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Feasibility Study on the Recovery of Commodity Chemicals and Agri-Products from Hog Manure

By

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A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfilment of the requirements of the degree of

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Abstract

An Extraction & Fractionation (EF) procedure is proposed that uses hog manure to generate value added products. Two fractions were generated, and analyzed for recovery of total and volatile solids, and total carbon and nitrogen. Metal concentration was determined using solid state ICP-AES; spectroscopic investigations (FTIR and ^{13}C – NMR) were also performed. The two significant fractions were a non-hydrolyzed fraction accounting for the largest portion of TS recovered; this was mainly carbohydrate based. The second fraction, termed the hydrolyzed fraction, represented a smaller fraction of total solids, and a high percentage of nitrogen recovery. Based on the results, two markets were identified for the products, with a third following development of a more efficient metal recovery procedure. A sustainability analysis showed the cost of producing the products using the EF procedure could range from 6 – 13 \$/kg TS, with clear improvements in environmental benefits when compared with conventional landspreading.

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Glossary

^{13}C – NMR – Carbon-13 nuclear magnetic resonance spectroscopy

Acidification – Addition of HCl to the solution following the alkaline hydrolysis. The HCl reduces solution pH, causing the HF to precipitate from solution.

Agri-product – A product from the EF procedure suitable for use in the agricultural industry as a source of nutrients and minerals.

Al – Aluminum

Alkaline hydrolysis – Second step in the EF procedure involving hydrolyzing the hog manure in a KOH solution at a temperature of 70° C producing a non-hydrolyzed component and a hydrolyzed component of the hog manure.

Annual loading rate – The amount of a given material placed on cropland in one season

Bioaccumulation – A physical/chemical process whereby compounds such as phosphorus and certain metals are retained in the soil matrix and accumulate over successive landspreading operations.

Broadcast landspreading – A technique in which hog manure is sprayed onto cropland using manure for a tanker truck or an irrigation canal.

C – Total percent carbon measured in the untreated hog manure or the NHF and HF using an Elemental Analyzer.

Ca – Calcium

Commodity chemical – A product from the EF procedure suitable for use in various industries; potential uses include production ethanol or organic acids, or the production of minerals and vitamins for use in hog production.

Cropland – Soil area where organic manures are landspread to supply nutrients for crop growth.

Crop N – The amount of nitrogen required by a particular crop in one season

Crop P – The amount of phosphorus required by a particular crop in one season

Crop production efficiency – General term used to describe the relative crop yield to the amount of energy used

Crop yield – The total amount of crop harvested in one growing season

Cu – Copper

Cultural energy – General term used to describe energy based on human labour and natural by-products as the basis of agricultural systems over modern sources of energy such as fossil fuels and inorganic fertilizers

Cumulative loading rate – The total amount of material that has accumulated on cropland over successive seasons

EF procedure – A chemical process applied to hog manure in which metals are first reduced in concentration and organic material is then recovered in several different forms.

Family farm production – Term used to describe a family run farming operation involving fewer than 1000 animals per farm. These operations tend to involve an integrative approach to crop and animal production.

Fe – Iron

Flushed manure – Hog manure that is collected using water.

FTIR – Fourier – transform infrared spectroscopy

HCl – Hydrochloric acid

HF – Hydrolyzed fraction of the hog manure. This material was solubilized into the KOH solution and was precipitated following acidification with HCl

Hog manure – Byproduct of the hog production industry which includes mainly excreta and urine, and to a lesser degree bedding and feed.

Hog manure management – A general, integrative term, implying the collection, storage, treatment and landspreading hog manure.

Hog manure slurry – Hog manure and water mixture diluted to 1 – 10 % solids in order to facilitate landspreading operations

ICP-AES – Inductively coupled plasma atomic emission spectroscopy

Incorporation – A physical operation in which hog manure is mixed with soil to a pre-determined depth following landspreading

Injection landspreading – A technique in which hog manure is applied beneath the soil surface using pressurized hoses

Inorganic fertilizer – Man made source of nitrogen, phosphorus and potassium for crops

Integrated nutrient management – A nitrogen, phosphorus and potassium management technique in which the inputs and outputs of these in soil are calculated on a yearly basis

Intensive hog production – Large scale production of hogs involving a production unit of more than 1000 animals per farm.

K – Potassium

KOH – Potassium hydroxide

Landspreading – Physical process whereby a solid or liquid organic material is applied and mixed to cropland.

Mg – Magnesium

N – Total percent nitrogen measured in the untreated hog manure or the NHF and HF using an Elemental Analyzer

Na – Sodium

NHF – Non-hydrolyzed fraction of the hog manure. This material is not solubilized by the alkaline hydrolysis

Non-gestating sow – Term used to describe a female hog that is within reproductive cycles

Nutrient sensitive cropland – Agricultural crop land that has excessive amounts of phosphorus bioaccumulation in the soil

%MRE – Percent metal removal efficiency

P – Phosphorus

Pre-treatment – First of two steps in the EF procedure involving washing the hog manure with HCl in order to solubilize metals present in the hog manure.

Scraped manure – Hog manure that is collected using gravitational or mechanical means such as pits or automated scrapers

Sustainable agriculture – A term used to describe consideration of economic, social and environmental aspects of agricultural operations.

TS – Mass of total solids measured in the untreated hog manure or the NHF and HF

VS – Percent volatile solids measured in the untreated hog manure or the NHF and HF

Zn – Zinc

Chapter 1 – Introduction

1.1. Preamble

Landspreading hog manure on cropland has historically been considered an adequate manner in which nutrients can be recycled on a farm (Miner *et al.*, 2000; Hatfield *et al.* <http://www.ars.usda.gov>; Ministry of Agriculture, Food and Rural Affairs, 2001; City of Ottawa, 2002; Weller *et al.*, 1977; Taiganides 1977). In recent years, intensification of the hog production industry, due to an increased demand for hog products, has led to dramatic increases in the quantity and nature of the manure that must be disposed of on land. The most distinguishing aspect of intensive hog production is the large quantities of manure produced in more dense areas (Taiganides, 1977; Hsu and Lo, 2000). This characteristic of intensive operations can reduce the effectiveness of landspreading by causing impacts such as bioaccumulation of compounds such as metals or phosphorus or deterioration of the soil matrix (Taiganides, 1977; El-Ahraf and Willis, 1996; Dinel *et al.*, 1998). The adoption of waste reduction strategies, technologies to more efficiently recycle hog manures, and stricter regulations regarding hog manure management on farms, are some of the methods employed by the public and private sector regulatory agencies to reduce the impact of intensive hog production industries on local ecology and public health.

The development of technologies that can reduce odours, reduce impacts from pathogenic organisms and concurrently extract nutrients and other potentially

useful commodities for resale (CETAC-WEST, 1999; Westerman and Bicudo, 2000; Chastain *et al.*, 2001) are becoming prominent areas of bio – technological research and innovation. Several researchers have suggested that the present state of agriculture (conventional agriculture with landspreading) may not be sustainable, given the trends and characteristics associated with intensive hog production (Biggelaar and Suvedi, 2000; Wallace, 1994; Dinel *et al.*, 1998; McSorley and Porazinska, 2001). Modern trends towards reducing the impact of intensive agricultural activities have been to develop different farming philosophies and practices such as organic farming or integrated nutrient and pest management (Sarkar and Singh, 1997; Orr *et al.*, 2001). Sustainable agriculture integrates technical, social and economic issues in order to reduce the impact of landspreading activities on human, ecological and community health (Biggelaar and Suvedi, 2000; Wallace, 1994; McSorley and Porazinska, 2001; Jones, 1993; Pannell and Schilizzi, 1999). By using hog manure as a raw material to produce valuable agricultural products and chemical commodities, farmers can simultaneously reduce the direct use of hog manure on land and generate a secondary source of income. This provides both a technical and social solution to issues related to inefficient and potentially dangerous, landspreading techniques.

The focus of this study was to examine the effectiveness of using hog manure as a raw material to produce value-added materials in the form of agricultural products (agri-products) and chemical commodities an Extraction and Fractionation (EF) procedure. The original concept of sequentially fractionating

organic material into different fractions, termed chemical commodities, was first introduced by Diné and Dumontet (1995); the background theory from their procedure was based on soil chemistry. The term “chemical commodity” is an adjective used to describe products from the EF procedure that could potentially have economic value attributed to their production, based on a suitable. Agri-products are used to describe the fraction of hog manure that is desirable from a crop nutrient perspective.

In consultation with Dr. Diné and other members of the project, the methodology for the extraction and fractionation of agri-products and chemical commodities was developed.

The EF procedure examined in this research consisted of sequentially pre – treating hog manure with HCl to reduce the metal content of the hog manure, followed by an alkaline hydrolysis with KOH to produce various products that will be examined for their potential to generate value added materials.

1.2. Purpose and Scope

The main purpose of this research is to examine the feasibility of the EF procedure to produce valuable agri-products and chemical commodities from hog manure. To achieve this objective, the following tasks were undertaken:

- Laboratory investigations involving the following tasks:
  - Batch, laboratory scale development and implementation of the EF procedure,
  - Analysis of metal content prior to and following pre – treatment with HCl,
  - Analysis of metal content in the products,
  - Characterization and analysis of the various fractions generated in EF procedure:
    - Fractions were dried and analyzed for the following variables:
      - Total solids yield,
      - % Volatile solids,
      - % Carbon,
      - % Nitrogen,
    - Fractions were examined using Fourier Transform Infrared Spectroscopy, to analyze functional groups present,
    - Fractions were examined using Carbon-13 Nuclear Magnetic Resonance Spectroscopy, to analyze carbon bonds present
- Sustainability analysis involving examination of technical, economical and environmental issues related to use of the EF procedure to produce various products on a batch basis.

Chapter 2 – Background Literature Review

2.1. Hog Manure and Manure Management

2.1.1. Hog Manure Generation Rates

The following two trends in the hog production industry are evident from the literature – 1. There is an increasing demand for hog products by consumers (Ministry of Agriculture, Food and Rural Affairs, 2000); – 2. The number of intensive hog production operations is increasing (Yeager, 2000; Schmidt *et al.*, 1996; Schmitt *et al.*, 1996; Miner *et al.*, 2000; Hatfield *et al.*, <http://www.ars.usda.gov>). Intensive livestock operations are defined by the City of Ottawa as farming operations that “...exceed 150 livestock units, or exceed 50 livestock units with a livestock density of more than 5 livestock units per tillable acre” (City of Ottawa, 2002). From the literature, it was evident that the number of family farms is decreasing, while the percentage of hogs being produced by intensive livestock operations is increasing (Weller and Willetts, 1977; Miner *et al.*, 2000; Miner, 1999; Hatfield *et al.*, <http://www.ars.usda.gov>; Yeager, 2000). This implies that the quantity of manure that needs to be disposed of is increasing, while simultaneously this manure is being concentrated in smaller areas, with a smaller land base available for landspreading that manure (Weller and Willetts, 1977; Honeyman, 1996; Hatfield *et al.*, <http://www.ars.usda.gov>; Hsu and Lo, 2000). Table 2-1 shows hog production trends in Ontario over a ten year period. These data show that demand for hog products is increasing. Tables 2-2 – 2-4 illustrate the trend in the hog production industry.

Table 2-1: Hog production trends in Ontario for various years (Adapted from Ministry of Agriculture: www.gov.on.ca/omafra/english/stats/livestock/pigs.html; 2000).

Type of Hog	% Change – 5 Years Ago (July 1995)	% Change – 10 Years Ago (July 1990)
Boars (> 6 months)	- 33.2	- 40.5
Sows and Bred Gilts	+ 1.3	+ 5.2
Hogs (under 20 kg)	+ 8.2	+ 9.1
Hogs (20 – 60 kg)	+ 1.9	+ 7.7
Hogs (> 60 kg)	+ 5.2	+ 13.1
Total Hogs	+ 4.4	+ 9.1

Table 2-2: Number of farms selling hogs in the US for various years, based on farm size (# hogs/farm) (Miner, 1999).

Year	Farm Size	
	1 to 1000 Hogs	> 1000 Hogs
1969	597,000	6,600
1978	454,700	15,800
1982	293,400	21,700
1987	215,000	24,000
1992	160,400	27,750

Table 2-3: Number of hog operations in the US for various years, based on farm size (Miner, 1999).

Farm Size	1994	1995	1996
1 to 999 animals	195,280	170,310	145,520
1000 to 1999 animals	8,070	7,720	7,050
> 2000 animals	4,630	4,750	4,880

Table 2-4: Number of hogs marketed by class size (Honeyman, 1996).

Annual Marketing's	% of Total Farms	% Total Marketing's
< 1000 head		
1978	96.8	66.4
1982	93.1	51.9
1987	89.9	42.5
1000 – 1999 head		
1978	2.4	16.3
1982	4.8	21.1
1987	6.7	21.9
2000 – 4000 head		
1978	0.7	10.3
1982	1.7	15.2
1987	2.7	18.5
> 5000 head		
1978	0.1	7.0
1982	0.4	11.8
1987	0.7	17.1

Hatfield *et al.* (<http://www.ars.usda.gov>) reported that the number of farms selling hogs has declined from 1,273,000 in 1959 to under 200,000 in 1990 in the U.S. Tables 2-1 – 2-4 clearly show that while the quantity of hog products being produced is increasing, the number of farms that are producing the hogs are decreasing in numbers, and thus, are increasing in size.

As urban sprawl and manure production increase, competition for available land will grow. This will result in a need for technologies that can reduce the amount of manure that is landspread, without wasting the nutrients already present in the manure. Increased use in bio-technologies such as the EF procedure will result

in a more efficient use of the wastes that are generated by the agricultural industry.

2.1.2. Hog Manure Characterization

Hog manure is a heterogeneous material of varying compositions and particle sizes (Dinel *et al.*, 1998; Zhang and Westerman, 1997). Variations in hog manure data exist due to differences in collection and storage, feed and bedding material, and the manner data are gathered and reported (Choudhary *et al.*, 1996). The heterogeneity in hog manure is illustrated in Tables 2-5 – 2-10. A high BOD value suggests the presence of organic matter and microbiological agents. The nutrient value of hog manure consists of nitrogen (N), phosphorus (P) and potassium (K), as well as several elements such as calcium (Ca) and magnesium (Mg). As previously mentioned, hog manure may also contain various metals and other potential pollutants. Table 2-5 shows characteristics of hog manure based on live animal weight; Table 2-6 shows data for excreta and urine only. Tables 2-7 and 2-8 show characteristics for scraped and flushed hog manures. Flushed manure is collected (and distributed) with water, and scraped manure is collected with a shovel or mechanical scraper. Flushed manures tend to have a lower solids content than scraped manures.

Table 2-5: Hog manure parameters based on total live weight (Taiganides, 1977).

Parameter (units)	Value
Wet Excreta Waste (% Live Wgt./day)	5.1
Total Solids (% Live Wgt.)	13.5
Volatile Solids (% Total Solids)	82.4
BOD (% Total Solids)	31.8
BOD/COD	30.7
N (% Total Solids)	5.6
P ₂ O ₅ (% Total Solids)	2.5
K ₂ O (% Total Solids)	1.4

Table 2-6: Hog manure parameters for excreta and urine only, and does not include bedding or feed (Elliott *et al.*, 1977).

Parameter	Percent
Feces/Urine Ratio	1.2
Total Solids (TS) = %DM	9.2
Volatile Solids (%TS)	80
BOD ₅ (%TS)	33
COD (%TS)	95
Total N (%TS)	7.5
Total P (%TS)	2.5
Total K (%TS)	4.9

Table 2-7: Characteristics of scraped hog manure (Miner *et al.*, 2000).

Parameter	Value
Volume (l)	30.3
Total Mass (kg)	29.5
Total Solids (TS), % wet weight	8
Volatile Solids (% TS)	80
Total N (% TS)	7
NH ₃ - N (% TS)	3.5
BOD ₅ (% TS)	30
Total P (% TS)	1.5

Table 2-8: Characteristics of flushed hog manure (Miner *et al.*, 2000).

Parameter	Value
Wastewater (l/day/1000 lb live wgt.)	378.5
Total Solids (TS) (kg/day/1000lb live weight)	22.7
TS, (% wet weight)	0.72
Volatile Solids (% TS)	80
BOD ₅ (% TS)	40
Total N (% TS)	6.5
NH ₃ – N (% TS)	3.2
Total P (% TS)	1.2

Data in Table 2-9 have been compiled from several sources by the author, and represent the ranges of characteristics observed for the variables of interest. The data presented in Table 2-10 show the range (and mean) of hog manure characteristics collected from different management systems. The nutrients shown in Table 2-10 represent those available to the crops.

Table 2-9: Liquid swine manure characteristics (Choudhary *et al.*, 1996).

Parameter	Min – Max Values Reported
pH	6.3 – 8.1
Dry Matter (%)	2.33 – 6.58
Total N (%)	6.3 – 11.6
NH ₄ ⁺ - N (%)	3.3 – 8.9
Total P (%)	1.7 – 4.38
K (%)	2.2 – 5.5
Ca (%)	3.12 – 6.33
Mg (%)	0.93 – 2.66
Na (%)	1.61 – 3.66

Table 2-10: Manure characteristics for various management systems (Hatfield *et al.*, <http://www.ars.usda.gov>).

Management System	Dry Matter (%)	NH ₄ – N	Total N	P	K
For Solid Manure		g / kg			
With Bedding	15 – 20 (18)	2.7 – 4.0 (3.1)	4.0 – 4.9 (4.5)	1.4 – 2.6 (1.8)	2.2 – 3.7 (3.0)
Without Bedding	17 – 20 (18)	2.2 – 3.6 (2.7)	3.1 – 4.5 (3.6)	1.0 – 2.0 (1.4)	2.2 – 3.3 (2.6)
For Liquid Manure		g / L			
Anaerobic Storage	2 – 7 (4)	2.5 – 3.7 (3.1)	3.4 – 6.6 (4.3)	0.7 – 1.6 (1.4)	1.2 – 3.0 (2.2)
Lagoon	0.3 – 2.0 (1)	0.2 – 0.6 (0.5)	0.4 – 0.7 (0.5)	0.05 – 0.2 (0.1)	0.2 – 0.6 (0.4)

The nutrient value of hog manure is well documented by researchers (Weller and Willetts, 1977; Taiganides, 1977; Miner *et al.* 2000, Ministry of Agriculture, Food and Rural Affairs, 2002). Table 2-11 shows the percent of total dry manure solids for various minerals and nutrients in liquid manure, as well as the N: P: K and C: N ratios.

Table 2-11: Mean nutrient and mineral content of liquid swine manure (Taiganides, 1977).

Parameter	Mean Value
Dry Matter	8.3
Organic Substances (% Dry Matter)	80.7
Total C (% Dry Matter)	34.9
Total N (% Dry Matter)	7.3
NH ₄ ⁺ - N (% Dry Matter)	4.3
P ₂ O ₅ (% Dry Matter)	3.8
K ₂ O (% Dry Matter)	2.8
CaO (% Dry Matter)	3.1
MgO (% Dry Matter)	0.96
Na ₂ O (% Dry Matter)	0.72
C : N (% Dry Matter)	4.8
N : P ₂ O ₅ : K ₂ O (% Dry Matter)	1 : 0.59 : 0.38

Not all nutrients contained in hog manure are available to plants (Miner *et al.*, 2000, Weller and Willetts, 1977). Nutrients can be immediately released into the atmosphere or groundwater upon placement, or they can be tightly bound into the soil matrix, and slowly released over time. The ability of plants to take up nutrients has a large impact on the manner, quantity and time frame in which manure can be ploughed into soil. The following two tables show the estimated availability of nutrients in hog manure, and the estimated crop nutrient requirements respectively.

Table 2-12: Estimated availability of nutrients in hog manure (Weller and Willetts, 1977).

Parameter (% wet weight)	% Available
Nitrogen	0.4
Phosphorus	0.3
Potassium	0.3

Table 2-13: Nutrient uptake for several common agricultural crops (Miner *et al.*, 2000).

Crop	Crop Yield/Hectare	Portion Harvested	N, kg	P, kg	K, kg
Reed canary grass	2.5 ton	All	163	16	136
Fescue, for hay	2.02 ton	All	125	12	122
Alfalfa, for hay	1.62 ton	All	89	9	71
Orchard grass, for hay	1.01 ton	All	30	4	43
Timothy, for hay	1.01 ton	All	24	3	36
Bluegrass, for hay	0.81 ton	All	24	5	6
Corn	80 bu*	Grain only	29	6	6
Corn	80 bu*	All	52	8	44
Corn for silage	150 bu*	All	84	16	81
Milo	70 bu*	Grain only	28	4.5	5.5
Milo	70 bu*	All	37	6	2.6

* Bushels

The types of micro-organisms in hogs and hog manure are shown in Table 2-14; though the table is not exhaustive, it does illustrate the need to ensure proper handling and management of the waste when using it to supply needed crop nutrients.

Table 2-14: Potentially transmittable organisms from hogs and hog manure (Elliott *et al.*, 1977).

Common Disease	Etiologic Agent	Method of Entry
Salmonellas	Salmonella sp.	Ingestion
Leptospirosis	Leptospira Pomona	Cutaneous and facial membranes
Anthrax	Bacillus anthracis	Cutaneous, inhalation, ingestion
Tuberculosis	Mycobacterium tuberculosis	Inhalation, ingestion
Tuberculosis	M. avium	Inhalation, ingestion
Tuberculosis	M. bovis	Inhalation, ingestion
Brucellosis	Brucella abortus	Ingestion, inhalation, direct contact
Brucellosis	B. melitensis	Ingestion, inhalation, direct contact
Erysipelas	Erysipelothrix rhusiopathiae	Ingestion, cutaneous
Colibacillosis	E. Coli (some stereotypes)	Ingestion
Hog Cholera	Virus	Direct contact, ingestion
Foot and Mouth	Virus	Direct contact, ingestion
Coccidiomycosis	Coccidioides immitus	Dust inhalation, cutaneous
Ringworm	Various Microsporum and Trichophyton	Direct contact
Coccidiosis	Eimeria sp.	Ingestion of oocytes
Balantidiasis	Balantidium coli	Ingestion of oocytes
Toxoplasmosis	Toxoplasma sp.	Unknown
Ascariasis	Ascaris lumbricoides	Ingestion
Sarcocystiasis	Sarcocystis sp.	Ingestion

Metals can be a concern in manures, as these can accumulate in surface and sub-surface soils as well as in the biomass (crops, livestock, etc.). The origin of metals in manure is mainly from diets, where trace quantities of metals are added as a normal constituent of hog feed (Luce and Maxwell, <http://www.ansi.okstate.edu>.) Tables 2-15 and 2-16 show average metal concentrations that have been previously reported (Asiegbu and Oikeh, 1995; Westerman and Bicudo, 2000).

Table 2-15: Metal content of swine manure (Asiegbu and Oikeh, 1995).

Parameter	Value
Al (ug)	1990
Ar (ppm)	0.05
P (%)	2.06
K (%)	1.08
Ca (%)	2.76
Mg (%)	0.95
Na (%)	0.15
Fe (%)	1.18
Zn (ug)	272.09
Cu (ug)	43.06
Cu (%)	27

Westerman and Bicudo (2000) showed extensive data with high levels of variability between hog manures collected from different management techniques. The most notable differences exist between the solid and liquid manures.

Table 2-16: Average concentration of various parameters in different forms of swine manure wastes (Westerman and Bicudo, 2000).

Parameter	Flushed Manure	Screened Liquid Manure	Lagoon Surface Liquid	Units	Separated Manure Solids	Units
pH	8.2±0.2	8.3±0.2	8.0±0.1	N/A	7.6±0.4	N/A
TKN	1368±277	1327±269	764±84	mg/l	18036±2022	µg/g
NH ₃ – N	980±175	963±163	659±61	mg/l	2917±641	µg/g
Org – N	388±127	363±132	105±43	mg/l	15120±920	µg/g
Total P	354±196	355±206	80±	mg/l	10435±2560	µg/g
Available P	ND	ND	ND	ND	5816±707	µg/g
OPO ₄ – P	180±68	178±62	70±3	mg/l	ND	ND
COD	7780±1676	7642±1657	1614155±	mg/l	ND	ND
TOC	1735±404	1816±479	715±94	mg/l	ND	ND
C/N Ratio	ND	ND	ND	ND	23.5±4.3	ND
Dry Matter	ND	ND	ND	ND	39.8±13.1	%
Total Solids	1.11±0.49	0.96±0.31	0.34±0.02	%	ND	ND
Volatile Solids	61.6±6.4	60.2±5.5	38.2±7.9	%TS	ND	ND
Total Sus. Sol.	8014±5044	6421±3122	565±97	mg/l	ND	ND
Na	222±35	232±53	166±11	mg/l	2210±437	µg/g
K	996±123	1037±165	764±61	mg/l	4577±644	µg/g
Ca	263±104	263±88	90±18	mg/l	37224±13890	µg/g
Mg	111±544	110±56	21±3	mg/l	4849±690	µg/g
Cu	8.0±5.94	8.5±5.8	0.4±0.2	mg/l	131±40	µg/g
Zn	11.2±6.8	11.2±6.2	0.8±0.4	mg/l	314±53	µg/g
Fe	31±20	32±17	5.1±1.5	mg/l	3208±831	µg/g
Crude Protein	ND	ND	ND	ND	10.3±0.6	%
Ash	ND	ND	ND	ND	15.0±11.4	%

One study of particular interest characterized different particle size ranges for various manures (Zhang and Westerman, 1997). In general, it was found that over half of the proteins in manure could be found in the smallest particle size range (<0.053 mm). Zhang and Westerman (1997) also reported findings from other studies that specifically examined hog manure. The authors reported data that showed for hog manure solids, 83 percent of the crude protein and 93 percent of the fat passed through a 0.25 mm sieve for all study cases. This

suggests that the smallest particle size range of swine manure may contain many of the compounds of interest to farmers and agronomists.

A study by Diné *et al.* (1998) examined colloidal fractions of hog manure using various spectroscopic investigations. Analytical methods used in the study were Pyrolysis-Field Ionization Mass Spectrometry (Py-FIMS), ^{13}C Nuclear Magnetic Resonance (^{13}C NMR) and Fourier – Transform Infra-Red Spectroscopy (FTIR). Py-FIMS and ^{13}C NMR results from their study are provided in Tables 2-17 and 2-18.

Table 2-17: Py – FIMS Results, showing various compound groups identified, as percent of Total Ion Intensity (TII) of colloidal mass spectrum (Diné *et al.*, 1998).

Compound Group	Group 1 (% of TII)	Group 2 (% of TII)	Group 3 (% of TII)
Carbohydrates	2.5	6.5	3.0
Phenols + Lignin Monomers	2.5	3.6	4.0
Lignin Dimers	0.3	0.5	0.2
Lipids	5.3	10.6	11.9
Alkyl Aromatics	3.0	4.0	2.9
N – Compounds	3.1	3.0	4.7
Sterols	10.1	12.7	10.2
Peptides	4.9	3.5	3.6
Suberins	1.5	1.6	0.9
Free Fatty Acids	3.4	6.8	9.5
Low Mass Signals (H_2O , CO etc.)	17.0	25.8	14.0
Total	53.6	78.6	64.9

Table 2-18: ^{13}C – NMR Integration results, showing suggested distribution of C in colloidal material (Dinel *et al.*, 1998).

C Type	Chemical Shift (ppm)	% of Total C
Aliphatic C (including C in sterols)	0 – 40	32.4
Protein C, peptide C, C in OCH_3 and sterols	41 – 60	18.0
Carbohydrate C	60 – 105	22.3
Aromatic C	105 – 150	15.3
Phenolic C	150 – 170	4.5
C in CO_2H groups	170 – 190	7.4

Results published by Dinel *et al.* (1998) appear to confirm the findings reported by Zhang and Westerman (1997), suggesting that the colloids (i.e. smaller particle size ranges) tend to contain the highest percentage of proteins and long chain polymers (aliphatic compounds).

It is evident that hog manure is a heterogeneous and variable material based on the data presented in Tables 2-5 through 2-18. Care must also be taken to ensure that differences observed in hog manure are not attributed to differences in the manner data are reported, or the water content of the hog manure. In addition, variability in hog manure can often be attributed to collection and storage methods, as well as feed characteristics.

2.1.3. Hog Manure Management

The most important factor differentiating many storage and treatment techniques is whether a solid, liquid or slurry manure is being handled. The solids content of manure is largely dependent upon the individual animal; once excreted, different management techniques will ultimately determine whether manure is to be handled as a solid or a liquid.

Figure 2-1 shows various management schemes for hog manure production. From this it can be seen that different decisions made in housing hogs will affect the ultimate nature of the manure. Shown in Figure 2-1 are the two main management options for hog manure production – open lot/pasture and confined production. Pasture production is generally not used by intensive livestock operations (Schmidt *et al.*, 1996; Schmitt *et al.*, 1996), as the manure is generally left “as excreted”, and is naturally spread by the animals (Hatfield *et al.*, <http://www.ars.usda.gov>). Management of hogs in this manner will not be further discussed, as manure left on pasture land does not lend itself to elaborate management alternatives. Open lot systems are similar to pasture systems in the nature of the manure collected, however, manure is often confined to a restricted area, thus ensuring that collection is more feasible, as compared to collection in a pasture management system.

Figure 2-1: Various management options for hog manure production (Dickey et al., <http://www.ianr.unl.edu/pubs/wastemgt/q531.htm#olmm>).

2.1.3.1. Open Lot Management

Figure 2-2 shows a typical open lot management system, often employed in small to medium sized operations (Dickey *et al.*, www.ianr.unl.edu; Hatfield *et al.*, <http://www.ars.usda.gov>). Open lot management techniques can vary widely in their design, ranging from dirt floors, to sloped concrete, and are not as common for intensive hog production due to high labour requirements from solids handling (Miner *et al.*, 2000). The use of bedding is also common in open lot systems, and as a result manure would have characteristics similar to those reported in Tables 2-7, 2-10 and 2-16.

Figure 2-2: Typical open lot management system for hogs (Dickey *et al.*, <http://www.ianr.unl.edu/pubs/wastemgt/g531.htm#olmm>).

Manure from the open lots can be scraped frequently, to reduce runoff and odours. Runoff can then be controlled by using either vegetative filters or holding ponds, a large number of different pond design considerations are used to control the organic loading and volume of runoff from an open lot (Dickey *et al.*, www.ianr.unl.edu; Miner *et al.*, 2000). Hatfield *et al.* (<http://www.ars.usda.gov>) have reported results that suggest that as much as 20 percent of the manure generated in an open lot runs off from the site, resulting in nitrogen losses, and potential surface or groundwater contamination (see Tables 2-19 and 2-20 for nutrient losses from different management systems).

2.1.3.2. Confined Housing

Intensive livestock operations tend to use closed confinement as a management technique in order to facilitate the collection of manure; these operations will

often exclude the use of bedding material, in order to produce a more uniform manure by-product (Hatfield *et al.*, <http://www.ars.usda.gov>). Manure emanating from confined management systems will come in either a liquid or solid form. Manure in a liquid form has been collected with water, termed flushed systems. In flushed systems, manure collection is facilitated by a sloped channel below the floor. Gutters can also be used to collect the manure, after which it is ejected into various confinement systems through the use of large volumes of water or high-pressure hoses. Manure collected in a flushed system inadvertently contains a higher water content (or lower solids content) than manure collected as a solid material (Miner *et al.*, 2000; Taiganides, 1977). Tables 2-8, 2-9, 2-11 and 2-16 represent data for flushed or liquid hog manures. Due to the high water contents of manures generated by closed systems, a significantly larger volume of waste tends to be produced by intensive operations of this nature.

In addition to the larger volumes of waste produced by flush handling systems, concerns with nutrient losses also exist (Dickey *et al.*, www.ianr.unl.edu; Hatfield *et al.*, <http://www.ars.usda.gov>; Miner *et al.*, 2000). Tables 2-19 – 2-22 provide data on expected nutrient losses for several hog and manure management techniques. The high nutrient losses resulting from management operations represent inefficiencies in the manner in which manure is stored and landspread. Nutrient loss can be considered as a loss of revenue for, as these nutrients are no longer available to supply to crops.

Table 2-19. Estimated nitrogen losses during storage, treatment, and handling for various manure management systems (Dickey *et al.*, <http://www.ianr.unl.edu>).

System	Nitrogen Loss* (%)
Liquid pit or silo storage – Liquid spreading	30 – 65
Anaerobic lagoon – Irrigation or liquid spreading	60 – 80
Bedded confinement – Solid spreading	30 – 40
Open lot – Solid spreading, runoff collected and irrigated	50 – 60

* Assumes incorporation into soil within a few hours. Manure that is not incorporated results in an additional 30 percent loss.

Table 2-20: Nitrogen loss during storage of manure from different management systems (Hatfield *et al.*, <http://www.ars.usda.gov>).

Management System	Type of Manure	Nitrogen Loss (%)
Daily Scraper System	Solid/Slurry	15 – 35
Bedded Manure	Solid	20 – 40
Anaerobic Pit	Liquid/Slurry	15 – 30
Aboveground Storage	Liquid/Slurry	10 – 30
Earth storage	Liquid/Slurry	20 – 40
Lagoon	Liquid	70 – 80

Nitrogen losses from lagoons can be high due to volatilization of ammonia from the surface layer. This characteristic of lagoon storage is advantageous for intensive livestock operations having a smaller land base available for landspreading. By using lagoons the nitrogen levels of the manure decline, while the phosphorus concentration remains relatively constant. Reduced nitrogen levels in manure allow the same quantity of waste to be disposed of on a smaller parcel of land (Hatfield *et al.*, <http://www.ars.usda.gov>).

Table 2-21: Estimated nitrogen losses over a four-day period for various application techniques (Hatfield *et al.*, <http://www.ars.usda.gov>).

Application Technique	Type of Manure	Nitrogen Loss (%)
Broadcast over soil	Solid	15 – 30
	Liquid	10 – 25
Broadcast followed by incorporation into soil	Solid	1 – 5
	Liquid	1 – 5
Direct Injection into soil	Liquid	0 – 2
Sprinkler irrigation	Liquid	15 – 35

Table 2-22: Estimated nitrogen losses during application of manure to crop or pastureland using various application techniques (Miner *et al.*, 2000).

Application Technique	Estimated % Nitrogen Loss
Hauling solid manure and bedding. Incorporating into soil within 24 hrs.	5
Hauling solid manure and bedding. Not incorporating into soil.	25
Hauling liquid manure in a tank from an anaerobic storage tank. Injected directly into soil.	2
Pumping liquid or slurry in a pipeline from an anaerobic storage tank or lagoon. Injected under pressure into soil.	3
Hauling liquid in a tank from an anaerobic storage tank. Sprayed onto crops, with no incorporation into soil.	20
Hauling liquid in a tank from an anaerobic storage tank. Sprayed onto crops, with incorporation into soil within 24 hrs.	5
Pumping liquid manure from anaerobic or slurry storage via pipe. Moving gun nozzle is used to spray onto soil.	30
Pumping liquid manure from an anaerobic storage tank, lagoon or stored slurry. Distribution using multiple high-pressure nozzles.	30
Pumping liquid manure from an anaerobic storage tank, lagoon or stored slurry. Distribution using multiple low-pressure nozzles.	20

2.1.3.3. Hog Manure Storage/Treatment

Following collection, manure is often stored on site, in a location that makes it accessible for landspreading or short distance hauling to other farms. Storage of manure can result in the production of odours and greenhouse gases (Miner *et al.*, 2000; Taiganides, 1977; Weller and Willetts, 1977, Elliot *et al.*, 1977). Several conventional storage/treatment options for liquid wastes and their characteristics are listed below.

- **Detention Basis**

- ▶ Relatively simple design and construction,
- ▶ Collects and stores wastes for long periods,
- ▶ Effluent may not be suitable for land application.

- **Anaerobic Lagoons**

- ▶ Can be used for biological treatment/stabilization of organic wastes,
- ▶ Produces a liquid effluent, generally suitable for land application,
- ▶ Can produce odours and greenhouse gases,
- ▶ Results in a significant reduction in N losses to the atmosphere in the form of ammonia.

- **Aerobic Lagoons**

- ▶ Similar to an “activated sludge” process,
- ▶ Utilizes suspended biological activity to reduce organic loading,
- ▶ Can be used for biological treatment/stabilization of organic wastes,
- ▶ Requires the use of aerators to add and mix dissolved oxygen,
- ▶ Complex in design, construction and operation,

- ▶ Can be used in combination with anoxic basins for complete removal of organics and COD
- ▶ Effluent is generally suitable for land application
- **Oxidation Ditch**
  - ▶ Modified activated sludge process without the use of an aeration tank
  - ▶ Requires the use of aerators to add and mix dissolved oxygen in an elongated ditch
  - ▶ Can be used for biological treatment/stabilization of organic wastes
  - ▶ Can often be complex in design, construction and operation
  - ▶ Effluent is generally suitable for land application

(Miner *et al.*, 2000; Weller and Willetts, 1977; Taiganides, 1977; Hatfield *et al.*, <http://www.ars.usda.gov>)

Complete treatment of hog manure results in the extraction and reuse of energy (methane), nutrients (nitrogen, phosphorus, potassium), or the generation of more valuable products from the animal waste (Miner *et al.*, 2000; Weller and Willetts, 1977; El-Ahraf and Willis, 1996). Examples of such systems would be anaerobic digestion in order to generate methane for energy production, or composting solid and liquid manures to produce a cleaner, more biologically stable product (Miner *et al.*, 2000). The largest disadvantage of many of these technologies is that there still often remains a sludge that can be contaminated with metals and potentially other compounds such as steroids or antibiotics. Other techniques such as solid-liquid separation have been shown to be reliable

methods to reduce odours and concentrate nutrients, with a large variety of designs available (Miner *et al.*, 2000; Zhang and Westerman, 1997; Weller and Willetts, 1977; Taiganides, 1977). In a study by Zhang and Westerman (1997), various solid-liquid separation technologies were examined, as well as separation efficiencies for various micro and macronutrients for a wide range of manures. Data specific to hog manure are shown in Table 2-23.

Table 2-23: Results from various studies on the removal of several nutrients (% removed) using different mechanical separators. (Zhang and Westerman, 1997).

Reference	TS	VS	COD	TKN	Total P
Stationary Screen					
Shutt <i>et al.</i>	9	-	24	-	-
Shutt <i>et al.</i>	35	-	69	-	-
Piccinini and Cotellini	6 – 31	5 – 38	0 – 32	3 – 6	2 – 12
Vibrating Screen					
Hegg <i>et al.</i>	3	-	6	-	-
Hegg <i>et al.</i>	10	-	1 – 14	-	-
Hegg <i>et al.</i>	27	-	24	-	-
Holmberg <i>et al.</i>	21 – 52	25 – 55	17 – 49	5 – 32	17 – 34
Shutt <i>et al.</i>	22	25	16	-	-
Piccinini and Cotellini	15 – 25	18 – 38	13 – 26	2 – 5	1 – 15
Holmberg <i>et al.</i>	50 – 67	54 – 70	48 – 59	33 – 51	34 – 59
Rotating Screen					
Hegg <i>et al.</i>	4 – 8	-	4	-	-
Piccinini and Cotellini	5 – 24	9 – 31	2 – 19	5 – 11	3 – 9
Belt Press					
Fernandes <i>et al.</i>	47 – 59	-	39 – 40	32 – 35	18 – 21
Centrifuge					
Piccinini and Cotellini	15 – 61	18 – 65	7.8 – 4.4	3.4 – 3.2	58 – 68

Total solids are considered a nutrient because compounds such as volatile solids and TKN are associated with the TS and, as a result, improving TS recovery would also suggest an improvement in the recovery of other nutrients. Zhang and Westerman (1997) reported a considerable range in capabilities of hog manure nutrient separation. The authors suggest the use of chemical precipitation to improve the separation efficiency. Zhang and Westerman (1997) presented results from various studies examining the use of a wide range of organic and inorganic compounds to improve the extraction of compounds from the manure. Chemical treatments that were examined include the use of ferric chloride, magnesium chloride, aluminum sulfate, calcium salts, calcium hydroxide, lignosulfonate, chitosan and various organic polymers. Results were reported as

percent increases in removal efficiencies for various nutrients, such as TKN, phosphorus or total solids (TS). Their results indicated that using different doses of chemicals and chemical combinations, TS removal efficiencies could be improved from 18 – 61 percent, VS removal could be improved by 8 – 66 percent, TKN by 21 – 44 percent and phosphorus removal could be improved by as much as 78 percent, when compared with using physical separation techniques alone. In addition, other researchers such as Westerman and Bicudo (2000) also found that by integrating chemical and physical techniques, enhanced removal of various compounds could be achieved. Their research involved using a mobile unit of the “Tangential Flow Separator” (TFS) that used a combination of screens, settling tanks, ferric chloride and a polymer. Removal efficiencies as high as 82 percent for total suspended solids (TSS) and 90 percent phosphorus were achieved. Results from their experiments with the TFS on flushed hog manure and lagoon effluent are shown in Table 2-24.

Table 2-24: Performance of the TFS system for separating various compounds from flushed hog manure and lagoon liquid (Westerman and Bicudo, 2000).

Parameter	Removal Efficiency (%) for flushed wastes	Removal Efficiency (%) for lagoon effluent
COD	49 ± 10	34 ± 8
TOC	18 ± 16	27 ± 30
TS	34 ± 11	9 ± 3
VS	50 ± 10	32 ± 4
TSS	82 ± 9	35 ± 30
TKN	22 ± 4	15 ± 7
NH ₃ – N	8 ± 3	7 ± 11
Total P	90 ± 9	80 ± 14
OPO ₄ – P	95 ± 4	92 ± 8
Cl	-210 ± 90	-130 ± 90
Cu	87 ± 9	-
Zn	87 ± 10	-
Fe	53 ± 12	-30 ± 80
Ca	25 ± 25	5 ± 30

The high variability in the removal efficiencies were attributed to the variation in influent parameters (not shown), as well as variation in particle size distribution. The use of chemical precipitation seems to be much more efficient when compared to results from a modern screw press separator shown in Table 2-25 (Chastain *et al.*, 2001). This application uses only physical separation and does not incorporate any additional chemical treatments.

Table 2-25: Removal efficiencies using a screw press separator, without the use of chemical treatment on deep pit stored hog manure (Chastain *et al.*, 2001).

Parameter	Removal based on average deep pit manure (%)
TS	12.1
VS	15.9
TKN	7.0
Organic – N	12.1
TP	12.1

Clearly solid - liquid separation for the purpose of concentrating nutrients will only be feasible when expensive chemical treatments supplement physical separation. In such cases, phosphorus removal has been shown to achieve 99 percent removal (Zhang and Westerman, 1997).

Other forms of hog manure treatment include composting (Miner *et al.*, 2000; Weller and Willetts, 1977; Taiganides, 1977), ozonation (Wu *et al.*, 1998) and electrolytic treatment (Ranalli *et al.*, 1996). Another form of treatment makes use of a “natural” food chain in order to grow organisms suitable for re-feeding to livestock. An example of such a system would be the use of dung beetles

(*Onthophagus Taurus*) to decompose animal manures (Weller and Willetts, 1977; Gittings *et al.*, 1994) or multi – stage treatment employing the use of sequential algal, zooplankton and fish ponds. This treatment breaks down and recycles valuable proteins and amino acids that can be found in hog manure (El-Ahraf and Willis, 1996).

The technologies reported herein illustrate the current state of hog manure management. With the exception of natural food chains, the technologies listed above only reduce the organic loading of the manures. However, the presence of compounds such as metals in the manures can still remain a concern. Hsu and Lo (2000) presented a study showing the how copper, manganese and zinc were extracted from composts derived from hog manures. Their research showed that by changing the pH of the extraction solution, the metal concentration of the compost was effected. This showed that changes in soil pH could result in the potential contamination of soils due to the leaching of metals. As a result of continued landspreading, these could accumulate and lead to poor soil quality (Dinel *et al.*, 1998). Hatfield *et al.* (<http://www.ars.usda.gov>) suggest that certain qualities of hog manure make it beneficial to improve soil structure and enhance soil fertility. However, there still remain many negative impacts associated with its continued land application, given the trends illustrated in Tables 2-1 to 2-4. This has also been suggested by other researchers such as Dinel *et al.* (1998).

2.1.4. Health and Environmental Issues

Beneficial uses of hog manure are most easily obtained by land application, in which the incorporation of manure into the soil matrix results in improved aeration and water retention capacity, and overall improvements in soil quality (Miner *et al.*, 2000; Meelu, 1996; Choudhary *et al.*, 1996). These qualities have made landspreading an important element of hog manure management. The trends illustrated in Tables 2-1 to 2-4, and an increased public awareness have led to the development of stricter legislation regarding manure and nutrient management throughout the world. In Ontario, legislation such as that of the City of Ottawa (2002) or the Ministry of Agriculture, Food and Rural Affairs (2001) are examples of this concern. However, the poor management of manure remains a concern to scientists and researchers, despite new guidelines and legislation specifically designed to address those concerns.

2.1.4.1. Health Effects

Many of the negative impacts associated with manure management can be avoided through relatively simple management decisions and technological solutions (Miner *et al.*, 2000, Miner, 1999; El-Ahraf and Willis, 1996). Some of the more common negative impacts that may arise due to management operations, with respect to both humans and livestock are listed below:

- Odours
- Dust and particulate emissions
- Pathogens/Vectors for disease transmission

- Nitrate contamination of surface/ground water (methemoglobinemia, otherwise known as “blue baby disease”
- Nitrate contamination of livestock drinking water and animal feed

For more detailed information of human health effects associated with landspreading hog manure, the reader is referred to Miner *et al.* (2000), El- Ahraf and Willis (1996), Miner (1999), Wu *et al.* (1998), Ranalli *et al.* (1996) or Hatfield *et al.* (<http://www.ars.usda.gov>).

2.1.4.2. Environmental Impacts

Environmental impacts that may arise due to landspreading operations vary in nature and extent of impact. From the generation data provided in Tables 2-2 to 2-4 it can be seen that the number of intensive hog farms is increasing, resulting in more localized sources of manure, often modeled as point sources (Weller and Willetts, 1977). It has also been shown that the majority of intensive livestock operations use flushing systems to manage their manure (Schmidt *et al.*, 1996; Schmitt *et al.*, 1996), resulting in the use of large volumes of water and production of large volumes of waste. The following list shows some potential environmental impacts that may arise from intensive hog operations and landspreading hog manure:

- Large demand of non-renewable resources (e.g., fossil fuels, water, inorganic fertilizers) (Heitschmidt *et al.*, 1996)
- Eutrophication of surface waters
- Groundwater contamination

- Greenhouse gas production
- Particulate air emissions
- Bio-accumulation of toxic compounds
- Odour
- Noise

Despite strict nutrient management legislation, difficulties continue to arise in preventing excessive build-up of unwanted compounds in agricultural land such as metals, phosphorus or antibiotics. The presence of nutrients in hog manure can make it a beneficial by-product of hog manure production, however, trends in the industry, and poor implementation of management and landspreading techniques, are turning hog manure into a problem rather than a beneficial by-product to the farmers and communities.

The effectiveness of landspreading manure is further questioned when less expensive, and more widespread inorganic fertilizers become more available. It has been suggested by Dinel *et al.* (1998) that due to economic pressures placed on operators of intensive livestock operations, landspreading is often chosen as the only form of disposal over more expensive haulage and treatment options. This can then lead to over application of manure on crop land. Though other researchers have suggested the beneficial qualities associated with landspreading hog manure (e.g., Weller and Willetts, 1977; Choudhary *et al.*, 1996), it is believed that these positive effects will only be fully achieved when the manure is spread over a large land base, such as in family farm operations.

More recent studies have focused on issues such as bioaccumulation of metals such as Cu and Zn, use and excretion of antibiotics or steroids in hogs, excessive phosphorus application due to the use of nitrogen as a basis for crop nutrient requirements, and excessive sodium build-up in soils (Dinel *et al.*, 1998; Choudhary *et al.*, 1996; Yeager, <http://www.ontla.on.ca>; Miner *et al.*, 2000, Miner, 1999). Compounds such as these are always present in hog manure, as they are provided in their diets (Luce and Maxwell, <http://www.ansi.okstate.edu>). Regardless of manure management techniques, compounds such as Mn, Na or Fe, are expected to be present in the manure at the time of application. Antibiotics used in hogs may also be present in hog manure (El-Ahraf and Willis, 1996; Dinel *et al.*, 1998), suggesting their escape to the environment may lead to the generation of newer, and perhaps more resistant forms of bacteria (www.hogwatch.org, 2002).

2.2. Sustainable Agriculture

A large number of studies have been undertaken to address the issue of achieving a sustainable agricultural industry. Many of the articles reviewed argued that current, conventional agricultural practices are not sustainable (e.g., Wallace, 1994; Meelu, 1996; Honeyman, 1996; Lyson, 2002). An unsustainable agricultural system implies that future generations may not be able to meet their basic nutrient needs in the same manner as we do today using conventional agricultural methods.

Current trends in agriculture are towards an increased use in cheaper, inorganic fertilizers to meet basic crop nutrient requirements. Table 2-26 illustrates fertilizer use throughout several decades in India.

Table 2-26: Fertilizer (N:P₂O₅: K₂O) consumption and food grain production in India (Meelu, 1996).

Year	Fertilizer Consumption ('000 tonnes)	Food Grain Production (million tones)
1964-1965	773	89.4
1969-1970	1,982	99.5
1974-1975	2,573	99.8
1979-1980	5,255	109.7
1984-1985	8,211	145.5
1989-1990	11,568	171.0
1994-1995	13,564	191.1

The concern of many researchers is that the efficiency of crop production, with respect to the increasing use of external inputs (e.g., inorganic fertilizers or fossil fuels), may be declining. This is illustrated by Heitschmidt *et al.* (1996), who compared cultural (labour) and energy inputs (fertilizers, fossil fuels) between agricultural management systems in Mexico and the United States. The main difference between the two systems is that the former has a greater reliance on cultural inputs and the latter has a greater reliance on external, energy inputs. Researchers have also suggested that as the amount of energy put into agricultural systems increases (inorganic fertilizer use, fossil fuels), crop yields may increase, however the overall efficiency of the crop production declines (Meelu, 1996; Roy *et al.*, 2001; McSorley and Porazinska, 2001; Wallace, 1994; McLaughlin *et al.*, 2000; Heitschmidt *et al.*, 1996). Table 2-27 provides a ratio of the energy output to energy input for both management systems.

Table 2-27: Energy output/cultural energy input ratios for corn production systems in Mexico and the United States (Heitschmidt *et al.*, 1996).

Item	Mexico	United States
Cultural/Energy Inputs (kcal/ha)	553,678	8,390,750
Grain Yield – Weight (kg/ha)	1,944	7,000
Grain Yield – Energy (kcal/ha)	6,901,200	24,500,000
Energy Output / Input Ratio (kcal/ha)	12.5	2.9

Examination of Table 2-27 shows that the energy output to energy input ratio is much higher in Mexico. This implies that less energy is required to produce the same unit of product. Put differently, the overall efficiency of the Mexican agricultural system is more efficient than the US. The total output of the Mexican system is lower for reasons which include land availability. Table 2-27 also suggests that a trade off could potentially be made between using extra labour rather than more widespread and simple inorganic fertilizer use. Benefits of a cultural based system include an increase in employment and an increased agricultural (and soil) production efficiency, due to the higher quantity of agricultural by-products that are recycled back into the soil.

Researchers suggest that the widespread availability, the simple ease of handling, and the declining costs of inorganic fertilizers are the direct causes of declining organic fertilizer use throughout the world (Meelu, 1996; McSorley and Porazinska, 2001). Researchers also suggest that there exists little difference in overall crop yields when comparing inorganic and organic sources of nutrients. This is illustrated in Table 2-28 which shows mean corn yields in Ontario for three

different manure management schemes and one inorganic fertilizer scheme in different textured soils.

Table 2-28: Mean corn yield (ton/hectare) for corn production based on inorganic and organic fertilizer (McLaughlin *et al.*, 2000).

Nutrient Source	Coarse Soil	Medium Soil	Fine Soil
Inorganic Fertilizer	8.84	7.90	6.78
Manure – surface applied	8.09	8.24	6.68
Manure – conventional inject	8.44	8.34	6.82
Manure – modified inject	8.31	8.20	6.38

Analysis of Table 2-28 shows that all four fertilizer sources resulted in similar corn yields. McLaughlin *et al.* (2000) stated that in Canada alone, the 0.7 million tonnes of nitrogen that are excreted annually by livestock would require approximately 35 to 48 PJ of energy to produce that same quantity of N in an inorganic fertilizer.

Studies by McLaughlin *et al.* (2000) and Choudhary *et al.* (1996) point to the value added potential of recycling organic agricultural wastes back into crops (generally through improved soil qualities and reduced energy costs), while other researchers suggest that continued application of manures to crop land may lead to excessive build-up of toxic and polluting compounds (Miner, 1999; El-Ahraf and Willis, 1996; Diné *et al.*, 1998). It has been suggested by Diné *et al.* (1998), that continued application of liquid hog manure on croplands, may result in clogging of soil pores due to suspended and settled colloidal matter found in

manure. Dinel *et al.* (1998) then speculated that this may result in a diminished soil infiltration rate; with an immense industry demand for water, this makes the long-term potential for the liquid landspreading of hog manure questionable. Other researchers point to the intensive energy demands arising from intensive agricultural operations, the largest being fossil fuels, inorganic fertilizer production and water demand (McLaughlin *et al.*, 2000; Heitschmidt *et al.*, 1996). Still other arguments raised include the immense agricultural subsidies that are continuously paid out (Wallace, 1994), insufficient land availability (Miner *et al.*, 2000), and soil bioaccumulation of phosphorus, metals and synthetic materials (Miner *et al.*, 2000; Miner, 1999; Dinel *et al.*, 1998; El-Ahraf and Willis, 1996; Choudhary *et al.*, 1996).

These issues suggest that ongoing use of manures on crop and pastureland in a conventional manner may be unsustainable, due to the trends in the hog production industry shown in Tables 2-1 through 2-4. Though beneficial qualities of landspreading manure are clearly established, these benefits are not possible in an intensive production scenario. The aspects of the EF procedure that may make it feasible from a sustainable agricultural perspective are that the main advantages of landspreading hog manure are maintained (e.g., beneficial nutrients and organic matter), while the negative components of the material can be extracted for reuse in other industries (e.g., metals). The EF procedure could potentially generate valuable products to provide an additional source of income and resources for both farmers and the communities.

2.3. Extraction and Fractionation

The extraction and fractionation of organic materials is an extensively researched topic (Schnitzer and Khan, 1972; Schnitzer and Khan, 1978; Schulten and Schnitzer, 1995; Schnitzer and Schulten, 1998, Dinel and Dumontet, 1995), and is closely related to soil chemistry. The most significant area of study in soil chemistry relevant to this research is presented.

The amount of soil organic matter (SOM) in soils can range from 0.1 percent in desert soils to 100 percent in organic soils (Schnitzer and Khan, 1978). SOM is further subdivided into two main fractions: a non-humic fraction and a humic fraction. The humic fraction of SOM consists of humin, humic acid and fulvic acid. The humic and fulvic fractions of SOM have been the main focus of soil chemists' research to date.

SOM can be fractionated into its various humic substances using different alkaline, neutral and acidic conditions. Various chemical processes will yield the "fractionated" humin, humic acid and fulvic acid components, having the following properties (Schnitzer and Schulten, 1998)

1. **Humic Acid (HA):** humic fraction that is soluble in dilute alkali or neutral salt solution, which is precipitated when the alkaline or neutral salt solution is acidified.

2. **Fulvic Acid (FA):** humic fraction that remains in solution when the alkaline or neutral salt solution is acidified, that is, it is soluble under alkaline, neutral and acidic conditions.
3. **Humin:** humic fraction that cannot be extracted from soils by dilute base, neutral or acid solutions.

Chapter 3 – Methodology

3.1. Experimental Procedure

The EF procedure that was used to generate agri-products and chemical commodities from hog manure is schematically represented in Figure 3-1. This illustrates the sequential metal reduction and alkaline hydrolysis fractionation in the EF procedure. Metal reduction was achieved by washing the manure in an aqueous HCl acid solution. Two different concentrations of HCl (0.1N and 1.0N) and a control were used to assess the metal removal efficiency (%MRE) of the different pre – treatment HCl solutions. Measurement of the metal concentration in the hog manure prior to pre – treatment provided baseline data from which the effectiveness of the two different HCl solutions could be determined.

The alkaline hydrolysis was performed using an aqueous KOH solution. The impact of different KOH concentrations (0.25N, 0.5N and 0.75N) on the main fractions was assessed. Figure 3-2 shows the nine individual experimental tests that were performed to assess the EF procedure and determine the best combination of HCl and KOH concentration. Each of the experimental tests were reproduced three times under the same conditions, and the standard deviation (SD) of the measured and calculated variables within each group was calculated using the standard equation for SD, shown below in equation 3 – 1:

$$(3 - 1) \quad SD = \sqrt{(\sum(y_i - y)/(n-1))}$$

In the equation for SD, ' y_i ' is an individual value within each replicate group, ' $\bar{y}$ ' is the average between replicates and ' n ' is the number of replicates.

Figure 3-1: Schematic representation of sequential EF procedure.

Figure 3-2: Experimental variables used to assess the EF procedure.

3.1.1. Hog Manure Collection and Storage

Hog manure was collected from the Central Experimental Farm in Ottawa, Canada. Manure was transported in a sealed plastic bucket and stored frozen in Ziploc bags. Prior to treatment, manure was thawed in a refrigerator for 24 hours and shaken vigorously to allow for accurate moisture content calculations.

Moisture content (MC) was determined by heating a pre-weighed wet sample of manure in a crucible at 60° C for 65 hours followed by cooling to room temperature in a dessicator. Cooled and dried samples were weighed and the moisture content was determined using equation 3 – 2.

$$(3 - 2) \quad MC = (Wet\ Mass - Dry\ Mass) \times (Wet\ Mass)^{-1} \times 100 \%$$

MC = moisture content

Wet Mass = mass of wet hog manure prior to drying

Dry Mass = mass of dried solids

3.1.2. Hog Manure Characterization

Collected manure consisted of excreta from non-gestating sows, with minimal amounts of urine, bedding and feed. Small amounts of wood chips were noted in dried samples, most likely originating from ingestion while feeding.

Initial characteristics, including metal content, of the untreated manure are provided in Tables 3-1 and 3-2, respectively, on a dry mass basis.

Table 3-1: Initial characteristics of untreated hog manure.

Parameter	Value	Units
Average Dry Matter	27.9 ± 0.34	% wet manure
Average Volatile Solids	85.4 ± 0.24	% TS
Average Total Carbon	42.8 ± 0.3	% TS
Average Total Nitrogen	1.83 ± 0.1	% TS

Table 3-2: Average metal concentrations (μg metal / g TS) in untreated hog manure.

Metal	Al	Ca	Cu	Fe	Mg
Concentration ($\mu\text{g/g}$)	450 ± 38	8435 ± 147	209 ± 33	712 ± 80	5387 ± 488
Metal	Zn	K	Na	P	
Concentration ($\mu\text{g/g}$)	660 ± 72	13584 ± 2200	7089 ± 149	14264 ± 1540	

Though P and K in Table 3-2 are not metals, these were measured in the hog manure using the same ICP technique used for metals such as Fe, Cu, Zn and Mg. Of the group of metals and other compounds scanned, many are required for effective crop growth, such as Mg and Ca. Other compounds such as Cu and Zn that are observed in the ICP results have been shown in literature to leach from soils and treated wastes given the pH of the soil and local precipitation. Based on background literature, these metals have been shown to solubilize in surface and groundwater providing a pathway for offsite migration. Removal of Cu and Zn using the EF procedure would thus result in a positive environmental effect from its implementation, when compared with conventional landspreading of partially treated hog manures. It should also be noted that the absence of compounds such as arsenic (As), cadmium (Cd) and nickel (Ni) in Table 3-2 may be because

these are not supplied to hogs in their feed, or they are present in the manure in concentrations below the detection limit of the equipment. In addition, mercury (Hg) was not scanned as special modifications in the digestion and ICP techniques would be required, and this was not feasible in the laboratory used for performing the ICP analysis. Possible reasons for the absence of As, Cd and Ni are further discussed in Chapter 4.

3.1.3. EF Procedure Implementation

3.1.3.1. Hog Manure Pre – Treatment

Two different strength HCl solutions (0.1N and 1.0N) and a control (no HCl pre – treatment) were used to determine the effectiveness of HCl to reduce the quantity of metals in the hog manure; in addition, the effect of pre – treatment on the products from the alkaline hydrolysis was also examined.

Approximately 55 g of dried hog manure was mixed with 300 ml of HCl (0.1N or 1.0N) in a 750 ml beaker, at room temperature for 24 hours using a stir bar on a Mirak Thermolyne Hot Plate/Stirrer. Pre – treated hog manure was separated from the liquid supernatant using a Centra GP8 Thermo IEC Centrifuge in a 750 ml nalgene bottle operating at 4700 – 4900 RPM for ten minutes. The supernatant was discarded, and the solid, pre – treated hog manure was washed with distilled water and then neutralized with 45 ml of 1.0 N KOH; the pH of the KOH and hog manure mixture was measured with an Orion Model 250A pH probe. Neutralized manure was then washed again with distilled water until all of

the KCl salt was removed; the removal of KCl salt was determined using the AgNO_3 Test for Cl.

3.1.3.2. Hog Manure Fractionation

Three different strength KOH concentrations were compared for their effects on the products from the EF procedure. However, the volume of water used for the different experiments did not remain the same, and as a result different masses of KOH were used, while the mass of hog manure remained the same. A range of 250 – 500 ml of aqueous KOH solution was mixed with approximately 46 g of the dried, pre – treated manure. Loss of dry matter was attributed to the colloidal matter observed in the wash water used to remove the KCl salt. The KOH solution and manure were heated to 70° C and stirred for one hour. The solid and liquid fractions were then separated using the centrifuge. The solid fraction was washed with distilled water, followed by neutralization with 1.0N HCl. The neutralized material was washed again with distilled water until all of the KCl salt was removed. The removal of KCl salt was determined using the AgNO_3 Test for Cl. The solid fraction was dried and was termed the non – hydrolyzed fraction (NHF) of the material. The dried mass of the NHF recovered from each experiment represented the yield of TS recovered in the NHF from the EF procedure. Experimental data for each of the experimental groups are provided in Appendix A.

The liquid supernatant contained dissolved material that was soluble in basic solutions. The pH of the liquid supernatant was reduced from a pH of 12 to a pH below 4 using 1.0N HCl. Below a pH of 4 the suspended colloidal matter was precipitated from solution. The flocs were removed from the solution using the centrifuge and washed with distilled water. This fraction was dried in an oven and the dry mass measured. The fraction precipitated and removed from solution was termed the hydrolyzed fraction (HF). The dry mass of the HF recovered from each experiment represented the yield of TS recovered in the HF from the EF procedure.

3.2. Product Analysis

Product analysis involved three main forms of analyses: 1) determining the metal concentration of the manure prior to and following pre – treatment with HCl; 2) calculating the % recovery of TS, VS, C and N in the NHF and HF and examining these based on the different HCl and KOH treatments illustrated in Figure 3-2; and 3) analyzing the NHF and HF using Fourier Transform Infrared Spectroscopy (FTIR) to examine the functional groups, and Carbon-13 Nuclear Magnetic Resonance Spectroscopy (^{13}C – NMR) to analyze the carbon bonds.

3.2.1. Metal Removal Efficiency

The metal content of untreated and pre – treated manure was determined using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) with a Thermo Jarrell Ash 6000 using Argon gas at approximately 10,000K. Samples

were digested with concentrated nitric acid (HNO₃). Approximately 1 gram of untreated or pre – treated manure sample and 20 ml of HNO₃ were mixed and covered with a watch glass and heated on a hot plate to 150 – 250° C for approximately 12 hours. Digestion was considered complete when the solution turned light yellow, and the solution volume had been reduced to 90 – 95% of the original volume. The digested solution was transferred into a volumetric flask of known volume and diluted with distilled water to the line on the flask, marking the known volume.

The metal removal efficiency (%MRE) between the untreated and pre – treated manure samples was determined using equation 3 – 3 below. Sample calculations are provided in Appendix B.

$$(3 - 3) \quad \%MRE = (M_u - M_{HCl}) \times (M_u)^{-1} \times 100\% [MM^{-1}]$$

%MRE = Metal removal efficiency (μg metal / (μg metal)

M_u = Metal Concentration in untreated manure (μg metal/g TS)

M_{HCl} = Metal Concentration in pre – treated manure (μg metal/g TS)

3.2.2. Product Recovery Analysis

3.2.2.1. Total Solids

From the yield of TS measured in the NHF and HF, and the mass of TS entering the process in the hog manure, the % TS recovery was calculated in the NHF and HF using equation 3 – 4 below. The superscripts 'f' and 'HM' represent either the NHF or HF, and hog manure, respectively.

$$(3 - 4) \quad \%TS_R^f = (M_{TS}^f \times (M_{TS}^{HM})^{-1}) \times 100\% [MM^{-1}]$$

$\%TS_R^f$ = % TS recovery in the HF or NHF (g TS/100 g TS)

M_{TS}^f = Yield of TS in fractions recovered from EF procedure (g TS)

M_{TS}^{HM} = Mass of TS entering procedure in the hog manure (g TS)

3.2.2.2. Volatile Solids

The %VS in the hog manure, and the NHF and HF was determined by placing a known amount of dry matter into a crucible of known mass and incinerating for 18 hours at 550° C, followed by cooling to room temperature in a dessicator for 48 hours. It is recognized that the solids that are volatilized at these high temperatures may not be available to microorganisms commonly found in surface soils. However, these less volatile materials may become available in more rigorous industrial operations such as ethanol or organic acid production. The mass of ash remaining in the crucible was measured. Using equation 3 – 5 the percent volatile solids (%VS) in the hog manure, NHF and HF was determined. IS represents inert solids.

$$(3 - 5) \quad \%VS = (Dry\ Mass - Ash) \times (Dry\ Mass)^{-1} \times 100\%$$

%VS = Percent VS in hog manure, NHF or HF (g VS/100g TS)

Dry Mass = Mass of dried hog manure, NHF or HF (g TS)

Ash = Mass of ash in the hog manure, NHF or HF following incineration (g IS/g TS)

The mass of VS entering the process in the hog manure was determined from the %VS measured in untreated hog manure in Table 3-1 and the mass of dried hog manure entering the process (TS). The product of these was the mass of VS entering the process, as shown in equation 3 – 6.

$$(3 - 6) \quad M_{VS}^{HM} = (\%VS^{HM}/100) \times M_{TS}^{HM} [M]$$

M_{VS}^{HM} = Mass of VS entering the process in the hog manure (g VS)

$\%VS^{HM}$ = % VS in the hog manure (g VS/100g TS)

M_{TS}^{HM} = Mass of TS entering the process in the hog manure (g TS)

From the %VS and measured TS yield in the NHF and HF, the yield of VS in the NHF and HF was calculated using equation 3 – 7.

$$(3 - 7) \quad M_{VS}^f = (\%VS^f/100) \times M_{TS}^f [M]$$

M_{VS}^f = Yield of VS in the NHF or HF fraction (g VS)

$\%VS^f$ = Percent VS (g VS/100g TS)

M_{TS}^f = Yield of TS in fraction (g TS)

The ratio of the yield of VS in the NHF or the HF, to the mass of VS entering the EF procedure in the hog manure is the %VS recovery in the NHF or HF. This is shown in equation 3 – 8 below.

$$(3 - 8) \quad \%VS_R^f = (M_{VS}^f \times (M_{VS}^{HM})^{-1}) \times 100\% (MM^{-1})$$

$\%VS_R^f$ = % VS recovered in either the NHF or HF (g VS/100g VS)

M_{VS}^f = Yield of VS in the NHF or HF determined from eq 3 – 6 (g VS)

M_{VS}^{HM} = Mass of VS entering the process determined from eq 3 – 5 (g VS)

3.2.2.3. Total %C

Using an Elemental Analyzer (CE Instruments (Italy), model 1110), the total %C in the hog manure, NHF and HF was measured. The samples were prepared by homogenizing dried fractions with a coffee grinder and compressing 5 – 15 µg of sample in a tinfoil cup. The prepared samples were analyzed at the University of Ottawa laboratory. Results were provided by the University as total %C (g

C/100g TS) in the hog manure, NHF or HF in an Excel data sheet. The yield of C in the hog manure, NHF and HF was calculated using equations 3 – 9 and 3 – 10 below.

$$(3 - 9) \quad M_C^{HM} = (\%C^{HM}/100) \times M_{TS}^{HM} [M]$$

M_C^{HM} = Mass of C entering the process in the hog manure (g C)

$\%C^{HM}$ = Percent C in the hog manure (g C/100g TS)

M_{TS}^{HM} = Mass of TS entering the process in the hog manure (g TS)

$$(3 - 10) \quad M_C^f = (\%C^f/100) \times M_{TS}^f [M]$$

M_C^f = Yield of C in either the NHF or HF (g C)

$\%C^f$ = Total %C in either the NHF or HF (g C/100g TS)

M_{TS}^f = Yield of TS in either the NHF or HF (g TS)

The ratio of the yield of C in the NHF or the HF to the mass of C entering the EF procedure in the hog manure is the %C recovery in the NHF or the HF. This is shown in equation 3 – 11 below.

$$(3 - 11) \quad \%C_R^f = (M_C^f \times (M_C^{HM})^{-1}) \times 100\% (MM^{-1})$$

$\%C_R^f$ = %C recovered in either the NHF or HF (g C/100g C)

M_C^f = Yield of C in the NHF or HF determined from eq 3 – 9 (g C)

M_C^{HM} = Mass of C entering the process determined from eq 3 – 8 (g C)

3.2.2.4. Total % N

Using an Elemental Analyzer (CE Instruments (Italy), model 1110), the total %N in the hog manure, NHF and HF was measured.

The samples were prepared by homogenizing dried fractions with a coffee grinder and compressing 5 – 15 µg of sample in a tinfoil cup. The prepared samples were analyzed in the University of Ottawa laboratory with an Elemental Analyzer. Results were provided by the University as total %N (g N/100g TS) in the hog manure, NHF or HF.

The yield of N in the hog manure, NHF and HF was calculated using equations 3 – 12 and 3 – 13.

$$(3 - 12) \quad M_N^{HM} = (\%N^{HM}/100) \times M_{TS}^{HM} [M]$$

M_N^{HM} = Mass of N entering the process in the hog manure (g N)

$\%N^{HM}$ = Percent N in the hog manure (g N/100g TS)

M_{TS}^{HM} = Mass of TS entering the process in the hog manure (g TS)

$$(3 - 13) \quad M_N^f = (\%N^f/100) \times M_{TS}^f [M]$$

M_N^f = Yield of N in either the NHF or HF (g N)

$\%N^f$ = Total %N in either the NHF or HF (g N/100g TS)

M_{TS}^f = Yield of TS in either the NHF or HF (g TS)

The ratio of the yield of N in the NHF or the HF to the mass of N entering the EF procedure in the hog manure is the %N recovery in the NHF or the HF. This is shown in equation 3 – 14 below.

$$(3 - 14) \quad \%N_R^f = (M_N^f \times (M_N^{HM})^{-1}) \times 100\% (MM^{-1})$$

$\%N_R^f$ = % N recovered in either the NHF or HF (g N/100g N)

M_N^f = Yield of N in the NHF or HF determined from eq. 3 – 12 (g N)

M_N^{HM} = Mass of N entering the process determined from eq. 3 – 11 (g N)

3.2.3. Fourier – Transform Infrared Spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) was used to analyze the functional groups in the NHF and HF, and compare these to published FTIR spectra for other organic materials. Samples were dried in an oven and then homogenized using a coffee grinder. Approximately 15 mg of sample was mixed with 400 mg of KBr in a crucible, and compressed into pellets using a force of 10 tons. Samples were analyzed using a Bomem Michelson 120 FTIR analyzer and the resultant spectra were generated using Bomem Grams 386 software. The spectra were provided in tabular format as a measure of % transmittance vs wavelength. The data were plotted using Microsoft Excel.

3.2.4. Carbon – 13 Nuclear Magnetic Resonance

Carbon – 13 Nuclear Magnetic Resonance Spectroscopy (^{13}C – NMR) was used to determine the presence of carbon bonds in NHF and HF, and compare these to published ^{13}C – NMR spectra for other organic materials. Dried and ground samples of the NHF and HF were supplied to the laboratory at the University of Ottawa. The scan was performed using a Bruker ASK 200, with a proton 90° pulse of 3.4 μsec , a contact time of 200 μsec , ^{13}C frequency of 50 MHz and a MAS spin speed of 4.5 MHz. The results of the ^{13}C – NMR analysis were provided as printouts showing the spectra and the relevant peaks observed by the scanner.

Chapter 4 – Results and Discussion

4.1. Pre – Treatment Metal Reduction

The purpose of pre – treatment with HCl was to reduce the metal concentration in the hog manure prior to fractionation with KOH. Table 4-1 shows the concentrations of metals in untreated hog manure, manure pre – treated with 0.1N HCl and manure pre – treated with 1.0N HCl on a dry mass basis determined using ICP-AES.

Table 4-1: Metal concentrations in untreated and pre – treated hog manures.

Metal	Concentration in Untreated Manure (μg metal / g TS)	Concentration in 0.1N Pre – Treated Manure (μg metal / g TS)	Concentration in 1.0N Pre – Treated Manure (μg metal / g TS)
Al	450 $\pm$ 38	428 $\pm$ 12	273 $\pm$ 100
Ca	8435 $\pm$ 147	6797 $\pm$ 489	2578 $\pm$ 545
Cu	209 $\pm$ 33	25 $\pm$ 9	39 $\pm$ 25
Fe	712 $\pm$ 80	207 $\pm$ 20	58 $\pm$ 30
Mg	5387 $\pm$ 488	951 $\pm$ 83	402 $\pm$ 126
Zn	660 $\pm$ 72	64 $\pm$ 15	118 $\pm$ 82
Na	7089 $\pm$ 149	1269 $\pm$ 730	389 $\pm$ 87
P	14264 $\pm$ 1540	8860 $\pm$ 480	1772 $\pm$ 592

The data in Table 4-1 showed a decline in concentration of most of the metals as the HCl concentration of the pre – treatment solution was increased, with the exception of Cu and Zn. These results indicate that different metal complexes can have varying solubilities at different solution pHs.

The data also show relatively high standard deviations for some metals such as Cu, Fe and Zn. Further examination into different sources of hog manure would result in a better understanding of the natural variability in metal concentrations from different manure sources based on variables such as feed characteristics.

Using equation 3 – 3, %MRE was calculated; results are presented in Table 4 – 2 for both HCl pre – treatment strengths.

Table 4-2: Metal removal efficiencies of metals in hog manure using 0.1N and 1.0N HCl.

Metal	Metal Removal Efficiency With 0.1 N HCl	Metal Removal Efficiency With 1.0 N HCl
Al	4.9%	39.3%
Ca	19.4%	69.4%
Cu	88.0%	81.3%
Fe	70.9%	91.9%
Mg	82.3%	92.5%
Zn	90.3%	82.1%
Na	82.1%	94.5%
P	37.9%	87.6%

Results in Table 4-2 showed %MRE in excess of 60% for Cu, Fe, Mg, Zn and Na for the 0.1N pre – treatment. Higher removal efficiencies were observed in hog manures pre – treated with 1.0N HCl. In addition, the data showed that for the

0.1N pre – treatment, the most to least extractable metals were $\text{Zn} > \text{Cu} > \text{Mg} > \text{Na} > \text{Fe} > \text{P} > \text{Ca} > \text{Al}$, while for 1.0N pre – treatments, the most to least extractable metals observed were $\text{Na} > \text{Mg} > \text{Fe} > \text{P} > \text{Zn} > \text{Cu} > \text{Ca} > \text{Al}$. Based on these observations, it can be seen that different metals behave differently in the HCl pre – treatment solutions.

Variations in the calculated %MRE data included high standard deviations for Cu, Fe and Zn, different “most to least extractable metals” observed for the two different HCl strengths, a decline in %MRE for Zn and Cu as solution pH was reduced, and a low %MRE observed for Al, Ca when compared with other metals such as Fe and Mg. Based on the experimental data in Appendix A, these variations can be explained by the different solubilities of the various metal complexes present in the manure, in the 0.1N and 1.0N HCl pre – treatment solutions. The change in solution pH, observed in the experimental data in Appendix A, appears to be a contributing factor in the solubility of the different metal complexes in the HCl pre – treatment solution. As different metal complexes can have different solubilities at different solution pHs, this could account for the variation that was observed in the %MRE data.

The presence of metal complexes in solution could be verified through future research. This could involve collection of the solution and wash waters following pre - treatment, and measurement of the metal concentration in the various solutions. Examination and comparison of the relative abundance of metal

complexes in solution vs. metal complexes that were not solubilized (i.e., still present in the hog manure), would allow for development of specific recovery processes based on metal complexes with similar solubilities. Recovery of metals from the EF procedure would provide a third product stream from the process, and thus an improved overall system recovery of the different compounds in the hog manure.

Further, variability in the %MRE for the metals could be attributable in part by the use of a single acid digestion technique to solubilize organic material in solution prior to analysis using ICP-AES. Though commonly used in most laboratories, the single acid digestion technique, in this case using concentration nitric acid (HNO_3), may not have completely solubilized all of the metals and the organic matter in the sample. The use of two or more acids to digest organic material could result in a more efficient digestion, thereby achieving better dissolution of metals in solution, and hence a more representative ICP analysis. A multiple acid digestion might also have revealed the presence of more harmful metals such as As, Cd and Ni. The presence of these, and their subsequent removal from the manure, would clearly be a benefit from the standpoint of implementing the EF procedure. In addition, the reduction of Cu and Zn that was observed with the acid pre-treatment of the manure illustrates how the use of the EF procedure prior to landspreading the manure could result in a positive effect on the soil health, by reducing the quantity of Cu and Zn that enter the environment.

4.2. Alkaline Hydrolysis and Product Recovery

The purpose of the alkaline hydrolysis with KOH was to fractionate the hog manure into a non – hydrolyzed (NHF) and a hydrolyzed fraction (HF). These could then be used to produce value-added products that can be employed as resources on farms, or as an additional source of revenue.

The NHF and HF produced in the experiments were analyzed for total solids (TS), volatile solids (VS), carbon (C) and nitrogen (N). The percent recovery of these was compared based on pre – treatment and KOH strength. Sample calculations are provided in Appendix B, using equations from Chapter 3.

4.2.1. Product Yield

The recovery of VS, C and N is based on the measured yield of TS in the NHF or HF, and the original mass of TS entering the process in the untreated hog manure.

Table 4-3 provides the average initial mass of dry hog manure used for each experiment in the EF procedure. The descriptor shown in the far left column describes the HCl – KOH strengths used for that particular experiment. Control experiments did not involve any pre – treatment with HCl. Also provided in Table 4-3 is the yield of TS in the NHF and HF (dry mass basis) recovered from the EF procedure for each of the experimental groups.

Data in Table 4-3 illustrate that the NHF accounted for a significantly larger quantity of TS recovered from the EF procedure. From the yield of TS, the yield of VS, C and N in the NHF and HF were calculated. The ratio of these to the total mass of TS, VS, C or N in the hog manure was calculated, which represented the percent recovery of either TS, VS, C or N in the NHF and HF.

Table 4-3: Initial hog manure starting dry mass, and the NHF and HF yields (dry mass basis) measured for the three pre – treatment and three hydrolysis groups.

HCl Strength (N) – KOH Strength (N)	Dry Hog Manure (Entering) (g TS)	NHF (Recovered) (g TS)	HF (Recovered) (g TS)
Control – 0.25	56.2 ± 0.8	36.0 ± 1.1	6.1 ± 0.4
1.0 – 0.25	55.9 ± 0.1	26.8 ± 0.3	2.4 ± 0.04
0.1 – 0.25	56.0 ± 0.1	40.6 ± 2.4	1.4 ± 0.7
Control – 0.5	53.9 ± 2.8	33.4 ± 0.2	3.4 ± 0.1
1.0 – 0.5	55.7 ± 0.0	23.2 ± 1.5	3.6 ± 0.9
0.1 – 0.5	55.7 ± 0.2	34.0 ± 0.9	6.4 ± 1.0
Control – 0.75	55.8 ± 0.1	35.8 ± 1.0	6.0 ± 0.2
1.0 – 0.75	55.8 ± 0.1	30.3 ± 0.2	1.4 ± 0.8
0.1 – 0.75	56.2 ± 0.1	34.2 ± 1.4	3.4 ± 0.3

4.2.2. Product Recovery

Percent recovery of TS, VS, C and N in the NHF and HF was calculated using equations 3 – 4, 3 – 8, 3 – 11 and 3 – 14, respectively. The recovery of each of these materials in the NHF and HF are presented in Tables 4 – 4 to 4 – 10. Values of N/A were reported for the 0.0/0.5 and 0.1/0.75 NHF, as well as the

0.0/0.5 HF experimental runs, as these were either missing or present in an insufficient mass required for particular analytical procedures.

4.2.2.1. Total Solids Recovery

The recovery of TS in the NHF and HF was determined using equation 3 – 4. Results are presented in Table 4-4, in terms of grams TS in the NHF or HF per 100 g TS in the hog manure. Sample calculations are provided in Appendix B.

The results in Table 4-4 below showed that 46.3 – 72.5% of the TS from the hog manure were recovered in the NHF, while 2.5 – 11.5% of the TS from the raw material were recovered in the HF. The data also showed that the lowest total %TS recovery was in manures pre – treated with 1.0N HCl. This suggested that the HCl may cause a greater solubilization of the dry matter in the hog manure, leading to a greater loss of recoverable TS in the hog manure. A low recovery of TS in the NHF and HF may result in a significant loss of valuable materials such as VS and N, reducing the overall efficiency of the EF procedure.

Table 4-4: %TS recovery in the NHF and HF for various hydrolysis strengths and pre – treatments.

HCl Strength (N) – KOH Strength (N)	NHF (gTS ^f /100gTS ^{HM})	HF (gTS ^f /100 gTS ^{HM})
Control – 0.25	64.1 ± 1.4	10.9 ± 1.1
1.0 – 0.25	53.6 ± 0.7	4.8 ± 0.1
0.1 – 0.25	72.5 ± 5.4	2.5 ± 1.4
Control – 0.5	62.0 ± 3.9	6.3 ± 0.7
1.0 – 0.5	46.3 ± 3.3	7.2 ± 1.9
0.1 – 0.5	61.0 ± 2.3	11.5 ± 2.1
Control – 0.75	64.2 ± 2.4	10.8 ± 0.5
1.0 – 0.75	60.6 ± 0.5	2.8 ± 1.5
0.1 – 0.75	60.9 ± 3.2	6.0 ± 0.8

4.2.2.2. Volatile Solids Recovery

The %VS measured in the raw material and the NHF and HF are presented in Table 4-5. The data showed that the %VS was highest in the HF, followed by the NHF and lowest in the hog manure (with the exception of the 0.1 – 0.5 treatment). It was also observed that the %VS was highest in manures pre – treated with 1.0N HCl. Manures pre – treated with 0.1N HCl had the second highest %VS and untreated manures had the lowest %VS.

Table 4-5: %VS (g volatile solids/100 g TS) measured in the raw material and the NHF and HF.

HCl Strength (N) – KOH Strength (N)	Raw Material (g VS ^{HM} /100g TS ^{HM})	NHF (g VS ^f /100g TS ^f)	HF (g VS ^f /100g TS ^f)
Control – 0.25	85.3 ± 0.3	87.9 ± 1.0	95.2 ± 0.0
1.0 – 0.25	85.3 ± 0.3	95.5 ± 0.5	96.1 ± 0.0
0.1 – 0.25	85.3 ± 0.3	92.3 ± 1.8	96.7 ± 0.5
Control – 0.5	85.3 ± 0.3	N/A	97.3 ± 0.0
1.0 – 0.5	85.3 ± 0.3	96.0 ± 0.5	97.3 ± 0.0
0.1 – 0.5	85.3 ± 0.3	87.4 ± 0.1	79.7 ± 0.6
Control – 0.75	85.3 ± 0.3	89.2 ± 0.0*	93.2 ± 0.9
1.0 – 0.75	85.3 ± 0.3	96.2 ± 0.0	97.1 ± 0.7
0.1 – 0.75	85.3 ± 0.3	N/A	95.7 ± 0.0

Published data on %VS of hog manure have reported values of approximately 80% (Tables 2-5 to 2-8 and 2-11). Published data often included manures with bedding, urine and feed present resulting in a lowered %VS. The manure used for these experiments contained limited amounts of urine and bedding, and thus a higher %VS was expected and obtained. Using equation 3-8, the %VS recovery was calculated for the different experimental runs; results are presented in Table 4-6. Yield data are provided in Appendix A, and sample calculations in Appendix B.

Table 4-6: %VS recovered in the NHF and HF.

HCl Strength (N) – KOH Strength (N)	NHF (g VS^f/100g VS^{HM})	HF (g VS^f/100g VS^{HM})
Control – 0.25	66.0 ± 1.7	12.0 ± 1.3
1.0 – 0.25	53.7 ± 0.7	4.9 ± 0.1
0.1 – 0.25	78.5 ± 6.8	2.8 ± 2.2
Control – 0.5	N/A	7.3 ± 0.8
1.0 – 0.5	46.8 ± 3.5	N/A
0.1 – 0.5	62.4 ± 2.2	10.7 ± 1.9
Control – 0.75	67.1 ± 2.5	11.7 ± 0.4
1.0 – 0.75	61.1 ± 0.5	2.8 ± 0.7
0.1 – 0.75	N/A	6.7 ± 0.9

Examination of the results in Table 4-6 showed that %VS recovery was highest in the HF in the control group hydrolyzed with 0.25N KOH, and lowest in the 0.1N pre – treated manure, hydrolyzed with the 0.25N KOH. For the NHF, the highest percent recovery was observed in manures pre – treated with 0.1N HCl and hydrolyzed with the 0.25N KOH. The lowest %VS recovery in the NHF was in the 1.0N HCl pre – treatment group, and hydrolyzed with the 0.5N KOH. Total %VS recovery between the NHF and HF ranged from 58.6 – 81.3%. The data showed that the NHF accounted for the largest proportion of %VS recovery from the hog manure as compared with the HF. This was because the NHF constituted the largest portion of the TS between the NHF and HF.

4.2.2.3. Carbon Recovery

Wood chips present in the raw material and in the NHF and HF, resulted in heterogeneous samples containing small pieces of wood fiber. As a result, sample weights for the Elemental Analyzer were doubled, using approximately 10 – 20 μg of sample instead of the normal 5 – 10 μg sample weight. The average %C data for the NHF and HF are presented in Table 4-7. The standard deviations in the data are provided by the operator of the elemental analyzer at the University of Ottawa. The values for the standard deviation are based on lab quality assurance and control (QA/QC) and are based on the standardized use of duplicates in the analysis. Results are provided as total carbon (or nitrogen) and do not indicate the different forms that the elements will take. Based on the information provided by the laboratory, the carbon measurements have a standard deviation of 0.3 and the nitrogen measurements have a standard deviation of 0.1.

Results from the carbon data showed that the HF was richest in C when compared with the raw material and the NHF, with the exception of the 1.0N/0.75N KOH experimental run. The %C in the HF ranged from 53.2 – 59.8%. The %C in the NHF ranged from 35.5 to 46.1%. The data showed the NHF had a lower percent carbon than the raw hog manure in the solutions hydrolyzed with 0.25N, as well as in the control experiments hydrolyzed with 0.75N KOH. The larger range of %C found in the NHF may be due to the heterogeneity of the samples.

Table 4-7: %C (g C^f / 100g TS^f) in the raw material and the NHF and HF.

HCl Strength (N) – KOH Strength (N)	Raw Material (g C^{HM}/100 g TS^{HM})	NHF (g C^f/100 g TS^f)	HF (g C^f/100 g TS^f)
Control – 0.25	42.8 ± 0.3	35.5 ± 0.3	54.0 ± 0.3
1.0 – 0.25	42.8 ± 0.3	41.9 ± 0.3	55.7 ± 0.3
0.1 – 0.25	42.8 ± 0.3	39.9 ± 0.3	54.6 ± 0.3
Control – 0.5	42.8 ± 0.3	N/A	59.2 ± 0.3
1.0 – 0.5	42.8 ± 0.3	46.1 ± 0.3	59.8 ± 0.3
0.1 – 0.5	42.8 ± 0.3	42.2 ± 0.3	58.4 ± 0.3
Control – 0.75	42.8 ± 0.3	38.6 ± 0.3	53.2 ± 0.3
1.0 – 0.75	42.8 ± 0.3	43.8 ± 0.3	58.3 ± 0.3
0.1 – 0.75	42.8 ± 0.3	43.1 ± 0.3	58.7 ± 0.3

Similar to the %VS data in Table 4-5, the %C data in Table 4-7 showed that in the NHF, the highest %C was measured in manures pre – treated with 1.0N HCl. The second highest %C was observed in the 0.1N HCl pre – treatment and the lowest %C was observed in the control experiments with no pre – treatment.

Using equation 3-11 and the %C data in Table 4-7, %C recovery was determined for the different experimental groups. Results are presented in Table 4-8, the yield data in Appendix A, and sample calculations in Appendix B.

Table 4-8: % Carbon recovery in the NHF and HF.

HCl Strength (N) – KOH Strength (N)	NHF (gC^f/100 gC^{HM})	HF (gC^f/100 gC^{HM})
Control – 0.25	53.2 ± 1.3	13.6 ± 0.8
1.0 – 0.25	47.1 ± 0.7	5.7 ± 0.2
0.1 – 0.25	67.8 ± 5.1	3.1 ± 1.8
Control – 0.5	N/A	8.9 ± 1.0
1.0 – 0.5	44.8 ± 3.2	9.0 ± 2.7
0.1 – 0.5	60.1 ± 3.6	15.7 ± 2.9
Control – 0.75	57.9 ± 0.6	13.4 ± 0.6
1.0 – 0.75	55.5 ± 1.9	3.4 ± 2.1
0.1 – 0.75	61.4 ± 3.1	8.2 ± 1.2

The %C recovery data in Table 4-8 showed similarities to the TS and VS recovery trends observed in Table 4-4 and 4-6. Total %C recovery between the NHF and HF ranged from 52.8% – 75.8%. The data also showed that total %C recovery was lowest in manures pre – treated with 1.0N HCl. The same trend that was noted in the TS and VS % recovery data.

The data also showed that the NHF accounted for the largest proportion of %C recovery from the hog manure when compared with the HF. This was because the NHF constituted the largest portion of the TS between the NHF and HF. The low %C recovery in the manures pre – treated with 1.0N HCl would not result in an efficient EF procedure, as a significant quantity of manure would be needed to

generate an economically viable process. The same trend was noted for the %TS and VS, suggesting that the efficiency of the EF procedure with regards to percent recovery data of VS and C could be based on the %TS recovery data.

4.2.2.4. Nitrogen Recovery

Results from the Elemental Analyzer for total %N in the raw material, the NHF and the HF are presented in Table 4-9.

The data presented below do not generally show the same trends as those observed for %VS and %C data in Tables 4-5 and 4-7. Examination of the data showed that the %N was consistently highest in the HF, when compared to the raw material and the NHF. Unlike the %VS and %C data however, the highest %N in the HF was observed in the control experiments, followed by the 0.1N HCl pre – treatment and lastly the 1.0N HCl pre – treatment. Further, these data appeared to suggest that nitrogen does not behave in the same fashion as the C or VS, and that it may be associated with different compounds in the hog manure. The data appeared to suggest that the solubility of N in HCl increased with an increasing concentration of HCl pre – treatment solution.

Table 4-9: Total % Nitrogen ($\text{g N}^f / 100 \text{ g TS}^f$) in the raw material and the NHF and HF.

HCl Strength (N) – KOH Strength (N)	Raw Material ($\text{g N}^{\text{HM}}/100 \text{ g TS}^{\text{HM}}$)	NHF ($\text{g N}^f/100 \text{ g TS}^f$)	HF ($\text{g N}^f/100 \text{ g TS}^f$)
Control – 0.25	1.8 ± 0.1	0.9 ± 0.1	6.7 ± 0.1
1.0 – 0.25	1.8 ± 0.1	0.7 ± 0.1	5.7 ± 0.1
0.1 – 0.25	1.8 ± 0.1	1.2 ± 0.1	6.5 ± 0.1
Control – 0.5	1.8 ± 0.1	N/A	7.8 ± 0.1
1.0 – 0.5	1.8 ± 0.1	0.6 ± 0.1	6.4 ± 0.1
0.1 – 0.5	1.8 ± 0.1	0.8 ± 0.1	7.2 ± 0.1
Control – 0.75	1.8 ± 0.1	0.5 ± 0.1	5.6 ± 0.1
1.0 – 0.75	1.8 ± 0.1	0.6 ± 0.1	5.2 ± 0.1
0.1 – 0.75	1.8 ± 0.1	0.5 ± 0.1	4.7 ± 0.1

Percent N data in Table 4-9 showed that for the HF, the %N was lowest in manures pre – treated with 1.0N HCl for the 0.25 and 0.5N KOH hydrolyses. In the case of the 0.75N KOH hydrolysis, the %N data deviates, and the lowest %N was observed in the 0.1N pre – treatment. The data showed that the nitrogen present in the raw material appeared to be affected more by the HCl pre – treatment when compared to the VS and C. The trends observed between the various pre – treatments and the control group for the HF appear to suggest that the solubility of N in the HCl increases as the HCl concentration increases. The higher solubility of N would lead to an increased amount of N in solution as a result of pre – treatment, resulting in a lower N concentration in the NHF and HF.

The data for the NHF did not readily show a consistent trend with respect to the %N in the different pre – treatment or KOH experimental groups.

Using the data from Tables 4-3 and 4-9, the %N recovery was calculated using equation 3-14. Results are presented in Table 4-10, with the yield data presented in Appendix A and sample calculations in Appendix B.

Table 4-10: % Nitrogen recovery in NHF and HF.

HCl Strength (N) – KOH Strength (N)	NHF (g N^f/100 g N^{HM})	HF (g N^f/100 g N^{HM})
Control – 0.25	30.1 ± 0.8	38.8 ± 1.7
1.0 – 0.25	17.5 ± 0.2	13.7 ± 0.8
0.1 – 0.25	48.0 ± 3.7	8.8 ± 5.6
Control – 0.5	N/A	27.3 ± 3.0
1.0 – 0.5	12.88 ± 0.6	22.53 ± 6.8
0.1 – 0.5	27.5 ± 3.7	45.1 ± 8.2
Control – 0.75	16.7 ± 0.2	33.3 ± 0.7
1.0 – 0.75	17.8 ± 2.5	7.1 ± 4.8
0.1 – 0.75	16.5 ± 2.2	15.5 ± 2.6

The most significant similarities between the data in Table 4-10, and the data in Tables 4-4, 4-6 and 4-8, is that the percent recovery of TS, VS, C and N for both the NHF and the HF was generally lowest in the 1.0N pre – treatments.

Further examination of the results in Table 4-10 showed the HF tended to have a higher percent recovery of N than the NHF. The results showed that the highest %N recovery in the HF was in the 0.1/0.5 treatment, and the lowest recovery was in the 1.0/0.75 treatment. For the NHF, %N recovery appeared to be significant in the 0.0/0.25, 0.1/0.25, and 0.1/0.5 treatments. The lowest %N recovery in the NHF was in the 1.0N pre – treatments, with the exception of the 0.75N hydrolysis.

The data presented on the recovery of TS, VS, C and N do not allow for a mass balance on the system, as colloidal matter generated in the pre – treatment step and the wash water used following the alkaline hydrolysis, resulted in the removal of small fraction of the solids, and thus, some removal of nitrogen and carbon. As a result, a complete system mass balance was not performed. An examination into the best combination of HCl and KOH is further examined, and used to provide a cost and sustainability analysis into the production of the NHF and HF.

In order to better understand the effects of HCl and KOH concentration on the percent recovery results in Tables 4-4, 4-6, 4-8 and 4-10, the data were plotted in Figures 4-1 to 4-4. These show percent recoveries plotted against HCl strength and KOH strength; Figures 4-1 and 4-2 represent the %TS, VS, C and N recovery in the HF and NHF vs. KOH strength for the three different HCl pre –

treatments. Figures 4-3 and 4-4 represent the %TS, VS, C and N recovery in the HF and NHF vs. HCl strength for the three different KOH hydrolyses.

Figures 4-1 to 4-4 illustrate some trends in the percent recovery data obtained for the NHF and HF. The most significant observation was that the percent recovery of TS, VS, and C in the HF were generally, within the same range, while the percent recovery of N in the HF was significantly higher. Figure 4-2 illustrates a similar, but slightly opposite trend for the NHF for percent recovery of N when compared with the TS, VS and C. The percent recovery of N for the NHF was lower than the percent recovery of TS, VS and C. These results illustrate that the solubility of N in HCl or KOH may be different than the solubility of VS and C in HCl or KOH. Further observation of the data in Figures 4-1 to 4-4 showed that percent recovery in the HF was much more sensitive to the HCl or KOH concentration than the NHF. This was attributed to the smaller quantity of material present in the HF when compared with the NHF. Based on the data observed, as well as the significant ranges of nitrogen recovered in the process, it is hypothesized that different forms of nitrogen, e.g. nitrates and ammonia, are present simultaneously in the organic fractions. This is shown in the background literature in Chapter 2.

Figure 4-1: Product recovery in the HF vs. KOH for the three different pre – treatment groups.

Figure 4-2: Product recovery in the NHF vs. KOH for the three different pre – treatment groups.

Figure 4-3: Product recovery in the HF vs. HCl for the three different hydrolyses.

Figure 4-4: Product recovery in the NHF vs. HCl for the three different hydrolyses.

Based on the results, it can be seen that the recovery of N fluctuates more than the TS, VS and C; this is most pronounced in the HF. Based on the data, and the likely presence of different forms of organic and inorganic nitrogen, fluctuations in N recovery is likely due to volatilization at higher pH's due to the alkaline hydrolysis. Based on the data however, it appears that the pre – treatment of the manure has an affect on the nitrogen recovery trend, and perhaps, the extent of volatilization of ammonia into the atmosphere. These losses could potentially be avoided by covering the beaker to prevent excessive ammonia losses.

The data plotted in Figure 4-1 showed that for the control groups, the percent recovery in the HF was reduced by increasing the concentration of KOH from 0.25N to 0.5N, followed by an increase in percent recovery as the concentration of KOH was increased from 0.5N to 0.75N. When examining both of the pre – treatment groups, the percent recovery in the HF reached an optimum at the 0.5N KOH strength, and was lower for the two extreme KOH strengths. These results showed that the percent recovery in the HF in the control group had an opposite trend to the percent recovery in the HF in the 0.1 and 1.0 N pre - treated hog manures. These observations could suggest that the HCl pre – treatment may have an effect on the availability of TS, VS, C and N at the different KOH strengths. This may be due to a change in the solubility of hydrolyzable products in the hog manure for the various HCl strengths. Based on the data in Figure 4-1, the 0.1N HCl pre – treatment followed by the alkaline hydrolysis with 0.5N KOH resulted in the highest recovery of nitrogen in the HF.

Examination of the NHF percent recovery data with HCl pre – treatment in Figure 4-2 showed a similar, but much less pronounced trend when compared with the data plotted in Figure 4-1 for the HF. This is likely due to the larger quantity of TS present in the NHF when compared with the HF, thus, this fraction would not be as sensitive to changes in system pH. The data for the NHF showed a much smaller difference between the control and two pre – treatment groups, when compared with the HF in Figure 4-1. The data also showed that the opposing trend in percent recovery between the control group and the pre – treatments that was observed for the HF in Figure 4-1, was not as evident for the NHF data in Figure 4-2. This suggested that the percent recovery for the NHF was not affected as much by the pre – treatment, when compared to the HF. As the most valuable agricultural product between the two fractions would most likely be the HF (due to the high N recovery, and the high %C and %VS values), the effects of pre – treatment on the NHF may not be as significant to the overall efficiency of the EF procedure, in terms of maximizing percent recovery of N.

The percent recovery data for the HF in Figure 4-3 was plotted against HCl pre – treatment strength for the three different KOH hydrolyses. A slightly different trend was observed in the HF when comparing these to the trends observed in Figure 4-1. As can be seen, the initial effect of increasing the HCl strength in the 0.25N and 0.75N KOH groups was a decline in the percent recovery, however, the opposite was observed in the 0.5N hydrolysis group. These data appear to confirm observations in Figure 4-1, and to a lesser degree in Figure 4-2, that

indicated that the 0.5N KOH strength may be the KOH concentration at which a change in the solubility of the hydrolyzable products can be noted. Similar to the data in Figure 4-1, the %N recovery was highest at the 0.1N HCl pre – treatment and 0.5N KOH hydrolysis group.

Data plotted in Figure 4-4 showed that the range of percent recovery observed for the NHF was much smaller when compared with the range of percent recovery in the HF. A similar conclusion can be drawn from examination of Figure 4-4 as that of Figure 4-2. The small range in percent recovery data observed in the NHF suggests that more consideration of the HF should be made when determining the most efficient pre – treatment and hydrolysis strength.

All of the data presented in Figures 4-1 to 4-4 showed that certain trends are evident from the percent recovery data in the NHF and HF. However, more research is required to determine the characteristics of the interactions between pre – treatment and KOH hydrolysis, and how these may affect recovery in the fractions. The significant range in nitrogen recovery may be attributed to the large range in pH that the alkaline solution undergoes, thereby causing losses in both organic matter due to solubility and ammonia due to volatilization.

In addition to comparing the effects of pre – treatment and hydrolysis strength, the metal concentrations in the NHF and HF were also examined in the 0.75N KOH hydrolysis group. Due to limited amounts of material for the 0.5N KOH

hydrolyses, the metal concentration data in the NHF and HF for the 0.5N experimental group were not available. In addition, the data showed that similar trends were observed in the 0.25N KOH hydrolyses, when compared with the 0.75N KOH experimental group, and thus only the 0.75N data are presented.

The results from the metal analysis in the NHF and HF showed similar trends to those observed for the metals in the untreated and pre – treated hog manures, in that some variation can be observed in the metal concentrations both between the NHF and HF and between the different HCl concentrations.

The results presented in Figures 4-5 and 4-6 showed that the concentration of Fe in the NHF and HF from the control group was generally lower than the Fe concentration in the NHF and HF from the 0.1N and 1.0N HCl pre – treated manures. The data also showed that in general, the concentration of Al, Mg, P and Ca was higher in the NHF, and in general, the concentration of Cu, Fe and Zn was similar in both the NHF and HF. The metal data in the two fractions complement the findings in Section 4.1 which suggested in general, the concentration of metals was reduced in the organic material following the HCl pre – treatment.

Figure 4-5: Metal concentration in the HF from untreated manure, and manures pre – treated with 0.1N and 1.0N HCl

Figure 4-6: Metal concentration in the NHF from untreated manure, and manures pre – treated with 0.1N and 1.0N HCl

4.3. Spectroscopic Analysis

In order to further examine the differences between the two fractions, and, in order to better identify potential end-uses for the NHF and HF, spectroscopic analyses were performed. Fourier-Transform Infrared Spectroscopy (FTIR) and Carbon – 13 Nuclear Magnetic Resonance Spectroscopy (^{13}C – NMR) were used to identify the functional groups and carbon bonds present in the NHF and HF.

4.3.1. Fourier – Transform Infrared Spectroscopy

The FTIR spectrum in Figure 4-7 shows typical peaks observed in the NHF, and the FTIR spectrum in Figure 4-8 shows typical peaks observed in the HF. Interpretation of the FTIR spectra was based on previously published literature from Diné *et al.*, (1998), Niemeyer *et al.*, (1992) and Bellamy (1975). Stretching and bending of the functional groups describe the range of wavelengths over which the molecular bonds are deformed.

Examination of the various spectra for both the NHF and the HF showed that in general, each had similar peaks. Interpretations are provided in Tables 4-11 and 4-12. Figure 4-7 shows an FTIR spectrum for the NHF from the 0.1N HCl/0.5N KOH experiment. This spectrum was chosen as the significant peaks were most easily identified, when compared with the spectra for the other pre – treatments and hydrolysis experiments. The FTIR spectra for the NHF from several different experiments are provided in Appendix A in Figures A1 – A8. Comparison of these with the spectra in Figure 4-7 showed that the significant peaks identified in

Table 4-11 for the NHF can, in general, also be identified in the spectra provided in Appendix A from the other experimental groups. This suggested that the functional groups identified by the peaks for the NHF may not be significantly affected by the pre – treatment or hydrolysis experiments.

Figure 4-7: Typical FTIR spectra for the NHF.

Table 4-11: Potential functional groups present in the NHF, identified using FTIR.

Observed Peak (cm ⁻¹)	Possible Functional Group*
≈ 3430	alcoholic OH, H ₂ O and/or possibly NH amine stretching
≈ 2930	CH stretching of aliphatic CH ₃
≈ 1660	Aromatic stretch of C = C and/or COO ⁻
≈ 1430	CH deformation of CH ₃ or CH ₂ bending
≈ 1380	CH ₃ deformation or symmetric COO ⁻ stretching
≈ 1250	CH deformation of CH ₃ or CH ₂ bending
≈ 1050	CO stretching of carbohydrates or C-OH stretch of aliphatic OH groups, or aromatic CH bending
≈ 560	Aromatic CH bending

Figure 4-8 shows an FTIR spectrum for the HF from the 0.1N HCl/0.5N KOH experiment. This spectrum was chosen as the significant peaks are most easily identified, when compared with the spectra for the other pre – treatments and hydrolysis experiments. The FTIR spectra for the HF from each of the experiments are provided in Appendix A in Figures A9 – A17. Comparison of these with the spectra in Figure 4-8 showed that the peaks identified in Table 4-12 can, in general, be identified in the spectra provided in Appendix A for the HF. This suggested that, similarly to the NHF, the functional groups indicated by the major peaks for the HF are not significantly affected by the pre – treatment or hydrolysis experiments.

Figure 4-8: Typical FTIR spectra for the HF.

Table 4-12: Potential functional groups present in the HF, identified using FTIR.

Observed Peak (cm^{-1})	Possible Functional Group
≈ 3410	alcoholic OH, H_2O and/or possibly NH amine stretching
≈ 2920	CH stretching of aliphatic CH_3
≈ 2850	CH stretching of aliphatic CH_2
≈ 1660	Aromatic stretch of $\text{C}=\text{C}$ and/or COO^-
≈ 1515	NH deformation and $\text{C}=\text{N}$ stretch, or aromatic $\text{C}=\text{C}$ stretch
≈ 1460	CH deformation of CH_3 or CH_2 bending
≈ 1415	CH deformation of CH_3 or CH_2 bending
≈ 1250	CH deformation of CH_3 or CH_2 bending
≈ 1030	CO stretching of carbohydrates or C-OH stretch of aliphatic OH groups, or CH_2 bending, or aromatic CH bending
≈ 820	Aromatic CH bending
≈ 540	Aromatic CH bending

Observation of Figures 4-7 and 4-8 shows many similarities between the FTIR spectrum for the NHF and the FTIR spectrum for the HF. Each showed broad bands at approximately 3400 cm^{-1} , indicating the possibility of alcoholic OH or water, or possibly NH stretching. A peak at approximately 2930 cm^{-1} was observed in the spectra for both the NHF and HF. In addition to this, the HF showed a second, smaller peak at approximately 2850 cm^{-1} , however this additional peak was not observed in the NHF. The peak at 2300 cm^{-1} for the both the NHF and HF is CO_2 entering the Bomem FTIR unit during installation of the KBr pellet. Both spectra showed activity below 1750 cm^{-1} , which suggested the presence of compounds such as aromatic $\text{C}=\text{C}$ bonds, COOH stretching, additional CH_3 and CH_2 stretching as well as further indication of OH functional groups. Specific interpretation of the spectra was difficult in the lower wavelength

regions for both spectra. From the FTIR analysis, it was clear that the differences between the two fractions are not readily obvious using FTIR analysis alone.

FTIR spectra for humic acid and cellulose are provided for comparative purposes. Figure 4-9 illustrates an FTIR spectrum for humic acid, originally published by Niemeyer *et al.* (1992). Figure 4-10 illustrates an FTIR spectrum for cellulose, originally published by (Cao and Tan, 2002). It should be noted that the spectrum for humic acid is plotted against absorbance and not transmittance.

Figure 4-9: FTIR spectrum for humic acid (HA) (Niemeyer *et al.*, 1992)

Figure 4-10: FTIR spectrum for cellulose (Cao & Tan, 2002).

The interpreted spectra for humic acid and cellulose are presented in Tables 4-13 and 4-14 respectively.

Table 4-13: Published FTIR spectra for humic acid (Niemeyer *et al.*, 1992).

Observed Peaks (cm ⁻¹)	Functional Group Assignment
3275	OH stretch of Phenolic OH (contribution from aliphatic OH, H ₂ O and NH)
2960	Asymmetric stretch of CH ₂
2600	OH stretch of H – Bonded COOH
1725	C = O stretch of COOH
1620	Aromatic C = C stretch and/or asymmetric COO ⁻ stretch
1395	Symmetric COO ⁻ stretch and/or CH bending of aliphatics
1200	C-O stretch and OH deformation of COOH
850	Aromatic CH out of plane bending

Table 4-14: FTIR spectra for cellulose (Cao and Tan, 2002).

Observed Peaks (cm ⁻¹)	Possible Functional Group
≈ 3360	OH stretch of Phenolic OH (contribution from aliphatic OH, H ₂ O and NH)
≈ 2900	Asymmetric stretch of CH ₂
≈ 1645	C=O stretch of amide, aromatic C=C, COO ⁻
≈ 1430	CH asymmetrical deformation of CH ₃ and CH bending of CH ₂
≈ 1370	Symmetric COO ⁻ stretch and/or CH bending of aliphatics, and/or CH symmetrical deformation of CH ₃
≈ 1340	CH – deformation
≈ 1280	C-OH stretch of phenolic OH
≈ 1240	C-OH stretch of phenolic OH and/or C-O stretch and OH deformation of COOH
≈ 1160	C – OH stretch of aliphatic OH
≈ 1060	C – O stretching of carbohydrates
≈ 615	Aromatic CH bending

The figures and interpretations from Niemeyer *et al.* (1992) and Cao and Tan (2002) show that there are many similarities between the spectra for the humic acid, cellulose, the NHF and the HF.

From the spectra obtained for the NHF and HF, and comparison of these with published FTIR spectra for humic acid and cellulose, it is clear that using FTIR alone, it is difficult to see significant differences between the two fractions. The use of Carbon – 13 Nuclear Magnetic Resonance Spectroscopy is used in order to further develop an understanding into the differences between the NHF and HF.

4.3.2. Carbon-13 Nuclear Magnetic Resonance (^{13}C – NMR)

^{13}C – NMR spectra were interpreted based on previously reported ^{13}C – NMR spectra for humic acid (Schnitzer and Schulten, 1998) and hog manure colloidal matter (Dinel *et al.*, 1998). Similar to FTIR stretching and bending of functional groups, significant chemical shift ranges observed in the ^{13}C – NMR spectra provide ranges over which specific carbon bonds are represented.

Figure 4-11: Typical ^{13}C – NMR Spectrum for the NHF

Figure 4-11 shows the ^{13}C – NMR spectrum obtained for the NHF in the 1.0N HCl/0.5N KOH experiment. Additional ^{13}C – NMR spectra for the NHF from other experimental groups are provided in Appendix A in Figures A18 through A21. Figure 4-11 shows significant chemical shifts are observed at 55.3, 61.9, 64.3, 71.6, 74.0, 83.2, 88.1 and 104.3 ppm. A comparison of this with the spectra in Figures A18 through A21 showed that in general, the most significant chemical shift range for the NHF occurred in the 60 – 105 ppm range in each of the experiments.

Figure 4-12: Typical ^{13}C – NMR Spectrum for the HF

Figure 4-12 shows the ^{13}C – NMR spectrum for the HF in the 0.0N HCl/0.75N KOH experiment. Additional ^{13}C – NMR spectra for the HF from other experimental groups are provided in Appendix A in Figures A22 through A26. Figure 4-12 shows a significantly broad range of signals, with peaks observed at 12.8, 15.0, 19.8, 25.0, 30.8, 33.2, 43.3, 56.3, 62.9, 72.7, 74.6, 82.4, 83.5, 105.5, 116.4, 130.6, 148.1, 173.2 and 181.2 ppm. A comparison of Figure 4-12 with Figures A22 through A26 did not show significant differences between the observed ranges for the different HCl and KOH strengths.

Table 4-15 shows a typical interpretation of various chemical shift ranges for different carbon bonds in a ^{13}C – NMR spectrum.

Table 4-15: ^{13}C – NMR spectra chemical shift range interpretation. (Dinel *et al.*, 1998).

Type of C	Chemical Shift (ppm)
Aliphatic C, associated w/ CH_3 and CH_2 ,	0 – 40
Protein C, Methoxyl groups	40 – 60
Carbohydrates C	60 – 105
Aromatic and Hetero - aromatic C	105 – 150
Phenolic C and Substituted Phenolic C	150 – 170
Carboxylic C (COOH)	> 170

Based on the interpretation by Dinel *et al.* (1998), the spectrum for the NHF showed mainly the presence of carbohydrate C, while the spectra for the HF showed the presence of aliphatic CH_3 and CH_2 , proteinaceous C and methoxyl groups, carbohydrate C, aromatic C and also phenolic and carboxylic C. In

general, the same observations were made for the NHF and HF spectra in Figures A18 through A26. The ^{13}C – NMR spectra illustrated that the HF was more complex in nature when compared to the NHF. This was attributed by the additional presence of signals observed between 0 – 180 ppm in the HF spectra. These findings appear to support previous observations in the %N recovery data, which showed that the HF contained a significantly higher fraction of the original nitrogen (Table 4-10). The results from both the FTIR and ^{13}C – NMR analysis appear to be complementary, and support each other.

In addition to examination of the ^{13}C – NMR spectra of the NHF and HF, previously published ^{13}C – NMR spectra for cellulose (Salloum *et al.*, 2002), hog manure colloidal matter (Dinel *et al.*, 1998) and humic acid (Schnitzer and Schulten, 1998) are presented for comparative purposes. These are shown in Figures 4-13, 4-14 and 4-15, respectively.

Figure 4-13: ^{13}C – NMR Spectrum for cellulose (Salloum *et al.*, 2002)

The spectrum for cellulose provided in Figure 4-13 is similar to that of the NHF generated in the EF procedure. This illustrates the aliphatic, cellulose – like nature of the NHF.

In addition, Figures 4-12, 4-14 and 4-15 illustrate similarities that can be observed among hog manure colloids, humic acid and the HF. Unlike the spectrum for the NHF in Figure 4-11, the spectra in Figures 4-12, 4-14 and 4-15 show a much broader range of significant chemical shifts. These similarities among the spectra illustrate the humic like nature of the HF. The results also suggest that in combination with the high percentage of C, VS and N also observed in the HF, this would potentially be an excellent source of organic matter and nitrogen.

Figure 4-14: ^{13}C – NMR Spectrum for hog manure colloidal matter (Dinel *et al.*, 1998)

Figure 4-15: ^{13}C – NMR Spectrum for humic acid (Schnitzer & Schulten, 1998)

4.4. Interpretation of NHF and HF Experimental Data Based on Soil Chemistry

Using theory presented by Schnitzer and Khan (1972); Schnitzer and Khan (1978), Schulten and Schnitzer (1995), Schnitzer and Schulten (1998) and Diné and Dumontet (1995) as described in Section 2.3, the NHF and HF from the EF procedure could be characterized as humin and humic – like material, respectively.

In order to illustrate the solubilization of the humic – like HF, and subsequent precipitation of this from solution, a series of chemical equations are provided. The first set of equations, “Reaction 1 and 2”, are used to illustrate the alkaline hydrolysis and solubilization of the HF.

The second set of equations, "Precipitation 1 and 2", is used to illustrate the precipitation of the HF from solution, and subsequent formation of KCl salt.

Ph-COOH represents the carboxylic groups attached to the phenyl aromatic ring present in the general hog manure structure (Ph). Ph-OH represents a phenolic functional group attached to the general structure. The hydrolysis with the KOH solution, involves an exchange between the carboxylic and phenolic functional groups present in the general structure of the hog manure. The K ion is dissociated from the KOH forming water with the H molecule disassociated from the COOH and OH functional groups.

From the experimental data observed in this study regarding the HF (Appendix A), and background soil chemistry theory presented in Section 2.3 (Schnitzer and Khan, 1978), it was shown that the $\text{Ph-COO}^-\text{K}^+$ and $\text{Ph-O}^-\text{K}^+$ associated with the HF, were soluble between a pH of 6 and 12. This can be verified by the significant chemical shifts greater than 150 ppm that were observed in ^{13}C – NMR in Figure 4-12. Lowering the pH below 5 precipitated the humic – like HF

from the solution. This is illustrated in the precipitation reactions; the formation of KCl salt should also be noted. As previously mentioned, removal of KCl salt from the NHF and HF was accomplished with distilled water, resulting in the solubilization of the KCl salt in the wash water, and the generation of wash waters that contained colloidal matter from either the NHF or the HF. The loss of colloidal matter in the experiment did not allow for the generation of mass balances, however, it can be assumed that the wash waters and colloidal matter that were collected would likely be either recycled back into the EF procedure, or the colloidal matter could be recovered, and combined with either the NHF or HF. Thus, the data presented herein can be considered to be conservative, and represents low recoveries. By maximizing the use of all of the products in the EF procedure, including colloidal matter in the wash water, the procedure would minimize the amount of sludge generated. This would need to be verified through further research, in which the colloidal matter from the pre – treatment and wash waters is collected and analyzed for carbon, nitrogen and metals.

The reduction of metal concentration was accomplished with the HCl pre – treatment, however these were not recovered in this study. The research showed that different metals behave differently at various pH levels in the pre – treatment solutions. This research could be combined with additional research that would allow for an effective mass balance around the metal data.

The data obtained from the percent recovery analysis of total solids showed that the NHF retained the highest portion of TS when compared with the HF. In addition, the FTIR and ^{13}C – NMR data showed that the NHF had many similarities to that of cellulose, attributed by the mainly carbohydrate based spectrum and comparison of this with a ^{13}C – NMR spectrum for cellulose. Based on observations made in the study, it is believed that the NHF could potentially be used to produce ethanol via fermentation processes, or other organic acids, for use in industry.

With respect to the HF, the significant presence of nitrogen illustrated in Tables 4-9 and 4-10, suggest that this may make a good source of nitrogen for crops. This would need to be verified through experiments that would examine the availability of the nitrogen in the HF to crops. In addition, the ^{13}C -NMR spectrum showed that this fraction contained many significant chemical shifts within similar ranges to those observed for hog manure colloids and humic acid. This characteristic, and the high fraction of volatile solids and carbon suggest that the HF may also be a good source of organic carbon.

The experimental data collected in this study show that on a technical level, the EF procedure can be used to generate a nutrient rich hydrolyzed fraction and a cellulose-based, energy rich, non-hydrolyzed fraction. The following section discusses issues related to the sustainability of the procedure, based on both economical and environmental considerations.

4.5. Sustainability Analysis

The sustainability analysis (SA) presented in this section combined observations made in published literature and the experimental data obtained in this study. The SA involves comparing the relative quantities of manure required via conventional landspreading techniques with the quantities of manure required to produce the HF to meet the crop N and P requirements, examination of potential technical issues related to implementation of the EF procedure, and examination of metal concentrations in soils, animal feed, untreated hog manure and the HF. In addition, the SA also involves a cost and environmental analysis of implementing the EF procedure.

4.5.1. Estimated Manure Quantities Based on Crop Nitrogen and Phosphorus Requirements

The quantity of wet manure required to meet crop nitrogen is first presented, followed by the quantity of wet manure required to meet crop phosphorus. Two cases were compared – Case 1 involved landspreading a wet hog manure slurry to provide crop N and P, and Case 2 involved examining the quantity of wet hog manure required for the EF procedure in order to produce a sufficient quantity of dried HF to provide crop N and P. In the comparison, conventional landspreading techniques were represented by Case 1, and the alternative use of the EF procedure to generate a sufficient quantity of HF to supply crop N and P requirements is presented in Case 2.

Equation 4 – 1 below was used to estimate the quantity of wet hog manure required for direct landspreading. Equation 4 – 2 was used to estimate the required quantity of wet hog manure to produce enough HF to supply crop nitrogen or phosphorus.

$$(4 - 1) \quad M_{WHM} = M_{N/P} \times (\%N/P_{HM})^{-1} \times (\%DM_{HM})^{-1} \times (\Psi)^{-1}$$

M_{WHM} = Mass of wet hog manure for Case 1 (kg wet manure/ha)
 $M_{N/P}$ = Mass of nitrogen or phosphorus required by crop (kg/ha)
 $\%N/P_{HM}$ = Nitrogen or Phosphorus content of dry hog manure (kg /100kg TS)
 $\%DM_{HM}$ = Slurry solids content – (0.1 kgTS/kg wet manure)
 Ψ = efficiency ($\Psi = 0.8$)

$$(4 - 2) \quad M_{eqWHM} = M_N \times (\%N_{HF})^{-1} \times (\%HF)^{-1} \times (\%DM_{HM})^{-1} \times (\Psi)^{-1}$$

M_{eqWHM} = Mass of wet hog manure required for Case 2 (kg wet manure/ha)
 $M_{N/P}$ = Mass of nitrogen or phosphorus required by crop (kg/ha)
 $\%N/P_{HF}$ = Nitrogen or phosphorus content of HF – 6.51% or 7.2% (kg N/100kg HF)
 $\%HF$ = HF Total Solids recovery – (kgHF/100kg TS)
 $\%DM_{HM}$ = TS of hog manure – 28% (kgTS/100kg wet hog manure)
 Ψ = efficiency ($\Psi = 0.8$)

Data from Tables 2-13, 4-1, 4-3, 4-9 and Figure 4-5 were used to determine the quantity of manure required to meet the nitrogen and phosphorus requirements using untreated hog manure and the HF for various crops. In addition, the moisture content of the manure was used to determine the mass of wet manure required to produce sufficient quantities of HF. In addition, as several %TS recoveries were observed for the HF, the two extreme cases are presented for Case 2. The first scenario for Case 2 involved using the HF with the highest TS recovery (0.1/0.5), and scenario 2 involved using the HF with the lowest TS

recovery (0.1/0.25). The range of TS is used rather than the range in %N or %P because the mass of total solids required has a greater effect on the quantity of material required for the EF procedure. As the calculation for crop nitrogen and phosphorus requirements is identical, both of nitrogen or phosphorus can be used in equations 4 – 1 and 4 – 2. The results for the nitrogen calculations are presented in Tables 4-16 and 4-17, and the phosphorus results are presented in Tables 4-18 and 4-19.

Table 4-16: Equivalent mass of wet manure required for conventional landspreading (Case 1) and for the EF Procedure using two different %TS recoveries (Case 2).

Crop	Crop N (kg N/ha)	Case 1 (kg/ha)	Case 2 Scenario 1 (kg/ha)	Case 2 Scenario 2 (kg/ha)
Fescue	125	85,383	67,396	342,879
Alfalfa	89	60,792	47,986	244,130
Orchard grass	30	20,492	16,175	82,291
Timothy	24	16,393	12,940	65,833
Bluegrass	24	16,393	12,940	65,833
Corn	29	19,809	15,636	79,548
Corn	52	35,519	28,037	142,638
Corn	84	57,377	45,290	230,415
Milo	28	19,126	15,097	76,805
Milo	37	25,273	19,949	101,492

The first two columns in Table 4-16 give type of crop and the required nitrogen for growth respectively. The data are based on a specific crop yield/hectare and reflects the quantity of nitrogen that is required to achieve a particular crop yield on one hectare. The next three columns show the equivalent quantities of wet hog manure required for each case. The data used for Case 1 assume manure nitrogen content as measured in the research of 1.83% (Table 4-9). Based on published data provided in Chapter 2, it was assumed that the manure slurry used for landspreading would be diluted to 10% solids. Both scenarios for Case 2 represent the equivalent quantity of wet manure that would be required for the EF procedure to generate enough HF to supply a particular crops' nitrogen requirement. In both cases nitrogen losses were assumed to be 20% (Table 2-21).

Wet manure requirements determined for conventional landspreading applications, based on the raw manure data collected in the experiment, are consistent with published data (Miner *et al.*, 2000). A comparison of the wet manure requirements with Case 2 – Scenario 1 data showed less manure would be required to meet the crop nutrient requirements when using a HF with a high percent recovery of TS when compared to wet manure requirements for Case 1. When using a low total solids recovery, as in Case 2 – Scenario 2, it was found that more manure was required for the EF procedure when compared with conventional landspreading. Both scenarios could, however, be used to an operator's advantage, assuming the low %TS recovery was still economically

feasible. In the 1st scenario, less manure is required, suggesting that the farmer may generate excess HF which can be sold to generate revenue. In the 2nd scenario, more manure is required, suggesting that more manure could be indirectly applied onto a smaller parcel of land, by first treating it with the EF procedure. This would reduce the need for additional offsite transportation and disposal costs of excessive quantities of manure, due to a small land base.

The data shown in Table 4-16 do not reflect the actual mass of HF that would be used to supply crop N. The data presented in Table 4-16 reflects the quantity of manure that would be required for the EF procedure to produce a sufficient quantity of HF. The actual mass of HF used for landspreading would be lower than the mass of wet hog manure that is conventionally applied to crops. In order to determine the actual mass of HF used to supply the crop requirements, the %HF and %DM_{HM} terms were dropped from equation 4 – 2, as shown in equation 4 – 3. It should be noted that the use of equation 4 – 3 also applies to the phosphorus calculation, and thus the 'N' terms in equation 4 – 3 can be replaced by P, representing phosphorus.

$$(4 - 3): \quad M_{HF} = M_{N/P} \times (\%N/P_{HF})^{-1} \times (\Psi)^{-1}$$

M_{HF} = Mass HF required for Case 2 (kg HF/ha)

$M_{N/P}$ = Mass of nitrogen or phosphorus required by crop – see Table 8 (kg /ha)

$\%N/P_{HF}$ = Nitrogen or Phosphorus content of HF (kg /kg HF)

Ψ = efficiency ($\Psi = 0.8$)

Table 4-17 shows the estimated masses of dried HF that would be landspread for both scenario 1 and scenario 2, for crop nitrogen requirements.

Table 4-17: Actual quantity of material required to meet crop nitrogen requirements.

Crop	Crop N (kg N/ha)	Case 1 (kg /ha)	Case 2 Scenario 1 (kg/ha)	Case 2 Scenario 2 (kg/ha)
Fescue	125	85,383	2,170	3,296
Alfalfa	89	60,792	1,545	2,347
Orchard grass	30	20,492	521	791
Timothy	24	16,393	417	633
Bluegrass	24	16,393	417	633
Corn	29	19,809	503	765
Corn	52	35,519	903	1,371
Corn	84	57,377	1,458	2,215
Milo	28	19,126	486	738
Milo	37	25,273	642	976

Results in Table 4-17 indicate that the actual mass of HF that is needed to meet crop nitrogen requirements would be significantly lower than the mass of untreated wet hog manure slurry that would be otherwise required. The improved ease of handling of the dried HF would be advantageous as less space would be required for storage and less fuel would be required for landspreading. In addition, the HF contains a significantly higher percentage of volatile solids and carbon than the hog manure, and thus, the use of the HF as a fertilizer would also result in positive effects on soil quality. Another major benefit of using the HF over wet manure slurry would be the biological stability of the EF product, making it safer for longer term storage, without concerns regarding nitrogen losses, greenhouse gas production or odours. It is also believed that the HF will contain less bacteria and pathogens when compared to wet hog manure; this is predominantly due to the HCl pre – treatment and alkaline hydrolysis. The presence of microorganisms in the HF was not actually determined, however, confirmation of this would result in a substantial improvement in protecting public safety and potable drinking water supplies.

In addition to crop N calculations, the same approach was used for comparing manure requirements based on crop P needs using equations 4 – 1 to 4 – 3. Results for the phosphorus computation are presented in Tables 4-18 and 4-19.

Table 4-18: Equivalent mass of wet manure required for conventional landspreading (Case 1) and for the EF Procedure using two different %TS recoveries (Case 2).

Crop	Crop P (kg P/ha)	Case 1 (kg /ha)	Case 2 Scenario 1 (kg/ha)	Case 2 Scenario 2 (kg/ha)
Fescue	12	16,826	178,149	1,845,033
Alfalfa	9	12,619	133,612	1,383,775
Orchard grass	4	5,609	59,383	615,011
Timothy	3	4,206	44,537	461,258
Bluegrass	5	7,011	74,229	768,764
Corn	6	8,413	89,074	922,517
Corn	8	11,217	118,766	1,230,022
Corn	16	22,434	237,532	2,460,044
Milo	4.5	6,310	66,806	691,887
Milo	6	8,413	89,074	922,517

Table 4-19: Actual quantity of material required to meet crop phosphorus requirements for case 1 and case 2.

Crop	Crop P (kg P/ha)	Case 1 (kg/ha)	Case 2 Scenario 1 (kg/ha)	Case 2 Scenario 2 (kg/ha)
Fescue	12	16,826	5,387	14,465
Alfalfa	9	12,619	4,040	10,849
Orchard grass	4	5,609	1,796	4,822
Timothy	3	4,206	1,347	3,616
Bluegrass	5	7,011	2,245	6,027
Corn	6	8,413	2,694	7,233
Corn	8	11,217	3,591	9,643
Corn	16	22,434	7,183	19,287
Milo	4.5	6,310	2,020	5,424
Milo	6	8,413	2,694	7,233

The phosphorus analysis showed that in the case of untreated hog manure, less wet manure is required per hectare for any given crop, to supply needed crop P, when compared to N requirements. This is consistent with current agricultural practices that show basing manure application rates on crop N leads to excessive build-up of P in agricultural soils. Manure application based on crop P requirements will result in crop N deficiencies. Thus, the data observed for the P and N content in the untreated hog manure used in these experiments is consistent with published literature and general findings in the agricultural industry regarding over application of P due to manure spreading scenarios based on crop N. A build up of P in soils occurs because the quantity of P required by crops is significantly less than the quantity of N required by crops, as shown in Table 2-13. As a result of the differences in the quantity of crop N and P needs, as well as over application of P onto soils, crop rotations are used to balance the P inputs and outputs. Build up of P in the soil has been linked to high P concentrations in surface waters due to run-off and leaching of P from agricultural soils.

Further examination of Table 2-18 shows that because the P concentration in the HF is so much lower than that of the untreated hog manure, a larger amount of manure is required to generate a sufficient quantity of HF from the EF procedure. The data in Table 2-18 show that by supplying the HF to soils based on crop N requirements (Table 2-16), the crops will lack sufficient P. These results show the opposite effect of supplying crop N needs using the HF when compared with

landspreading untreated hog manure, in that instead of over-application of P to soils, there will in fact be an under-application of P to soils, when basing application rates on crop N.

This suggests that use the HF to meet crop nutrient needs would not result in excessive P build-up in soils, and would in fact require supplemental P addition for crop growth. The lack of P build-up in soils would be a large environmental benefit from the use of the HF as an agri-product.

4.5.2. Metal Analysis in the HF and Agricultural Soils

In addition to P build-up in soils, care must also be taken to ensure that other metals such as Cu and Zn do not accumulate in crop land due to excessive application of manures known to contain these compounds.

The data presented in this section involves a brief analysis of the potential for Cu and Zn to escape into the environment, and either become solubilized in groundwater or entrained in the soil matrix due to complexation. The published data presented in this section includes metal content in hog feeds, soil background metal data for As, Cd, Cu, Ni and Zn in various parts of the world and soil remediation criteria for these metals in Ontario. In addition, published data is compared with the metal concentrations observed in the untreated hog manure and the HF in order to hypothesize on the potential for bioaccumulation of these in crop land due to their relative concentrations.

Table 4-20 below shows metal concentrations in various hog feeds obtained from the Alberta Ministry of Agriculture, Food and Rural Development, (www.agric.gov.ab.ca/index.html). Based on the published data for the hog feed characteristics, it can be seen that the concentration of the various metals and minerals in the hog feed can vary. These differences in metal concentrations in hog feed could lead to differences in the metal concentrations in hog manure, as described in Chapter 2. In addition, the crude make-up of the hog feeds can lead to differences in digestibility and retention of the various metal complexes and minerals.

Table 4-20: Metals in two different types of hog feed. (Alberta Ministry of Agriculture, Food and Rural Development, www.agric.gov.ab.ca/index.html).

Metal	Fish Meal	Soy Meal
Fe ($\mu\text{g/g}$)	624	180
Cu ($\mu\text{g/g}$)	10.7	18.2
Zn ($\mu\text{g/g}$)	102	75
Mg ($\mu\text{g/g}$)	18	35
Ca ($\mu\text{g/g}$)	557	68
P ($\mu\text{g/g}$)	303	81
K ($\mu\text{g/g}$)	78	236

The data showed that the metal content of the hog manure used in these experiments had a higher concentration than both of the different feed characteristics shown in Table 4-20. A mass balance of the actual quantity of metals ingested by the hogs and the quantity leaving would provide a better understanding regarding the metal retention of the hogs.

Perhaps of more importance to metals and their potential for accumulation in crop land is the examination of the soil background metal concentration, and comparison of these with the concentration of metals that are applied to the soil. Table 4-21 shows the background soil metal concentration ranges in various parts of the world published by several different researchers.

Table 4-21: Soil background metal concentration ranges observed in various parts of the world.

Metal	Background Soil Concentration ($\mu\text{g/g}$)			
	Quebec ¹	Taiwan ²	Ohio ³	Allaway, US ³
As	5 – 15	ND* – 10.8	N/A**	N/A**
Cd	0.9 – 1.5	1.02 – 3.41	0 – 2.9	0.01 – 7
Cu	40 – 100	7.15 – 35.1	11 – 37	2 – 100
Ni	30 – 100	18.6 – 66.7	9 – 38	10 – 1000
Zn	110 – 230	30.1 – 392	47 – 138	10 – 300

Notes:

* ND – not detected; **N/A – data not available

1 – Quebec Ministry of Environment (MENV), www.menv.gouv.qc.ca

2 – Food and Fertilizer Technology Center <http://www.agnet.org>

3 – Ohio State University, www.ohioonline.ag.ohio-state.edu/rc275/index.html

Based on the data in Table 4-21, it can be seen that in general the soil background metal concentration remains within the same order of magnitude for all of the different locations. Large fluctuation in the data is to be expected due to the significant number of factors which can effect soil metal concentration, notwithstanding different land uses. Factors such as regional differences, cultural differences, geophysical differences and climatic differences will all play major roles in determining soil background data. It is likely that the data for Quebec will be most representative of background soil metal concentrations in the Ottawa region, simply based on proximity.

In order to determine the loading rate of manures onto soil, the concentration of metals in the manure must be known, as well as the local soil background metal concentration. By knowing these values, the maximum quantity of manure that can be applied to soils, without leading to metal bioaccumulation can be determined. Factors involved in determining the loading rate must include the assimilative nature of soils on the application of metals. In addition, liming soils to maintain an alkaline soil pH will reduce leaching of metals into the groundwater. Table 4-22 below shows the background metal concentration of soils in New York, the maximum allowable annual loading rate of biosolids and lastly the maximum cumulative concentration of metals allowed in the soils. All of the data is based on one hectare.

Table 4-22: Soil metal loading rates for based on USEPA guidelines (Tucker *et al.*, 2003).

Metal	Max. Annual Loading Rate (kg/ha/yr)*	Max. Allowable Cumulative Loading Rate (kg/ha)
As	2	41
Cd	1.9	39
Cu	75	1500
Ni	21	420
Zn	140	2800

Using data obtained from the experiment, the quantity of Cu and Zn that would be applied to one ha of crop land was determined, based on using both crop N and crop P nutrient requirements. Results from this analysis show that when using untreated hog manure, basing manure application on corn N requirements, resulted in the deposition of 1.16 kg/ha/yr of Cu and 3.66 kg/ha/yr of Zn. In

comparison, using the HF to supply crop nutrients show that basing HF application on crop N resulted in the deposition of 0.26 kg/ha/yr of Cu and 0.46 kg/ha/yr of Zn. These results show that the use of both the HF and the hog manure used in this experiment would not result in excessive application of Cu and Zn to crop land, based on both annual and cumulative maximum allowable metal loading rates. However, the data do show that use of the HF following pre – treatment will result in a lowered rate of Cu and Zn deposition in the soil, thereby extending the lifespan of the agricultural land. Benefits such as these should be factored in the analysis when comparing the relative benefits of landspreading untreated hog manure vs. the HF.

4.5.3. Energy and Resource Use in the EF Procedure

In addition to direct environmental impacts such as P and N application and lowered Cu and Zn application, consideration should also be given to physical restraints of implementing the EF procedure on a large scale basis. This consideration should involve both technical issues related to implementing the procedure and the non-renewable resource and energy uses associated with implementing the EF procedure.

Based on observations made in this study, certain technical issues have been identified, as well as sources of non-renewable resource use. These are first listed and then discussed.

- Difficulty in achieving a cost – effective manner in increasing system pH from low values to higher values observed in the alkaline hydrolysis. In addition, significant changes in solution pH may result in high volatilization of ammonia – N from the process,
- Raising temperature of the solution and manure mixture to 70° C for the alkaline hydrolysis will increase the energy requirements of the procedure,
- Mixing the hog manure in either the pre – treatment or alkaline hydrolysis solution will increase energy requirements of the procedure,
- Large quantities of HCl and KOH required for the EF procedure,
- High process water demand.

A significant range in pH can be observed in the experimental data in Appendix A. These data show that both economical and technical issues relating to achieving the range of pH and, limiting the amount of ammonia volatilization due to a high alkaline solution pH need to be addressed. The difficulties in increasing the pH from a low, acidic value, to a high, alkaline value, can be significant and costly. The system pH measured in this research ranged from below 4 to above 12. This suggests that either significant quantities of material be used to increase the pH of the pre – treatment solution, such as lime, or a trade – off in hydrolysis efficiency be made. The latter situation could involve using a more dilute alkaline solution with a pre – treatment solution of a slightly higher pH. Such impacts of reducing the HCl concentration (e.g. to 0.05N) and using the lowest strength KOH solution should be further explored in future research. Based on the data

obtained in this research, use of the 0.1N HCl solution with the 0.25N KOH hydrolysis solution resulted in a TS and N recovery in the HF of 2.5% and 8.8% respectively. Implications of a low TS recovery in the HF were examined in Table 4-16. Based on these data, for 100 tons of hog manure on a dry basis (e.g. 357 tons of wet manure at 28% solids), 2.5 tons of HF would be recovered on a dry basis, and 8.8% of the nitrogen from the original hog manure would be recovered. Thus, the mass of nitrogen that would be recovered in this scenario would be 0.165 tons of N. These results suggest that only a high value of N would allow for cost effective use of an EF procedure using 0.1N HCl and 0.25N KOH. In addition, the high amount of manure that would be required to generate a sufficient quantity of HF to supply either crop N (or P) would be significantly larger, increasing costs of manure collection and storage.

Another problem associated with pH is increased amounts of ammonia volatilization as the system pH is increased. The high system pH suggests that the loss of nitrogen during the alkaline hydrolysis may be significant if precautions are not taken to ensure these losses are minimized. Reducing the system temperature would assist in lowering volatilization rates, or the use of a closed reactor vessel to prevent the release of ammonia to the atmosphere could also reduce nitrogen losses. The former solution could however, result in a decline in the amount of material that is hydrolyzed from the hog manure. Further, the latter option will require more capital expenditure due to increased complexity. These trade – offs should be considered in a cost analysis of the EF procedure.

In addition to issues relating to the system chemistry, costs associated with energy consumption must also be considered. The associated value of energy that will be required to increase the system temperature to 70° C and to mix the various pre – treatment and hydrolysis solutions with the hog manure could be significant. In addition, energy requirements from fossil fuel use regarding collection, storage and loading manure into the process must also be considered. By considering the density and weight of the manure, as well as the size and volume capacity of the equipment required to haul the manure will be required in this analysis. Other energy requirements will arise in mixing and drying equipment, pumps required to move the water, and conveyers required to move the manure within the process. From the data gathered in this research, the most significant sources of energy requirements will likely arise from the high water demand of the process, the high demand for energy to heat, mix and process the hog manure, and also the use of HCl and KOH used for the pre – treatment and alkaline hydrolysis. These variables are further explored in the cost analysis in the following section. In addition, the value of the HF and NHF are considered, by examining the value of N and P in the HF and the potential energy content of the NHF.

4.5.4. Cost Analysis

Based on the experimental data obtained in from these experiments (provided in Appendix A), a cost estimate of implementing the EF procedure was made. In addition, the environmental benefits and drawbacks associated with landspreading and implementing the EF procedure are also compared. The

complete cost breakdown summarized in this section can be found in Tables A19 through A21, and involve costs associated with using the 0.1N HCl and 0.5N KOH solutions. The costs associated with generating the HF and NHF that were considered in the cost analysis are listed below:

- Quantity of water,
- Quantity of 1.0N HCl solution,
- Quantity of concentrated KOH pellets,
- Amount of energy required to raise solution temperature

Using these values using the unit costs for each, the costs for the EF procedure were determined, and summarized in Table 4-23 below.

Table 4-23: Summary of cost estimates for implementing the EF procedure.

Parameter	Cost for treating 100 tons of (TS)	Cost/kg TS
Water	\$ 4,542	0.045 \$/kg TS
HCl	\$ 291,774	2.92 \$/kg TS
KOH	\$ 358,577	3.59 \$/kg TS
Energy	\$ 2,807	0.028 \$/kg TS
Total Cost	\$ 657,700	6.58 \$/kg TS
Adjusted Cost	\$ 1,315,401	13.15 \$/kg TS

The total cost of the energy provided in Table 4-23 does not include fossil fuels and energy needs to operate the system. In order to overcome these unknowns, the total cost is adjusted by a factor of safety of two. Based on this data, the cost of applying the HF to one hectare of soil, using the application rate of corn in Table 4-17 of 503kg/ha would cost \$ 6,614 based on the adjusted cost of the EF procedure. Based on these results, a comparison of these costs with the costs

associated with landspreading will reveal that landspreading untreated hog manure is less costly than using the EF procedure. However, this analysis does not associate any value to the HF or the NHF. The analysis does not take into account the reduced need for controlling runoff of P from crop land or the reduced application rate of Cu and Zn to soils. Determining the value of these benefits, though beyond the scope of this research, must be considered when performing a fair comparison between landspreading untreated hog manure vs. using the hog manure to generate valuable products. Table 4-24 below is used to illustrate the environmental benefits and drawbacks associated with landspreading untreated hog manure, and using hog manure to generate valuable products.

Table 4-24: Environmental benefit and drawback comparison.

Benefits		Drawbacks	
HM*	HF**	HM*	HF**
Improvements in soil quality	Improvements in soil quality	Potential for contamination of streams from over application of P	Increased investment in technology
Reduced need for inorganic fertilizers	Reduced need for inorganic fertilizers	Intensification of hog production industry is making landspreading more difficult, due to a decline in available land	Increased demand for water
	Reduced amount of metal deposition on land	Potential contamination of drinking water	High demand of HCl and KOH
	Reduced amount of P application to crop land	Odour	
	Production of NHF to generate energy		
	Reduced odour during landspreading		
	Potential for recovery of minerals and vitamins from hog manure		

HM* – conventional application of untreated hog manure to soils

HF** – use of untreated hog manure to generate products using EF procedure

The information in Table 4-24 shows advantages to using the EF procedure over conventional landspreading untreated hog manure. The generation of two additional products from the procedure, when compared to the single value of untreated hog manure based on nutrient content is a clear advantage of the EF procedure. In addition, the health of the soil will be improved through the reduced application of metals and phosphorus. In addition, hog manure cannot be landspread on “nutrient sensitive” soils. Nutrient sensitive soils are those deficient in nitrogen, but have large quantities of P and minerals. The reduced P and mineral content of the HF would allow for this to be potentially safely applied without concern of over P application. This last point suggests that the HF could be used in areas where untreated hog manures cannot be used; this implies that potentially a “niche market” could be developed for the HF, in areas where soils are considered to be “nutrient sensitive”. In these areas, farmers have classically only had the option of using inorganic fertilizers with a specific nutrient content, whereas the use of the HF could present a second alternative in these scenarios.

The information presented in this research suggests that it is possible to generate a nutrient rich fraction from hog manure (HF) and a potentially energy rich fraction from the hog manure (NHF). In addition, the research showed that using a 0.1N HCl pre – treatment followed by a 0.5N KOH hydrolysis would result in the recovery of over 70% of the TS and N from the hog manure in the NHF and HF. Further examination of the data showed that the HF could be applied to crop land at lower quantities than hog manure based on crop N requirements.

Based on this, the data showed that a reduced quantity of P, Cu and Zn would be applied to the land. In addition, the cost of generating both the HF and NHF was determined to range from approximately 6 – 13 \$/kg (dry basis). The data also suggested that the environmental benefits associated with using the EF procedure surpassed those benefits associated with conventionally landspreading hog manure. Further, the data also suggested that the environmental drawbacks of implementing the EF procedure are lower than the drawbacks associated with landspreading untreated hog manure. Based on the technical, economic and environmental assessment of the data obtained in this research, it is concluded that it is feasible to use the EF procedure to recover commodity chemicals from untreated hog manure.

Chapter 5 – Conclusions & Recommendations

5.1. Conclusions

Metal removal data showed that for all of the metals scanned in the untreated and pre – treated manures, washing untreated manure with HCl, reduces their concentration in the hog manure. For the 0.1N pre – treatment the most to least extractable metals were $Zn > Cu > Mg > Na > Fe > P > Ca > Al$. The 1.0N pre – treatment showed a different order of the most reduced to the least reduced metal concentrations, namely, $Na > Mg > Fe > P > Zn > Cu > Ca > Al$. This difference was attributed to different solubilities of the metals at the various HCl solution strengths.

The metal concentrations measured in the NHF and HF generated from untreated and pre – treated manures showed similar trends to those observed for the metal concentrations in the untreated and pre – treated manures. In general, the metal concentrations for both the NHF and HF were lower in the pre – treated experimental runs when compared with the control groups. It was also observed that the metal concentrations of Al, Mg, P and Ca were higher in the NHF when compared with their concentration in the HF. Conversely, the concentrations of Cu, Fe and Zn were higher in the HF when compared with their concentration in the NHF. In addition, the concentration of Fe was lower in the control group as compared with the pre – treatment groups for both the NHF and HF. The metal data that was observed in this research suggested that different metals

complexes have different solubilities at different pHs, and thus future research should be directed to measuring the concentration of metals in the manure and in solution. This additional metal data would then allow for a complete balance of the metal complexes throughout pre – treatment. The experimental data collected in this study suggests that a recovery process developed toward the metals would result in the production of a viable product. Potential end uses of metals could include their use as a feed additive to provide basic nutritional metal requirements for livestock.

Percent recovery analysis for the TS, VS and C showed that the NHF accounted for the largest amount of material that was recovered in the EF procedure, while the HF accounted for a much smaller portion. The data also showed that, in general, the HF accounted the most significant portion of the N recovered from the hog manure.

Experimental data showed that the 0.1N pre – treatment, followed by an alkaline hydrolysis with 0.5N KOH resulted in the best recovery of TS, VS, C and N in the HF. The best recovery for the NHF was in the 0.1N pre – treatments, followed by the 0.25N KOH hydrolysis.

In addition to product recovery analysis, FTIR and ^{13}C – NMR spectra were examined in the NHF and HF. These showed that the NHF is mainly composed of carbohydrates, aliphatic compounds, OH functional groups, (likely arising from

alcohol, water and to a lesser degree carboxylic and phenolic compounds), and has similar characteristics to cellulose – like materials. The spectral data for the HF showed a more complex structure, having humic acid – like characteristics. The structural data showed the presence of more aromatic compounds with carboxylic and phenolic functional groups.

Examination of the NHF showed that this contained a relatively high amount of carbon, though little nitrogen. This suggested that the NHF could be used as a substrate or additive for ethanol production or organic acids. In addition, the HF contained a higher percentage of volatile solids and carbon, and was rich in nitrogen when compared with the NHF; this suggested that the HF could be used as a source of nitrogen and organic matter for agricultural crops.

A sustainability analysis was also performed. The main findings from this are summarized below.

- Based on crop N needs and the concentration of N in the untreated hog manure and the HF, the data showed that less manure was required to supply crop N when using the HF with a high TS recovery when compared with using untreated hog manure. In contrast, using a HF with a low TS recovery resulted in more manure being required to supply crop N needs, when compared with using untreated hog manure,

- Because the P concentration in the untreated manure was reduced, the quantity of P in the HF results in a diminished quantity of P accumulation in soils, suggesting the HF could be used in a “niche market” involving “nutrient sensitive” soils,
- The significant range in pH that was measured between the pre – treatment and alkaline hydrolysis could result in significant operational costs associated with expenditure on chemicals. In addition, the high pH measured during the alkaline hydrolysis will likely result in significant losses of ammonia from the process in large scale industry applications. The loss of nitrogen due to ammonia volatilization at high pHs will likely require capital expenditure in order to prevent or minimize nitrogen losses to the atmosphere at these pHs.
- Economic evaluation of large scale implementation of the EF procedure on a batch basis, treating 100 tons of dry solids, showed a total cost of \$637,000; this was doubled to account for data gaps resulting in a cost of \$1,300,000. The unit cost of implementing the EF procedure was determined to range from 6.37 – 13.00 \$/kg on a dry basis.
- Comparison of environmental benefits and drawbacks of implementing the EF procedure vs. continued use of conventional landspreading of untreated hog manure, showed that the EF procedure resulted in more environmental benefits and less environmental drawbacks when compared with conventional landspreading. Benefits associated with implementing the EF procedure include: generating potentially three

products from untreated hog manure, one of which can replace conventional manure application on land and reduced application of P, Cu and Zn on soils. The main drawback of implementing the EF procedure is the increased use of water and the need for large quantities of HCl and KOH,

- Based on the research performed herein, the technical implementation of the EF procedure is feasible. Significant environmental benefits and lowered drawbacks appear to be achievable by implementing the EF procedure. Advantages in terms of increased soil life due to lowered P, Cu and Zn deposition, as well as the potential to generate “niche markets” must be also be included in these comparisons.

5.2. Recommendations

The following are general recommendations and suggested future courses of research arising from this study:

- Further analysis into the extraction of metals, and concentration of these into a product that can be used as a feed or feed supplement for livestock.
- Further examination into the distribution of metals between the non – hydrolyzed and hydrolyzed fractions of the raw material.
- Further analysis into other contaminants such as steroids or antibiotics that have been reported to be present in hog manures. Examination of their extraction and potential for re-use are also suggested.
- Further examination into other potential pre – treatment and hydrolysis solutions.
- This research focused on the concentration of the KOH solution (normality), and not the mass of KOH actually used for hydrolysis. The mass of hog manure used for each experimental run remained very similar, suggesting that by adjusting the actual mass of KOH added to the manure and not the concentration of the KOH solution, a greater effect on product yield may be achieved. Further analysis into the effect of mass of KOH used on product yield are suggested.
- All of the manure used in this study came from one source, and as a result, may not be representative of the ‘real world’ scenario. It is expected that manure from intensive operations will contain a lower solids content, suggesting that dewatering steps may be necessary prior to the EF procedure. Water collected from this additional step could be recycled into the EF procedure, reducing the demand for water in the procedure.
- Examination into recovery of additional total solids or nitrogen from the supernatant colloids following extraction of the HF, and the colloids in the wash waters generated in the EF procedure.

- Economic/Market based studies determine the potential value of the products generated in the EF procedure, through examinations such as Cost – Benefit analysis.
- Bench – Scale replication on a continuous basis.

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Appendix A – Experimental Data

Sample	Crucible Wt. (gr)	Wet+Crucible (gr)	Wet Weight (gr)	Dry + Crucible (gr)	Dry Weight (gr)	Moisture Content (%)	SD
K/6	62.8107	80.6229	17.8122	67.8762	5.0655	71.5616	
A2/A1	59.4764	73.9067	14.4303	63.4715	3.9951	72.3145	
A-98	58.2757	74.675	16.3993	62.8339	4.5562	72.2049	
P1-7MC	62.636	73.594	10.958	65.7072	3.0712	71.9730	
B4	63.7088	79.3015	15.5927	68.1057	4.3969	71.8015	
8-A0	62.5678	80.3356	17.7678	67.4756	4.9078	72.3781	
4	66.5568	81.1876	14.6308	70.5763	4.0156	72.5271	

Avg 72.1087	0.3443

Table A2 HCl Pretreatment of Wet Hog Manure

Discarded						
Solution Volume (ml)						
ID	HCl Strength (N HCl)	Wet Mass (g)	(250 ml DW + 170 ml 3 N) (250 ml DW + 170 ml 3 N) (250 ml DW + 170 ml 3 N)			
R1B3	1.0	199.8				
R2B3	1.0	200.6				
R3B3	1.0	200.7				
Avg						
R4B3	0.1	200.29	250			
R5B3	0.1	200.27	250			
R6B3	0.1	198.38	250			
Avg						
R10B3	1.0	200.3	183.3			
R11B3	1.0	200.4	183.3			
R12B3	1.0	199.8	183.3			
Avg						
R1B4	0.1	200.2	262.5			
R2B4	0.1	200.7	262.5			
R3B4	0.1	200.8	262.5			
Avg						
R7B4	1.0	200.1	250			
R8B4	1.0	200	250			
R9B4	1.0	199.5	250			
Avg						
R10B4	0.1	201.8	250			
R11B4	0.1	200.8	250			
ID	HCl Strength (N HCl)	Total DW Volume (ml)	Neutralized?	Collected	Vol. 1.0 N KOH (ml)	Mass K Added (g)
				Init pH		
R1B3	1.0	945	Yes	11	25	0.975
R2B3	1.0	330	Yes	6.7	29	1.131
R3B3	1.0	1125	Yes	6.82	12	0.488
Avg		800				0.858
R4B3	0.1	130	No	N/A	N/A	N/A
R5B3	0.1	120	No	N/A	N/A	N/A
R6B3	0.1	N/A	No	N/A	N/A	N/A
Avg		125				
R10B3	1.0	375	Yes	7.66	61	2.379
R11B3	1.0	375	Yes	7.65	60	2.34
R12B3	1.0	375	Yes	7	60	2.34
Avg		375				2.353
R1B4	0.1	250	No	4.92	0	N/A
R2B4	0.1	250	No	N/A	N/A	N/A
R3B4	0.1	250	No	N/A	N/A	N/A
Avg		250				
R7B4	1.0	500	Yes	6.85	50	1.95
R8B4	1.0	500	Yes	8.05	51	1.989
R9B4	1.0	500	Yes	7.18	50	1.95
Avg		500				1.963
R10B4	0.1	375	No	N/A	N/A	N/A
R11B4	0.1	375	No	N/A	N/A	N/A

Table A3: Alkaline Hydrolysis of Hog Manure (HM)

ID	Prewash Strength (N HCl)	Hydrolysis Strength (N KOH)	Initial Wet Mass (g)	Dry Mass (g) (if Applicable)	Mass KOH Used (g)	Solution Volume (ml)	Mass K Added (g)
R1B1	-----	0.5	179.21	N/A	14	370.79	8.75
R2B1	-----	0.5	199.7	N/A	13.97	350.3	8.73
R3B1	-----	0.5	200.5	N/A	14.11	349.5	9.83
Avg			193.14		14.03		9.77
R1B3	1.0	0.5	199.8	44.86	7.03	250	4.90
R2B3	1.0	0.5	200.6	51.60	7.03	250	4.90
R3B3	1.0	0.5	200.7	46.95	7.03	250	4.90
Avg			200.37	47.74	7.03		4.90
R4B3	0.1	0.5	200.29	49.49	10	360	6.96
R5B3	0.1	0.5	200.27	47.31	10	351	6.96
R6B3	0.1	0.5	198.38	49.81	10	349	6.96
Avg			199.65		10		6.96
R7B3	---	0.25	205.1	N/A	7	349	4.88
R8B3	---	0.25	198.6	N/A	7	348	4.88
R9B3	---	0.25	200.9	N/A	7	352	4.88
Avg			201.53		7		4.88
R10B3	1.0	0.25	200.3	37.59	4.67	250	3.25
R11B3	1.0	0.25	200.4	37.24	4.67	250	3.25
R12B3	1.0	0.25	199.8	38.6	4.67	250	3.25
Avg			200.17		4.67		3.25
R1B4	0.1	0.25	200.2	50.6	4.9	350	3.41
R2B4	0.1	0.25	200.7	47.88	4.9	350	3.41
R3B4	0.1	0.25	200.8	49.11	4.9	350	3.41
Avg			200.57		4.9		3.41
R4B4	---	0.75	199.6	N/A	16.93	250	11.79
R5B4	---	0.75	199.9	N/A	16.71	250	11.64
R6B4	---	0.75	200.3	N/A	16.85	250	11.73
Avg			199.93		16.83		11.72
R7B4	1.0	0.75	200.1	45.81	14.7	350	10.24
R8B4	1.0	0.75	200	43.37	14.7	350	10.24
R9B4	1.0	0.75	199.5	45.73	14.7	350	10.24
Avg			199.87		14.7		10.24
R10B4	0.1	0.75	201.8	51.77	14.77	350	10.29
R11B4	0.1	0.75	200.8	50.14	14.77	350	10.29
Avg			201.3		14.77		10.29

* Does not include water originally present in manure

Table A4: Non-Hydrolyzed Fraction (NHF) DW Wash & Yield Data

ID	Total wash water volume (ml)	Number of washes	Average volume/wash (ml/wash)	Residue yield (g)	Neutralized?	pH	Vol. 1.0 N HCl (ml)	Mass Cl Added (g)
R1B1	500	5	50.75	33.27	Yes	7.17	8	N/A
R2B1	100	6	100	33.16	Yes	7.31	8	N/A
R3B1	100	6	100	33.63	Yes	7.21	5	N/A
R1B3	1250	5	250	24.72	Yes	7.17	8	0.28
R2B3	1250	5	250	23.61	Yes	7.31	8	0.28
R3B3	1285	5	257	21.17	Yes	7.21	5	0.18
Av9	1261.67							
R4B3	1000	4	250	34.63	Yes	7.6	26	0.92
R5B3	1000	4	250	32.62	Yes	7.42	26	0.89
R6B3	1000	4	250	34.6	Yes	7.4	26	0.92
Av9	1000							
R7B3	1000	4	250	37.36	Yes	7.21	12	0.43
R8B3	1000	4	250	34.69	Yes	7.36	10	0.36
R9B3	1000	4	250	36.02	Yes	7.43	12	0.43
Av9	1000							
R10B3	750	6	125	26.83	Yes	7.26	5	0.18
R11B3	750	6	125	26.5	Yes	7.67	5.5	0.20
R12B3	750	6	125	27.2	Yes	7.35	5	0.18
Av9	750							
R1B4	500	2	250	44.04	Yes	7.55	2	0.07
R2B4	500	2	250	39.33	Yes	7.22	3.5	0.12
R3B4	500	2	250	38.55	Yes	7.51	11	0.39
Av9	500							
R4B4	750	3	250	37.26	Yes	7.51	35	1.24
R5B4	750	3	250	35.32	Yes	7.88	27	0.96
R6B4	750	3	250	34.63	Yes	7.5	28	0.99
Av9	750							
R7B4	1000	4	250	30.18	Yes	6.4	17	0.60
R8B4	1000	4	250	30.09	Yes	6.85	17	0.60
R9B4	1000	4	250	30.5	Yes	7.04	16	0.57
Av9	1000							
R10B4	950	4	237.5	35.59	Yes	6.9	22	0.78
R11B4	950	4	237.5	32.96	Yes	6.61	20	0.71
Av9	950							

Table A6: Hydrolyzed Fraction (HF) Wash & Yield Data

ID	Total wash water volume (ml)	Number of washes	Average volume/wash (ml/wash)	HF Yield (g)
R1B1	---	---	---	3.59
R2B1	250	4	100	3.48
R3B1	250	4	100	3.25
Av9	250			
R1B3	---	---	---	2.33
R2B3	---	---	---	4.18
R3B3	---	---	---	4.25
Av9				
R4B3	---	---	---	7.34
R5B3	---	---	---	6.82
R6B3	---	---	---	5.06
Av9				
R7B3	250	1	250	5.66
R8B3	250	1	250	6.68
R9B3	250	1	250	5.84
Av9	250			
R10B3	375	3	125	2.44
R11B3	375	3	125	2.4
R12B3	375	3	125	2.49
Av9	375			
R1B4	375	3	125	0.79
R2B4	375	3	125	1.06
R3B4	375	3	125	2.29
Av9	375			1.38
R4B4	390	2	195	5.7
R5B4	360	2	180	6.3
R6B4	370	2	185	6
Av9	373.33			
R7B4	500	2	250	1.61
R8B4	500	2	250	0.5
R9B4	500	2	250	2.07
Av9	500			1.39
R10B4	250	2	125	3.69
R11B4	285	2	142.5	3.02
Av9	267.5			

Table A7: NHF and HF Yield Summary Table

ID	Prewash Strength (N HCl)	Hydrolysis Strength (N KOH)	NHF yield (g)	HF Yield (g)	Total Wash Water Used (ml)
R1B1	-----	0.5	33.27	3.59	N/A
R2B1	-----	0.5	33.16	3.48	N/A
R3B1	-----	0.5	33.63	3.25	N/A
Avg					N/A
R1B3	1.0	0.5	24.72	2.33	2195
R2B3	1.0	0.5	23.61	4.18	1580
R3B3	1.0	0.5	21.17	4.25	2410
Avg					2061.67
R4B3	0.1	0.5	34.63	7.34	1130
R5B3	0.1	0.5	32.62	6.82	1120
R6B3	0.1	0.5	34.6	5.06	N/A
Avg					1125
R7B3	-----	0.25	37.36	5.66	1250
R8B3	-----	0.25	34.69	6.68	1250
R9B3	-----	0.25	36.02	5.84	1250
Avg					1250
R10B3	1.0	0.25	26.83	2.44	1500
R11B3	1.0	0.25	26.5	2.4	1500
R12B3	1.0	0.25	27.2	2.49	1500
Avg					1500
R1B4	0.1	0.25	44.04	0.79	1125
R2B4	0.1	0.25	39.33	1.06	1125
R3B4	0.1	0.25	38.55	2.29	1125
Avg					1125
R4B4	-----	0.75	37.26	5.7	1140
R5B4	-----	0.75	35.32	6.3	1110
R6B4	-----	0.75	34.83	6	1120
Avg					1123.33
R7B4	1.0	0.75	30.18	1.61	2000
R8B4	1.0	0.75	30.09	0.5	2000
R9B4	1.0	0.75	30.5	2.07	2000
Avg					2000
R10B4	0.1	0.75	35.59	3.69	1575
R11B4	0.1	0.75	32.86	3.02	1610
Avg					1592.5

Table A8: NHF and HF Yield and Standard Deviation

ID	Prewash	Hydrolysis	Dry Weight (g)	SD	NHF Yield (g)	Std. Dev.	HF Yield (g)	SD
R1B1	---	0.5	50.00		33.27		3.59	
R2B1	---	0.5	55.72		33.16		3.48	
R3B1	---	0.5	55.94		33.63		3.25	
			53.89	2.75	33.35	0.20	3.44	0.14
R1B3	1.0	0.5	55.74		24.72		2.33	
					23.61		4.18	
					21.17		4.25	
					23.17	1.48	3.59	0.89
R4B3	0.1	0.5	55.88		34.63		7.34	
R5B3	0.1	0.5	55.88		32.62		6.82	
R6B3	0.1	0.5	55.35		34.60		5.05	
			55.70	0.25	33.95	0.94	6.41	0.98
R7B3	---	0.25	57.22		37.36		5.66	
R8B3	---	0.25	55.41		34.69		6.68	
R9B3	---	0.25	56.05		36.02		5.84	
			56.23	0.75	36.02	1.09	6.06	0.44
R10B3	1.0	0.25	55.88		26.83		2.44	
R11B3	1.0	0.25	55.91		26.50		2.4	
R12B3	1.0	0.25	55.74		27.20		2.49	
			55.85	0.07	26.84	0.29	2.44	0.04
R1B4	0.1	0.25	55.86		44.04		0.79	
R2B4	0.1	0.25	56.00		39.33		1.06	
R3B4	0.1	0.25	56.02		38.55		2.29	
			55.96	0.07	40.64	2.43	1.38	0.65
R4B4	---	0.75	55.69		37.26		5.7	
R5B4	---	0.75	55.77		35.32		6.3	
R6B4	---	0.75	55.88		34.83		6	
			55.78	0.08	35.80	1.05	6.00	0.24
R7B4	1.0	0.75	55.83		30.18		1.61	
R8B4	1.0	0.75	55.80		30.09		0.5	
R9B4	1.0	0.75	55.66		30.50		2.07	
			55.76	0.07	30.26	0.18	1.39	0.66
R10B4	0.1	0.75	56.30		35.59		3.69	
R11B4	0.1	0.75	56.02		32.86		3.02	
				56.16	0.14	34.23	1.365	0.335

Table A9: %Volatile Solids and %Inert Solids Measurement

Raw Hog Manure - No - Pre - Treatment						
Sample	Dry Weight (gr)	Ash + Crucible (gr)	Ash (gr)	Volatile Solids (gr)	VS (%)	IS (%)
K	6.0826	58.6243	0.8741	5.2085	85.6295	14.3705
L	6.9496	58.1203	1.0031	5.9465	85.5661	14.4339
A1	7.9989	64.122	1.2103	6.7886	84.8692	15.1308
D9/8	7.8637	61.0324	1.1393	6.7244	85.5119	14.4881
I	9.0915	58.7726	1.3574	7.7341	85.0696	14.9304
O	6.1381	57.3659	0.9086	5.2295	85.1974	14.8026
B	5.9832	55.8704	0.8792	5.104	85.3055	14.6945
G	6.472	58.4563	0.954	5.518	85.2596	14.7404
J	7.8371	58.7732	1.1361	6.701	85.5036	14.4964
E	5.1076	57.7229	0.7388	4.3688	85.5353	14.4647

Avg	85.3448	14.6552
Std. Dev.	0.24764	0.24764

Table A10: NHF %Inert Solids and %Volatile Solids

ID	Crucible (g)	Crucible + Dry (g)	Dry (g)	Crucible + Ash (g)	Ash (g)	Inert Solids Content (%)	SD	Organic Content (%)	SD
R1B3	9.7638	10.7246	0.9608	9.8057	0.0419	4.3609		95.6391	
R2B3	11.2048	12.4053	1.2005	11.2548	0.05	4.1649		95.8351	
R3B3	11.4366	12.1759	0.7393	11.4621	0.0255	3.4492		96.5508	
					Avg.	3.9917	0.4799	96.0083	0.4799
R4B3	11.8858	13.3913	1.5055	12.0763	0.1905	12.6536		87.3464	
R5B3	12.1322	14.166	2.0338	12.3845	0.2523	12.4053		87.5947	
R6B3	11.9353	13.5183	1.583	12.1354	0.2001	12.6406		87.3594	
					Avg.	12.5665	0.1397	87.4335	0.1397
R7B3	11.4202	12.8112	1.391	11.5963	0.1761	12.6600		87.3400	
R8B3	13.4857	14.5525	1.0668	13.6207	0.135	12.6547		87.3453	
R9B3	11.5647	12.3909	0.8262	11.6543	0.0896	10.8448		89.1552	
					Avg.	12.0532	1.0464	87.9468	1.0464
R10B3	11.2981	11.7563	0.4582	11.3163	0.0182	3.9721		96.0279	
R11B3	10.7504	11.8107	1.0603	10.7992	0.0488	4.6025		95.3975	
R12B3	10.904	11.7918	0.8878	10.948	0.044	4.9561		95.0439	
					Avg.	4.5102	0.4984	95.4898	0.4984
R1B4	10.9858	12.2589	1.2731	11.0741	0.0883	6.9358		93.0642	
R2B4	11.2013	11.9246	0.7233	11.2469	0.0456	6.3044		93.6956	
R3B4	11.2478	12.7731	1.5253	11.3963	0.1485	9.7358		90.2642	
					Avg.	7.6587	1.8263	92.3413	1.8263
R6B4	11.1866	11.5648	0.3782	11.2274	0.0408	10.7679		89.2121	
					Avg.	10.7679	0.0000	89.2121	0.0000
R7B4	11.5555	12.1997	0.6442	11.5803	0.0248	3.8497		96.1503	
					Avg.	3.8497	0.0000	96.1503	0.0000

Table A11: HF %Inert and %Volatile Solids

ID	Crucible (g)	Crucible + Dry (g)	Dry (g)	Crucible + Ash (g)	Ash (g)	Inert Solids Content (%)	SD	Organic Content (%)	SD
R1B1					0.0313	2.67979		97.32021	
R2B1					Avg	2.67979	0	97.32021	0
R3B1	11.4952	12.6632	1.168	11.5265					
R1B3	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
R2B3	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
R3B3	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
R4B3	11.78	13.5738	1.7938	12.1566	0.3766	20.99454		79.00546	
R5B3	11.4356	14.035	2.5982	11.9516	0.5158	19.84457		80.15543	
R6B3	11.1324	13.3018	2.1694	11.5693	0.4389	20.13921		79.86079	
					Avg	20.32610	0.59733	79.67390	0.59733
R7B3	11.1957	12.256	1.0603	11.2462	0.0505	4.76280		95.23720	
R8B3									
R9B3					Avg	4.76280	0	95.23720	0
R10B3									
R11B3	11.1884	12.2832	1.0948	11.2311	0.0427	3.9003		96.0997	
R12B3					Avg	3.9003	0.0000	96.0997	0.0000
R1B4	11.4937	11.6537	0.16	11.4996	0.0059	3.6875		96.3125	
R2B4					0.012	2.9340		97.0660	
R3B4	11.2872	11.6962	0.409	11.2992		3.3107	0.5328	96.6893	0.5328
					Avg				
R4B4					0.0929	7.4403		92.5597	
R5B4	11.4927	12.7413	1.2486	11.5856	0.0316	6.1122		93.8878	
R6B4	11.1853	11.7023	0.517	11.2169		6.7763	0.9391	93.2237	0.9391
					Avg				
R7B4	10.1875	10.5289	0.3414	10.1856	0.0081	2.3726		97.6274	
R8B4					0.0131	3.3444		96.6556	
R9B4	11.8116	12.2033	0.3917	11.8247		2.8585	0.6872	97.1415	0.6872
					Avg				
R10B4					0.0341	4.2796		95.7204	
R11B4	11.205	12.0018	0.7968	11.2391			0.0000	95.7204	0.0000
					Avg	4.2796			
							0.0000	95.7204	0.0000

N/A: Insufficient Quantity of Material

Table A12: Average %VS in the NHF and HF

Prewash	Hydrolysis	NHF	HF
None	0.500	N/A	97.320
1.0	0.500	96.008	N/A
0.1	0.500	87.433	79.674
None	0.250	87.947	95.237
1.0	0.250	95.490	96.100
0.1	0.250	92.341	96.689
None	0.750	89.212	93.224
1.0	0.750	96.150	97.142
0.1	0.750	N/A	95.720

N/A: Insufficient Quantity of Material

Table A13: %N and %C in Raw Hog Manure

ID	%N	SD	%C	SD
Run 1	1.74		43.56	
Run 1 - dupl	1.87		43.00	
Run 2	1.85		43.47	
Run 2 - dupl	2.05		42.11	
Run 3	1.86		42.87	
Run 3 - dupl	1.89		40.92	
Run 4	1.74		42.24	
Run 4 - dupl	1.83		43.46	
Run 5	1.71		42.10	
Run 5 - dupl	1.64		43.96	
Run 6	1.91		41.88	
Run 6 - dupl	1.90		42.79	
Run 7	1.88		43.28	
Run 7 - dupl	1.72		42.85	
Avg.	1.83	0.11	42.75	0.82

Table A14: %N and %C for the NHF

ID	Total N (%)	SD	Total C (%)	SD
R1B3				
R2B3	0.55		45.95	
R2B3 - dupl	0.58		46.16	
Avg	0.57	0.02	46.06	0.15
R4B3				
R5B3	0.77		41.97	
R5B3 - dupl	0.88		40.99	
R6B3 - NMR	0.97		43.07	
R6B3 - NMR - dupl	0.70		42.72	
Avg	0.83	0.12	42.19	0.92
R9B3	1.02		40.24	
R9B3 - dupl	0.94		38.14	
R9B3 - NMR	0.70		31.99	
R9B3 - NMR - dupl	0.72		31.55	
Avg	0.85	0.16	35.48	4.37
R10B3	0.64		42.28	
R10B3 - dupl	0.73		41.73	
R11B3	0.66		41.99	
R11B3 - dupl	0.64		41.77	
Avg	0.67	0.04	41.94	0.25
R1B4	1.26		40.04	
R1B4 - dupl	1.18		39.82	
Avg	1.22	0.06	39.93	0.15
R4B4				
R5B4				
R6B4	0.46		38.57	
R6B4 - dupl	0.46		38.61	
Avg	0.46	0.00	38.59	0.03
R7B4	0.57		45.20	
R7B4 - dupl	0.63		45.11	
R7B4 - dupl	0.52		42.53	
R7B4 - dupl	0.68		42.18	
Avg	0.60	0.07	43.76	1.62
R10B4	0.53		43.03	
R10B4 - dupl	0.48		43.20	
Avg	0.50	0.04	43.12	0.12

Table A15: %N and %C for the HF

ID	Total N (%)	SD	Total C (%)	SD
R1B1				
R2B1 - NMR	7.81		59.17	
Avg	7.81		59.17	
R1B3				
R2B3				
R3B3 - NMR	6.39		59.81	
Avg	6.39		59.81	
R4B3				
R5B3 - NMR	7.20		58.42	
Avg	7.20		58.42	
R7B3	6.99		56.26	
R8B3 - NMR	6.21		51.58	
R8B3 - NMR (dupl)	6.39		51.83	
R9B3	7.11		56.30	
Avg	6.67	0.44	53.99	2.29
R10B3	5.38		56.25	
R11B3	5.03		54.79	
R11B3 - dupl	7.05		56.33	
R12B3	5.45		55.37	
Avg	5.73	0.90	55.68	0.74
R1B4	6.36		53.93	
R2B4	6.20		55.60	
R3B4	6.82		54.09	
R3B4 - dupl	6.67		54.67	
Avg	6.51	0.28	54.57	0.76
R4B4	5.86		53.16	
R4B4 - dupl	5.73		52.17	
R6B4	5.42		53.81	
R6B4 - dupl	5.41		53.77	
Avg	5.61	0.23	53.23	0.76
R7B4	5.56		59.06	
R8B4	4.23		56.39	
R9B4	5.64		59.42	
R9B4 - dupl	5.33			
Avg	5.19	0.66	43.72	1.66
R10B4	4.90		59.98	
R10B4 - dupl	4.92		59.75	
R11B4	4.72		59.66	
R11B4 - dupl	4.42		55.38	
Avg	4.74	0.23	58.69	2.21

Table A16: Volatile solids yield in the hog manure, the NHF and the HF.

HCl Strength (N) – KOH Strength (N)	Raw Material (g VS ^{HM})	NHF (g VS')	HF (g VS')
Control – 0.25	48.0 ± 0.8	31.7 ± 1.2	5.8 ± 0.5
1.0 – 0.25	47.7 ± 0.1	25.6 ± 0.3	2.4 ± 0.04
0.1 – 0.25	47.8 ± 0.1	37.5 ± 3.2	1.2 ± 1.0
Control – 0.5	46.0 ± 2.9	N/A	3.4 ± 0.2
1.0 – 0.5	47.5 ± 0.1	22.8 ± 1.6	N/A
0.1 – 0.5	47.5 ± 0.3	29.7 ± 1.0	5.1 ± 0.9
Control – 0.75	47.6 ± 0.1	31.9 ±	5.6 ± 0.2
1.0 – 0.75	47.6 ± 0.1	29.1 ± 0.2	1.4 ± 0.3
0.1 – 0.75	48.0 ± 0.2	N/A	3.2 ± 0.5

Table A17: Carbon yield in the hog manure, the NHF and HF.

HCl Strength (N) – KOH Strength (N)	Raw Material (g C ^{HM})	NHF (g C ^f)	HF (g C ^f)
Control – 0.25	24.03 ± 0.4	12.78 ± 0.5	3.27 ± 0.1
1.0 – 0.25	23.90 ± 0.04	11.26 ± 0.2	1.36 ± 0.04
0.1 – 0.25	23.94 ± 0.04	16.23 ± 1.2	0.75 ± 0.4
Control – 0.5	23.04 ± 1.4	N/A	2.04 ± 0.1
1.0 – 0.5	23.81 ± 0.1	10.67 ± 0.8	2.15 ± 0.7
0.1 – 0.5	23.81 ± 0.1	14.32 ± 0.8	3.74 ± 0.7
Control – 0.75	23.85 ± 0.04	13.82 ± 0.1	3.19 ± 0.1
1.0 – 0.75	23.85 ± 0.04	13.24 ± 0.5	0.61 ± 0.5
0.1 – 0.75	24.03 ± 0.1	14.76 ± 0.8	1.97 ± 0.3

Table A18: Nitrogen yield in the raw material and the NHF and HF.

HCl Strength (N) – KOH Strength (N)	Raw Material (g N ^{HM})	NHF (g N ^f)	HF (g N ^f)
Control – 0.25	1.03 ± 0.02	0.31 ± 0.01	0.40 ± 0.01
1.0 – 0.25	1.02 ± 0.0	0.18 ± 0.002	0.14 ± 0.01
0.1 – 0.25	1.02 ± 0.0	0.49 ± 0.04	0.09 ± 0.1
Control – 0.5	0.99 ± 0.1	N/A	0.27 ± 0.01
1.0 – 0.5	1.02 ± 0.0	0.13 ± 0.01	0.23 ± 0.1
0.1 – 0.5	1.02 ± 0.01	0.28 ± 0.04	0.46 ± 0.1
Control – 0.75	1.02 ± 0.002	0.17 ± 0.002	0.34 ± 0.01
1.0 – 0.75	1.02 ± 0.0	0.18 ± 0.03	0.07 ± 0.1
0.1 – 0.75	1.03 ± 0.0	0.17 ± 0.02	0.16 ± 0.03

Table A19: Technical Data for the EF Procedure

Wet Manure (g):	199
Moisture Content (%)	72
Total Solids (g TS)	56

System Inputs: Total

Hog Manure (g TS)	56
Volume Water (m)	1,703
- Wash Water (m)	1,125
- Pre - Treatment Water (m)	225
- Hydrolysis Water (m)	353
HCl - 1.0N (m)	158
- Pre - Treatment HCl (m)	25
- Neutralization HCl (m)	26
- Acidification HCl (m)	107
KOH - concentrated pellets (g)	10
- Neutralization KOH (g)	0
- Hydrolysis KOH (g)	10

System Sizing: Total

Batch Solution Volume (m)	1,500

System Energy Inputs: Total

Energy required to mix batch solutions	
Energy required to heat water (J):	97,525
Delta T (C)	55

Note:

Energy requirement is to heat hydrolysis solution volume from a temperature of 15 degrees C to a temperature of 70 degrees C. The energy to maintain the system temperature for a period of one hour is assumed to be twenty percent of the amount of energy required to heat the water initially.

2 - Data based on using 100 tons of dry hog manure

Note: it is assumed that the hog manure had an original moisture content of 72%

System Inputs: Total

Hog Manure (ton TS)	100
Volume Water (L)	3,053,285
- Wash Water (L)	2,016,997
- Pre - Treatment Water (L)	403,399
- Hydrolysis Water (L)	632,889
HCl - 1.0N (L)	263,276
- Pre - Treatment HCl (L)	44,622
- Neutralization HCl (L)	46,615
- Acidification HCl (L)	191,839
KOH - concentrated pellets (ton)	18
- Neutralization KOH (ton)	0
- Hydrolysis KOH (ton)	18

System Sizing: Total

Batch Solution Volume (L)	2,689,329

System Energy Inputs: Total

Energy required to mix batch solutions	
Energy required to heat water (MJ):	174,852
Delta T (C)	55

1J = 2.78 x 10⁶ kWh (Georgia State University)

System Inputs: Normalized per g dry hog manure (TS)

Hog Manure (g TS)	1
Volume Water (m/g TS)	30.53
- Wash Water (m/g TS)	20.17
- Pre - Treatment Water (m/g TS)	4.03
- Hydrolysis Water (m/g TS)	6.33
HCl - 1.0N (m/g TS)	2.83
- Pre - Treatment HCl (m/g TS)	0.45
- Neutralization HCl (m/g TS)	0.47
- Acidification HCl (m/g TS)	1.92
KOH - concentrated pellets (g/g TS)	0.18
- Neutralization KOH (g/g TS)	0.00
- Hydrolysis KOH (g/g TS)	0.18

System Sizing: Normalized per g dry hog manure (TS)

Batch Solution Volume (m/g TS)	26.89

System Energy Inputs: Normalized per g dry hog manure (TS)

Energy required to mix batch solutions	N/A
Energy required to heat water (J/g TS):	1748.52
Delta T (C)	55

Table A20: Unit Costs Associated with EF Procedure**Unit Costs of Inputs**

Electricity Rate (\$/kWh) ¹	\$	0.06
Fuel Cost (\$/L) ²	\$	0.0145
Cost of Water (\$/cu. m) ³	\$	1.49
Cost of 1.0N HCl (\$/L) ⁴	\$	1.03
Cost of KOH pellets (\$/ton) ⁴	\$	20,000.00
Value of N (\$/kg)	\$	0.496
Value of P (\$/kg)	\$	0.485

Notes:

1 - Data based on data from the Independent Electricity Market Operator (www.theimo.com)
The cost of electricity shown is the average cost in May 2003.

2 - Data based on United States Department of Energy (<http://tonto.eia.doe.gov/oog/info/gdu/gasdiesel.asp>)

3 - Data based on cost of water in the City of Ottawa for August 2002
The data includes a water consumption charge, transmission charge and the cost for sewer and wastewater

4 - Data obtained from Fisher Scientific (www.fishersci.com/catalogs), and adjusted for bulk sales
Cost of HCl is based on unit cost of 200 L of concentrated 6.0N HCl

5 - Based on data from Zublena *et al.*, 1997

Table A21: Economic Costs of Generating HF and NHF Using the EF Procedure

Data based on using 100 tons of dry hog manure per day**System Input Costs: Total**

Volume Water (\$)	
- Wash Water (\$)	\$ 4,542.16
- Pre - Treatment Water (\$)	\$ 3,000.55
- Hydrolysis Water (\$)	\$ 600.11
HCl - 1.0N (\$)	\$ 941.51
- Pre - Treatment HCl (\$)	\$ 291,774.24
- Neutralization HCl (\$)	\$ 46,166.81
- Acidification HCl (\$)	\$ 48,013.48
KOH - concentrated pellets (\$)	\$ 197,593.95
- Neutralization KOH (\$)	\$ 358,577.17
- Hydrolysis KOH (\$)	\$ 358,577.17

System Sizing Costs: Total

Batch Solution Volume (\$)

N/A

System Energy Costs: Total

Energy required to mix batch solutions (\$)	N/A
Energy required to heat water (\$):	\$ 2,807.37
Fossil Fuel Costs (\$)	N/A
Miscellaneous Energy Costs (\$)	N/A

Total Cost to treat 100 tons of dry solids(\$)	\$ 657,700.94
Factor of Safety for Unknowns	2
Total Assumed Cost (\$)	\$ 1,315,401.87

System Input Normalized Costs for Batch Treatment

Volume Water (\$/kg TS)	
- Wash Water (\$/kg TS)	\$ 0.045
- Pre - Treatment Water (\$/kg TS)	\$ 0.030
- Hydrolysis Water (\$/kg TS)	\$ 0.006
HCl - 1.0N (\$/kg TS)	\$ 0.009
- Pre - Treatment HCl (\$/kg TS)	\$ 2.92
- Neutralization HCl (\$/kg TS)	\$ 0.46
- Acidification HCl (\$/kg TS)	\$ 0.48
KOH - concentrated pellets (\$/kg TS)	\$ 1.98
- Neutralization KOH (\$/kg TS)	\$ 3.59
- Hydrolysis KOH (\$/kg TS)	\$ 3.59

System Sizing: Normalized Costs for Batch Treatment

Batch Solution Volume (\$/kg TS)

N/A

6.583

System Energy Inputs: Normalized Costs for Batch Treatment

Energy required to mix batch solutions (\$/kg TS)	
Energy required to heat water (\$/kg TS):	\$ 0.028
Fossil Fuel Costs (\$)	
Miscellaneous Energy Costs (\$)	

Normalized Cost to treat 100 tons of dry solids(\$/kg TS)	\$ 6.58
Factor of Safety for Unknowns	2
Total Assumed Cost (\$/kg TS)	\$ 13.15

Figure A1: FTIR Spectrum for the NHF (0.0/0.25)

Figure A2: FTIR Spectrum for the NHF (0.0/0.75)

Figure A3: FTIR Spectrum for the NHF (0.1/0.25)

Figure A4: FTIR Spectrum for the NHF (0.1/0.5)

Figure A5: FTIR Spectrum for the NHF (0.1/0.75)

Figure A6: FTIR Spectrum for the NHF (1.0/0.25)

Figure A7: FTIR Spectrum for the NHF (1.0/0.5)

Figure A8: FTIR Spectrum for the NHF (1.0/0.75)

Figure A9: FTIR Spectrum for the HF (0.0/0.25) **Figure A10:** FTIR Spectrum for the HF (0.0/0.5)

Figure A11: FTIR Spectrum for the HF (0.0/0.75)

Figure A12: FTIR Spectrum for the HF (0.1/0.25)

Figure A13: FTIR Spectrum for the HF (0.1/0.5) **Figure A14: FTIR Spectrum for the HF (0.1/0.75)**

Figure A15: FTIR Spectrum for the HF (1.0/0.25) **Figure A16: FTIR Spectrum for the HF (1.0/0.5)**

Figure A17: FTIR Spectrum for the HF (1.0/0.75)

Figure A18: ^{13}C - NMR spectrum of the NHF (0.0N HCl/0.25N KOH)

Figure A19: ^{13}C - NMR spectrum of the NHF (0.1N HCl/0.25N KOH)

Figure A20: ^{13}C - NMR spectrum of the NHF (0.0N HCl/0.75N KOH)

Figure A21: ^{13}C - NMR spectrum of the NHF (0.1N HCl/0.75N KOH)

Figure A22: ^{13}C - NMR spectrum of the HF (0.1N HCl/0.25N KOH)

Figure A23: ^{13}C - NMR spectrum of the HF (1.0N HCl/0.25N KOH)

Figure A24: ^{13}C - NMR spectrum of the HF (0.1N HCl/0.5N KOH)

Figure A25: ^{13}C - NMR spectrum of the HF (0.0N HCl/0.75N KOH)

Figure A26: ^{13}C - NMR spectrum of the HF (0.1N HCl/0.75N KOH)

Appendix B – Sample Calculations

Note: For all equations, the superscript 'f' represents either the NHF or HF, and the superscript 'HM' represents hog manure.

1. Moisture Content (MC)/Dry Matter (DM)

$$\text{MC} = (\text{Wet Mass} - \text{Dry Mass}) \times (\text{Wet Mass})^{-1} \text{ [MM}^{-1}\text{]} \\ \text{DM} = 1 - \text{MC}$$

From Table A1 in Appendix A, for untreated manure:

$$\begin{aligned} \text{Wet Mass} &\approx 17.8122\text{g (TS + H}_2\text{O)} \\ \text{Dry Mass} &\approx 5.0655\text{g TS} \\ (\text{Wet} - \text{Dry}) &\approx 12.7467\text{g H}_2\text{O} \\ \therefore \text{MC} &\approx 12.7467\text{g (H}_2\text{O)}/17.8122\text{g TS} \end{aligned}$$

$$\Rightarrow \text{MC} \approx 0.72 \text{ (g H}_2\text{O/g TS)}$$

$$\Rightarrow \text{DM} \approx 1 - 0.72 \approx 0.28 \text{ (g DM/g TS)}$$

2. % Volatile Solids (%VS)/Inert Solids (%IS)

$$\begin{aligned} \% \text{VS} &= (\text{Dry Mass} - \text{Ash}) \times (\text{Dry Mass})^{-1} \times 100\% [\text{MM}^{-1}] \\ \% \text{IS} &= 100\% - \% \text{VS} \end{aligned}$$

From Table A9 in Appendix A, for untreated hog manure:

$$\begin{aligned} \text{Dry Mass} &\approx 6.0826\text{g TS} \\ \text{Ash} &\approx 0.8741 \text{ g IS} \\ (\text{Dry} - \text{Ash}) &\approx 5.2085 \text{ g VS} \\ \therefore \% \text{VS} &\approx (5.2085 \text{ g VS}/6.0826 \text{ g TS}) \times 100\% \end{aligned}$$

$$\Rightarrow \% \text{VS} \approx 85.6\%$$

$$\Rightarrow \% \text{IS} \approx 100 - 85.6 = 14.4\%$$

3. Metal Removal Efficiency (%MRE)

$$\%MRE = (M_u - M_{HCl}) \times (M_u)^{-1} \times 100\% [MM^{-1}]$$

M_u = Metal Concentration in untreated manure ($\mu\text{g metal/gTS}$)

M_{HCl} = Metal Concentration in pre – treated manure ($\mu\text{g metal/gTS}$)

From Table 4 – 1, for Mg concentration:

$$M_u \approx 5387 (\mu\text{g Mg/g TS})$$

From Table 4 – 1, for Mg concentration in 0.1N pre – treated manures:

$$M_{HCl} \approx 951 (\mu\text{g Mg/g TS})$$

$$M_u - M_{HCl} \approx 4436 (\mu\text{g Mg/g TS})$$

$$\therefore \%MRE \approx 4436/5387 \times 100\%$$

$$\Rightarrow \%MRE \approx 82.3\% \text{ reduction in Mg concentration (Table 4-2)}$$

4. Product Recovery:

a. Total Solids Recovery (%TS_R^f)

$$\%TS_R^f = (M_{TS}^f \times (M_{TS}^{HM})^{-1}) \times 100\% [MM^{-1}]$$

M_{TS}^f = yield of total solids in fraction (gTS)

M_{TS}^{HM} = mass of total solids in hog manure (gTS)

From Table 4-3 for NHF for Control – 0.25:

$$M_{TS}^f \approx 36.0 \text{ g}$$

$$M_{TS}^{HM} \approx 56.2 \text{ g}$$

$$\therefore \%TS_R^f \approx (36/56.2) \times 100\%$$

$$\Rightarrow \%TS_R^f \approx 64.1\% \text{ recovery TS from hog manure in NHF, in Table 4-4}$$

b. Volatile Solids Yield (M_{VS}^f)

$$M_{VS}^f = (\%VS^f/100) \times M_{TS}^f [M]$$

$\%VS^f$ = percent volatile solids (gVS/100gTS)

M_{TS}^f = yield of total solids in fraction (gTS)

From Table 4-5, for NHF for Control – 0.25:

$$\%VS^f \approx 87.9\% \text{ (g VS/100g TS)}$$

From Table 4-3, for NHF for Control – 0.25:

$$M_{TS}^f \approx 36.0 \text{ g TS}$$

$$\therefore M_{VS}^f \approx (0.879 \times 36.0 \text{ g TS})$$

$$\Rightarrow M_{VS}^f \approx \text{yield of VS in the 0.0/0.25 NHF was } 31.7 \text{ g (Table A16)}$$

i. Volatile Solids Recovery ($\%VS_R^f$)

$$\%VS_R^f = (M_{VS}^f \times (M_{VS}^{HM})^{-1}) \times 100\% (MM^{-1})$$

M_{VS}^f = yield of volatile solids in fraction (gVS)

M_{VS}^{HM} = mass of volatile solids in the hog manure (gVS)

From Table A16, for NHF for Control – 0.25:

$$M_{VS}^f \approx 31.7 \text{ g VS}$$

From Table A-16, for the hog manure, for Control – 0.25:

$$M_{VS}^{HM} \approx 48.0 \text{ g VS}$$

$$\therefore \%VS_R^f \approx (31.7/48.0) \times 100\%$$

$$\Rightarrow \%VS_R^f \approx 66.04\% \text{ of the volatile solids from the hog manure are recovered in the NHF (Table 4-6)}$$

c. Carbon Yield (M_C^f)

$$M_C^f = (\%C^f/100) \times M_{TS}^f [M]$$

$\%C^f$ = total %C in fraction (gC/100gTS)

M_{TS}^f = yield of total solids in fraction (gTS)

From Table 4-7, for NHF for Control – 0.25:

$$\%C^f \approx 35.48\% \text{ (gC/100gTS)}$$

From Table 4-3, for NHF for Control – 0.25:

$$M_{TS}^f \approx 36.0 \text{ g TS}$$

$$\therefore M_C^f \approx (0.3548 \times 36.0)$$

$\Rightarrow M_C^f \approx \text{yield of C in the 0.0/0.25 NHF was 12.8 g of carbon (Table A17)}$

i. Carbon Recovery ($\%C_R^f$)

$$\%C_R^f = (M_C^f \times (M_C^{HM})^{-1}) \times 100\% (MM^{-1})$$

M_C^f = yield of carbon in the NHF (gC)

M_C^{HM} = mass of carbon in the hog manure (gC)

From Table A-17, for NHF for Control – 0.25:

$$M_C^f \approx 12.8 \text{ gC}$$

From Table A-17, for hog manure, for Control – 0.25:

$$M_C^{HM} \approx 24.03 \text{ gC}$$

$$\therefore \%C_R^f \approx (12.8/24.03) \times 100\%$$

$\Rightarrow \%C_R^f \approx 53.2\% \text{ of C from the hog manure is recovered in the NHF (Table 4-8)}$

d. Nitrogen Yield (M_N^f)

$$M_N^f = (\%N^f/100) \times M_{TS}^f [M]$$

$\%N^f$ = total %N in fraction (gN/100gTS)

M_{TS}^f = yield of total solids in fraction (gTS)

From Table 4-9, for HF for Control – 0.25:

$$\%N^f \approx 6.67\% \text{ (gN/100gTS)}$$

From Table 4-3, for HF for Control – 0.25:

$$M_{TS}^f \approx 6.1 \text{ g TS}$$

$$\therefore M_N^f \approx (0.0667 \times 6.1)$$

$$\Rightarrow M_N^f \approx \text{yield of N in the 0.0/0.25 HF was 0.40 g (Table A18)}$$

i. Nitrogen Recovery ($\%N_R^f$)

$$\%N_R^f = (M_N^f \times (M_N^{HM})^{-1}) \times 100\% (MM^{-1})$$

M_N^f = mass of nitrogen in fraction (gN)

M_N^{HM} = mass of nitrogen in hog manure (gN)

From Table 4-18, for HF for Control – 0.25:

$$M_N^f \approx 0.40 \text{ gN}$$

From Table 4-18, for hog manure, for Control – 0.25:

$$M_N^{HM} \approx 1.03 \text{ gN}$$

$$\therefore \%N_R^f \approx (0.40/1.03) \times 100\%$$

$$\Rightarrow \%N_R^f \approx 38.8\% \text{ of N from the original starting material recovered in the HF (Table 4-10)}$$

5. Wet Manure Requirements based on Crop Nitrogen Requirements (for Table 4-11)

a. Conventional Landspreading of Wet Manure (M_{WHM})

Assumptions:

N losses are 20%

Manure slurry at time of application is 10% solids (10%TS)

$$M_{WHM} = M_N \times (\%N_{HM})^{-1} \times (\%DM_{HM})^{-1} \times (\Psi)^{-1}$$

M_{WHM} = Mass of wet hog manure for Case 1 (kg wet manure/ha)

M_N = Mass of nitrogen required by crop (kg N/ha)

$\%N_{HM}$ = Nitrogen content of dry hog manure – 1.83% (kg N/100kg TS)

$\%DM_{HM}$ = Slurry solids content – 10% (kgTS/100kg wet manure)

Ψ = efficiency ($\Psi = 0.8$ for nitrogen losses of 20%)

From Table 2-13, for Alfalfa:

$$M_N = 89 \text{ kgN/ha}$$

From Table 4-9, for raw material:

$$\%N_{HM} = 1.83\%$$

Assuming: %solids = 0.1; $\Psi = 0.8$

$$\therefore M_{WHM} \approx ((89/0.0183)/(0.1 \times 0.8))$$

$\Rightarrow M_{WHM} \approx 60,792 \text{ kg of wet manure are required to supply 89 kg of Nitrogen to one hectare of alfalfa.}$

b. Equivalent quantity of wet manure required for EF procedure (high TS recovery) (M_{WHM}) (For Table 4-11)

Assumptions:

N loss of 20%

Hog Manure solids content of 28% (gTS/gWet Manure)

$$M_{eqWHM} = M_N \times (\%N_{HF})^{-1} \times (\%HF)^{-1} \times (\%DM_{HM})^{-1} \times (\Psi)^{-1}$$

M_{eqWHM} = Mass of wet hog manure required for Case 2 (kg wet manure/ha)

M_N = Mass of nitrogen required by crop (kg N/ha)

$\%N_{HF}$ = Nitrogen content of HF – 6.51% or 7.2% (kg N/100kg HF)

$\%HF$ = HF Total Solids recovery – 2.5% or 11.5% (kgHF/100kg TS)

$\%DM_{HM}$ = TS of hog manure – 28% (kgTS/100kg wet hog manure)

Ψ = efficiency ($\Psi = 0.8$ for nitrogen losses of 20%)

From Table 2-13, for Alfalfa:

$$M_N = 89 \text{ kg/ha}$$

From Table 4-9, for HF (0.1/0.5):

$$\%N_{HF} \approx 7.20\% \text{ (kgN}^{HF}/100 \text{ kgTS}^{HF})$$

From Table 4-4, for HF (0.1/0.5):

$$\%HF \approx 11.5\% \text{ (kgTS}^{HF}/100\text{kgTS}^{HM})$$

Assuming $\%DM_{HM} \approx 0.28$, $\Psi = 0.8$

$$\therefore M_{eqWHM} \approx (89/0.072)/(0.115 \times 0.28 \times 0.8)$$

$\Rightarrow M_{eqWHM} \approx 47,986 \text{ kg of wet manure are required for the EF procedure to produce a sufficient quantity of high TS recovery HF, for 1 ha of alfalfa.}$

c. Equivalent quantity of wet manure required for EF procedure (low TS recovery) (M_{eqWHM}) (For Table 4-11)

Assumptions:

N loss of 20%

Hog Manure solids content of 28% (gTS/g Wet Manure)

$$M_{eqWHM} = M_N \times (\%N_{HF})^{-1} \times (\%HF)^{-1} \times (\%DM_{HM})^{-1} \times (\Psi)^{-1}$$

M_{eqWHM} = Mass of wet hog manure required for Case 2 (kg wet manure/ha)

M_N = Mass of nitrogen required by crop (kg N/ha)

$\%N_{HF}$ = Nitrogen content of HF – 6.51% or 7.2% (kg N/100kg HF)

$\%HF$ = HF Total Solids recovery – 2.5% or 11.5% (kgHF/100kg TS)

$\%DM_{HM}$ = TS of hog manure – 28% (kgTS/100kg wet hog manure)

Ψ = efficiency ($\Psi = 0.8$ for nitrogen losses of 20%)

From Table 2-13, for Alfalfa:

$$M_N = 89 \text{ kg/ha}$$

From Table 4-9, for HF (0.1/0.25):

$$\%N_{HF} \approx 6.51\% \text{ (kgN}^{HF}\text{/100 kgTS}^{HF}\text{)}$$

From Table 4-4, for HF (0.1/0.25):

$$\%HF \approx 2.5\% \text{ (kgTS}^{HF}\text{/100kgTS}^{HM}\text{)}$$

Assuming $\%DM_{HM} \approx 0.28$, $\Psi = 0.8$

$$\therefore M_{eqWHM} \approx (89/0.0651)/(0.025 \times 0.28 \times 0.8)$$

$\Rightarrow M_{eqWHM} \approx 244,130 \text{ kg of wet manure are required for the EF procedure to produce a sufficient quantity of low TS recovery HF, for 1 ha of alfalfa.}$

6. Mass of HF Required (high TS recovery) (M_{HF}) (For Table 4-12)

Assumptions:

20% nitrogen losses

$$M_{HF} = M_N \times (\%N_{HF})^{-1} \times (\Psi)^{-1}$$

M_{HF} = Mass HF required for Case 2 (kg HF/ha)

M_N = Mass of nitrogen required by crop – see Table 8 (kg N/ha)

$\%N_{HF}$ = Nitrogen content of HF – 6.51% or 7.2% (kg N/kg HF)

Ψ = efficiency ($\Psi = 0.8$ for nitrogen losses of 20%)

From Table 2-13 in Chapter 2, for Alfalfa:

$$M_N = 89 \text{ kg/ha}$$

From Table 4-9, for HF (0.1/0.5):

$$\%N_{HF} \approx 7.20\% \text{ (kgN}^{HF}/100 \text{ kgTS}^{HF}\text{)}$$

$$\therefore M_{HF} \approx (89/0.072)/0.8$$

$\Rightarrow M_{HF} \approx 1545 \text{ kgN/ha of high TS recovery HF are required to meet crop N requirements}$

7. Mass of HF Required (low TS recovery) (M_{HF}) (For Table 4-12)

Assumptions:

20% nitrogen losses

$$M_{HF} = M_N \times (\%N_{HF})^{-1} \times (\Psi)^{-1}$$

M_{HF} = Mass HF required for Case 2 (kg HF/ha)

M_N = Mass of nitrogen required by crop – see Table 8 (kg N/ha)

$\%N_{HF}$ = Nitrogen content of HF – 6.51% or 7.2% (kg N/kg HF)

Ψ = efficiency ($\Psi = 0.8$ for nitrogen losses of 20%)

From Table 2-13, for Alfalfa:

$$M_N = 89 \text{ kg/ha}$$

From Table 4-9, for HF (0.1/0.25):

$$\%N_{HF} \approx 6.51\% (\text{kgN}^{HF}/100 \text{ kgTS}^{HF})$$

$$\therefore M_{HF} \approx (89/0.0651)/0.8$$

$\Rightarrow M_{HF} \approx 1709 \text{ kgN/ha}$ of low TS recovery HF are required to meet crop N requirements