats' diets had no effect on body weight gain during gestation or lactation or on the number and size of pups. Clinoptilolite (60%) at 5% and ammonium carbonate at 4% levels by weight reduced the weight loss of dam after lactation; however, it reduced the weight gain of female rats due to dilution effect on the feed (Pond and Lee, 1984). Nestorov (1984) reported 17% and 3.6% greater weight gain in young beef cattle (steer) and

chickens (broilers) when clinoptilolite at 4.3% and, 0.5%, 1% and 1.5% by weight was added to cattle's and chickens' regular diet respectively (Table 2.2).

A zeolite (clinoptilolite) added diet in hogs at lower CP and energy level reported better results in body weight gain to feed intake ratio. A clinoptilolite-added diet in hogs with 16.5% CP and 3.1 Mcal/kg energy resulted in greater litter size, greater piglet weight at birth and greater piglet weight gain during lactation (Kyriakis et al., 2002) and also, 18.2% CP and 3.2 Mcal/kg energy showed similar impact on body weight gain; however, it reduced the number of piglets with splay-legs and with swelling and reddening of vulva (Papaioannou et al., 2002). CP at 15.2% levels in hog's diet resulted in improved daily body weight gain (Pond et al., 1988); however, 16% CP resulted in no effect on body weight gain to feed intake ratio (Pond and Yen, 1982). Similarly, Nestorov (1984) found increase in body weight gain and correction of diarrhea in hogs due to 14.6% of CP and 2.9 Mcal/kg energy in diets (Table 2.2).

So, the literature shows that the use of clinoptilolite has both positive and negative impacts on hog's body weight and body weight gain rate, and greater % clinoptilolite at lower supplement rates by weight in diet with lower CP and energy levels give better results on hog's body weight gain.

2.5 Effect of zeolite (clinoptilolite) on carcass quality and heavy metal concentration

Zeolite (clinoptilolite) has no effect on carcass quality, heavy metal concentrations in kidney, liver and muscle tissues; or their market values. The toxic cation absorption capacity of zeolite prevented adverse effect on metabolic functions in hogs (Pond et al., 1993) resulting in no effect on meat quality. It had no adverse effect on edible parts of muscles, liver, heart and kidneys (carcass) (Nestorov, 1984; Fokas et al., 2004) due to their absorption capacity on lead (Pb), arsenic (As) and cadmium (Cd) (Pond et al., 1993). According to Nestorov (1984), histochemical studies on intestinal tracts of

hogs fed with 10% clinoptilolite showed no adverse effects on tissues and organoleptic evaluation of meat. Pond and Yen (1983) found no effect of zeolite A on plasma potassium (K), sodium (Na) and magnesium (Mg) levels in hogs. Clinoptilolite (85%) at 2.5%, 5% and 7.5% levels by weight in hog's diet reduced blood plasma NH_3 levels; however, zeolite A (95% clinoptilolite) at 1%, 2% and 3% by weight showed no adverse effect on blood plasma NH_3 level (Shurson et al., 1984). Tests on male castrated hogs by adding clinoptilolites (60% and 72%) at 5% level of supplement resulted in no effect on blood haemoglobin, haematocrit, plasma urea-N, serum protein, albumin, alkaline phosphate, Ca and P; however clinoptilolite reduced the increase of liver Cd due to the addition of Cd in feed (Pond and Lee, 1984). According to Vrzgula and Bartko (1984) there were no substantial differences in liver function, serum blood counts or in metabolic concentrations between the zeolite and control groups. Similarly, dietary use of zeolite showed no influence on performance and carcass quality of growing and fattening hogs (Pearson et al., 1985). Therefore, zeolite species (with different % clinoptilolite) at different supplement levels with traditional feed could play a vital role in achieving the goal of manure nutrient reduction and maintain the quality and quantity of meat.

2.6 Effect of diet manipulation on manure characteristics

Very few scientific articles reported on the rheological properties of manure products and most of such efforts focused on liquid manure or manure slurry (Landry et al., 2004). Kumar et al. (1972) found that the viscosity of dairy cattle slurry decreased with the increase of sample dilution and temperature. The rheological properties of livestock slurry depended on manure moisture content or total solid (TS) content, particle size and viscosity; and the TS of manure slurries showed directly proportional relationships with viscosity (Chen and Shetler, 1983; Landry et al., 2004; and Keener, 2005). The feces with finer particles in zeolite fed hogs possess lower TS and carbon (C), and hence lower viscosity. Keener (2005) reported a

viscosity increase of 10 to 80-fold going from 0% TS (liquid) to 5% and 10% TS. Manure slurry, below 5% TS content, showed Newtonian flow properties and above 5% it showed non-Newtonian (pseudo plastic) flow properties and behaved like real plastic materials due to the dependence of its viscosity on applied shear rate (El-Mashad et al., 2005 and Kumar et al., 1972).

Zeolite in swine diet showed positive impacts on viscosity which is reported to reduce crust formation during storage and, required less energy and cost for pumping, transportation and land spreading (Backhurst and Harker, 1974; Chen, 1986). The clinoptilolite at 5% level in hog's diet resulted in firmer, better-formed and less odoriferous feces (Vrzgula and Bartko, 1984). Supplementation of synthetic amino acids with reduced intact protein levels in hog's diet significantly reduced N excretion and odour production (Sutton et al., 1999). Reduction of manure odour due to dietary manipulation with clinoptilolite (Le et al., 2007) indicated more thorough digestive process resulting in finer particle size of feces (Mumpton, 2006). Manure characteristics are considered as predominant parameters for affecting the cost at the local level for manure pre-treatment, handling, transportation and field application; as well as to address the environmental adversities due to intensive swine farming. Therefore, this study was conducted to examine the physical and chemical properties of manure obtained from clinoptilolite fed hogs, and also, to test the effect of clinoptilolite on quality and quantity of meat production.

2.7 Conclusion

Research in recent days has been directed towards the source reduction of manure nutrients through diet manipulation by adding natural feed additives such as zeolite (clinoptilolite). A review of literature revealed that clinoptilolite has both positive and negative impacts on hog performance and manure characteristics such as nutrient content (N, P and K), odour, TS, viscosity; and maintenance of meat quality. The effectiveness of zeolite however, depends on its species, properties, supplement level of clinoptilolite

by weight, %CP and energy levels used in diets as well as the age, weight and feeding conditions of experimental hogs. Besides positive impacts, there are reports of negative results such as decrease of ovulation rate of young sows, reduction of number of piglets with splay-legs, decrease of nitrogen ingestion efficiency and increase of N excretion in feces, decrease of liver and kidney weight in grower hogs, reduction of energy absorption efficiency due to clinoptilolite in hog's diet at different supplement levels by weight and production of feces with higher TS content.

Most of the research work on zeolite has been reported at supplement levels of 2%, 2.5%, 5%, 7.5% and 10% by weight; and it has resulted in better feed conversion, higher body weight gain at lower supplemental levels in diet. Also, previous studies focused on feed conversion, body weight gain, and manure nutrient reduction (to some extent) due to clinoptilolite supplement in hog's diet, however, its effect on manure characteristics is another important part of the studies. More research needs to be done on the effect of zeolite on manure physical and chemical characteristics. Therefore, the present study was designed to test the effect of clinoptilolite at 4% level with higher CP and energy percentage in diets, on manure characteristics such as nutrient content (N, P and K), odour, TS, TC, viscosity, shear stress and shear rate (Chapter III); and on hog performance, carcass quality and quantity (Chapter IV).

2.8 References

- Agriculture and Agri-Food Canada (AAFC). 1998. Research strategy for hog manure management in Canada. Cat. no. A42-77/1998E. Department of Supply and Services. Ottawa. Canada.
Available at <http://dsp-psd.pwgsc.gc.ca/Collection/A42-77-1998E.pdf> (accessed February 2007).
- Backhurst, J.R., and J.H. Harker. 1974. Evaluation of physical properties of pig manure. *Journal of Agricultural Engineering and Research*. 19:199-207.
- Barrington, S.F., and K. El Moueddeb. 1995. Zeolite as pig manure additive to control odour and conserve N. Canadian Society of Agricultural Engineering. Paper no. 95-510, Saskatoon, Canada.
- Beauchemin, S., R.R. Simard, and D. Cluis. 1998. Forms and concentration of phosphorus in drainage water of twenty-seven tile-drained soils. *Journal of Environmental Quality*. 27:721-728.
- Beaulieu, M.S., and F. Bedard. 2001. A geographic profile of Canadian livestock. Research paper. Cat. no. 21-601-MIE-no. 062. Agriculture Division. Jean Talon Building, Twelfth floor, Ottawa, ON. K1A OT6.
- Bernal, M.P., and J.M. Lopez-Real. 1993. Natural zeolites and sepiolite as ammonium and ammonia adsorbent materials. *Bioresource Technology*. 43:27-33.
- Bolinder, M.A., R.R. Simard, S. Beauchemin, and K.B. MacDonald. 2000. Risk of water contamination by phosphorus. *Canadian Journal of Soil Science*. 80(1):153-163.
- Burton, C.H., and C. Turner. 2003. Manure management: Treatment strategies for sustainable agriculture. Second edition. Silsoe Research Institute. Silsoe, UK. p. 21.
- Cai, L., J.A. Koziel, Y. Liang, A. Nguyen, and H. Xin. 2007. Evaluation of zeolite for control of odorants emissions from simulated poultry manure storage. *Journal of Environmental Quality*. 36:184-193.
- Castro, M., and A. Elias. 1978. Effect of the inclusion of zeolite in final

- molasses-based diets on the performance of growing-fattening pigs. Cuban Journal of Agricultural Sciences. 12:69-75.
- Chambers, P.A., M. Guy, E.S. Roberts, M.N. Charlton, R. Kent, C. Gagnon, G. Grove, and N. Foster. 2001. Nutrients and their impact on the Canadian environment. Agriculture and Agri-Food Canada, Environment Canada, Fisheries and Oceans Canada, Health Canada and Natural Resources Canada. p. 241.
- Chen, Y.R. 1986. Rheological properties of sieved beef cattle manure slurry: Rheological model and effects of temperature and solids concentration. Agricultural Wastes. 15:17-33.
- Chen, Y.R., and E.L. Shetler. 1983. Temperature effect on rheological properties of cattle manure slurry. Journal of Testing and Evaluation. 11(6):360-364.
- Coffey, M.T., and D.W. Pilkington. 1989. Effect of zeolite-A on the performance and carcass quality of swine. Journal of Animal Science. 67(2):36.
- Cool, W.M., and J.M. Willard. 1982. Effect of clinoptilolite on swine nutrition. Nutrition Reports International. 26(5):759-766.
- Cromwell, G.L., L.W. Turner, J.L. Taraba, R.S. Gates, M.D. Lindemann, S.L. Traylor, W.A. Dozier, and H.J. Monegue. 1998. Manipulation of swine diets to reduce odours and harmful gaseous emissions from manure. Final report. p. 12. Available at <http://www.porkboard.org/environment/Research/researchReports/197PDF/97-1791-Cromwell-U%20of%20KY.pdf> (accessed 15 March 2007).
- Elliot, M.A., and H.M. Edwards Jr., 1991. Comparison of the effects of synthetic and natural zeolite on laying hen and broiler chicken performance. Poultry Science. 70:2115-2130.
- El-Mashad, H.M., W.K.P. van Loon, G. Zeeman and G.P.A. Bot. 2005. Rheological properties of dairy cattle manure. Bioresource Technology. 96:531-535.

- Emfema. 2005. International association of the European manufacturers of major, trace and specific feed minerals secretariat. Wetstraat-Rue de la Loi 223/3B-1040 Brussels, Belgium. Available at <http://www.emfema.org/minerals> (accessed February 2007).
- Falconer, I.R., and A.R. Humpage. 2005. Health risk assessment of cyanobacterial (blue-green algal) toxins in drinking water. *International Journal of Environmental Research and Public Health*. 2(1):43-50.
- Fokas, P., G. Zervas, K. Fegeros, and P. Zoiopoulos. 2004. Assessment of Pb retention coefficient and nutrient utilization in growing pigs fed diets with added clinoptilolite. *Animal Feed Science and Technology*. 117:121-129.
- Forsberg, C.W., J.P. Phillips, S.P. Golovan, M.Z. Fan, R.G. Meidinger, A. Ajakaiye, D. Hilborn, and R.R. Hacker. 2003. The Enviropig physiology, performance, and contribution to nutrient management advances in a regulated environment: The leading edge of change in pork industry. *Journal of Animal Science*. 81(2):68-77. Also available at <http://www.uoguelph.ca/enviropig> (accessed February 2007).
- Godelitsas, Ath., and Th. Armbruster. 2003. Microporous and Mesoporous Materials. 61:3.
- Hagedorn, T.K., D.R Ingram, S.J. Kovar, V.N. Achee, D.G. Barnes, and S.M. Laurent. 1990. Influence of sodium zeolite-A on performance, bone condition and liver lipid content of white leghorn hens. *Poultry Science*. 69(1):169.
- Han, I.D., H.K. Part, and C.S. Kim. 1976. Studies on the nutritive value of zeolite. II. Effects of zeolite rich hull mixture on the performance of growing-finishing swine. *Korean Journal of Animal Science*. 18:225.
- Hofmann, N., and M.S. Beaulieu. 2001. A geographic profile of manure production in Canada. Research paper. Cat. no. 21-601-MIE-no.077. Agriculture Division. Jean Talon Building, Twelfth floor, Ottawa, ON. K1A OT6.

http://www.gracedavison.com/eusilica/Adsorbents/product/zeolite_molecular_sieve.htm (accessed March 2007).

- Jamieson, A., C.A. Madramootoo, and P. Enright. 2003. Phosphorus losses in surface and subsurface runoff from a snowmelt event on an agricultural field in Quebec. *Canadian Biosystems Engineering*. 45.
- Jongbloed, A.W., and N.P. Lenis. 1998. Environmental concerns about animal manure. *Journal of Animal Science*. 76:2641-2648.
- Keener, H.M. 2005. Evaluation of manure flow-ability. Department of food, agricultural and biological engineering. Ohio State University, Ohio Agricultural Research and Development Centre, 1680 Madison Avenue, Wooster, OH, 44691.
- Kondo, N., and B. Wagai. 1968. Experimental use of clinoptilolite-tuff as a dietary supplement for pigs. *Yotonkai*. p. 1-4.
- Kovar, S.J., D.R Ingram, T.K Hagedorn, V.N Achee, D.G. Barnes, and S.M. Laurent. 1990. Broiler performance as influenced by sodium zeolite-A. *Poultry Science*. 69(1):174.
- Kumar, M., H.D. Bartlett, and N.N. Mohsenin. 1972. Flow properties of animal slurries. *Transactions of the American Society of Agricultural Engineers*. 15(4):718-722.
- Kyriakis, S.C., D.S. Papaioannou, C. Alexopoulos, Z. Polizopoulou, E.D. Tzika, and C.S. Kyriakis. 2002. Experimental studies on safety and efficacy of the dietary use of a clinoptilolite-rich tuff in sows: a review of recent research in Greece. *Microporous and Mesoporous Materials*. 51:65-74.
- Landry, H., C. Lague, and M. Roberge. 2004. Physical and rheological properties of manure products. *Transactions of the American Society of Agricultural and Biological Engineers*. 20(3):277-288.
- Le, P.D., A.J.A. Aarnink, A.W. Jongbloed, C.M.C. van der Peet Schwering, N.W.M. Ogink, and M.W.A. Verstegen. 2007. Effects of crystalline amino acid supplementation to the diet on odour from pig manure. *Journal of Animal Science*. 85:791-801.

- Lindley, J.A., D.W. Johnston, and C.J. Clanton. 1988. Effect of handling and storage systems on manure value. *Applied Engineering in Agriculture*. 4:246-252.
- Ma, C.S., S.K. Yang, C.M. Tzeng, and H.K. Wu. 1984. Effect of feeding clinoptilolite on embryo survival in swine. In W.G. Pond and F.A. Mumpton (ed.) *Zeo-agriculture: Use of natural zeolites in agriculture and aquaculture*. International committee on natural zeolites. Westview Press, Boulder, CO. p. 155-160.
- Martin-Kleiner, I., Z. Flegar-Mestric, R. Zado, D. Breljak, S. Stanovic Janda, R. Stojkovic, M. Marusic, M. Radacic and M. Boranic. 2001. The effect of the zeolite clinoptilolite on serum chemistry and hematopoiesis in mice. *Food and Chemistry Toxicology*. 39:717-727.
- McCrory, D.F., and P.J. Hobbs. 2001. Additives to reduce ammonia and odour emissions from livestock wastes: A review. *Journal of Environmental Quality*. 30:345-355.
- McMullen, L.K., and P. Holden. 2001. Phytase fact sheet. Iowa State University Swine Specialist. Available at <http://extension.agron.iastate.edu/immag/pubs/phytase.doc> (accessed February 2007).
- Mumpton, F.A. 2006. Using zeolites in agriculture: Zeolite product website. Available at <http://www.zeolite-products.com> (accessed April 2007).
- Mumpton, F.A., and P. H. Fishman. 1977. The application of natural zeolites in animal science and aquaculture. *Journal of Animal Science*. 45:1188-1203.
- Nestorov, N. 1984. Possible applications of natural zeolites in animal husbandry. In: W.G. Pond and F. A. Mumpton (ed.) *Zeo-Agriculture: Use of natural zeolite in agriculture and aquaculture*. International committee on natural zeolites. Westview Press, Boulder, CO. p. 163.
- Olver, M.D. 1997. Effect of feeding clinoptilolite (zeolite) on the performance of three strains of laying hens. *British Poultry Science*. 38:220-222.
- Papaioannou, D.S., S.C. Kyriakis, A. Papasteriadis, N. Roumbies, A.

- Yannakopoulos, and C. Alexopoulos. 2002b. A field study on the effect of in-feed inclusion of a natural zeolite (clinoptilolite) on the health status and performance of sows/gilts and their litters. *Research in Veterinary Science*. 72:51-59.
- Pearson, G., W.C. Smith, and J.M. Fox. 1985. Influence of dietary zeolite on pig performance over the live weight range 25-87 kg. *New Zealand Journal of Experimental Agriculture*. 13:151-154.
- Perraki, Th., and A. Ourfanoudaki. 2004. Mineralogical study of zeolites from Pentelofos area, Thrace, Greece. *Applied Clay Science*. 25:9-16.
- Pond, W.G., and J.T. Lee. 1984. Physiological effects of clinoptilolite and synthetic zeolite A in animals. In W.G. Pond and F.A. Mumpton (ed.) *Zeo-agriculture: Use of natural zeolites in agriculture and aquaculture*. International committee on natural zeolites. Westview Press, Boulder, CO. p. 129-146.
- Pond, W.G., and J.T. Yen. 1983. Protection by clinoptilolite or zeolite NaA against cadmium-induced anemia in growing swine. *Proceedings of the society for experimental biology and medicine*. 173:327-337.
- Pond, W.G., and J.T. Yen. 1982. Response of growing swine to dietary clinoptilolite from two geographic sources. *Nutrition Reports International*. 25:837-848.
- Pond, W.G., J.T. Yen, and V.H. Varel. 1988. Response of growing swine to dietary copper and clinoptilolite supplementation. *Nutrition Reports International*. 37:797-803.
- Pond, W.G., K.J. Ellis, K.J. Krook, and P.A. Schoknecht. 1993. Modulation of dietary Pb toxicity in pigs by clinoptilolite. In: *Proceedings of zeolite '93, fourth conference on the occurrence, properties and utilization of natural zeolites*. International committee on natural zeolites. Suny-College at Brockport, Brockport, New York. p. 170-172.
- Poulsen, H.D., and N. Oksberg. 1995. Effect of dietary inclusion of a zeolite (clinoptilolite) on performance and protein metabolism of young growing pigs. *Animal Feed and Science Technology*. 53:297-303.

- Sheppard, R.A. 1984. Characterization of zeolitic materials in agricultural research. In W.G. Pond and F.A. Mumpton (ed.) *Zeo-agriculture: Use of natural zeolites in agriculture and aquaculture*. Westview Press, Boulder, CO. p. 81-90.
- Shurson, G.C., P.K. Ku, E.R. Miller, and M.T. Yokoyama. 1984. Effects of zeolite A or clinoptilolite in diets of growing swine. *Journal of Animal Science*. 59(6):1536-1545.
- Smith, K.A., D.R. Charles, and D. Moorhouse. 2000. Nitrogen excretion by farm livestock with respect to land spreading requirements and controlling nitrogen losses to ground and surface waters. Part 2: Pigs and poultry. *Bioresource Technology*. 71:183-194.
- Statistics Canada. 2007. Statistics Canada Agriculture Division. Cat. no. 23-010-XIE. Hog statistics. Ottawa: Statistics Canada, ON. K1A 0T6. 6(1):32-35. Available at <http://www.statcan.ca/english/freepub/23-010-XIE/23-010-XIE2007001.pdf> (accessed March 2007).
- Sutton, A.L., K.B. Kephart, M.W.A. Verstegen, T.T. Canh, and P.J. Hobbs. 1999. Potential for reduction of odorous compounds in swine manure through diet modification. *Journal of Animal Science*. 77:430-439.
- Tsitsishvili, G.V., T.G. Andronikashvili, N.PH. Kvashali, R.M. Bagishvili, and Z.A. Zurabashvili. 1977. Agricultural applications of natural zeolites in the Soviet Union. Institute of physical and organic chemistry, Academy of sciences of the Georgian S.S.R., Jykia 5, Tbilisi 380086, Georgia, U.S.S.R.
- Vidal, C. 2000. Twenty years of agriculture in Europe – ever larger holdings but different economic situations, *Statistics in focus, agriculture and fisheries*, Theme 5 – 9/2000, Eurostat, Luxembourg.
- Vrzgula, L., and P. Bartko. 1984. Effects of clinoptilolite on weight gain and some physiological parameters of swine. In: W.G. Pond and F.A. Mumpton (ed.) *Zeo-agriculture: Use of natural zeolites in agriculture*

and aquaculture. International committee on natural zeolites.

Westview Press, Boulder, CO. p. 129-146 and p. 161-167.

Woestyne, M.V., and W. Verstraete. 1995. Biotechnology in the treatment of animal manure. In Biotechnology in animal feeds and animal feeding. VCH Verlagsgesellschaft mbH, Weinheim, Germany. p. 311-327.

Yannakopoulos, A., A. Tserveni-Gousi, A. Kassoli-Four-Naraki, A. Tsirambides, K. Michailidis, A. Filippidis, and U. Lutat. 2000. Effects of dietary clinoptilolite-rich tuff on the performance of growing-finishing pigs. In: Natural zeolites for the third millenium. Eds Coela, C. and Mumpton, F.A. N Napoli, Italy: De Frede Editore. p. 471-481.

ZeoponiX, Inc. and Boulder Innovative Technologies, Inc. 2000. Zeolite: The versatile mineral. 2910 Juilliard Street, Boulder, CO 80305 USA. Available at <http://www.zeoponix.com/zeolite.htm> (accessed March 2007).

Table 2.1: General physical properties of zeolite¹.

Properties	Unit	Descriptions
Specific density	Kg/m ³	2.16
Bulk density	Kg/m ³	0.85 – 1.1
Hardness	Mohs scale	3.5 – 4
Alkaly stability	pH	7 – 11
Acid stability	pH	2 – 7
Moisture content	%	7 – 9
Absorbing gases	-	NH ₃ , H ₂ S
Color	-	Greenish, Ivory

¹ Emfema (2005).

Table 2.2: Zeolite (clinoptilolite) tests as feed additives at different supplement levels in swine, cattle, chicken, lamb, and rat's mice and rat's diets.

Animal types	Animal age (weeks)	Zeolite used % (by weight)	Clinoptilolite % in zeolite	Impacts		Zeolite origin/Feed composition	References
				Beneficial	Adverse		
<u>Swine</u>							
Cross bred sows	-	2	85	Higher litter size & higher piglet wt. at birth, & higher piglet wt. gain during lactation	Reduction of no. of piglets with splay-legs, & with swelling and reddening of vulva	Zeolite originated from North eastern Greece, 21.6% crude protein (CP) & 3.4 MJ/kg metabolic energy included in diets	Papaioannou et al., 2002
Cross bred gilts & sows	-	2	77	Higher litter size & higher piglet wt. at birth, & higher piglet wt. gain during lactation	No adverse or side effects		
Grower hogs	-	3	70	-	Klinofeed resulted in lower wt. gain due to its dilution effect on feed value, increased N excretion in feces however, it decreased in urine, & did not significantly improved protein retention	0 & 3% Klinofeed with 17% CP & 3.5 Mcal/kg included in diet as feed additives	Poulsen & Oksbjerg, 1995
Grower hogs	-	2	90	Improved daily body wt. gain & feed intake	Clinoptilolite decreased liver & kidney wt., liver K also decreased	Female weanling pigs were used for the test, clinoptilolite was fine powder of <34 mesh with 15.4% CP and 3.4 Mcal/kg energy	Pond et al., 1988
Grower hogs	-	4 & 8	-	-	Clinoptilolite had no significant effects on growth rate, feed conversion rate, & carcass quality due to same CP & energy levels supplemented to all pigs		
						Zeolite originated from Japan, all the hogs received same levels of CP & energy in diets	Pearson et al., 1985

Table 2.2: Zeolite (clinoptilolite) tests as feed additives at different supplement levels in swine, cattle, chicken, lamb, and rat's mice and rat's diets (contd.).

Animal types	Animal Age (weeks)	Zeolite used % (by weight)	Clinoptilolite % in zeolite	Impacts		Zeolite origin/Feed composition	References
				Beneficial	Adverse		
Grower hogs	7	0.5	85	Metabolic energy utilization improved due to clinoptilolite & zeolite A	No effect on body wt. gain, feed intake & gain/feed ratio	15.6% of CP & 3.2 Kcal/kg of energy present in diet with 95% zeolite A at 0.3% by weight	Shurson et al., 1984
Grower hogs	13	5	85	No effect on hog performance & also, no effect on metabolic energy utilization	-	13.5% of CP & 3.2 Kcal/kg of energy present in diet with 95% zeolite A at 1.0% by weight	Shurson et al., 1984
Grower hogs	1	2.5, 5 & 7.5	85	Clinoptilolite reduced odourous p-cresol in feces	Zeolite A showed linear decrease of mineral retention in hogs stomach (Ca, Fe, Mg, Na & P)	13.5% of CP & 3.2 Kcal/kg of energy present in diet with 95% zeolite A at 0, 1, 2 & 3% by weight	Shurson et al., 1984
Grower hogs	2	2.5, 5 & 7.5	85	Clinoptilolite reduced blood plasma NH ₃ level	Zeolite A showed no adverse effect on blood plasma NH ₃ level No effect on blood hemoglobin, hematocrit, plasma urea-N, serum protein, albumin, alkaline phosphate, Ca & P;	Zeolite A (95% clinoptilolite) at 0, 1, 2 & 3% by weight were mixed with diets	Shurson et al., 1984
Castrated hogs (male)	5	5	60 & 72	-	decrease of wt. gains were observed in both cases however, New Mexico zeolite showed lower gain rate than other	Zeolite possess 60% (New Mexico, <50 mesh) & 72% (Idaho, <16 or 50 mesh) clinoptilolite at 17% CP & 3.5 Mcal/kg energy level	Pond and Lee, 1984
Weanling pigs	10	5	60	Feed conversion rate was not affected, clinoptilolite solved diarrheal problem	Lowering of wt. gain reported in both cases	5% clinoptilolite & 4% ammonium carbonate with 15% CP & 3.4 Mcal/kg energy mixed in diets separately	Pond and Lee, 1984

Table 2.2: Zeolite (clinoptilolite) tests as feed additives at different supplement levels in swine, cattle, chicken, lamb, and rat's mice and rat's diets (contd.).

Animal types	Animal age (weeks)	Zeolite Used % (by weight)	Clinoptilolite % in zeolite	Impacts		Zeolite origin/Feed composition	References
				Beneficial	Adverse		
Grower hogs	4 to 5	3	60	No trt. effects were noticed except clinoptilolite slightly increased wt. gain, liver Cd increased with addition of Cd in feed however, the increase was less with clinoptilolite	-	Clinoptilolite with granular or <50 mesh from New Mexico & synthetic zeolite A with or without 92ppm Cd were used as feed additives	Pond and Lee, 1984
Hogs	-	3 & 5	95	Decrease of urinary P	Increase of urinary energy loss due to tyrosine, reduction of energy absorption efficiency of hogs due to zeolite A; increase of N excretion & fecal excretion of Ca, Fe, K, Na & P; & also increase of urinary Ca, Fe, Mg & Na; lower N ingestion efficiency caused increase of urine p-cresol	Zeolite A with or without 3% tyrosine at 4.0 Mcal/kg energy level was included as feed additives in diet	Shurson et al., 1984
Sows	72 to 108	2.5 & 5	-	Due to dilution effect of clinoptilolite on feed energy & CP levels the wt. gains were significantly less with 5% clinoptilolite in comparison to 0 & 2.5%, feeding of 2.5 & 5% clinoptilolite decreases ovulation rate by 1 & 2.2 ova respectively however didn't significantly affect the embryo survival rate	-	Zeolite originated from Taipei, Taiwan; & fed as powder (<120 mesh) after drying at 400°C with 15.9% CP & 3.1 Mcal/kg energy in diets	Ma et al., 1984

Table 2.2: Zeolite (clinoptilolite) tests as feed additives at different supplement levels in swine, cattle, chicken, lamb, and rat's mice and rat's diets (contd.).

Animal types	Animal age (week)	Zeolite Used % (by weight)	Clinoptilolite % in zeolite	Impacts		Zeolite origin/Feed composition	References
				Beneficial	Adverse		
Grower hogs	12	5	40 to 60	Daily wt. gain increased by 17%, serum blood characteristics not affected by clinoptilolite however increase of blood serum Ca, Mg, P, Na, K, Co & Fe; Se & Mn levels dropped; liver function was not affected by clinoptilolite; decrease of Se & Mn levels noticed	-	Zeolite originated from Nizmy Hrabovec, Czechoslovakia	Vrzgula and Bartko, 1984
Grower hogs	12	5	40 to 60	Wt. gain increased by 20%, diarrhetic hogs with clinoptilolite produce firmer feces after 6 hrs & treated hogs gained wt. twice as fast as compared to non treated hogs	Reduction in daily wt. gain at first 30 days however after 30 days there was no such problem noticed	Zeolite originated from Nizmy Hrabovec, Czechoslovakia	Vrzgula and Bartko, 1984
Grower hogs	-	5	40 to 60	Wt. gain/feed conversion increased from 0.44 to 0.54 kg body wt./kg feed; clinoptilolite corrected the diarrhea, & significant wt. gain observed	No difference noticed in clinical observations	Zeolite originated from Nizmy Hrabovec, Czechoslovakia; CP of 15.3% & digestible energy of 2.9 Kcal/kg were included in diets	Nestorov, 1984
Grower hogs	-	5 & 10	95	Clinoptilolite at 10% produced higher wt. gain & better feed conversion, the larger particle size of clinoptilolite resulted in better stomach stability and improved performance, clinoptilolite produced hogs with 24% less body fat but with more muscle mass	Feces contained more solids, more Ca ingestion through bone deposition however same K ingestion & clinoptilolite produced more NH ₃ in jejunum	Zeolite (particle size 2.4 to 3.4 mm) from Ash Meadows, California; 18.5% CP & 3.3 Kcal/kg energy included in diets as feed additives	Cool and Willard, 1982

Table 2.2: Zeolite (clinoptilolite) tests as feed additives at different supplement levels in swine, cattle, chicken, lamb, and rat's mice and rat's diets (contd.).

Animal types	Animal age (week)	Zeolite Used % (by weight)	Clinoptilolite % in zeolite	Impacts		Zeolite origin/Feed composition	References
				Beneficial	Adverse		
Grower hogs	5	10	85	No effect on body wt. gain, feed intake & gain/feed ratio	No effect on blood traits (Ca, Mg, alkaline phosphatase, hemoglobin, hematocrit, protein)	Zeolite (New Mexico) with particle size < 50 mesh & 19% CP & 3.4 Mcal/kg energy included in diets.	Pond & Yen, 1982
Grower hogs	5	5	85	No effect on body wt. gain, feed intake & gain/feed ratio	-	Zeolites (New Mexico) with particle size < 50 mesh. 14% CP & 3.2 Mcal/kg	Pond & Yen, 1982
Grower hogs	5	5	85 & 92	Lowest wt. gain with 92% clinoptilolite & slower daily wt. gain with 85% clinoptilolite in diets	No toxic effects	Clinoptilolite content of zeolite from New Mexico (size <50 mesh) & Idaho (<16) were 85 & 92% respectively	Pond & Yen, 1982
Grower hogs	-	2.5, 5, 7.5 & 10	-	Clinoptilolite at 5% and 7.5% produced higher but not significant wt. gain & better feed conversion	Clinoptilolite produced dry feces with higher total solid content	Feed of molasses, soybeans & yeast with 16% CP & 3.8 Kcal/kg energy included in diets; zeolites from Cuba	Castro and Elias, 1978
<u>Cattle</u>							
Steers	-	4.3	-	Mean daily wt. gain of clinoptilolite fed steers were 17% higher than regular diets fed steers	-	Granulated urea-clinoptilolite mixture (called Carbazin) was tested in young beef cattle. Carbazin contained clinoptilolite ground to <0.1mm, urea, dicalcium phosphate, a mineral nutrition mixture, & a binding agent	Nestorov, 1984

Table 2.2: Zeolite (clinoptilolite) tests as feed additives at different supplement levels in swine, cattle, chicken, lamb, and rat's mice and rat's diets (contd.).

Animal types	Animal age (week)	Zeolite used % (by weight)	Clinoptilolite % in zeolite	Impacts		Zeolite origin/Feed composition	References
				Beneficial	Adverse		
<u>Chicken</u>							
Broilers	Pre-starting, starting & finishing periods	0.5, 1.0& 1.5	-	Zeolite fed bird's body wt. gain was 3.6% higher than the regular diet fed birds	-	Clinoptilolite from Kurdzali, Bulgaria. The natural CLI-rich ore ground to <0.1mm & pretreated to Ca > K & K > Ca forms, contained 67-72% SiO ₂ , 10-13%Al ₂ O ₃ , <1.5% Fe ₂ O ₃ , ≤0.25% TiO ₂ , 1.5-3.5% CaO, 0.3-0.8% MgO, 2.5-5.0% K ₂ O	Nestorov, 1984
<u>Lambs</u>							
Male lambs	-	3	60	Clinoptilolite improved wt. gain when fed with corn, soybean & urea both improved wt. gain when added to diet of corn alone	Zeolite A decreased the weight gain	Zeolite originated from New Mexico, granular or <50 mesh in size, synthetic zeolite A was also tested as feed additives to regular feed (corn & urea)	Pond and Lee, 1984
Lambs	-	5	-	Mean daily wt. gain of clinoptilolite fed lambs were 5% higher than regular diets fed lambs	-	Clinoptilolite from Kurdzali, Bulgaria. The natural CLI-rich ore ground to <0.1mm & pretreated to Ca > K & K > Ca forms, contained 67-72% SiO ₂ , 10-13%Al ₂ O ₃ , <1.5% Fe ₂ O ₃ , ≤0.25% TiO ₂ , 1.5-3.5% CaO, 0.3-0.8% MgO, 2.5-5.0% K ₂ O	Nestorov, 1984

Table 2.2: Zeolite (clinoptilolite) tests as feed additives at different supplement levels in swine, cattle, chicken, lamb, and rat's mice and rat's diets (contd.).

Zeolite origin/Feed composition								References
Animal types	Animal age (week)	Zeolite used % (by weight)	Clinoptilolite % in zeolite	Impacts				
				Beneficial	Adverse			
<u>Mice</u>								
<u>Mice</u>								
<u>and rats</u>								
Female mice	12	12.5, 25& 50	85	In serum, clinoptilolite increased K by 20%, but not Na & Cl; & for the mice with tumours, clinoptilolite improved declined Na& Cl in the blood serum	-	Fine powdered zeolite (particle size< 4.3 µm) originated from Southern Serbia, fed to the mice with implanted tumour cells	Martin-Kleiner et al., 2001	
Growing rats (adult)	-	20	60	Clinoptilolite absorbed less N than its full binding capacity due to its less purity (60%)	Higher pH at lower stomach releases some N from clinoptilolite	Sampling was done after 30 minutes of stomach injection with 20% Clinoptilolite or ammonium carbonate solution, zeolite originated from New Mexico which was <50 mesh in size	Pond and Lee, 1984	
Weanling rats	-	5	60	No effect on wt. gain due to clinoptilolite or ammonium carbonate	Addition of both lowered wt. gain due to their diluting effect on feed	Clinoptilolite (5%) & ammonium carbonate (4%) with 15% CP & 3.4 Mcal/kg digestible energy used as feed additives, zeolite originated from New Mexico (<50 mesh in size)	Pond and Lee, 1984	

Table 2.2: Zeolite (clinoptilolite) tests as feed additives at different supplement levels in swine, cattle, chicken, lamb, and rat's mice and rat's diets (contd.).

Animal types	Animal age (week)	Zeolite used % (by weight)	Clinoptilolite % in zeolite	Impacts		Zeolite origin/Feed composition	References
				Beneficial	Adverse		
Female rats (adult)	-	5	60	Addition of both clinoptilolite &/ or ammonium carbonate had no effect on wt. gain of pups, clinoptilolite when used with ammonium carbonate reduced the wt. loss of dam after lactation	Ammonium carbonate reduced the dam wt. after lactation	Clinoptilolite (5%) & ammonium carbonate (4%) with 15% CP & 3.4 Mcal/kg digestible energy used as feed additives, zeolite originated from New Mexico (<50 mesh in size)	Pond and Lee, 1984
Female rats	-	5	60 & 72	No effect on body wt. gain during gestation or lactation or number & size of pups	-	New Mexico (granular or < 50 mesh size) & Idaho (<16 & 50 mesh size) used as feed additives in diets with 17% CP & 3.5 Mcal/kg digestible energy & also with or without antimicrobial agent replacing zeolite	Pond and Lee, 1984
Female rats	-	3	60 & 72	Treatment had no effect on body weight gain	-	New Mexico (granular or < 50 mesh size) & Idaho (<16 & 50 mesh size) used as feed additives in diets with 17% CP & 3.5 Mcal/kg digestible energy & also with or without antimicrobial agent replacing zeolite	Pond and Lee, 1984

CONNECTING STATEMENT TO CHAPTER THREE

Intensification of swine farming results in an excess nutrient accumulation in soil and water bodies, affecting both terrestrial and aquatic ecosystems. Zeolite as a swine feed additive is expected to lower the manure nutrient content so that the negative impact due to the excessive application can be reduced. Zeolite application in swine manure is expected to have a positive impact on shear viscous properties (shear stress and shear rate), and its application as a swine feed additive is expected to change the physical characteristics (friction coefficient and velocity) of manure at the production source. This change in manure properties is expected to reduce handling, pumping and transportation costs that could encourage swine farmers to shift their excess manure to regions with a deficit; and minimize the nutrient overloading problems in fresh water bodies. Therefore, the following chapter investigates the effect of zeolite (90%+ clinoptilolite) as a feed additive on manure characteristics such as total solids (TS), total carbon (TC) and nutrient (TN, TP and TK) content; manure viscosity, shear stress and shear rate; and manure odour.

CHAPTER THREE

EFFECT ON MANURE CHARACTERISTICS OF SUPPLEMENTING GROWER HOG RATION WITH CLINOPTILOLITE

ABSTRACT

Diet manipulation, such as zeolite (clinoptilolite) supplementation, can reduce manure nutrient content but such a practice may negatively impact on manure handling properties. Therefore, the objective of the present study was to measure the impact on manure physico-chemical properties of supplementing grower hog rations with 4% zeolite (90%+ clinoptilolite). The manure was produced in triplicate by feeding one of four experimental rations, each to three hogs for 4 weeks. During the last week, the hogs were placed in metabolic cages to individually collect, measure and characterize their manure. The four rations consisted of a control with 100% crude protein (CP) and energy requirements (R1), and a three 4% zeolite added rations with a CP and energy of 100% and 100%; 90% and 90% and; 90% and 85% (R2, R3 and R4), respectively. Ration R2 gave the best results in terms of lower manure nutrient content, but had a higher level of urine as compared to the control ration R1. The rations R3 and R4 produced manure mostly with a higher total solid (TS) level. The addition of zeolite to the ration improved the flow characteristics of the manure, especially for rations R3 and R4. Zeolite manually added to manure had no effect on its viscosity even if it increased the manure TS (%). Rations R3 and R4 emitted less odours after an aging period of 67 days, as compared to ration R1; ration R2 produced less odours than ration R1, although not statistically significant ($P>0.05$). Thus, swine diets supplemented with a zeolite (clinoptilolite) can lower the manure nutrient content without altering its physical properties. Further research is required with rations containing different levels of CP and energy.

Keywords: Clinoptilolite, grower hogs, viscosity, odour, manure physical characteristics.

3.1 Introduction

In many regions of North America and Europe, the intensification of livestock farms has resulted in the land application of manure nutrients in excess of that required by crops (Burton and Turner, 2003; Statistics Canada, 2007). As a result, agricultural soils have become overloaded with nutrients, such as nitrogen (N) and phosphorous (P), and their drainage and erosion has enriched downstream lakes and rivers. The resulting aquatic plant growth, including the rapid algae bloom, has increased the incidents of oxygen (O₂) depletion in water bodies leading to fish kills and drinking water deterioration (Falconer and Humpage, 2005).

Because livestock manures are generally rich in N, especially in the form of ammonium, its management has contributed to over 50% of the total atmospheric ammonia (NH₃) emissions in Europe (ECETOC, 1994; Jarvis and Pain, 1990; Klaasen, 1994; Summer and Hutchings, 2001). In Canada, livestock manure produced 70% of all atmospheric NH₃, and the application of chemical fertilizer increased this percentage to 90% (Kurvits and Marta, 1998). As a result, N is being deposited on land and water surfaces at rates exceeding 20 kg/ha, which is affecting sensitive ecosystems such as wetlands and the Mediterranean Sea (Asman et al., 1998; Asman and van Jaarsveld, 1991).

Reducing the nutrient load of livestock manures can help to mitigate the problems associated with soil, water and air contamination. According to Jongbloed and Lenis (1998), only a 30 to 35% of minerals such as N and P, are absorbed by the digestive track of hogs, as opposed to 70% for carbohydrates. Therefore, any feed additive which improves mineral digestion can have a major impact on manure nutrient load and soil enrichment in areas with a high livestock density.

Clinoptilolite is a specific type of zeolite, which when used as swine feed additive, can potentially improve nutrient digestion and lower odour emissions from urine and feces (Sutton et al., 1999). Furthermore, Sutton et al.

(1999) reported a reduction in manure NH₃ emissions of 28 to 79%, as a result of zeolite diet supplementation. The primary odour-producing compound in swine manure evolves from the poor digestion of specific carbohydrates and the excessive feeding of proteins. Zeolite supplementation in a grower hog ration resulted in a lower manure N and P levels (Cromwell et al., 1998; Sutton et al., 1999; Jongbloed and Lenis, 1998). Zeolite improved the digestibility of crude protein (CP) and nitrogen-free extracts (Han et al., 1976), and reduced the dietary CP requirements while minimizing the manure NH₃ emissions (Otto et al., 2003).

If a zeolite can have a positive impact on manure nutrient digestion at inclusion rates of 2 to 10%, it can also change the properties of manure, a topic which has not been intensively researched. Because zeolite does not break down within the digestive track of livestock (Leung et al., 2006), it can potentially increase the total solids (TS) content of manures. For example, when included in a ration at a rate of 4% by weight, a zeolite can increase the manure TS from 5 to 6%, assuming that 70% of the feed carbohydrates are digested. Accordingly, the supplementation with zeolite of livestock ration can increase the kinematic viscosity of manure which in turn, can require a more handling and pumping energy.

The kinematic viscosity of manure was found to increase with TS (Chen and Shetler, 1983; Chen, 1986; Landry et al., 2004). Keener (2005) reported a 10 to 80 fold increase in kinematic viscosity for a TS going from 0 to 5 and 10%, respectively. Manure slurries are known to be Newtonian fluids for TS under 5% (Kumar et al., 1972) and non-Newtonian pseudoplastic fluids above 5% (Landry et al., 2004). Hashimoto and Chen (1976) suggested the use of a rheological consistency coefficient (K), and a rheological behaviour index (n), to express the variation in manure viscosity with its TS. For a shear rate of 10 s⁻¹, Landry et al. (2004) used a similar expression to predict the apparent viscosity of swine manure as a function of TS:

$$\eta_{\text{app}} = 4 \times 10^{-6} \text{ TS}^{4.6432} \quad (3.1)$$

Where,

TS is total solids of the manure in % and η_{app} is the apparent viscosity in Pa-s.

Therefore, the objective of this paper was to observe the effect of zeolite (90%+ clinoptilolite), as grower hog feed additive, on the characteristics of manure produced, namely: mass, TS, mineral content, total carbon (TC), loss of N during storage, flow characteristics and odour emissions. The evolution of TS, TN and TC was measured during an aging period of 67 days at a 24 °C, whereas the flow characteristics, viscosity and odour emissions were measured at the end of this period. In a second experiment designed to observe the effect of zeolite on manure viscosity, without the effect of fat in the ration, 0%, 2% and 4% zeolites were added to the fresh swine manure to measure its viscosity.

3.2 Methods and materials

3.2.1 Experimental materials

The experimental manures were produced with grower hogs housed at the swine unit of the Macdonald Campus Experimental Farm, of McGill University, Montreal, Canada. All hogs were cross-bred ($\frac{1}{2}$ Duroque, $\frac{1}{4}$ Landrace and $\frac{1}{4}$ Yorkshire).

These hogs were raised in a grower room measuring 14.75 m \times 7.20 m and 3.05 m in height, with 16 pens of 3.00 m \times 1.84 m, offering 0.92 m²/hog. A central alleyway serviced the two lateral rows of 8 pens with a fully slatted floor. The feeders were placed against the alleyway and hogs were offered feed ad libitum. The grower room was ventilated at a rate ranging from 5 to 48 L/s/hog, using a central air inlet with baffles pivoting against weights and a fan bank in one corner of the end wall.

The stainless steel metabolic cages used in this experiment were housed in a laboratory measuring 16.25 m \times 7.6 m and 3.05 m in height, ventilated at a rate of 5 to 48 L/s/hog and maintained at 24 °C. The metabolic

cages measured 0.60 m in width by 1.8 m in length and the bars inside the cage could be adjusted to restrain the hog in a position close to the feeder, while still allowing the animal to lie down and get up. Under the plastic mesh flooring of each cages, two trays were used to collect the urine and feces; the top tray was perforated to allow the urine to drain into the second non-perforated tray. Females were used for this experiment to facilitate the collection of the feces and urines in the trays at the back of the cages.

The four experimental rations (control or R1, and the 4% zeolite added rations, R2, R3 and R4) were prepared from corn and soybeans by Agri-brands Purina Canada Inc, St-Hubert, Quebec (Table 3.1). The rations R1 and R2 were formulated to meet the nutrient requirements for finishing grower hogs (NRC, 1998) while rations R3 and R4 offered 90% of the crude protein (CP) and 90 or 85% of the energy requirements, respectively.

Supplied by KMI mines of Nevada, USA, a zeolite (90%+ clinoptilolite) at the rate of 4% was incorporated into the rations R2, R3 and R4. Its clinoptilolite content was determined by Core Laboratories Inc. of Calgary, Canada, using XR diffraction and by comparing the fingerprint to that of a pure sample (Table 3.2).

3.2.2 Methods

Twenty four female hogs weighing 30 (\pm 2) kg were randomly assigned to one of four groups where each group was housed in a single pen inside the grower room. Each pen was randomly assigned to one of the four diets fed ad libitum until the hogs weighed 60 (\pm 5) kg, a process which took three weeks. Three hogs from each pen were then randomly selected and transferred into individual metabolic cages where they continued to receive the same ration.

In the metabolic cages, the hogs were offered feed and water ad libitum. From the third to the seventh day (over four days), the feces and urine produced by each hog were collected separately, weighed at the end of the

period, mixed together and analyzed for TS, TC and nutrients (TN, TP and TK). This manure was used to determine the effect of zeolite supplementation on manure characteristics. Thus for each one of the four experimental rations, three manure samples (one per experimental hog) were collected, aged and tested for various parameters.

The research protocol, including the care and feeding of the animals, was approved by the Animal Care Committee of McGill University in accordance with the Canadian Council on Animal Care Guidelines (Appendix).

The twelve large manure samples were aged in a room maintained at 24 °C for 67 days, in 20 litre (L) containers with a depth of 0.4 m. During this period, water was added to the manure at a rate of 1L per month, to prevent from drying out. The aging of manure at 24 °C for slightly over two months was presumed to represent a normal Canadian storage period of 6 months at 10 °C, as microbial activity doubles with every 10 °C of temperature. The effect of supplementing hog rations with a zeolite (90%+ clinoptilolite) was measured by sampling all manures at the beginning and end of this 67 days period, and analyzing these samples for TS, TC, TN, TP and TK; and by measuring their odour emission and flow rate at various TS under an hydraulic head of 1.8 m.

For each ration, triplicate manure samples were analyzed for odour emission by uniformly spreading over a sand surface inside an air tunnel where the air was blown at a rate of 3 m/s. Air was sampled at the inlet and outlet of the tunnel to determine its threshold dilution using six panellists and a forced-choice dynamic olfactometer (CEN, 2006; Choinière and Barrington, 1998).

The Brookfield rotary viscometer could not be used to measure the viscosity of the manure samples collected from the metabolic cages because of its limitations to values above 10^{-2} Pa-s (10 centipoises). Therefore, a laboratory apparatus was set-up to compare the flow rate of each manure sample exposed to a hydraulic head of 1.8 m (Fig. 3.1). This apparatus

consisted of a long funnel feeding manure into a 9 mm inside diameter (D) rubber tube emptying into a bucket, under a pressure head of 1.8 m. The time required to feed 6 L of well mixed manure into this apparatus measured its flow rate, v , and therefore the resulting friction factor, f , according to Daily and Harleman (1966):

$$v = V/t / (\pi D^2/4) \quad (3.2)$$

$$f = 2gh_L/(L/D)/v^2 \quad (3.3)$$

Where,

v is the velocity of manure flowing through the rubber tubing, m/s; V is the volume of manure fed through the rubber tubing, 0.006 m³; t is the time required to feed V through the apparatus, s; D is the inside diameter of the rubber tubing, 0.009 m; f = friction factor; g is the gravitational constant, 9.81 m/s²; h_L is the hydraulic manure head, 1.8 m; and L is the length of the rubber tubing and funnel neck, 1.6 m.

Before each flow test, the apparatus was filled with part of the well mixed manure sample, and immediately after, 6 L of this same manure was poured into the funnel while keeping its level constant. The time required to have a 6 L sample flow through the apparatus was measured using a stop watch. Because the manure sample was well mixed before hand and the entire process took less than 2 minutes, the manure solids had little time to settle. Each one of the twelve manure samples collected from the metabolic cages were used at its original TS and then at two other dilutions, except for the manures from ration R2 which were already quite dilute, as compared to the others.

To further understand the impact of zeolite on manure viscosity, zeolite was added to fresh manure from the same large sample to measure the resulting viscosity. The first test consisted in comparing manure flow properties using once more the funnel apparatus, but with a hydraulic head of 0.3 m. The second test consisted in measuring the manure viscosity with a standard Brookfield rotary viscometer (Model LVDVE 115, Serial No. E8216, Middleboro, MA) equipped with 4 different spindles (S61, S62, S63 and S64).

A large fresh manure samples with an initial TS content of 10% was split into triplicate sets of sub-samples where the first set was placed aside as control, while the second and third received 2% and 4% zeolite, respectively. The viscosity of each set of sub-sample was measured with the Brookfield rotary viscometer first with its original 10% TS, and then once diluted to 8%, 6%, 4% and 2%. The dynamic viscosity of each manure treatment was measured using a 500 ml volume of each manure sample.

3.2.3 Analytical method

Total solids (TS) were determined in triplicate by drying 100 g samples at 103 °C for 24 h (VWR, Sheldon Manufacturing Inc., Model No. 1327F, Serial No. 09020405, USA). The TS values were calculated as:

$$TS(\%) = \{(C - A)/(B - A)\} \times 100 \quad (3.4)$$

Where,

A is the weight of the container; B is the weight of the container with the wet sample, and; C is the weight of the container with the dry sample.

Total carbon (TC) was determined by incinerating dried samples at 500 °C, calculating the volatile fraction from the ash content, and dividing the volatile fraction by 1.83 to obtain the TC content. The total nitrogen (TN) was assumed equal to the Total Kjeldahl Nitrogen (TKN) since very little nitrate-nitrite was found in the manure samples. All TN, total phosphorous (TP) and total potassium (TK) analysis were obtained from a sample digested at 500 °C using sulphuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2). TN was quantified from this digested sample using an ammonia sensitive probe connected to a pH meter (Corning Model 450, NY, USA) after adjusting the pH to 13, and TP and TK were quantified colorimetrically using a spectrophotometer (Hach DR 2800, Type LPG, Loveland, CO, USA) after adjusting the pH to 7.0. All pH adjustments were done with 1 and 5 M NaOH solutions and 1 M solution of HCl.

3.2.4 Statistical analysis

The effect of different rations on the properties of manure was analyzed using ANOVA (SAS, 2004) for a completely randomized design (CRD). The standard deviation for the various parameters reported was calculated using Excel (Microsoft, 2003).

3.3 Results and discussion

3.3.1 Effect of zeolite on nutrient content

Table 3.3 presents the quantity and quality of manure produced by the hogs fed one of the four rations in triplicate. This table also reports the changes in manure TS, TN and TC over the 67 days period. The quantity of manure produced was not statistically different ($P>0.05$) except for that produced by ration R3 where hogs on ration R3 produced more manure than those on rations R1 and R4. The TS (%) differed among the manures produced from the different rations, but the mass of total solids (kg) did not. The manure produced by the hogs on ration R4 had the most TS (%), followed by rations R3 and R1 with an intermediate level, and ration R2 with the lowest TS (%). Rations R1 and R2 produced the least total mass of TS ($P>0.05$), followed by ration R4 and then ration R3. The mass of TS was greater in ration R3 than ration R4 ($P<0.05$), and ration R4 produced a greater TS mass than rations R1 and R2 ($P<0.05$). Accordingly, supplementing the ration of hogs with a zeolite can have an impact on manure mass and TS (%). Based on other metabolic studies conducted with the same ration and zeolite (Wan, 2005), the energy and crude protein (CP) level of the ration along with the addition of zeolite, for a given hog growth stage, can have an impact on the final TS (%) level of the ration.

In terms of total nitrogen (TN), no ration produced manure with a statistically different quantity ($P>0.05$), especially because of the large variation in results. Nevertheless, ration R2 produced the least TN, while rations R3 and R4 produced the highest levels. Ration R2 produced manure with statistically less total phosphorous (TP), followed by that of ration R1,

and then by that of rations R3 and R4 with the most. Rations R1 and R2 produced significantly less total potassium (TK) than that of rations R3 and R4. Thus, zeolite supplementation had a positive effect on lowering the TP content of the manure; it may also have a positive effect on lowering that of TN, if the experiment was repeated using more subjects.

Over the period of 67 days, only the manure TN content changed significantly ($P < 0.05$). The TKN analyses are said to represent the TN content of the manure because of their low nitrite/nitrate levels. The ration R2 lost the most nitrogen (18%), followed by the R3 and R4 rations with 9% and 8% loss respectively; and then the R1 (control) ration with 4% loss. Therefore, the supplementation of zeolite in the ration did not reduce the volatilization of NH_3 from the manure in storage. This loss of N during storage was neither related to initial N nor initial TS content. These results are different from those observed by Sutton et al. (1999), likely because of the high storage temperature which enhances ammonia volatilization.

3.3.2 Effect of zeolite on manure flow and viscosity

Fig 3.2a illustrates the velocity resulting from having each of 12 manure samples, flow through a 9 mm inside diameter rubber tube under a hydraulic head of 1.8m. The regression analysis of the data indicated that the resulting velocity was linearly related to manure TS:

$$v_{R1} = 4.1684 - 0.3826 \text{ TS} \quad R^2 = 0.98 \quad (3.5)$$

$$v_{R2} = 6.3857 - 0.6857 \text{ TS} \quad R^2 = 0.65 \quad (3.6)$$

$$v_{R3} = 7.4654 - 0.6749 \text{ TS} \quad R^2 = 0.64 \quad (3.7)$$

$$v_{R4} = 10.987 - 0.7406 \text{ TS} \quad R^2 = 0.64 \quad (3.8)$$

Where,

v is the velocity of manure flowing through the rubber tubing, m/s, and its suffix indicates the ration tested, and TS is the total solids of the manure in %. For the same TS (%), rations R1 produced manure with a statistically lower velocity, followed by the manure from rations R2 and R3, and then manure from ration R4.

The resulting velocity was used to compute the friction coefficient, and the following power regression equations:

$$f_{R1} = 1.49 \times 10^{-7} \times TS^{6.7408} \quad R^2 = 0.93 \quad (3.9)$$

$$f_{R2} = 1.034 \times 10^{-14} \times TS^{14.90} \quad R^2 = 0.67 \quad (3.10)$$

$$f_{R3} = 6.79 \times 10^{-8} \times TS^{6.6225} \quad R^2 = 0.72 \quad (3.11)$$

$$f_{R4} = 1.42 \times 10^{-6} \times TS^{4.059} \quad R^2 = 0.58 \quad (3.12)$$

Where,

f is the friction coefficient obtained from Eq. (3.3) for manure flowing through the rubber tubing, dimensionless, and its suffix indicates the ration tested, and TS is the total solids of the manure in %.

In terms of friction coefficient, all rations demonstrated the same friction coefficient below a 7% TS, but for the higher TS values, the friction coefficient changed significantly with rations, ration R1 giving the highest value followed by the rations R2, R3 and R4; in decreasing order of significance ($P < 0.05$). The greater difference between rations R1 and R2, versus rations R3 and R4, likely resulted from the higher ration fat level. Rations R1 and R2 were formulated with a 7% fat whereas rations R3 and R4 were formulated with a 2% fat.

Interestingly enough, the flow apparatus (Fig 3.1) was initially tested using water (results not shown). As compared to the flow rate obtained with water at the same temperature, the manure from rations R3 and R4 demonstrated higher flow rate for TS under 7.5% and 9%, respectively. Manures from ration R2 demonstrated the same flow rate as water for TS content under 7.5%, and manure from ration R1 demonstrated lower flow rates as compared to water for TS down to 6.5%. The behaviour of the manure produced from ration R1 is typical of that reported by Loerh (1984) which indicates that below 4% TS, the manure behaves like water. But, for the manure produced from a diet supplemented with zeolite, the swine manure could show lower viscosity values, thus reducing the energy required for pumping, as compared to water and highly diluted manures.

To further verify the effect of zeolite on manure viscosity, more tests were conducted in the laboratory whereby zeolite was directly added to manure samples (Figs. 3.3a, 3.3b, 3.3c and 3.3d). Adding 2% and 4% zeolite to manure with 4%, 6%, 8% and 10% TS, did not significantly change its viscosity ($P>0.05$), despite the fact that the zeolite did increase the TS of the manure. The relationship between manure TS (excluding the addition of solids from zeolite) and the resulting apparent viscosity (Pa-s), at a shear rate of 10 s^{-1} (as used by Landry et al., 2004) gave the following regression equation:

$$\eta_{\text{app}} = 4.62 \times 10^{-4} \text{ TS}^{2.552} \quad R^2 = 0.93 \quad (3.13)$$

Where,

TS is total solids of the manure in % and η_{app} is the apparent viscosity in Pa-s. This equation differs from that obtained by Landry et al. (2004) (Eq. 3.1) likely because of the ration formulations. Nevertheless for a 4% manure TS, Eq. (3.13) gives an apparent viscosity of $1.6 \times 10^{-3} \text{ Pa-s}$, which is close to the observed $1.0 \times 10^{-3} \text{ Pa-s}$ value reported by Loerh (1984).

3.3.3 Odour

The odour emissions obtained inside the wind tunnels for the manure produced from the control ration R1 and the zeolite rations R2, R3 and R4 are illustrated in Table 3.4. The manure obtained from rations R3 and R4 released significantly less odours than that from the rations R1 and R2. The ration R1 produced the most odorous manures without being statistically different from that of ration R2.

It appears that the rations with zeolite can have a positive effect on reducing manure odour emissions, especially when the CP and energy content is reduced. Zeolite inclusion in the ration may have a secondary effect on odour emission by increasing the manure TS content, and slowing down the aging process. This was also observed by Hobbs (1996).

3.4 Conclusions

For 60 (\pm 5) kg grower hogs fed a normal finishing ration with 100% of the CP and energy requirements, 4% zeolite (90%+ clinoptilolite) as feed additive was found to reduce manure TS (%), TC and TP; to have an insignificant but lowering effect on manure TN (concentration and mass), and to have no effect on manure mass and TK. For the same hogs fed 4% zeolite added to a ration with 85% to 90% of the CP and energy, the manure produced had a higher mass and TS but more or less the same nutrient mass.

Once the manure was aged, zeolite added in the ration was found to have little effect on manure flow characteristics, as compared to the manure produced by animals on the same ration, but without zeolite (ration R2 compared to ration R1). When a zeolite was added to a ration with less fat, CP and energy, the resulting manure demonstrated a higher flow rate for the same hydraulic head, as compared to a manure produced using a control ration. These comparisons are made on the same TS basis.

When considering both the chemical and flow characteristics of the manures produced and the same normal barn dilution, ration R2 (4% zeolite and 100% energy and CP) would give a slightly more diluted manure as compared to the control R1, but much easier to handle. Furthermore, the rations R3 and R4 would produce manure with higher TS but just as easy to handle as that produced with the control ration.

When zeolite was manually added to fresh swine manure, it was found to have no significant effect on manure viscosity, despite the fact that the addition of zeolite increased the TS. Thus, adding zeolite to the ration of grower hogs is likely not to affect the flow properties of the manure, despite the increase in TS (%).

Finally, the rations with 4% zeolite and a lower CP and energy level produced manures with less odour emissions after a 67 days of aging period at 24 °C. The manure produced from 4% zeolite added ration, with full CP and energy level, did emit fewer odours but not at a statistically different level as compared to that produced using the control ration.

Therefore, zeolite supplemented rations warrant further investigations, as they can reduce manure nutrient content while not affecting its handling properties.

3.5 Acknowledgement

The Fédération des producteurs de porcs du Québec (Quebec, Canada), the Natural Science and Engineering Research Council of Canada (NSERC), Promix (Upton, Québec, Canada) and KMI Zeolites (Nevada, USA) are thanked for their generous financial support.

3.6 References

- Asman, W.A.H., and H.A. van Jaarsveld. 1991. A variable resolution transport model applied for NH_x in Europe. *Atmospheric Environment*. 26A:445-464.
- Asman, W.A.H., M.A. Sutton, and J.K. Schjørring. 1998. Ammonia: emission, atmospheric transport and deposition. *New Phyt.* 139:27-48.
- Burton, C.H., and C. Turner. 2003. *Manure management: Treatment strategies for sustainable agriculture*. Second edition. Silsoe Research Institute. Silsoe, UK. p. 9.
- CEN. 2006. Air quality - determination of odour concentration by dynamic olfactometry. prEN13725, European committee for standardization, 36 rue de Stassart, B-1050 Brussels.
<http://www.aerox.nl/images/eurstandard.pdf> (accessed August 2004).
- Chen, Y.R. 1986. Rheological properties of sieved beef cattle manure slurry: Rheological model and effects of temperature and solids concentration. *Agricultural Wastes*. 15:17-33.
- Chen, Y.R., and E.L. Shetler. 1983. Temperature effect on rheological properties of cattle manure slurry. *Journal of Testing and Evaluation*. 11(6):360-364.
- Choinière, D., and S. Barrington. 1998. The conception of an automated dynamic olfactometer. *Canadian Society of Agricultural Engineering*, Paper no. 98, Saskatchewan, Canada. p. 208.
- Cromwell, G.L., L.W. Turner, J.L. Taraba, R.S. Gates, M.D. Lindemann, S.L. Traylor, W.A. Dozier, and H.J. Monegue. 1998. Manipulation of swine diets to reduce odours and harmful gaseous emissions from manure. Final report. Department of animal science and department of biosystems and agricultural engineering, University of Kentucky, Lexington. Kentucky 40546. p. 12. Available at <http://www.porkboard.org/environment/research/researchreports/1997pdf/97-1791-cromwell-abs.pdf> (accessed 14 March 2007).
- Daily, J.W., and D.R.F. Harleman. 1966. *Fluid dynamics*. Addison-Wesley

Publishing Company Inc., Readings Massachusetts, USA.

- ECETOC. 1994. Ammonia missions to air in Western Europe, Technical report no. 62. European centre for ecotoxicology and toxicology of chemicals. Brussels, Belgium. p. 196.
- Falconer, I.R., and A.R. Humpage. 2005. Health risk assessment of cyanobacterial (blue-green algal) toxins in drinking water. *International Journal of Environmental Research and Public Health*. 2(1):43-50.
- Han, I.D., H.K. Part, and C.S. Kim. 1976. Studies on the nutritive value of zeolites. II. Effects of zeolite rich hull mixture on the performance of growing-finishing swine. *Korean Journal of Animal Science*. 18:225.
- Hashimoto, A.G., and Y.R. Chen. 1976. Rheology of livestock waste slurries. *Transactions of the American Society of Agricultural Engineers*. 19(5):930-934.
- Hobbs, P.J. 1996. Odor emission from swine manure. In: *International round table on swine odor control*. Proceedings June 1996. Iowa State University, Iowa, USA.
- Jongbloed, A.W., and N.P. Lenis. 1998. Environmental concerns about animal manure. *Journal of Animal Science*. 76:2641-2648.
- Keener, H.M. 2005. Evaluation of manure flow-ability. Department of food, agricultural and biological engineering. Ohio state university, Ohio agricultural research and development centre, 1680 Madison Avenue, Wooster, OH, 44691.
- Klaasen, G. 1994. Options and costs of controlling ammonia emissions in Europe. *European Reviews of Agricultural Economics*. 21:219-240.
- Kumar, M., H.D. Bartlett, and N.N. Mohsenin. 1972. Flow properties of animal slurries. *Transactions of the American Society of Agricultural Engineers*. 15(4):718-722.
- Kurvits T., and T. Marta. 1998. Agricultural NH₃ and NO_x emissions in Canada. In: *Nitrogen, the Confer-N-s, first international nitrogen conference*. Noordwijkerhout, the Netherlands. p. 187-193.

- Landry, H., C. Lague, and M. Roberge. 2004. Physical and rheological properties of manure products. *Transactions of the American Society of Agricultural and Biological Engineers*. 20(3):277-288.
- Leung, S., S.F. Barrington, and B. El-Husseini. 2006. Effect of particle size on physico-chemical properties of clinoptilolite as feed additive. *Microporous and Mesoporous Materials*. p. 49-57.
- Loerh, R. 1984. *Pollution control for agriculture*. Academic Press Inc., Harcourt Brace Javanovich Publishers, New York, USA.
- Microsoft. 2003. *Microsoft Office Excel 2003*. Mississauga, Ontario, Canada.
- Mumpton, F.A. 2006. Using zeolites in agriculture: Zeolite product website. Available at <http://www.zeolite-products.com> (accessed April 2007).
- National Research Council (NRC). 1998. *Nutrients requirements of pig*. Tenth edition. National Academy Press, Washington DC.
- Otto, E.R., M. Yokoyama, S. Hengemuehle, R.D. von Bermuth, T. van Kempen, and N.L. Trottier. 2003. Ammonia, volatile fatty acids, phenolics, and odor offensiveness in manure from growing pigs fed diets reduced in protein concentration. *Journal of Animal Science*. 81:1754-1763.
- SAS Institute. 2004. *SAS/STAT User's guide*. SAS for Windows. Version 9.1. SAS Institute, Inc., Cary, NC, USA.
- Sommer, S.G., and N.J. Hutchings. 2001. Ammonia emission from field applied manure and its reduction-invited paper. *European Journal of Agronomy*. 15:1-15.
- Statistics Canada. 2007. *Statistics Canada Agriculture Division*. Cat. no. 23-010-XIE. *Hog statistics*. Ottawa: Statistics Canada, Ontario. K1A 0T6. 6(1):32-35. Available at <http://www.statcan.ca/english/freepub/23-010-XIE/23-010-XIE2007001.pdf> (accessed March 2007).
- Sutton, A.L., K.B. Kephart, M.W.A. Verstegen, T.T. Canh, and P.J., Hobbs. 1999. Potential for reduction of odorous compounds in swine manure

through diet modification. *Journal of Animal Science*. 77:430-439.

Wan, Y. 2005. Metabolic effects of zeolite as natural feed supplement for grower pigs. A M. Sc. thesis submitted to McGill University, Montreal, Quebec, Canada.



Fig 3.1: Experimental set-up to compare hog manure flow characteristics.

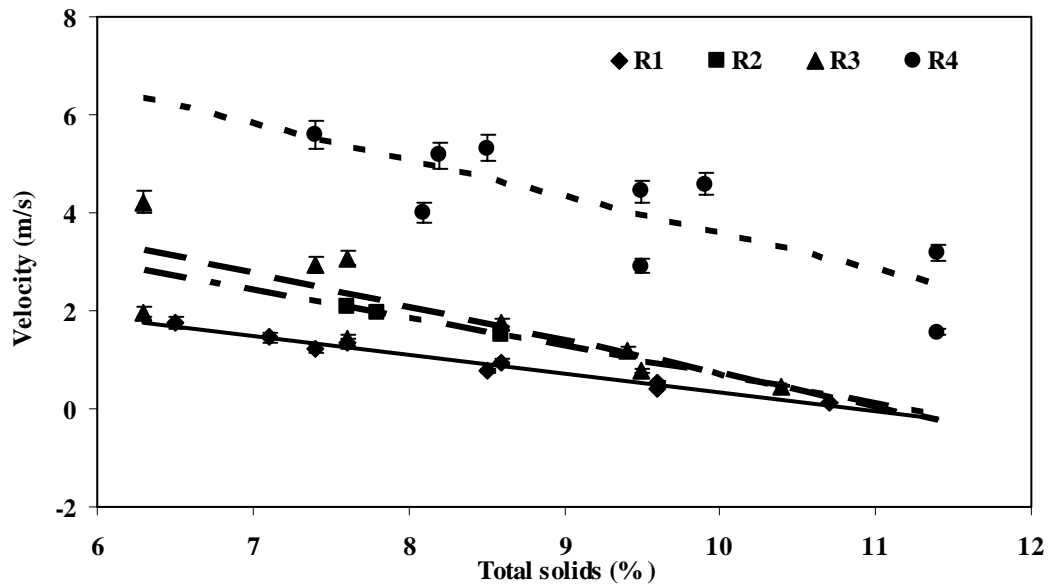


Fig 3.2a: Velocity as a function of manure total solids (TS) obtained with manures from the four experimental rations, exposed to a 1.8m hydraulic head flowing through a 9mm inside diameter rubber tube.

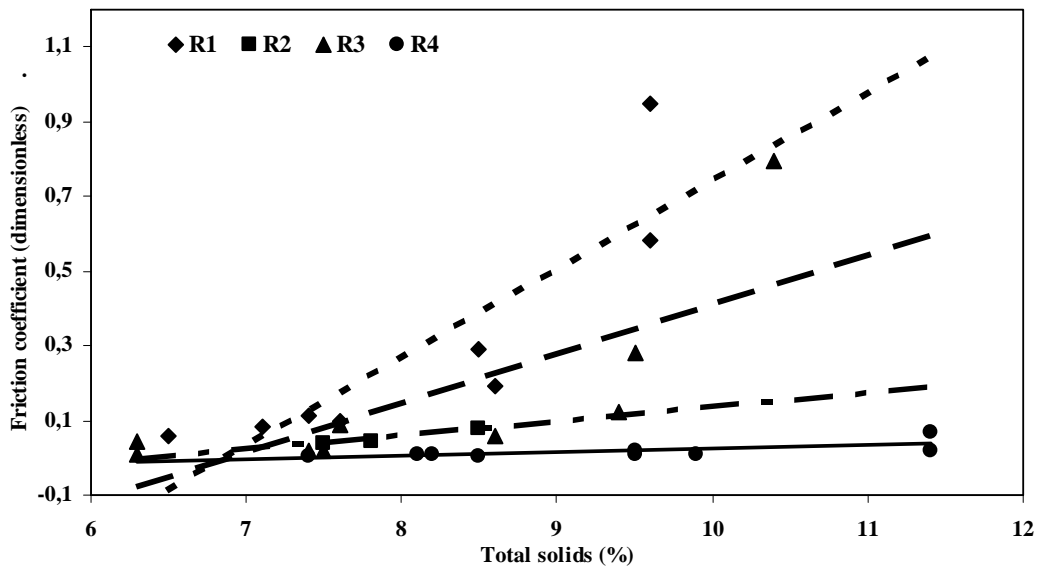


Fig 3.2b: Friction coefficient as a function of manure total solids (TS) for the samples obtained from each four rations, and flowing through a 9mm inside diameter rubber tube exposed to a 1.8m hydraulic head.

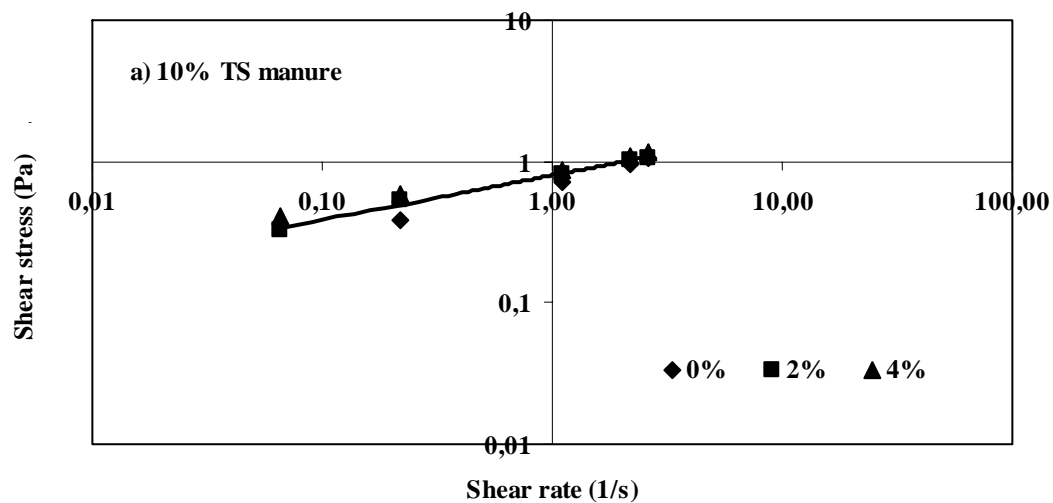


Fig 3.3a: Effect of manure zeolite content (0%, 2% and 4%) and TS (10%) on shear viscous properties.

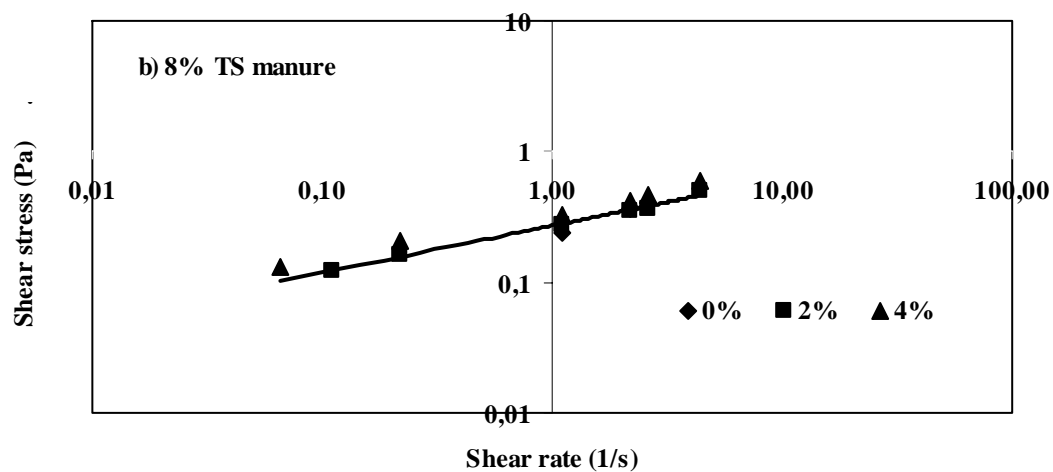


Fig 3.3b: Effect of manure zeolite content (0%, 2% and 4%) and TS (8%) on shear viscous properties.

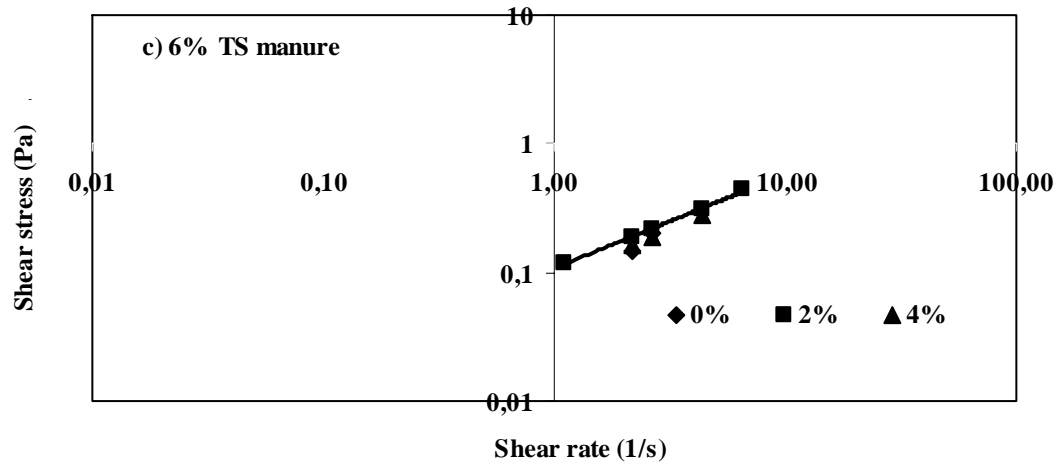


Fig 3.3c: Effect of manure zeolite content (0%, 2% and 4%) and TS (6%) on shear viscous properties.

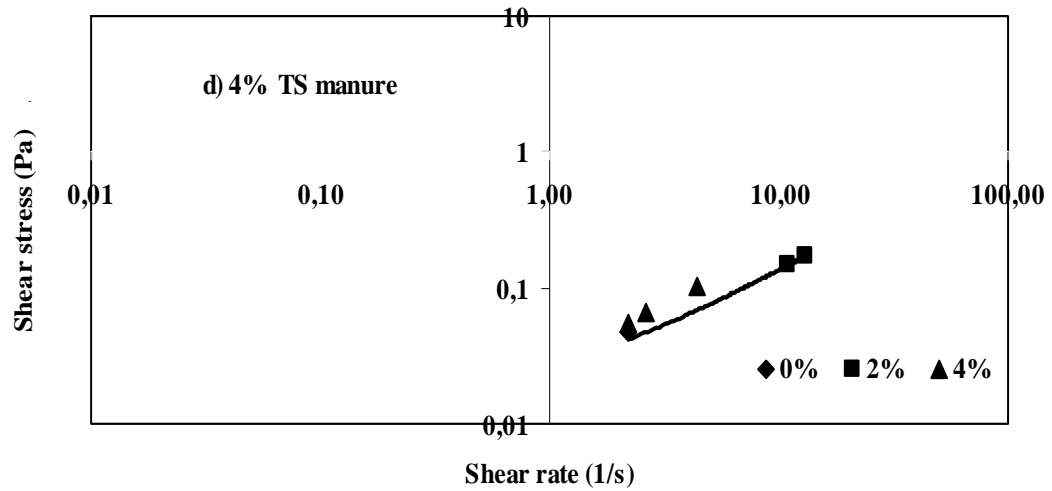


Fig 3.3d: Effect of manure zeolite content (0%, 2% and 4%) and TS (4%) on shear viscous properties.

Table 3.1: Composition of feed supplied to swine during the test.

Property	R1	R2	R3	R4
Crude protein (%)	17.2	17.2	15.5	15.5
Crude fat (%)	7	7	2	2
Crude fiber (%)	5	5	5	5
Na (%)	0.2	0.2	0.2	0.2
Ca (%)	0.75	0.75	0.75	0.75
P (%)	0.65	0.65	0.65	0.65
Cu (mg/kg)	125	125	125	125
Zn (mg/kg)	100	100	100	100
Vitamin A (I.U./kg ¹)	5400	5400	5400	5400
Vitamin D3 (I.U./kg)	1200	1200	1200	1200
Vitamin E (I.U./kg)	40	40	40	40
Selenium (mg/kg)	0.3	0.3	0.3	0.3
Zeolite (%)	0	4	4	4
Energy (Kcal)	3250	3250	2925	2760
Crude Protein (%)	100	100	90	90
Energy (%)	100	100	90	85

Note : R1 - control ration with 100% CP and 100% energy; R2- 4% zeolite ration with 100% CP and 100% energy; R3 – 4% zeolite ration with 90% CP and 90% energy; R4 – 4% zeolite ration with 90% CP and 85% energy in diets;¹ international units per kilogram.

Table 3.2: Bulk composition^a of experimental zeolite by percent weight.

Elements	Chemical symbol	Weight (%)
Quartz	SiO ₂	Trace to 1
Plagioclase	NaAlSi ₃ O ₈ - CaAl ₂ Si ₂ O ₈	Trace to 1
Calcite	CaCO ₃	1
Dolomite	[CaMg]CO ₃	Trace to 1
Clinoptilolite	KNa ₂ Ca ₂ (Si ₂₈ Al ₇)O ₇₂ ·24H ₂ O	97 to 98
Opal	SiO ₂ .nH ₂ O	0
Muscovite/Illite	KAl ₂ [AlSi ₃ O ₁₀][OH] ₂	0
NH ₄ ⁺ -N adsorption capacity at pH =2 and T = 39°C (Cmol ⁺ /kg of zeolite) ^b		122.68

^a Bulk composition analysis of the experimental zeolite was carried out by Core Laboratories Inc. (AB); ^b Leung et al. (2006).

Table 3.3: Characteristics of the raw and aged manure.

Characteristics	Rations							
	R1		R2		R3		R4	
	I	F	I	F	I	F	I	F
Mass, kg	7.05 ^a (2.08)	8.39 (2.08)	8.85 ^{a,b} (2.34)	11.22 (3.03)	10.07 ^{a,b} (2.52)	12.1 (1.43)	6.38 ^b (1.47)	7.78 (1.23)
TS, %	17.2 ^b (2.3)	14.6 (1.7)	11.6 ^a (0.87)	7.8 (0.30)	17.0 ^b (3.3)	14.5 (2.7)	23.0 ^c (0.4)	19.1 (0.4)
TS, kg	1.21 ^a (0.40)	1.21 (0.23)	1.03 ^a (0.31)	0.88 (0.25)	1.71 ^c (0.05)	1.73 (0.17)	1.47 ^b (0.18)	1.49 (0.27)
TC, % dm	38.4 ^c (0.76)	38.7 (0.76)	30.8 ^a (1.92)	29.2 (0.24)	32.5 ^{a,b} (3.91)	35.0 (0.14)	37.0 ^{b,c} (3.05)	34.0 (0.33)
TC, kg	0.46 ^b (0.01)	0.47 (0.01)	0.32 ^a (0.02)	0.26 (0.03)	0.56 ^c (0.07)	0.61 (0.02)	0.54 ^{b,c} (0.04)	0.51 (0.05)
TKN, mg/l	6450 (1380)	5220 (520)	4320 (265)	2780 (640)	5520 (890)	4190 (450)	8290 (2130)	6230 (160)
TKN, g	45.5 (9.4)	43.8 (4.36)	38.2 (11.2)	31.2 (7.2)	55.6 (9.0)	50.7 (5.5)	52.9 (13.6)	48.5 (5.3)
TP, mg/l	4054 ^c (430)	-	2058 ^a (141)	-	2861 ^b (981)	-	7217 ^d (630)	-
TP, g	28.9 ^a (9.3)	-	20.3 ^a (6.6)	-	30.5 ^a (7.8)	-	46.8 ^d (7.2)	-
TK, mg/l	7749 ^b (3360)	-	4493 ^a (3850)	-	13 670 ^c (4 200)	-	13 822 ^c (3 400)	-
TK, g	50.2 ^a (10.4)	-	36.6 ^a (18.2)	-	143.2 ^b (44.0)	-	129.56 ^b (31.9)	-

Note: The value in parenthesis is the standard deviation; R1 - control ration with 100% CP and 100% energy; R2- 4% zeolite ration with 100% CP and 100% energy; R3 – 4% zeolite ration with 90% CP and 90% energy; R4 – 4% zeolite ration with 90% CP and 85% energy in diets; I - initial value (day 0); F - final value after aging (day 67); TC is expressed in terms of % dry matter (dm); the values with a different letter as superscript differ significantly ($P<0.05$).

Table 3.4: Manure odour level at different feed rations.

Rations	Average odour level (odour unit/m ³)
R1	503 (24)
R2	371 (116)
R3	232 (46)
R4	320 (92)

Note: The value in parenthesis is the standard deviation; R1 - control ration with 100% CP and 100% energy; R2- 4% zeolite ration with 100% CP and 100% energy; R3 – 4% zeolite ration with 90% CP and 90% energy; R4 – 4% zeolite ration with 90% CP and 85% energy in diets.

CONNECTING STATEMENT TO CHAPTER FOUR

The previous chapter (i.e., Chapter III) showed that zeolite (clinoptilolite), as a feed additive at different supplemented level in hog's diet can lower manure nutrient content without altering its physical properties. So, zeolite (clinoptilolite) has potential to reduce the environmental adversities resulting from the intensive hog farming practice. Further, the impacts due to the addition of zeolite on hog performance, carcass quality and quantity need to be investigated. Therefore, the following chapter investigates the effect of zeolite (clinoptilolite) as feed additives on grower hog's feed intake, feed conversion, body weight, body weight gain, carcass quality and heavy metal concentrations in kidney, liver and muscle tissues.

CHAPTER FOUR

EFFECT OF CLINOPTILOLITE DIET SUPPLEMENTATION AND LOWER CRUDE PROTEIN AND ENERGY LEVELS ON GROWER HOG PERFORMANCE

ABSTRACT

Clinoptilolite is a zeolite which has been used as feed additive to improve nutrient digestion and lower manure nutrient content, but without consistently producing positive results. For rations containing 4% zeolite (90%+ clinoptilolite), the present study verified the effect on grower hog performance of varying the level of crude protein (CP) and energy. A total of 192 grower hogs were randomly assigned to one of two rooms, where those in room one received feed supplemented with zeolite while the others received a control diet. The experiment was repeated while reversing the treatment per room. Three levels of CP and energy were used for the zeolite supplemented ration. Initially, the hogs weighed 23.9 (\pm 1.0) kg and were fed ad libitum up to a live body weight of 100 (\pm 5.0) kg. At every two weeks and for 12 weeks, feed intake and feed conversion were averaged for each 6 hog per pen while body weight, weight gain and carcass qualities were measured on individual hog. At slaughter, kidney, liver and muscle samples were obtained and analyzed for heavy metal content. Although no significant differences were found, ration R3 (4% zeolite, 90% CP and 90% energy) gave better results during 6 out of 12 weeks of monitoring, as compared to the control ration. This indicates that more research is needed to adjust the ration with hog growth stage. No significant results were observed in terms of feed conversion; nevertheless, hogs on ration R2 and R3 had a better CP conversion and those on ration R3 had a better energy conversion. Hogs on ration R3 produced leaner carcasses, leading to a better market price. The heavy metal content of the carcasses was not significantly affected ($P>0.05$) by zeolite supplementation.

Keywords: Clinoptilolite, swine performance, carcass quality, heavy metal concentration.

4.1 Introduction

From 2000 to 2006, the number of hogs per farm in Canada increased from 790 to 1,160 while the number of farms dropped from 16,780 to 12,560 (Statistics Canada, 2007), still resulting in a 10% increase in hog numbers. Similar intensification trends were reported for the European Union and the United States, and have resulted in the concentration of manure production in localized regions (Burton and Turner, 2003). As a result and for these regions, manure land nutrient applications exceed crop nutrient requirements, resulting in soil enrichment. Manure odour nuisance and water body eutrophication are other issues resulting from this intensification (Jongbloed and Lenis, 1998).

This manure management issue can be resolved either by dewatering or transporting further to better disperse the mass of nutrients, or by manipulating the diet to lower the manure nutrient content. Clinoptilolite is a zeolite which has been tested as a natural feed additive to improve feed digestion and swine performance (feed intake, feed conversion, body weight and weight gain) while also lowering manure nutrient content.

Zeolite (clinoptilolite) in the diet of hogs was found to improve feed efficiency (Pond et al., 1988; Coffey and Pilkington, 1989; and Yannakopoulos et al., 2000) as well as the digestibility of crude protein (CP) and nitrogen-free extracts (Han et al., 1976). However, feed use efficiency in hogs depended on age, weight and feeding conditions (Vrzgula and Bartko, 1984; Nestorov, 1984). Sows fed a diet supplemented with 2% clinoptilolite produced more numerous litters, greater piglet weight at birth and greater piglet weight gain during lactation (Papaioannou et al., 2002). Also supplemented at 2% level, clinoptilolite reduced p-cresol in the feces of hogs while increasing that of the urine along with its energy loss due to low energy absorption (Shurson et al., 1984). Using 5% zeolite (77% clinoptilolite) in the diet of hogs, Barrington and El Moueddeb (1995) observed a feed conversion improved by 0.15 kg/kg of body weight gain. Castro and Elias (1978) reported a 12% increase in feed efficiency of hogs fed a 7.5% zeolite in their diet in

comparison to the control diet. Among the treatment levels of 0%, 5% and 10%, zeolite (95% clinoptilolite) at 10% level showed better feed conversion (Cool and Willard, 1982).

Poulsen and Oksberg (1995) reported feces with a higher nitrogen (N) content, a higher feed conversion and a lower daily weight gain for young hogs fed clinoptilolite (70%) at 3%. Clinoptilolite at 5% supplementation in the diet of hogs lowered the daily weight gain (Pond and Yen, 1982; Pond and Lee, 1984). In comparison to regular diet, clinoptilolite at 5% and 10% levels in the diet resulted in a weight gain of 27% (Kondo and Wagai, 1968) and 8% (Nestorov, 1984), respectively. According to Ma et al. (1984), clinoptilolite at 5% level resulted in less weight gain in comparison to 0% and 2.5% levels in hog's diet. However, the effectiveness of zeolite on growth increase depended on zeolite species and supplement level (Mumpton, 2006). Clinoptilolite added to the diet of hogs with 16.5% CP and 3.1 Mcal/kg energy resulted in a larger litter, greater piglet weight at birth and greater piglet weight gain during lactation (Kyriakis et al., 2002) whereas, 18.2% CP and 3.2 Mcal/kg energy had a similar impacts on body weight gain (Papaioannou et al., 2002). With 15.2% CP in the diet of hogs, there are reports of improved daily body weight gain (Pond et al., 1988); however, 16% CP resulted in no effect on body weight gain to feed ratio (Pond and Yen, 1982). Nestorov (1984) found a higher weight gain and the correction of diarrhea in hogs fed a diet containing 14.6% CP and 2.9 Mcal/kg energy.

Similarly, zeolite has a positive impact on carcass quality and its market values. The toxic cation absorption capacity of zeolite prevented the adverse effect on metabolic function in hogs (Pond et al., 1993). Zeolite had no adverse effect on the quality of muscle, liver, heart and kidneys tissues (Nestorov, 1984; Fokas et al., 2004) due to its absorption capacity for lead (Pb), arsenic (As) and cadmium (Cd) (Pond et al., 1993). According to Nestorov (1984), histochemical studies on the intestinal tract of hogs fed 10% clinoptilolite showed no evidence of adverse effects on the tissues and organoleptic evaluation of meat. Pond and Yen (1983) found no effect of

zeolite A on plasma potassium (K), sodium (Na) and magnesium (Mg) levels in hogs.

From the literature review, zeolite (clinoptilolite) at low levels of supplementation increase the feed efficiency and weight gain of hogs while showing no negative impact on carcass quality. The clinoptilolite added to hog diets at lower CP and energy levels reported better results in body weight gain to feed ratio. The present study was designed to test the effect of supplementing grower hog diets with zeolite (clinoptilolite) while reducing the level of CP and energy. The effects measured were feed intake and feed conversion, body weight and body weight gain, carcass quality and heavy metal concentrations in kidney, liver and muscle tissues.

4.2 Materials and methods

4.2.1 Experimental ration

Four experimental rations were tested. The control ration, R1, contained no zeolite and offered 100% of the crude protein (CP) and energy requirements (Table 4.1). The rations R2, R3 and R4 all contained 4% zeolite (90%+ clinoptilolite) but 100%, 90% and 90% of the CP with 100%, 90% and 85% of the energy required, respectively (NRC, 1998). The feed was prepared from corn and soybean, by Agri-brands Purina Canada Inc, St-Hubert, Quebec. The experimental zeolite (90%+ clinoptilolite) was supplied by the KMI mine, Nevada, USA (Table 4.2).

4.2.2 The experimental hogs

This trial used two groups of 192 crossbred female hogs ($\frac{1}{2}$ Duroc, $\frac{1}{4}$ Landrace and $\frac{1}{4}$ Yorkshire) with an initial average body weight of 23.9 (± 1.0) kg. The groups were tested one at the time. Within each group, the hogs were randomly assigned to one of three rations, either the control or one of two zeolite rations. During the first feed trial, the hogs in room 1 were fed the control diet, R1, while the hogs in room 2 were fed the zeolite rations R3 and

R4. During the second trial, the hogs in room 1 were fed the zeolite rations R2 and R4 while the hogs in room 2 were fed the control diet R1.

4.2.3 The experimental rooms

The experiment was conducted at the piggery unit of Macdonald Campus, McGill University, Ste-Anne-de-Bellevue, Montreal, Canada.

These hogs were raised in a grower room measuring 14.75 m × 7.20 m and 3.05 m in height, with 16 pens of 3.00 m × 1.84 m, offering 0.92 m²/hog. A central alleyway serviced the two lateral rows of 8 pens with a fully slatted floor. The feeders were placed against the alleyway and offered feed ad libitum. The grower room was ventilated at a rate ranging from 5 to 48 L/s/hog, using a central air inlet with baffles pivoting against weights and a fan bank in one corner of the end wall.

The research protocol, including the care and feeding of the animals was approved by the Animal Care Committee of McGill University in accordance with the Canadian Council on Animal Care Guidelines (Appendix).

4.2.4 Methodology

The first group of 192 hogs was tested in the fall of 2004 while the second group was tested during the winter of 2005. For each group and after each hog was randomly assigned to a pen of six, all subjects were weighed and each pen was randomly assigned one of the two experimental rations in the zeolite room. All feeders were weighed empty.

Throughout the trial, all feed placed in the feeder was weighed daily. At every two week interval and for a period of 13 to 14 weeks, all subjects were weighed along with the feeders to calculate feed intake and feed conversion. All hogs were measured using an electronic scale (Sensteck Manufacturing Company, Model No. 2500, Serial No. 542014, Saskatoon,

Canada). The initial ration was a starter with a high level of CP. At week 6, the starter ration was replaced by a grower ration, and on week 10, the finisher ration was introduced (Table 4.1).

At a live weight of 110.9 (\pm 9.0) kg, the hogs were sent to slaughter. For the last group only and at the slaughtering house, the kidney, part of the liver and a muscle sample were collected from 15 hogs fed each one of the three rations.

All kidney, liver and muscle tissues were digested with nitric acid (HNO₃) before being analyzed for heavy metals. The heavy metals were quantified by Inductively Coupled Plasma (ICP) analysis (Varian, VISTA-MPX, CCD Simultaneous: ICP-OES, Australia Pvt. Ltd).

4.2.5 Statistical analysis

For feed intake and feed conversion, each pen was considered to be an experimental unit. Body weight, body weight gains, carcass quality and heavy metal concentrations were measured on individual hog. The trial was repeated by switching rooms to eliminate room effect.

All data were analyzed using the GLM procedure of SAS (2004) with completely randomized design (CRD) methods. Feed intake, feed conversion, body weight and body weight gains were analyzed by ANOVA with mixed model procedure in SAS (2004) using repeated measures.

The model for feed intake and feed conversion was:

$$y_{ijk} = \mu + \text{rat}_i + \text{week}_j + \text{rat.week}_{ij} + e_{ijk} \dots\dots\dots(4.1)$$

Where,

y_{ijk} = dependent variable; μ = overall mean; rat_i = fixed effect of i^{th} ration ($i = 1, 2, 3, 4$) on feed intake and feed conversion; week_j = fixed effect of j^{th} week ($j = 2, 4, \dots\dots, 12$) on feed intake and feed conversion rate; and e_{ijk} = residual errors.

The model for body weight and body weight gain was:

$$y_{ijkl} = \mu + \text{rat}_i + \text{pig}_j + \text{week}_k + \text{rat.week}_{ik} + e_{ijkl} \dots\dots\dots(4.2)$$

Where,

y_{ijkl} = dependent variable; μ = overall mean; rat_i = fixed effect of i^{th} ration ($i = 1, 2, 3, 4$) on body weight and body weight gains; pig_j = random effect of j^{th} pig ($1, 2, 3, \dots$) on body weight and body weight gains; $week_k$ = fixed effect of k^{th} week ($k = 2, 4, \dots, 12$) on body weight and body weight gains; and e_{ijkl} = residual errors.

The model for carcass quality and heavy metal concentrations was:

$$y_{ij} = \mu + rat_i + e_{ij} \dots\dots\dots(4.3)$$

Where,

y_{ij} = dependent variable; μ = overall mean; rat_i = fixed effect of i^{th} ration ($i = 1, 2, 3, 4$) on carcass quality and heavy metal concentrations; and e_{ij} = residual errors.

4.3 Results and discussion

4.3.1 Body weight and body weight gain

The control ration gave the best body weight and body weight gain at the end of the trial (Tables 4.3a and 4.3b). The effect of supplementing zeolite was not statistically different ($P>0.05$) as compared to the control ration R1. However, ration R3 produced a weight gain which was as good and even better during the weeks 0-2, 2-4 and 6-8, as compared to the control ration R1. During weeks 10-12, ration R4 produced a better weight gain than that of the control. As for ration R2, it did not perform better than the control ration R1, for all weeks.

Therefore, zeolite may be able to improve weight gain, but the CP and energy levels of the ration likely need to be adjusted with animal age. Because the zeolite ration R3 contains less CP, it can lead to the production of manure with less nitrogen (N).

4.3.2 Feed intake and feed conversion

The zeolite rations lead to feed intake and feed conversion which were not significantly different ($P>0.05$) as compared to that of the control ration

R1. Nevertheless, after 12 weeks, rations R2, R3 and R4 lead to the consumption of slightly more feed in comparison to control ration R1 (Table 4.3c). Feed consumption increased with lower ration energy values.

When CP and energy conversions are calculated, rather than the feed conversion, the rations R2 and R3 performed better in terms of CP, and ration R3 performed better in terms of energy, as compared to ration R1. Even though these results are not significant ($P>0.05$), zeolite may have the potential to improve the conversion of some nutrients, but more research is needed to determine the right CP and energy adjustment, when zeolite is supplemented. This adjustment likely needs to be adjusted with hog's growth stage.

4.3.3 Carcass quality and heavy metal contamination

Inclusion of 4% zeolite in the ration of hogs had a significant effect on the fat percentage ($P<0.01$) of the carcass but no significant effect ($P>0.05$) on the muscle percentage in comparison to the control ration (Table 4.4). Carcass index was significantly affected by the addition of zeolite in the ration ($P<0.01$). This positive impact results from the use of less energy, leading to the production of leaner carcasses.

For all heavy metals analyzed, the tissues from hogs fed rations R2, R3 and R4 did not contain significantly more elements than that of the hogs on the control ration R1 (Tables 4.5a, 4.5b and 4.5c). Zeolite added to the rations had a particle size distribution ranging from 0.05 to 0.50 mm. Furthermore, clinoptilolite is known to resist degradation under conditions of low pH and moderate temperatures as found in the stomach of hogs (Leung et al., 2006). Therefore, zeolite releases a very small amount of heavy metals in the stomach of animals which does not lead to tissue contamination.

4.4 Conclusions

Rations containing 4% zeolite (90%+ clinoptilolite) and various levels of crude protein (CP) and energy were fed to hogs, along with a control ration,

to observe the effect on body weight and body weight gain, feed intake and feed conversion, and carcass quality. Although no significant differences were found, ration R3 (4% zeolite, 90% CP and 90% energy) gave better results during 6 out of 12 weeks of monitoring as compared to the control ration. This indicates that more research is needed to adjust the ration with hog growth stage. No significant results were observed in terms of feed conversion; nevertheless, hogs on rations R2 and R3 had a better CP conversion and those on ration R3 had a better energy conversion. Hogs on ration R3 produced leaner carcasses, leading to a better market price. The heavy metal content of the carcasses was not significantly affected by zeolite supplementation.

4.5 Acknowledgements

The Fédération des producteurs de porcs du Québec (Quebec, Canada), the Natural Science and Engineering Research Council of Canada (NSERC), Promix (Upton, Québec, Canada) and KMI Zeolites (Nevada, USA) are thanked for their generous financial support.

4.6 References

- Barrington, S.F., and K. El Moueddeb. 1995. Zeolite as pig manure additive to control odour and conserve N. Canadian Society of Agricultural Engineering. Paper no. 95-510, Saskatoon, Canada.
- Burton, C.H., and C. Turner. 2003. Manure management: Treatment strategies for sustainable agriculture. Second edition. Silsoe Research Institute. Silsoe, UK. p. 9.
- Castro, M., and A. Elias. 1978. Effect of the inclusion of zeolite in final molasses-based diets on the performance of growing-fattening pigs. Cuban Journal of Agricultural Sciences. 12:69-75.
- Coffey, M.T., and D.W. Pilkington. 1989. Effect of zeolite-A on the performance and carcass quality of swine. Journal of Animal Science. 67(2):36.
- Cool, W.M. and J.M. Willard. 1982. Effect of clinoptilolite on swine nutrition. Nutrition Reports International. 26(5):759-766.
- Fokas, P., G. Zervas, K. Fegeros, and P. Zoiopoulos. 2004. Assessment of Pb retention coefficient and nutrient utilization in growing pigs fed diets with added clinoptilolite. Animal Feed Science and Technology. 117:121-129.
- Han, I.D., H.K. Part, and C.S. Kim. 1976. Studies on the nutritive value of zeolite. II. Effects of zeolite rich hull mixture on the performance of growing-finishing swine. Korean Journal of Animal Science. 18:225.
- Jongbloed, A.W., and N.P. Lenis. 1998. Environmental concerns about animal manure. Journal of Animal Science. 76:2641-2648.
- Kondo, N., and B. Wagai. 1968. Experimental use of clinoptilolite-tuff as a dietary supplement for pigs. Yotonkai. p. 1-4.
- Kyriakis, S.C., D.S. Papaioannou, C. Alexopoulos, Z. Polizopoulou, E.D. Tzika, and C.S. Kyriakis. 2002. Experimental studies on safety and efficacy of the dietary use of a clinoptilolite-rich tuff in sows: a review of recent research in Greece. Microporous and Mesoporous Materials.

51:65-74.

- Leung, S., S.F. Barrington, and B. El-Husseini. 2006. Effect of particle size on physico-chemical properties of clinoptilolite as feed additive. *Microporous and Mesoporous Materials*. p. 49-57.
- Ma, C.S., S.K. Yang, C.M. Tzeng, and H.K. Wu. 1984. Effect of feeding clinoptilolite on embryo survival in swine. In W.G. Pond and F.A. Mumpton (ed.) *Zeo-agriculture: Use of natural zeolites in agriculture and aquaculture*. International Committee on Natural Zeolites. Westview Press, Boulder, CO. p. 155-160.
- Mumpton, F.A. 2006. Using zeolites in agriculture: Zeolite product website. Available at <http://www.zeolite-products.com> (accessed April 2007).
- National Research Council (NRC). 1998. Nutrients requirements of pig. Tenth edition. National Academy Press, Washington, DC.
- Nestorov, N. 1984. Possible applications of natural zeolites in animal husbandry. In: *Zeo-Agriculture – Use of natural zeolites in agriculture and aquaculture*. (W. G. Pond and F. A. Mumpton, editors). International Committee on Natural Zeolites. Westview Press, Boulder, CO. p. 163.
- Papaioannou, D.S., S.C. Kyriakis, A. Papasteriadis, N. Roumbies, A. Yannakopoulos, and C. Alexopoulos. 2002. A field study on the effect of in-feed inclusion of a natural zeolite (clinoptilolite) on the health status and performance of sows/gilts and their litters. *Research in Veterinary Science*. 72:51-59.
- Pond, W.G., and J.T. Lee. 1984. Physiological effects of clinoptilolite and synthetic zeolite A in animals. In W.G. Pond and F.A. Mumpton (ed.) *Zeo-agriculture: Use of natural zeolites in agriculture and aquaculture*. International Committee on Natural Zeolites. Westview Press, Boulder, CO. p. 129-146.
- Pond, W.G., and J.T. Yen. 1982. Response of growing swine to dietary clinoptilolite from two geographic sources. *Nutrition Reports International*. 25:837-848.

- Pond, W.G., and J.T. Yen. 1983. Protection by clinoptilolite or zeolite NaA against cadmium-induced anemia in growing swine. *Proceedings of the Society for Experimental Biology and Medicine*. 173:327-337.
- Pond, W.G., J.T. Yen, and V.H. Varel. 1988: Response of growing swine to dietary copper and clinoptilolite supplementation. *Nutrition Reports International*. 37(4):795-803.
- Pond, W.G., K.J. Ellis, K.J. Krook, and P.A. Schoknecht. 1993. Modulation of dietary Pb toxicity in pigs by clinoptilolite. In: *Proceedings of Zeolite '93, Fourth conference on the occurrence, properties and utilization of natural zeolites*. International Committee on Natural Zeolites. SUNY-College at Brockport, Brockport, New York. p. 170-172.
- Poulsen, H.D., and N. Oksberg. 1995. Effect of dietary inclusion of a zeolite (clinoptilolite) on performance and protein metabolism of young growing pigs. *Animal Feed and Science Technology*. 53:297-303.
- SAS Institute. 2004. *SAS/STAT User's guide*. SAS for Windows. Version 9.1. SAS Institute, Inc., Cary, NC, USA.
- Shurson, G.C., P.K. Ku, E.R. Miller, and M.T. Yokoyama. 1984. Effects of zeolite A or clinoptilolite in diets of growing swine. *Journal of Animal Science*. 59(6):1536-1545.
- Statistics Canada. 2007. *Statistics Canada Agriculture Division*. Catalogue no. 23-010-XIE. *Hog statistics*. Ottawa: Statistics Canada, ON. K1A 0T6. 6(1):32-35. Available at <http://www.statcan.ca/english/freepub/23-010-XIE/23-010-XIE2007001.pdf> (accessed March 2007).
- Vrzgula, L., and P. Bartko. 1984. Effects of clinoptilolite on weight gain and some physiological parameters of swine. In: W.G. Pond and F.A. Mumpton (ed.) *Zeo-agriculture: Use of natural zeolites in agriculture and aquaculture*. International Committee on Natural Zeolites. Westview Press, Boulder, CO. p.161-167.
- Yannakopoulos, A., A. Tserveni-Gousi, A. Kassoli-Four-Naraki, A. Tsirambides, K. Michailidis, A. Filippidis, and U. Lutat. 2000.

Effects of dietary clinoptilolite-rich tuff on the performance of growing-finishing pigs. In: Natural zeolites for the third millenium. Eds Coela, C. and Mumpton, F.A. N Napoli, Italy: De Frede Editore. p. 471-481.

Table 4.1: Experimental feed composition for 100% crude protein and energy.

Property	Starter	Grower	Finisher
Crude protein (%)	17.2	15.5	14.0
Crude fat (%)	7	7	2
Crude fiber (%)	5	5	5
Na (%)	0.2	0.2	0.2
Ca (%)	0.75	0.75	0.75
P (%)	0.65	0.65	0.65
Cu (mg/kg)	125	125	125
Zn (mg/kg)	100	100	100
Vitamin A (I.U./kg ¹)	5400	5400	5400
Vitamin D3 (I.U./kg)	1200	1200	1200
Vitamin E (I.U./kg)	40	40	40
Selenium (mg/kg)	0.3	0.3	0.3
Zeolite (%)	0	4	4
Energy (Kcal)	3250	3250	2925

¹ International units per kilogram.

Table 4.2: Bulk composition^a of experimental zeolite by percent weight.

Elements	Chemical symbol	Weight (%)
Quartz	SiO ₂	Trace to 1
Plagioclase	NaAlSi ₃ O ₈ - CaAl ₂ Si ₂ O ₈	Trace to 1
Calcite	CaCO ₃	1
Dolomite	[CaMg]CO ₃	Trace to 1
Clinoptilolite	KNa ₂ Ca ₂ (Si ₂₈ Al ₇)O ₇₂ ·24H ₂ O	97 to 98
Opal	SiO ₂ .nH ₂ O	0
Muscovite/Illite	KAl ₂ [AlSi ₃ O ₁₀][OH] ₂	0
NH ₄ ⁺ -N adsorption capacity at pH =2 and T = 39°C (Cmol ⁺ /kg of zeolite) ^b		122.68

^a The bulk composition analysis of the experimental zeolite was carried out by Core Laboratories Inc. (AB); ^b Leung et al. (2006).

Table 4.3a: Least square mean (LSM) values for body weight.

Rations	Weeks						
	0	2	4	6	8	10	12
R1	23.4 (0.16)	35.1 (0.26)	46.7 (0.30)	60.0 (0.33)	72.9 (0.42)	87.0 (0.56)	100.8 (0.60)
R2	22.9 (0.23)	33.8 (0.36)	45.9 (0.43)	59.2 (0.46)	71.9 (0.59)	85.4 (0.79)	98.6 (0.85)
R3	23.0 (0.39)	34.6 (0.56)	47.2 (0.64)	59.8 (0.69)	73.3 (0.87)	85.7 (1.14)	98.1 (1.22)
R4	23.4 (0.39)	35.2 (0.56)	47.4 (0.64)	58.8 (0.69)	72.0 (0.87)	84.9 (1.14)	98.7 (1.22)

Note: The values inside the parenthesis are standard errors (SE); R1 - control ration with 100% CP and 100% energy; R2- 4% zeolite ration with 100% CP and 100% energy; R3 – 4% zeolite ration with 90% CP and 90% energy; R4 – 4% zeolite ration with 90% CP and 85% energy in diets; the values with a different letter as superscript differ significantly ($P<0.05$) within the ration groups.

Table 4.3b: Least square mean (LSM) values for body weight gain.

Rations	Weeks					
	2	4	6	8	10	12
R1	11.8 (0.14)	11.6 (0.18)	13.3 (0.18)	12.9 (0.21)	14.2 (0.28)	13.7 (0.26)
R2	10.9 (0.20)	12.1 (0.26)	13.3 (0.25)	12.7 (0.30)	13.5 (0.39)	13.1 (0.37)
R3	11.7 (0.31)	12.8 (0.39)	12.8 (0.38)	13.6 (0.45)	12.5 (0.57)	12.6 (0.53)
R4	11.7 (0.31)	12.2 (0.39)	11.3 (0.38)	13.1 (0.45)	12.8 (0.57)	13.7 (0.53)

Note: The values inside the parenthesis are standard errors (SE); R1 - control ration with 100% CP and 100% energy; R2- 4% zeolite ration with 100% CP and 100% energy; R3 – 4% zeolite ration with 90% CP and 90% energy; R4 – 4% zeolite ration with 90% CP and 85% energy in diets; the values with a different letter as superscript differ significantly ($P<0.05$) within the ration groups.

Table 4.3c: Least square mean (LSM) values for feed intake.

Rations	Weeks					
	2	4	6	8	10	12
R1	131.4 (1.47)	137.7 (1.97)	139.8 (4.67)	216.5 (7.48)	186.9 (4.46)	222.7 (3.94)
R2	132.8 (2.17)	150.4 (2.89)	145.7 (6.76)	229.2 (10.79)	200.6 (6.46)	231.5 (5.71)
R3	132.5 (3.36)	154.6 (4.25)	128.0 (9.37)	207.6 (14.84)	224.2 (8.98)	245.5 (7.97)
R4	150.4 (3.44)	158.1 (4.38)	190.3 (9.68)	301.8 (15.33)	215.1 (9.27)	259.1 (8.22)

Note: The values inside the parenthesis are standard errors (SE); R1 - control ration with 100% CP and 100% energy; R2- 4% zeolite ration with 100% CP and 100% energy; R3 – 4% zeolite ration with 90% CP and 90% energy; R4 – 4% zeolite ration with 90% CP and 85% energy in diets; the values with a different letter as superscript differ significantly ($P<0.05$) within the ration groups.

Table 4.3d: Least square mean (LSM) values for feed conversion.

Rations	Weeks					
	2	4	6	8	10	12
R1	1.9 (0.03)	2.0 (0.03)	1.8 ^a (0.07)	2.8 (0.11)	2.3 (0.06)	2.8 (0.07)
R2	2.1 (0.04)	2.1 (0.05)	1.9 ^{ab} (0.10)	3.1 (0.15)	2.5 (0.08)	3.0 (0.10)
R3	1.9 (0.06)	2.0 (0.07)	1.7 ^{ab} (0.14)	2.6 (0.21)	3.0 (0.12)	3.3 (0.14)
R4	2.2 (0.06)	2.2 (0.07)	2.8 ^b (0.14)	3.9 (0.21)	2.9 (0.12)	3.2 (0.14)

Note: The values inside the parenthesis are standard errors (SE); R1 - control ration with 100% CP and 100% energy; R2- 4% zeolite ration with 100% CP and 100% energy; R3 – 4% zeolite ration with 90% CP and 90% energy; R4 – 4% zeolite ration with 90% CP and 85% energy in diets; the values with a different letter as superscript differ significantly (P<0.05) within the ration groups.

Table 4.4: Effect of control and zeolite rations on carcass quality.

Items	R1	R2	R3	R4
Weight of the carcass, kg	91.2	90.9	90	90
Fat, %	21.1	21.5	20.5	20.1
Muscle, %	60.2	61.5	60.8	62.7
Index	54.9	108	3.4	57.2
Value,\$/hog	152.1	155	149.7	153.1
Variation, \$/hog	0	-0.37	0.96	1

Note: R1 - control ration with 100% CP and 100% energy; R2- 4% zeolite ration with 100% CP and 100% energy; R3 – 4% zeolite ration with 90% CP and 90% energy; R4 – 4% zeolite ration with 90% CP and 85% energy in diets.

Table 4.5a: Effect of control and zeolite rations on heavy metals concentration in the hog liver tissue.

Heavy metals	Concentration (wet basis)		
	R1	R2	R4
Al, mg/kg	13.5 (26.5)	18.2 (9.00)	8.1 (10.3)
Fe, mg/kg	81.9 (52.2)	76.8 (61.8)	88.3 (44.3)
K, mg/kg	69.6 (43.9)	53.4 (13.1)	73.3 (34.4)
Zn, g/kg	53.0 (38.0)	89.0 (42.0)	87.0 (40.0)
Cr, mg/kg	2.90 (5.30)	0.40 (1.10)	0.20 (0.50)
Cu, mg/kg	7.70 (13.9)	7.80 (4.00)	14.50 (8.9)
Ni, mg/kg	1.80 (0.70)	0.40 (0.90)	0.00 (0.20)
Ca, mg/kg	384.0 (480)	779.0 (555)	401.0 (397)
Mg, mg/kg	241.0 (77.0)	227.0 (36.0)	256.0 (54.0)
Na, mg/kg	416.0 (96.0)	400.0 (66.0)	406.0 (76.0)
P, mg/kg	1344.0 (541)	1376.0 (260)	1620.0 (370)
S, mg/kg	889.0 (354)	1793 (1046)	902.0 (221)

Note: The value in parenthesis is the standard deviation; R1 - control ration with 100% CP and 100% energy; R2- 4% zeolite ration with 100% CP and 100% energy; R4 – 4% zeolite ration with 90% CP and 85% energy in diets.

Table 4.5b: Effect of control and zeolite rations on heavy metal concentration in hog kidney tissue.

Heavy metals	Concentration (wet basis)		
	R1	R2	R4
Al, mg/kg	15.5 (14.3)	34.8 (20.5)	9.5 (14.4)
Fe, mg/kg	39.5 (24.9)	24.6 (43.5)	27.5 (14.1)
K, mg/kg	40.9 (30.4)	60.6 (30.8)	58.9 (41.0)
Zn, g/kg ¹⁴	4.00 (5.30)	6.80 (8.80)	0.00 (0.00)
Cr, mg/kg	1.60 (1.70)	3.70 (3.50)	2.80 (2.20)
Cu, mg/kg	3.00 (3.20)	4.70 (0.60)	0.10 (0.20)
Ni, mg/kg	366.0 (477)	440.0 (385)	248.0 (379)
Ca, mg/kg	285.0 (101)	252.0 (90)	202.0 (42)
Mg, mg/kg	241.0 (77)	227.0 (36)	256.0 (54)
Na, mg/kg	740.0 (179)	661.0 (220)	636.0 (137)
P, mg/kg	1406 (560)	1402 (673)	1069 (257)
S, mg/kg	1018 (382)	943.0 (297)	700.0 (176)

Note: The value in parenthesis is the standard deviation; R1 - control ration with 100% CP and 100% energy; R2- 4% zeolite ration with 100% CP and 100% energy; R4 – 4% zeolite ration with 90% CP and 85% energy in diets.

Table 4.5c: Effect of control and zeolite rations on heavy metal concentration in hog muscle tissue.

Heavy metals	Concentration (wet basis)		
	R1	R2	R4
Al, mg/kg	13.3 (9.90)	57.7 (93.4)	9.30 (8.20)
Fe, mg/kg	27.7 (33.9)	20.1 (44.6)	14.5 (10.1)
K, mg/kg	2.30 (6.30)	26.8 (82.5)	0.10 (0.40)
Zn, g/kg	1.70 (4.50)	2.40 (5.50)	0.10 (0.40)
Cr, mg/kg	795.0 (814)	427.0 (344)	501.0 (684)
Cu, mg/kg	247.0 (45)	303.0 (98.0)	235.0 (47.0)
Ni, mg/kg	581.0 (26)	897.0 (61.0)	65.0 (39.0)
Ca, mg/kg	336.0 (73)	307.0 (96.0)	318.0 (77.0)
Mg, mg/kg	752.0 (139)	884.0 (348)	701.0 (140)
Na, mg/kg	713.0 (139)	1063.0 (571)	711.0 (120)
P, mg/kg	105.0 (76.0)	56.0 (32.0)	72.0 (56.0)
S, mg/kg	VSD	1.50 (5.40)	0.20 (0.70)

Note: The value in parenthesis is the standard deviation; R1 - control ration with 100% CP and 100% energy; R2- 4% zeolite ration with 100% CP and 100% energy; R4 – 4% zeolite ration with 90% CP and 85% energy in diets; VSD – very small to detect.

CHAPTER FIVE

GENERAL CONCLUSION

Zeolite (90%+ clinoptilolite) shows potential as a swine feed additive to reduce nutrient excretion and odour generation. High cation exchange capacity, molecular sieving properties and stability under high temperatures and acidic conditions, existing inside a hog's stomach; facilitate the reduction of nutrients in swine manure. Therefore, zeolite (90%+ clinoptilolite) could reduce nutrient overloading problems associated with intensive swine operations. Their wide geographic distribution, natural occurrence, and abundance of large, high grade deposits all over the world make zeolite's application economically feasible. In this context, the experiments were carried out to test the effect of clinoptilolite as a grower hog feed additive on manure physico-chemical properties, feed conversion, and weight gain and carcass quality.

This study showed that zeolite (90%+ clinoptilolite) can be used as a swine feed additive to reduce manure nutrient content without altering its physical properties. Swine diets supplemented with zeolite (90%+ clinoptilolite) also lowered manure odour, which helped in reducing nuisance factor and promoting easy handling and field application. The odour reduction also encourages the farmers to shift their excess manure to intensive cropping regions of the country so that nutrient accumulation and leakage problems due to the excessive manure application in and around the intensive swine farming regions can be reduced. Similarly, source reduction of manure nutrients (TN, TP and TK) and odours, reduces its adverse environmental effects; and also improves the public's general perception of the swine industry.

The addition of 4% zeolite (90%+ clinoptilolite) as a swine feed additive resulted in no significant changes ($P>0.05$) in feed intake, feed conversion rate, body weight and body weight gain. Also, the analysis of heavy metal concentrations (Al, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb and Zn) on samples of kidney, liver and muscle tissues showed no significant difference ($P>0.05$) between hogs fed with zeolite vs. traditional feed. Overall, the effect of 4% zeolite (90%+ clinoptilolite)

supplemented feed with a 100% CP and energy level showed better swine performance with lowered manure nutrient (TN, TP and TK) content and odours, without any change in physical properties or carcass quality.

The experimental test results obtained from this study can be used as a basis for future research into:

1. the impact of zeolite at different % levels of clinoptilolite with different supplement levels in hog's diet;
2. the impact of zeolite (clinoptilolite) application with rations containing different levels of crude protein (CP) and energy;
3. the rheological properties of manure products at different levels of temperature;
4. the adjustment of different rations with hog's growth stage;
5. an economic study of using zeolite as feed additives.

APPENDICES



McGill University Animal Care Committee
AMENDMENT to Animal Use Protocol

www.mcgill.ca/ags/animal/

ACTION	DATE
CCs	
DB	J. F. H. 10/10/05
APPROVED	

Principal Investigator: Suzelle Barrington Protocol # 4481
 Protocol Title: Zoolite as natural feed additive to reduce environmental impact of manure Phone: 398-7776
 Unit, Dept. & Address: Bioresource Engineering Fax: 398-8387
 Email: suzelle.barrington@mcgill.ca Level: _____ Funding: NSERC-FPPQ

1. ADDITIONAL ANIMALS REQUESTED: (justify additional animal numbers in box 5 below)										
Species	Strain	Supplier / Source	# Animals Purchased	# By Breeding	Age	Sex	Weight	# Needed at One Time	#/Cage	Total Per Year

2. ADDITIONAL PERSONNEL: If an undergraduate student is involved, the role of the student and the supervision received must be described. Training is mandatory for all personnel listed. Refer to www.animalcare.mcgill.ca for details. Each person listed in this section must sign to indicate that s/he has read the main protocol.				
Name	Classification	Animal Related Training	Occupational Health & Safety Program	Signature
Kirsten Nagle	undergraduate student	Training under Denis Hatcher for one month before the trial	yes	<i>Kirsten Nagle</i>

3. CHANGE IN FUNDING SOURCE AND/OR TITLE (title of grant must appear on the cover page of the animal protocol)


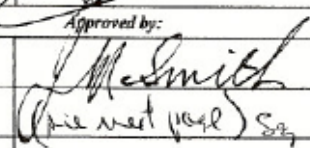
4. OTHER: (including housing, procedure, anaesthetic/analgesic, problems anticipated) If additional procedures, specify how many and which animals are to be used.

5. WHY ARE THESE AMENDMENTS NECESSARY? If requesting additional animals, justify the numbers

Approval Signatures:		Date
Principal Investigator/ Course Director	<i>[Signature]</i>	<i>Jan 30th 2005</i>
Chair, Facility Animal Care Committee	<i>[Signature]</i>	<i>Feb 14/2005</i>
UACC Veterinarian		
Chairperson, Ethics Subcommittee (Level or Teaching Protocols Only)		

Note: the above modifications are valid until the expiration date of the main protocol.

22 FEB. 2005

	McGill University Animal Use Protocol – Research	Protocol #: <u>4461</u> Investigator #: <u>939</u> Approval End Date: <u>MAY 31, 2005</u> Facility Committee: <u>AGR</u>												
Title: <u>Zeolite as natural swine feed additive to reduce the environmental impact of manure</u> <small>(must match the title of the funding source application)</small>														
<input type="checkbox"/> New Application <input checked="" type="checkbox"/> Renewal of Protocol # <u>4461</u> <input type="checkbox"/> Pilot Category (see section 11): <u>B</u>														
1. Investigator Data: Principal Investigator: <u>Suzelle Barrington</u> Phone #: <u>514-398-7776</u> Unit/Department: <u>Department of Bioresource Engineering</u> Fax#: <u>514-398-8387</u> Address: <u>Macdonald Stewart MS1024, Macdonald Campus</u> Email: <u>suzelle.barrington@mcgill.ca</u>														
2. Emergency Contacts: Two people must be designated to handle emergencies. Name: <u>Suzelle Barrington</u> Work #: <u>514-398-7776</u> Emergency #: <u>(450) 825-2530</u> Name: <u>Denis Hatcher</u> Work #: <u>514-398-8644</u> Emergency #: <u>(514) 457-9276</u>														
3. Funding Source: External <input checked="" type="checkbox"/> Internal <input type="checkbox"/> Source (s): <u>NSERC and FPPO</u> Source (s): _____ Peer Reviewed: <input checked="" type="checkbox"/> YES <input type="checkbox"/> NO** Peer Reviewed: <input type="checkbox"/> YES <input type="checkbox"/> NO** Status: <input checked="" type="checkbox"/> Awarded <input type="checkbox"/> Pending Status: <input type="checkbox"/> Awarded <input type="checkbox"/> Pending Funding period: <u>until summer 2005</u> Funding period: _____		For Office Use Only: <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <th style="text-align: center;">ACTION</th> <th style="text-align: center;">✓</th> <th style="text-align: center;">DATE</th> </tr> <tr> <td style="text-align: center;">CCs</td> <td></td> <td></td> </tr> <tr> <td style="text-align: center;">DB</td> <td style="text-align: center;">✓</td> <td style="text-align: center;">May 7th 2004</td> </tr> <tr> <td colspan="3" style="text-align: center;">APPROVED</td> </tr> </table>	ACTION	✓	DATE	CCs			DB	✓	May 7 th 2004	APPROVED		
ACTION	✓	DATE												
CCs														
DB	✓	May 7 th 2004												
APPROVED														
** All projects that have not been peer reviewed for scientific merit by the funding source require 2 Peer Review Forms to be completed e.g. Projects funded from industrial sources. Peer Review Forms are available at www.mcgill.ca/rgo/animal/														
Proposed Start Date of Animal Use (d/m/y): <u>June 1st 2004</u> or ongoing <input checked="" type="checkbox"/>														
Expected Date of Completion of Animal Use (d/m/y): <u>June 1st 2005</u> or ongoing <input type="checkbox"/>														
Investigator's Statement: The information in this application is exact and complete. I assure that all care and use of animals in this proposal will be in accordance with the guidelines and policies of the Canadian Council on Animal Care and those of McGill University. I shall request the Animal Care Committee's approval prior to any deviations from this protocol as approved. I understand that this approval is valid for one year and must be approved on an annual basis. Principal Investigator's signature:  Date: <u>March 24th 2004</u> Approved by: 														
Chair, Facility Animal Care Committee:		Date: <u>30 March 2004</u>												
University Veterinarian:	<u>(see next page) S2</u>	Date:												
Chair, Ethics Subcommittee (as per UACC policy):		Date:												
Approved Animal Use	Beginning: <u>June 1, 2004</u>	Ending: <u>MAY 31, 2005</u>												
<input type="checkbox"/> This protocol has been approved with the modifications noted in Section 13.														

	McGill University Animal Use Protocol – Research	Protocol #: Investigator #: Approval End Date: Facility Committee:
Title: <u>Zeolite as natural swine feed additive to reduce the environmental impact of manure</u> <small>(must match the title of the funding source application)</small>		
<input type="checkbox"/> New Application <input checked="" type="checkbox"/> Renewal of Protocol # 4461 <input type="checkbox"/> Pilot Category (see section 11): <u>B</u>		
1. Investigator Data:		
Principal Investigator: <u>Suzelle Barrington</u>		Phone #: <u>514-398-7776</u>
Unit/Department: <u>Department of Bioresource Engineering</u>		Fax #: <u>514-398-8387</u>
Address: <u>Macdonald Stewart MS1024, Macdonald Campus</u>		Email: <u>suzelle.barrington@mcgill.ca</u>
2. Emergency Contacts: Two people must be designated to handle emergencies.		
Name: <u>Suzelle Barrington</u>	Work #: <u>514-398-7776</u>	Emergency #: <u>(450) 825-2530</u>
Name: <u>Denis Hatcher</u>	Work #: <u>514-398-8644</u>	Emergency #: <u>(514) 457-9276</u>
3. Funding Source:		For Office Use Only:
External <input checked="" type="checkbox"/> Internal <input type="checkbox"/> Source (s): <u>NSERC and FPPO</u> Source (s): _____ Peer Reviewed: <input checked="" type="checkbox"/> YES <input type="checkbox"/> NO** Peer Reviewed: <input type="checkbox"/> YES <input type="checkbox"/> NO** Status: <input checked="" type="checkbox"/> Awarded <input type="checkbox"/> Pending Status: <input type="checkbox"/> Awarded <input type="checkbox"/> Pending Funding period: <u>until summer 2005</u> Funding period: _____		
** All projects that have not been peer reviewed for scientific merit by the funding source require 2 Peer Review Forms to be completed e.g. Projects funded from industrial sources. Peer Review Forms are available at www.mcgill.ca/rgo/animal/		
Proposed Start Date of Animal Use (d/m/y): <u>June 1st 2004</u>		or ongoing <input checked="" type="checkbox"/>
Expected Date of Completion of Animal Use (d/m/y): <u>June 1st 2005</u>		or ongoing <input type="checkbox"/>
Investigator's Statement: The information in this application is exact and complete. I assure that all care and use of animals in this proposal will be in accordance with the guidelines and policies of the Canadian Council on Animal Care and those of McGill University. I shall request the Animal Care Committee's approval prior to any deviations from this protocol as approved. I understand that this approval is valid for one year and must be approved on an annual basis.		
Principal Investigator's signature: _____		Date: _____
Approved by:		
Chair, Facility Animal Care Committee:	_____	Date: _____
University Veterinarian:	<u>[Signature]</u>	Date: <u>May 5, 2004</u>
Chair, Ethics Subcommittee (as per UACC policy):	_____	Date: _____
Approved Animal Use	Beginning: _____	Ending: _____
<input type="checkbox"/> This protocol has been approved with the modifications noted in Section 13.		

 Canadian Food Inspection Agency
Agence canadienne d'inspection des aliments
Animal Health & Production Division
Ottawa, Ontario
K1A 0Y9
Fax: (613) 228-6614

October 16, 2003

JCG:STF

Mr. J.C. Guilmain
J.C. Guilmain, Inc.
1034 Rang 20
Upton, Québec
J0H 2E0

Re: Application for Temporary Feed Registration

Dear Mr. Guilmain:

This letter is to inform you that a temporary registration (Registration No. T990700) is being granted for KMI zeolite (Registration No. T990700) to authorize the disposal of swine from this research trial that have been fed diets containing 4% and 6% KMI zeolite for slaughter. This temporary registration expires on March 31, 2005.

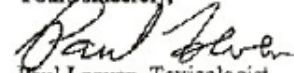
If you wish to register KMI zeolite in the future at levels greater than 2% in livestock feed, then the following information will be required:

1. Tissues from the current study should be held and analysed for heavy metals (arsenic, cadmium, chromium and lead) for liver, kidney and muscle from three pigs fed diets containing 4% and 6% KMI zeolite; and
2. Histopathology (as discussed previously) will be required for muscle, kidney and liver for four pigs at levels fed.

Please note that this ingredient has only been evaluated for safety and not for efficacy. Therefore, currently KMI zeolite is only approved as a flowing/anti-caking agent not to exceed to 2% in finished feed.

You have been charged fees in the amount of CAN\$304.95 for the consideration of this application and this fee has been paid in full. If you have any questions, please do not hesitate to contact me at (613) 225-2342 ext. 4140.

Yours sincerely,


Paul Loeven, Toxicologist,
Feed Section.

c.c. Jacques Fafard, CFIA Québec Area Office
Catherine Italiano, CFIA Headquarters
✓ Dr. Suzelle Barrington, McGill University

P:\New Ingredients\Zeolite On/Temporary reg for KMI zeolite 6% Oct. 16, 2003.mpd



 Canadian Food Inspection Agency
Agence canadienne d'inspection des aliments
Animal Health & Production Division
Ottawa, Ontario
K1A 0Y9
Fax: (613) 228-6614

March 31, 2005

Mr. J.C. Guilmain
J.C. Guilmain, Inc.
1034 Rang 20
Upton, Québec
J0H 2E0

Feuilles de transmission par télécopieur		Date	March 31/05	# de pages	1
Post-it® Fax Note		70710			
To / À	Dr. Suzelle Barrington		Paul Loeven		
Co./Dept. / Département			Feed Section / CFIA		
From / À	(514) 348-8387		(613) 225-2342 ext. 4140		
Fax / À	(514) 348-8387		(613) 228-6614		

JCG.SIF


Re: Application for Extension of Temporary Feed Registration

Dear Mr. Guilmain:

This letter is to inform you that an extension has been granted until May 31, 2005 for the temporary registration (Registration No. T990700) of KMI zeolite in order to allow the current research trial to be completed in which swine are being fed diets containing 4% and 6% KMI zeolite. The extension had been requested by Dr. Suzelle Barrington, the researcher conducting this research trial with KMI zeolite in swine. KMI zeolite is currently registered as an anti-caking/flowing agent in feed (Registration No. 990668) and may be added up to 2% of the total diet.

If you have any questions, please do not hesitate to contact me at (613) 225-2342 ext. 4140.

Yours sincerely,


Paul Loeven, Toxicologist,
Feed Section.

cc: Jacques Fafard, CFIA Québec Area Office
Janice Weightman, CFIA Headquarters
Dr. Suzelle Barrington, McGill University

P:\New Ingredients\Zeolite Ore\temporary reg for KMI zeolite 6% extension Mar. 31, 2005.wpd

Canada

**McGill University Animal Care Committee
Certification of Animal Training For Species
Other Than Laboratory Rodent/Rabbit**

Please Print Clearly:

Trainee's Name: Jagannath tiwari Work Phone
#: N/A

Status: (Grad. Student, Undergrad, Post. Doc., Faculty etc): Grad Student

Building and Room: Macdonald Stewart

Dept./Faculty/Institution: Animal Science/ FAES/ McGill


Email: injayanti@hotmail.com Supervisor: Dr. Suzelle Barrington
This is to document that the above-mentioned person has been trained to work with

Swine (species) through a hands-on personal tutorial
session on October 29th 2005 (date),

in/at Macdonald Campus Farm (location).

The training included the following procedures and methods:

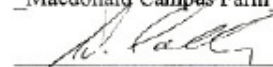
Swine Basic Handling



(Signature of trainer)

Philip Lavoie (Name of trainer)

Macdonald Campus Farm (Trainer's Department/Faculty/Institution)



(Certified by Animal Training Coordinator)

Note:

- *Trainer must supply a copy of this to the Animal Training Coordinator,
fax: 398-4644*
- *Trainee should keep this certificate as other institutions may request it*



McGill University
Environmental Health and Safety

THIS IS TO CERTIFY THAT

Jagannath Tiwari

Department of Bioresource Engineering
SUCCESSFULLY COMPLETED CORE TRAINING IN

**Workplace Hazardous Materials Information System
(W.H.M.I.S.)**

ON

Wednesday, January 17, 2007

Pietro Gasparini
Environmental Health & Safety Officer

Valid Until Sunday, January 17, 2010

Wayne Wood
Manager, Environmental Health & Safety

17th October 2007

The undersigned parties allow Jagannath Tiwari to publish the following two papers in the thesis:

Tiwari, J., S. Barrington, X. Zhao. 2007. Effect on manure characteristics of supplementing grower hog ration with clinoptilolite. Microporous and Mesoporous Materials.

Tiwari, J., S. Barrington, X. Zhao. 2007. Effect of clinoptilolite diet supplementation and lower crude protein and energy levels on grower hog performance. Journal of Animal Science.



Suzelle Barrington



Xin Zhao