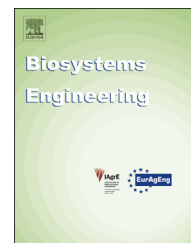




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## Research Paper

# Characteristics of volatile fatty acids in stored dairy manure before and after anaerobic digestion



Laura H. Page<sup>a</sup>, Ji-Qin Ni<sup>a,\*</sup>, Albert J. Heber<sup>a</sup>, Nathan S. Mosier<sup>a</sup>,  
Xingya Liu<sup>a</sup>, Hung-Soo Joo<sup>b</sup>, Pius M. Ndegwa<sup>b</sup>, Joseph H. Harrison<sup>c</sup>

<sup>a</sup> Department of Agricultural and Biological Engineering, Purdue University, 225 S. University Street, West Lafayette, IN 47907, USA

<sup>b</sup> Department of Biological Systems Engineering, Washington State University, PO Box 646120, Pullman, WA 98935, USA

<sup>c</sup> Department of Animal Sciences, Washington State University, Research and Extension Center, 2606 West Pioneer, Pulyallup, WA 98371, USA

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Volatile fatty acids (VFA) are among the most abundant volatile organic compounds in dairy manure and are associated with odour nuisance. This paper presents research results of VFA production during a three-month storage of dairy manure from four different sources: a dairy barn (raw), the inlet of an anaerobic digester (influent), the digester outlet (effluent), and the effluent after solid separation (effluent SS). Manure from each source was studied in two lab-scale reactors that were continuously ventilated with fresh air in the manure headspace to simulate manure storage conditions. Two manure samples were taken weekly in the top and bottom manure layers from each reactor for VFA analysis. Five VFA (formic acid, acetic acid, propionic acid, butyric acid, and 2-methylbutyric acid) were identified in all reactors using high performance liquid chromatography (HPLC). The dominant VFA was formic acid for the influent and acetic acid for the other three manure sources. The overall average concentrations of the five VFA were  $1963 \pm 685$  (mean  $\pm$  standard deviation),  $14,175 \pm 4825$ ,  $286 \pm 98$ , and  $169 \pm 80$  mg l<sup>-1</sup> for the raw, influent, effluent, and effluent SS, respectively. The “pre-consumer” organic wastes mixed with dairy manure in the influent significantly increased the total VFA concentrations and the proportion of individual VFA. Concentrations of VFA demonstrated highly temporal and spatial variations. Anaerobic digestion significantly reduced formation of VFA in the effluent and effluent SS. However, the complexity of VFA characteristics made it difficult to reliably model and predict the concentrations and compositions of VFA in dairy manure.

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## 1. Introduction

Manure, or slurry, from dairy farm contains about 2–8% of total solid (TS) and is typical wastewater from animal agriculture. Dairy manure naturally contains microorganisms

that aid in manure degradation, but the breakdown results in the release of many compounds, including volatile organic compounds (VOC), that can negatively impact the environment. Volatile organic compounds are regulated by the U.S. EPA (CMA, 1998) and can be divided into several subgroups, which include volatile fatty acids (VFA) (Schiffman, Miller,

\* Corresponding author. Tel.: +1 765 496 1733; fax: +1 765 496 1115.

E-mail address: [jqin@purdue.edu](mailto:jqin@purdue.edu) (J.-Q. Ni).

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Suggs, & Graham, 1995). About 300 VOC have been detected and quantified at animal facilities and 36 VOC, many of them are VFA that are associated with odour nuisance, have been found in pig manure (Ni, Robarge, Xiao, & Heber, 2012). Because VFA are usually among the most abundant VOC identified in animal manure, they have been used as an indicator of the total VOC content in manure (Conn, Topp, & Lazarovits, 2007; Zhu, Riskowski, & Torremorell, 1999).

Anaerobic digestion (AD) of dairy manure is an effective technology to generate renewable energy through the production of biogas that contains 55–65% of methane, as well as an important technology in the reduction of environmental pollution. Under anaerobic conditions, microbial decomposition of animal manure results in the production of VFA and other organic compounds (Cooper & Cornforth, 1978). The VFA act as important intermediates in the production of methane. Acetogens further degrade VFA to acetate, carbon dioxide, and hydrogen. It is these products that are converted by methanogens to methane (Gerardi, 2003). It is recognised that methanogens can use directly only acetic acid, formic acid, and hydrogen, while butyric and propionic acids must first be converted to the former compounds by acetogenic bacteria (Dinopoulou, Rudd, & Lester, 1988). The microorganisms responsible for the production and consumption of VFA are sensitive to manure properties including pH, temperature, and ammoniacal nitrogen (Lu, Chen, He, & Shao, 2008).

Biological degradation of manure can result in the release of odourous compounds (Mackie, Stroot, & Varel, 1998). Odours produced from manure are a complex mixture of ammonia, hydrogen sulfide, and VOC (El-Mashad, Zhang, Arteaga, Rumsey, & Mitloehner, 2011). There are no federal guidelines to regulate and control odours in the environment. However, odours can be a nuisance and may create negative psychological responses by those impacted. Although it is the sulphurous, phenol, and indole compounds that appear to contribute the most to malodour (Le, Aarnink, Ogink, Becker, & Versteegen, 2005), some studies have demonstrated that VFA are strongly correlated with odour generation (e.g., Hobbs, Misselbrook, & Pain, 1998; Miller & Varel, 2003; Ndegwa, 2003). The odour contribution from VFA is dependent upon individual VFA concentrations as well as total VFA concentration (Ndegwa, 2003). Short chain fatty acids including acetic and formic acids may be present in manure in much higher concentrations; but long-chain and branching VFA such as butyric and 2-methylbutyric acids have been shown to have more offensive odour (Hensen et al., 2006; Zhu et al., 1999). Le et al. (2005), in a review article, concluded that there were significant differences between odourous compounds in general, and VFA in particular. The wide variations were most likely due to differences in sampling and measuring methods and different sources of samples. The use of multiple sources and replications of each source is beneficial to avoid wrong conclusions based on such differences. However, due to the affinity of VFA to adsorb to surfaces, it can be difficult to make gas-phase measurements. Therefore, some studies of odourous compound emissions have been based on VFA concentration in the liquid phase (Blanes-Vidal et al., 2009; Hansen, Kai, & Moller, 2006).

Manure is usually stored on-farm under different management practices and environmental conditions before its

use as fertiliser for crops. While stored, manure in the zone below the surface layer naturally undergoes AD (Cooper & Cornforth, 1978; Lovanh, Loughrin, Cook, Rothrock, & Sistani, 2009). Volatile fatty acids in separated solid and liquid fractions of pig manure decreased during storage and the decrease was affected by temperature (Popovic & Jensen, 2012). Characterising VFA in stored dairy manure related to AD is important for assessing the environmental impact of AD, including odour pollution and greenhouse gas emissions, because most of the successful agricultural AD systems in the USA are on dairy farms (USEPA, 2011).

However, VFA are still one of the least-well known groups of compounds present within animal manure (Alanis, Ashkan, Krauter, Campbell, & Hasson, 2010; Rabaud, Ebeler, Ashbaugh, & Flocchini, 2003; Sun et al., 2008). There are only a few published studies on VFA in dairy manure. In addition, no research in the literature has compared and characterised the VFA regarding their temporal and spatial variations in stored non-AD treated and AD-treated dairy manure. The objective of this paper was to study the characteristics of five VFA, i.e., formic, acetic, propionic, butyric, and 2-methylbutyric acids related to different manure sources and the treatments of these sources with AD and post-AD solid–liquid separation.

## 2. Materials and methods

### 2.1. Dairy manure and manure preparation

Dairy manure from four different sampling locations, two undigested (non-AD) and two digested (AD-treated), was collected at the end of September 2011 in NW Washington State at the Qualco anaerobic digester complex, which was constructed in 2008 (WSDA, 2011). The hydraulic retention time of the Qualco digester was approximately 16 days. The two non-AD sources were the manure from a dairy barn (raw) and a mixture of dairy manure and “pre-consumer” wastes (WSDA, 2011) to the digester (influent). The two AD-treated manure sources were from the outlet of the digester (effluent) and the effluent after solids separation before storing in a lagoon (effluent SS).

The pre-consumer wastes included several different biological wastes. Recorded daily inputs into the digester showed that, during the 16 days prior to the day of manure effluent collection for this study, the digester had been fed with 6.9% “Blood” that was waste from a ruminant slaughter plant; 1.2% “Fish” consisting of bread crumbs and waste fish from fish stick processing; 23.6% “Trap”, a byproduct consisting of grease trap waste; and 68.3% dairy manure. On the day of the influent manure collection, the digester was fed with a mixture of 5.9% “Blood”, 4.0% “Trap”, and 90.1% dairy manure.

The four sources of manure were collected and frozen in four sealed plastic containers prior to shipment. The frozen containers were shipped to Purdue University where they were kept at room temperature for six days to thaw completely before filling eight manure-testing reactors (R1–R8). Prior to filling, manure in each container was mixed with a power mixer until the mixture was homogenous. Manure was continuously stirred while loading the reactors to

**Table 1 – Overview of manure preparation.**

Container	Sampling date	Sampling location	Reactor	Reactor filling
1	20/Sep/11	Raw manure from dairy barn	1 and 2	5/Oct/11 (day 0)
2	22/Sep/11	Influent to AD containing raw dairy manure and pre-consumer wastes	3 and 4	5/Oct/11 (day 0)
3	22/Sep/11	Effluent from AD	5 and 6	11/Oct/11 (day 6)
4	22/Sep/11	Effluent from AD after separation of solids	7 and 8	11/Oct/11 (day 6)

ensure uniformity in replicate reactors. Reactors R1–R4 were filled on test day 0 and R5–R8 were filled on day 6 (Table 1).

## 2.2. Laboratory test for simulated manure storage

Manure from each source was tested in two laboratory-scale reactors measuring 610 mm high and 380 mm diameter and made of white polyvinyl chloride. The inside surfaces of the reactors were lined with Tedlar films, except for the bottoms of the reactors. The reactors were housed in a temperature-controlled walk-in chamber at about 20 °C (Fig. 1).

Each reactor was initially filled with manure to a height of 254 mm and was continuously ventilated with 6.5 l min<sup>-1</sup> of fresh air in the manure headspace for three months to simulate manure storage conditions on dairy farms (Fig. 2). The exhaust air from each reactor and the reactor inlet fresh air were sampled weekly or biweekly for odour evaluation, and measured for 10 min approximately every 90 min for gas emission evaluation. Results of odour and gas emissions will be presented elsewhere.

## 2.3. Manure sampling for regular analysis

Before filling the reactors, two manure samples were taken from each container after the source manure was completely mixed with the power mixer on days 0 and 6. One manure sample was taken from each reactor at the end of the test on day 107 after the manure was completely mixed (Table 2). These 16 manure samples were shipped to an external laboratory (Midwest Laboratories, Inc., Omaha, NE, USA) for analysis with a “basic manure package,” which included moisture/TS, total nitrogen (TKN), phosphate, potash, sulphur, calcium, magnesium, sodium, iron, manganese, copper, zinc, pH, and ammoniacal nitrogen.

## 2.4. Manure sampling for volatile fatty acid analysis

Two manure samples were taken weekly for VFA concentration analysis from each reactor. A total of 224 samples were taken during the 3-month study (Table 2). One weekly sample was taken from the top manure layer within 25 mm below the surface and another was taken from the bottom manure layer within 50 mm above the reactor base (Fig. 2). Samples were taken using 5-ml plastic pipettes. The manure height in each reactor was measured with a ruler prior to manure sampling. Based on the measurement, a pipette was marked accordingly to ensure the top layer was measured within 25 mm below the surface. Each manure sample contained 5–8 ml of liquid manure depending on the amount of solids present in the sample. Samples with high solids content needed to be larger to ensure enough liquid portion for analysis.

## 2.5. Analyses of volatile fatty acid samples

Analyses of VFA were conducted via high performance liquid chromatography (HPLC) using a Waters 2695 separations module (Waters Technologies Corporation, Milford, MA, USA) with a Waters 2414 refractive index detector at the Laboratory of Renewable Resources Engineering, Purdue University. The column was a Bio-Rad Aminex<sup>®</sup> HPX-87H (Bio-Rad Laboratories, Hercules, CA, USA), and the mobile phase was 5 mM aqueous sulphuric acid. Manure samples were centrifuged for 10 min at 3000 g followed by two 5-min successive sessions at 16,000 g to remove manure solids. Samples were then filtered using a 25-mm nylon 0.2 µm filter before being analysed with the HPLC system. Data analyses of VFA were performed via Waters HPLC software (Empower, Waters Technologies, Milford, MA, USA).

Concentrations of VFA were calculated after calibrations of all five acids were conducted using external standards (Fig. 3). Linear regressions for each compound (determined by retention time) were obtained between peak areas for three injections of samples containing known concentrations of each compound at four levels of concentrations. Mean differences among VFA concentrations within the same reactor and between replicate reactors were assessed with a general linear model (GLM) procedure using PROC GLM (SAS v.9.2, SAS Inst. Inc., Cary, NC, USA).

## 3. Results and discussion

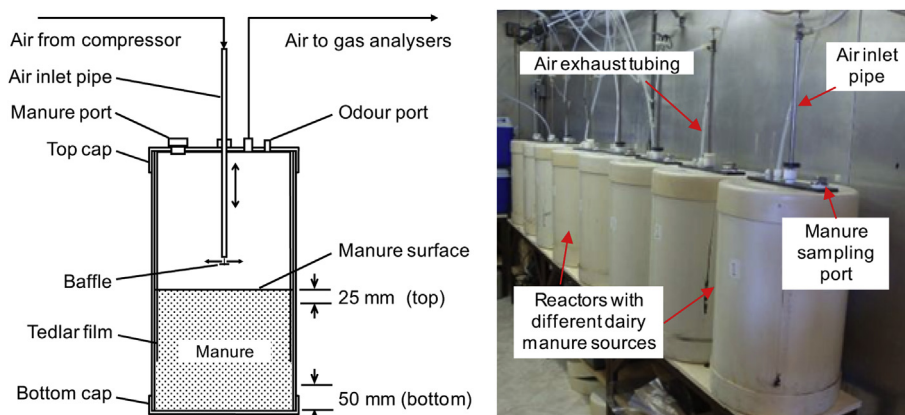
### 3.1. Characteristics of source and end-test manure

#### 3.1.1. Overview

The regular manure analysis revealed differences among initial samples of all four types of source manure before the three-month laboratory study. The differences in the initial samples from each manure source were as much as 4 units for pH, 4.7% for TS, 0.07% for ammoniacal nitrogen (NH<sub>4</sub>-N), 0.15% for organic nitrogen (N), 0.11% for TKN, 0.05% for phosphorous (P<sub>2</sub>O<sub>5</sub>), and 0.01% for total sulphur (S) (Table 3). In the end-of-test manure samples, there were variations not only among the four groups, but also between the two replicate reactors within the same group, especially in reactors containing influent manure (R3 and R4). The properties of influent manure between R3 and R4 were the most different compared with the two replicates of the other three sources. For example, R3 had 0.7 unit higher pH, 1% lower TS, and 0.03% lower P<sub>2</sub>O<sub>5</sub> than R4. The results demonstrated that the characteristics of manure could change substantially after months of storage.

#### 3.1.2. pH

The pH of the influent manure ranged from 4.4 for the initial manure to 6.2 for the end-test manure in R3. This range of pH



**Fig. 1 – Reactor setup. Left: Cross section of reactor (not to scale). Right: Reactors filled with dairy manure under storage test in a temperature-controlled chamber.**

is close to the optimum pH for acid fermentation necessary for the formation of VFA (Gerardi, 2003). The influent manure pH was much lower compared with the raw manure pH largely due to the pre-consumer wastes added into the influent. Studies have shown that accumulation of VFA result in a decrease in pH (Ghasimi, Idris, Chuah, & Tey, 2009; Ndegwa, 2003).

The pH for raw and effluent manure sources remained between 8.3 and 8.7 from the start to the end of the study. The lack of a significant change in pH in these manure sources may indicate a well-buffered manure solution (Patni & Jui, 1985). However, by the end of the experiment there was an increase in pH of all four manure sources. This may be due to the degradation of VFAs or protein which could have resulted in the production of ammonia to counterbalance VFA production (Lu et al., 2008; Yu & Fang, 2001).

3.1.3. Total solids

The analysis of TS in the manure samples taken prior to reactor filling and at the end of the experiment showed a reduction in solids content in manure only for R3 (Table 3). The percent of TS increased for AD-treated sources and remained the same for raw manure. The increase in solids may be due to the loss of moisture through evaporation at the manure surface (Misselbrook et al., 2005). Influent manure had the highest

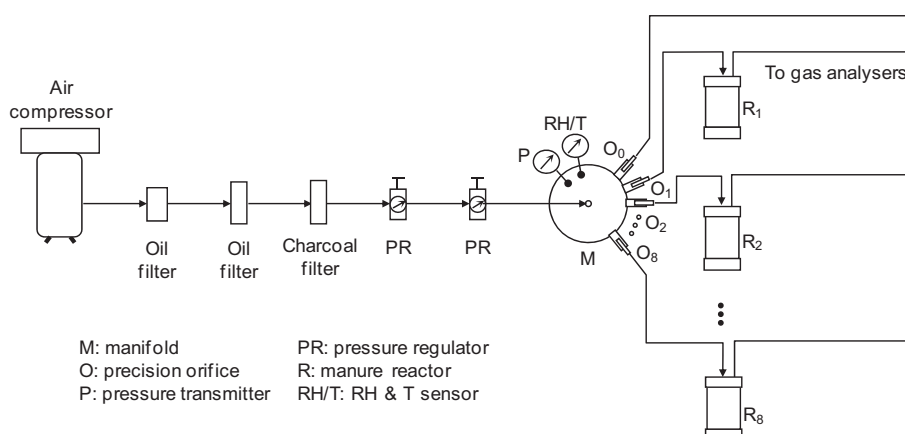
initial TS which could play a large role in microbial activities in the manure as well as the production of VFA (El-Mashad et al., 2011; Zhu, Ndegwa, & Luo, 2001). Emission of VOCs has been shown to be directly proportional to percentage solids in manure (Conn et al., 2007; Zahn et al., 2001).

3.1.4. Ammoniacal nitrogen, organic nitrogen, and total nitrogen

The ammoniacal nitrogen (NH<sub>4</sub>-N) content was the highest in the influent manure at the end of the experiment most likely due to the mineralisation of organic nitrogen to ammonium (Frear, Liao, Ewing, & Chen, 2011). However, organic nitrogen contents increased from the start to the end-of-test for all manure sources except for raw manure. The TKN was higher in the influent manure than in the raw manure due to the addition of pre-consumer wastes. The amount of ammonia (NH<sub>3</sub>) that is released from manure mainly depends on several factors, including manure pH, concentrations of ammoniacal nitrogen in the manure, temperature, and air velocity over manure surface (Ni, 1999).

3.1.5. Phosphorus and total sulphur

Phosphorus and total sulphur concentrations increased from the initial samples to the end samples in all manure sources except for the effluent (R5 and R6) in sulphur (Table 3). Influent



**Fig. 2 – Schematic of the test setup (not to scale).**



**Table 2 – Overview of manure sampling schedule and total number of samples.**

Test day	Regular samples	VFA samples	Operation
0	4		Source sampling in containers 1 and 2 (2/container)
6	4		Source sampling in containers 3 and 4 (2/container)
7–98		224	Weekly sampling in reactors (2/reactor and 16/week)
107	8		End-test sampling in reactor (1/reactor)

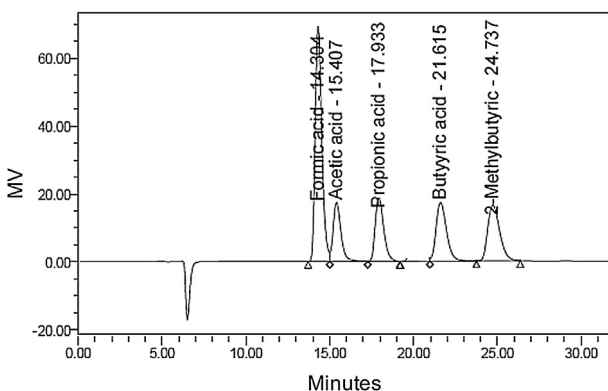
manure contained the highest amounts of both phosphorus and total sulphur in start and end-of-test samples. Although the absolute concentrations were still low at the end of the test for all manure sources, the relative rate of increase was substantial for some reactors. For example, the sulphur concentrations in raw manure (R1 and R2) doubled after three months of storage. Nutrients such as these are needed for normal growth of the bacteria involved in AD (Ghasimi et al., 2009).

### 3.2. Characteristics of individual volatile fatty acid concentrations

#### 3.2.1. Overview

The five different VFA shown in the standard graph (Fig. 3), including formic, acetic, butyric, propionic, and 2-methylbutyric acids, were detected in all four manure sources. The highest concentrations of VFA were found in the non-AD influent manure (R3 and R4, Table 4). Previous experiments have revealed acetic and propionic acids as the main fermentation products from dairy manure (Cooper & Cornforth, 1978; Dinopoulou et al., 1988; El-Mashad et al., 2011). In this study, however, acetic acid was the predominant VFA only in three sources (the raw manure and the two effluent manure sources), but not in the influent manure (R3 and R4). Manure conditions in influent manure favoured the production of butyric acid, most likely due to the addition of pre-consumer wastes. Concentrations of propionic acid were lower than acetic acid only in the raw manure (R1 and R2).

The concentrations of five VFA exhibited temporal variations over the 3-month experiment (Figs. 4–9). This agreed with several previous studies, which also showed that the proportion of individual VFA in manure could change over time due to different rates of degradation or formation between VFA (Conn et al., 2007; Moller, Sommer, & Ahring, 2004; Popovic & Jensen, 2012). Patni and Jui (1985) reported the changes in VFA concentrations in dairy manure slurry with different solids contents during undisturbed storage in covered tanks.

**Fig. 3 – Acid standard test.**

Their results also showed that the concentration of the predominant VFA constituent (acetic acid) governed the trend for changes in the concentration of total VFA in stored manure.

Moreover, the concentrations of the five VFA demonstrated spatial variations. The GLM analysis revealed significant differences ( $P < 0.05$ ) in acid concentrations among all treatments, between replicate reactors with the same source manure, as well as within the same reactor. Most concentration differences were found in comparisons between the top and bottom layers of manure, demonstrating spatial variations in VFA concentrations in the manure. The concentrations of VFA in the top layer were generally lower than in the bottom layer. This was most likely due to the more rapid decomposition of VFA by the aerobic and facultative bacteria due to exposure to air (Cooper & Cornforth, 1978; Patni & Jui, 1985; Zhang & Zhu, 2003).

The weekly sample analyses revealed that although formic acid in R3 and R4, and acetic acid in R1 and R2 exhibited a general trend of decreasing in concentrations over time, the two VFA did not show the same tendency in all eight reactors. In addition, the concentrations of the other three VFA (propionic acid, butyric acid, and 2-methylbutyric acid) exhibited more irregular temporal variations. These characteristics of the five VFA made it difficult to reliably model and predict their dynamics in dairy manure.

#### 3.2.2. Formic acid

Formic acid is the simplest carboxylic acid. Reactors containing influent manure had extremely high concentrations of formic acid for the first 4 weeks. Its highest concentration was  $27,100 \text{ mg l}^{-1}$  at the bottom of R4 on day 14. The formic acid concentrations in R3 and R4 dropped down to zero with very small fluctuations around day 56. Formic acid concentrations ranged from 0 to  $905 \text{ mg l}^{-1}$  in raw manure reactors and AD-treated manure reactors (Fig. 4). The most reasonable explanation for this is that the pre-consumer wastes added to the influent manure introduced substantial formic acid that was then broken down rapidly by microbial activity. The considerable reduction in formic acid concentrations in R3 and R4 after day 42 could be due to the initiation of methanogenesis because methanogens can directly use formic acid (Dinopoulou et al., 1988; Lu et al., 2008).

#### 3.2.3. Acetic acid

As the predominant VFA in most of the manure sources, concentrations of acetic acid increased in reactors containing raw manure (R1 and R2) until around day 21 and then declined steadily (Fig. 5). Although acetic acid was not the predominant VFA in the influent manure (R3 and R4), its absolute concentrations in the influent manure were the highest among the four manure sources (Table 4). Concentrations of acetic acid in R3 top and bottom reached the maximum concentrations of 3340 and

**Table 3 – Results of selected parameters from regular analysis of the four manure sources.**

Parameter	Raw manure			Influent			Effluent			Effluent (SS <sup>a</sup> )		
	Initial		End	Initial		End	Initial		End	Initial		End
	C1	R1	R2	C2	R3	R4	C3	R5	R6	C4	R7	R8
pH	8.3	8.4	8.4	4.4	6.2	5.5	8.3	8.5	8.6	8.4	8.6	8.7
Total solids (TS), %	2.8	2.8	2.8	6.1	5.2	6.2	1.9	2.4	2.4	1.4	1.8	1.7
Ammoniacal nitrogen (NH <sub>4</sub> -N), %	0.08	0.05	0.04	0.06	0.15	0.14	0.13	0.07	0.05	0.11	0.04	0.03
Organic nitrogen (N), %	0.07	0.06	0.07	0.20	0.21	0.24	0.06	0.08	0.09	0.05	0.07	0.08
Total nitrogen (TKN), %	0.15	0.11	0.11	0.26	0.36	0.38	0.19	0.15	0.14	0.16	0.11	0.11
Phosphorous (P <sub>2</sub> O <sub>5</sub> ), %	0.08	0.10	0.10	0.10	0.11	0.14	0.07	0.08	0.08	0.05	0.07	0.06
Total sulfur (S), %	0.01	0.02	0.02	0.02	0.03	0.03	0.02	0.02	0.02	0.02	0.02	0.02

<sup>a</sup> Separation of solids.

3880 mg l<sup>-1</sup> on days 21 and 28, respectively (Fig. 5). The concentrations declined until day 49 and then gradually increased with some fluctuation. In R4, acetic acid concentrations began to decrease on day 21, but began to increase on day 42 and continued to increase until day 91, when the concentration dropped more than 2000 mg l<sup>-1</sup>. The maximum acetic acid concentration among all reactors was 4870 mg l<sup>-1</sup> at the bottom of R4 on day 84. There were large differences in acetic acid concentrations for the influent manure compared with the AD-treated manure. The maximum acetic acid concentration in AD-treated manure was only 660 mg l<sup>-1</sup> and it occurred on day 70 at the bottom of R7 (effluent SS). Concentrations of acetic acid in both R5 and R6 (effluent) bottom layer increased after day 7, but began gradually decreasing after days 14 and 21, respectively. The top layers of the AD-treated reactors all had lower concentrations of acetic acid compared with the bottom layers. The temporal and spatial variations in acetic acid concentrations in different reactors demonstrated characteristics that were more complex than previously reported.

### 3.2.4. Propionic acid

Concentrations of propionic acid were highest in reactors containing influent manure (R3 and R4), reaching a maximum concentration of 2900 mg l<sup>-1</sup> on day 84 (Fig. 6). The propionic acid concentrations in reactors containing raw manure (R1 and R2) increased until about day 35 and then completely degraded by the last day of sampling. Concentrations of propionic acid in AD-treated manure reached a maximum of 240 mg l<sup>-1</sup> in R5. Concentrations did not exceed 70 mg l<sup>-1</sup> for R6, R7 and R8. Because R5 and R6 were replicates, the difference in propionic acid between the two reactors demonstrated a significant variation within the same treatment.

### 3.2.5. Butyric acid

Butyric acid concentrations ranged only from 0 to 501 mg l<sup>-1</sup> for raw manure reactors (R1 and R2). Concentrations of butyric acid did not exceed 51 mg l<sup>-1</sup> in any AD-treated reactor (R5–R8). Reactors containing the influent manure (R3 and R4) had the highest concentrations of butyric acid, ranging from 1150 to 6390 mg l<sup>-1</sup>. In both the top and bottom layers of R3 and R4, butyric acid concentrations increased until day 35 and 42, respectively, then gradually declined (Fig. 7). When comparing with the formic and butyric acid in R3 and R4, the concentrations of butyric acid did not begin to increase until formic acid concentrations declined. All correlation factors ranged from

–0.969 to –0.985, showing high correlations between the two VFA, when the correlation coefficients for top and bottom layers in R3 and R4 were calculated for the period during which formic acid concentration reached 0 mg l<sup>-1</sup> or when butyric acid reached its peak concentration. Formic acid accumulation can inhibit acidogenesis, and those bacteria responsible for producing butyric acid seem to be more affected (Lu et al., 2008).

### 3.2.6. 2-Methylbutyric acid

The concentrations of 2-methylbutyric acid were very low compared with all other VFA. The maximum concentration of 740 mg l<sup>-1</sup> occurred in R3 in the bottom layer on the last day of sampling. Concentrations of 2-methylbutyric acid in raw manure stayed fairly static, reaching a maximum concentration of 183 mg l<sup>-1</sup>. On day 56, concentrations of 2-methylbutyric acid in raw manure began to decline until the VFA could no longer be detected. Concentrations in the influent manure were below those in raw manure until day 35 and continued to increase until day 84 for R4. At all time points and in both top and bottom manure layers, the concentrations of 2-methylbutyric acid for AD-treated manure were below 75 mg l<sup>-1</sup> (Fig. 8).

## 3.3. Effects of manure sources and manure treatment on volatile fatty acid concentrations

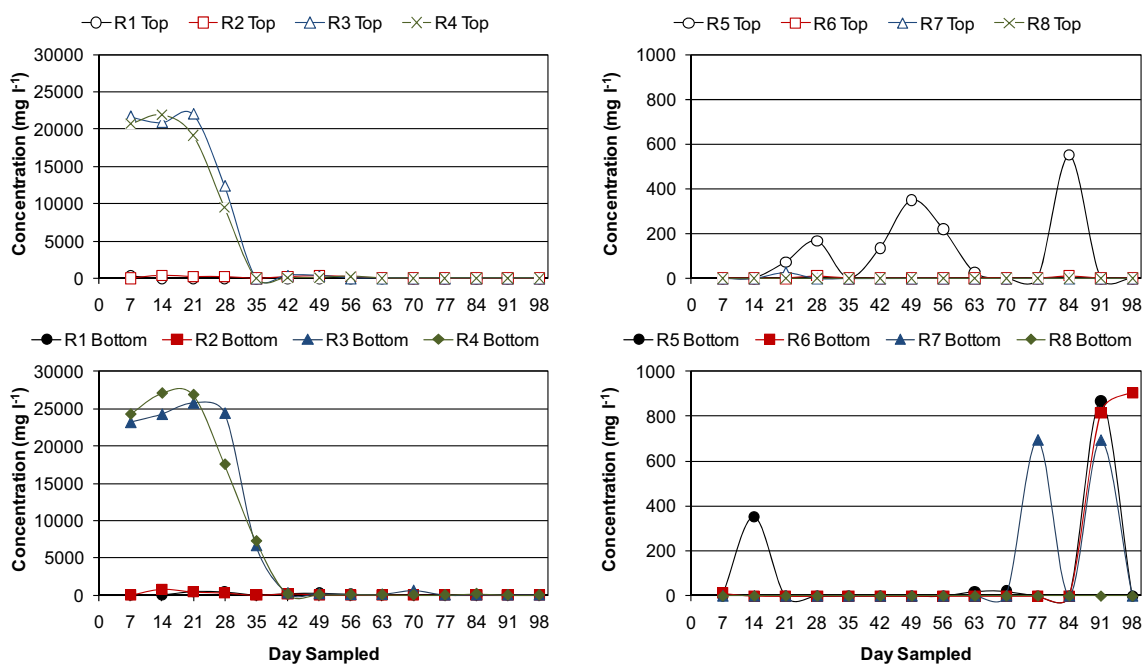
### 3.3.1. Effect of pre-consumer wastes on volatile fatty acids in anaerobic digestion influent

The influent manure reactors (R3 and R4) had the highest VFA concentrations among all reactors (Table 4). Their total VFA of 14,175 ± 4825 mg l<sup>-1</sup> (mean ± standard deviation) during the entire study was more than 6 times higher than that from the raw dairy manure (1963 ± 4825 mg l<sup>-1</sup>). In addition, while acetic acid was the most common VFA present in all other three manure sources, formic acid was dominant in the influent manure source (R3 and R4). Furthermore, butyric acid concentrations were higher than acetic and propionic acid concentrations in the influent manure, instead of lower as in the other three manure sources. These characteristics showed that the addition of pre-consumer wastes in dairy manure in the influent resulted in not only higher VFA concentrations, but also different proportions of VFA compared with the raw dairy manure, which was dominated by acetic and propionic acids.

According to a recent study in Washington State (Frear et al., 2011), the addition of pre-consumer wastes can

**Table 4 – Mean  $\pm$  standard deviation and range (in parentheses) of VFA concentrations in each reactor from 14 top layer (T) and 14 bottom layer (B) weekly manure samples.**

Reactor	Layer	VFA concentration ( $\text{mg l}^{-1}$ )					
		Formic acid	Acetic acid	Propionic acid	Butyric acid	2-Methylbutyric	Total VFA (sum of 5)
1	T	20 $\pm$ 75 (0–281)	1298 $\pm$ 967 (103–2595)	424 $\pm$ 232 (0–729)	130 $\pm$ 142 (0–501)	82 $\pm$ 48 (0–127)	1867 $\pm$ 648 (103–3677)
1	B	107 $\pm$ 180 (0–528)	1424 $\pm$ 1346 (76–3383)	661 $\pm$ 347 (18–1381)	129 $\pm$ 145 (0–348)	88 $\pm$ 60 (0–155)	2302 $\pm$ 804 (94–5365)
2	T	101 $\pm$ 122 (0–334)	1098 $\pm$ 941 (66–2312)	285 $\pm$ 307 (0–875)	79 $\pm$ 85 (0–204)	74 $\pm$ 49 (0–129)	1567 $\pm$ 588 (66–3432)
2	B	135 $\pm$ 245 (0–827)	1318 $\pm$ 1228 (78–2976)	552 $\pm$ 337 (0–1149)	122 $\pm$ 127 (0–291)	90 $\pm$ 67 (0–183)	2119 $\pm$ 737 (78–4704)
1 and 2	T and B	91 $\pm$ 169 (0–294)	1284 $\pm$ 1109 (81–2764)	480 $\pm$ 332 (5–1008)	115 $\pm$ 125 (0–260)	84 $\pm$ 55 (0–144)	1963 $\pm$ 685 (85–4223)
3	T	5545 $\pm$ 9248 (0–21,994)	2300 $\pm$ 534 (1416–3343)	1488 $\pm$ 354 (1028–2040)	2284 $\pm$ 1104 (1299–4925)	294 $\pm$ 201 (0–642)	11,412 $\pm$ 4417 (4571–29,032)
3	B	7516 $\pm$ 11,197 (0–25,720)	2992 $\pm$ 481 (2264–3881)	1813 $\pm$ 178 (1458–2146)	3047 $\pm$ 1110 (1623–4958)	424 $\pm$ 274 (43–740)	15,102 $\pm$ 5446 (7898–33,029)
4	T	5117 $\pm$ 8775 (0–21,948)	2969 $\pm$ 933 (1322–4423)	2103 $\pm$ 244 (1844–2491)	3727 $\pm$ 1631 (1153–6158)	280 $\pm$ 165 (58–507)	13,532 $\pm$ 4224 (5731–28,501)
4	B	7386 $\pm$ 11,226 (0–27,075)	3399 $\pm$ 1010 (1975–4873)	2265 $\pm$ 422 (1337–2900)	4106 $\pm$ 1756 (1713–6390)	317 $\pm$ 194 (49–573)	16,673 $\pm$ 5483 (5658–34,514)
3 and 4	T and B	6391 $\pm$ 9950 (0–23,529)	2915 $\pm$ 853 (1872–3701)	1917 $\pm$ 427 (1519–2097)	3291 $\pm$ 1558 (1601–5388)	329 $\pm$ 214 (54–561)	14,175 $\pm$ 4825 (6307–30,648)
5	T	108 $\pm$ 166 (0–550)	89 $\pm$ 78 (0–203)	18 $\pm$ 64 (0–240)	6 $\pm$ 10 (0–28)	13 $\pm$ 20 (0–62)	225 $\pm$ 95 (0–550)
5	B	90 $\pm$ 242 (0–867)	282 $\pm$ 196 (55–584)	42 $\pm$ 58 (0–217)	14 $\pm$ 17 (0–42)	30 $\pm$ 26 (0–72)	439 $\pm$ 170 (75–1232)
6	T	2 $\pm$ 4 (0–12)	76 $\pm$ 96 (0–334)	1 $\pm$ 4 (0–13)	4 $\pm$ 9 (0–26)	8 $\pm$ 14 (0–35)	89 $\pm$ 51 (0–408)
6	B	124 $\pm$ 312 (0–905)	237 $\pm$ 186 (0–543)	16 $\pm$ 23 (0–64)	13 $\pm$ 16 (0–35)	26 $\pm$ 25 (0–61)	400 $\pm$ 181 (0–964)
5 and 6	T and B	90 $\pm$ 214 (0–420)	171 $\pm$ 171 (45–379)	19 $\pm$ 46 (0–84)	9 $\pm$ 14 (0–28)	19 $\pm$ 23 (0–47)	286 $\pm$ 98 (98–607)
7	T	2 $\pm$ 7 (0–27)	42 $\pm$ 92 (0–331)	1 $\pm$ 4 (0–14)	4 $\pm$ 9 (0–23)	6 $\pm$ 13 (0–32)	55 $\pm$ 43 (0–400)
7	B	99 $\pm$ 251 (0–693)	175 $\pm$ 231 (0–660)	6 $\pm$ 13 (0–46)	7 $\pm$ 15 (0–46)	15 $\pm$ 17 (0–52)	293 $\pm$ 163 (0–772)
8	T	0 $\pm$ 0 (0–0)	61 $\pm$ 111 (0–387)	2 $\pm$ 8 (0–31)	6 $\pm$ 10 (0–24)	8 $\pm$ 13 (0–34)	76 $\pm$ 54 (0–476)
8	B	0 $\pm$ 0 (0–0)	225 $\pm$ 238 (0–597)	12 $\pm$ 23 (0–70)	14 $\pm$ 18 (0–51)	16 $\pm$ 21 (0–56)	257 $\pm$ 135 (0–760)
7 and 8	T and B	25 $\pm$ 130 (0–173)	126 $\pm$ 192 (0–325)	5 $\pm$ 14 (0–23)	8 $\pm$ 14 (0–30)	11 $\pm$ 16 (0–38)	169 $\pm$ 80 (0–398)



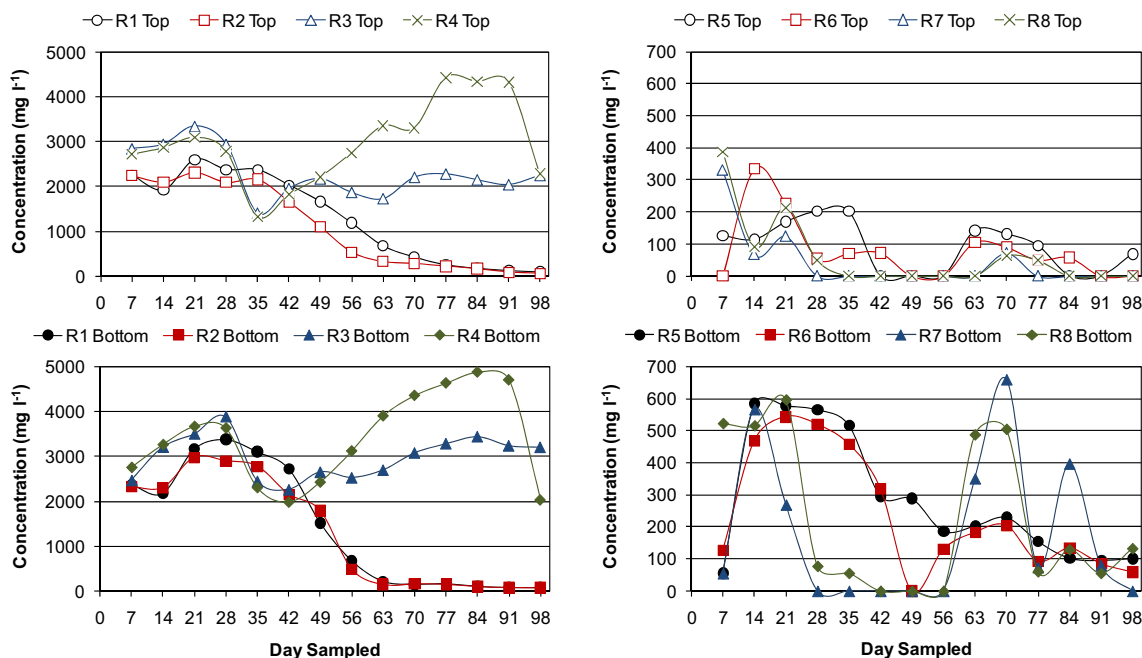
**Fig. 4 – Comparison of formic acid concentrations in the four manure sources. Top Left: Top layer of non-AD. Top Right: Top layer of AD-treated. Bottom Left: Bottom layer of non-AD. Bottom Right: Bottom layer of AD-treated.**

significantly increase biogas production over dairy manure alone by adding nutrients as well as creating more favourable conditions in the manure for microorganisms involved in the different phases of digestion that lead to methanogenesis. The main products of the first phase of AD, anaerobic acidogenesis, are acetic and butyric acids when the substrate added has easily degradable carbohydrates (Dinopoulou et al., 1988). The extremely high VFA concentrations in the influent manure in this study could provide some supporting evidence

to the increased biogas production in Washington State, where all of the operating dairy digesters use a combination of manure and some quantity of pre-consumer organic waste-derived materials (WSDA, 2011).

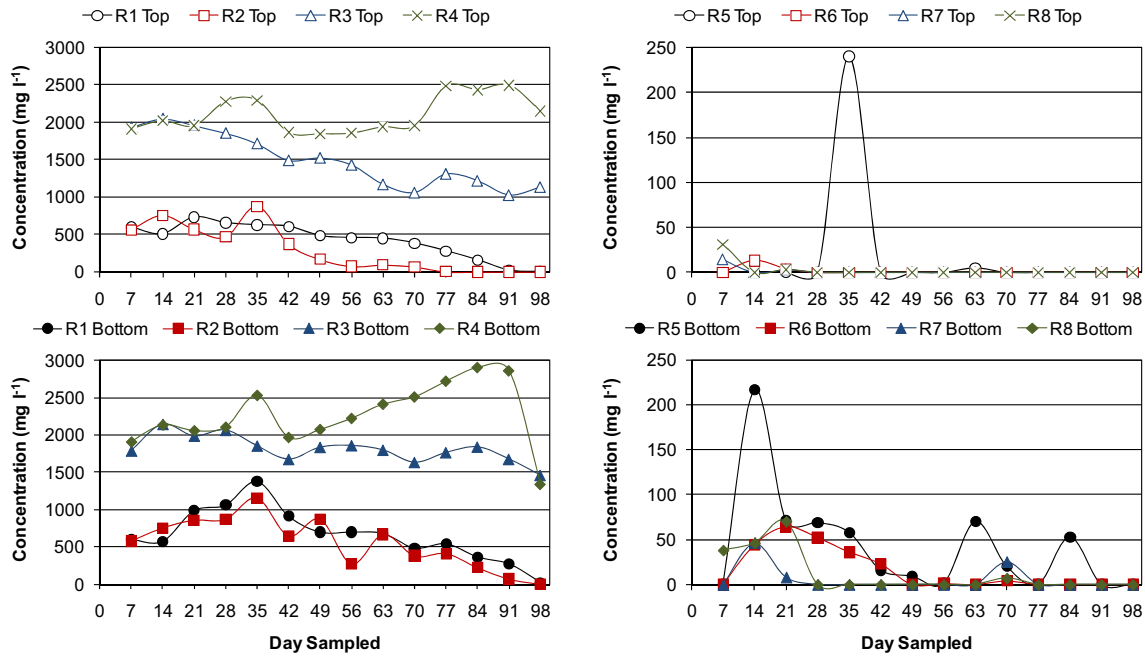
3.3.2. Effect of anaerobic digestion and separation of solids on volatile fatty acids in stored manure

The total VFA (sums of five VFA) presented in Table 4 and Fig. 9 clearly show the differences among various manure sources.



**Fig. 5 – Comparison of acetic acid concentrations in the four manure sources. Top Left: Top layer of non-AD. Top Right: Top layer of AD-treated. Bottom Left: Bottom layer of non-AD. Bottom Right: Bottom layer of AD-treated.**

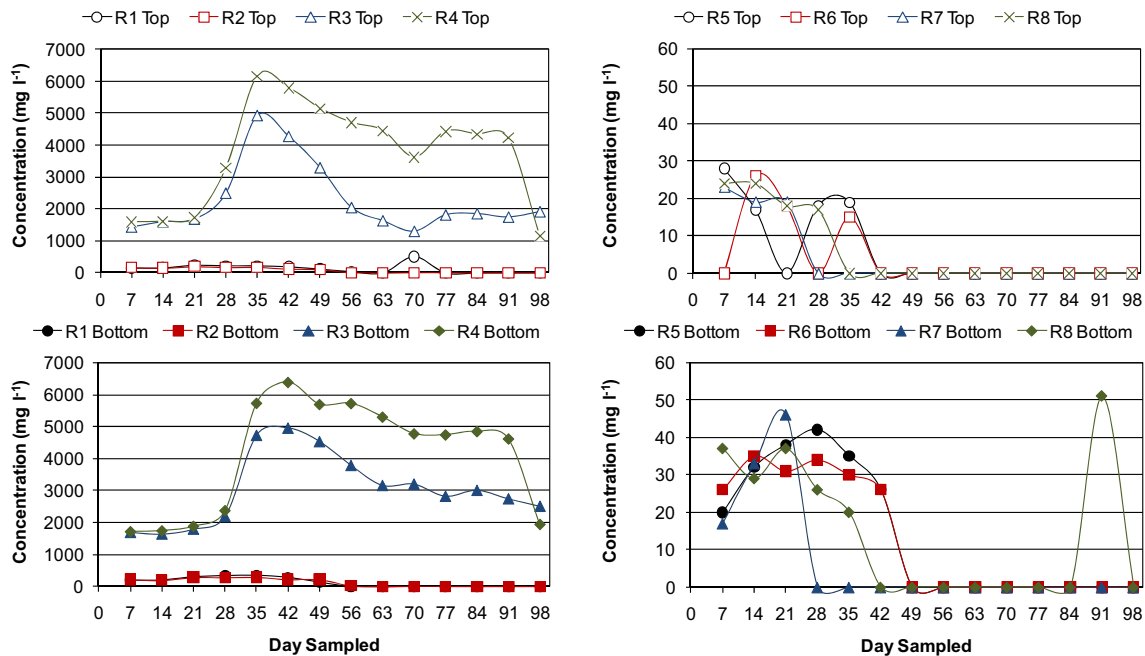




**Fig. 6 – Comparison of propionic acid concentrations in the four manure sources. Top Left: Top layer of non-AD. Top Right: Top layer of AD-treated. Bottom Left: Bottom layer of non-AD. Bottom Right: Bottom layer of AD-treated.**

In general, the manure before AD (R1–R4) had significantly higher total VFA compared with the manure after AD ( $P < 0.05$ ). Additionally, concentrations of all individual VFA in the AD-treated manure never exceeded  $1000 \text{ mg l}^{-1}$  (Figs. 4–8) and were significantly lower than in non-AD treated manure. This demonstrated that the Qualco AD system greatly reduced VFA concentrations in stored manure. Moreover, although both AD-treated effluent manure sources contained

significantly lower concentrations of all five VFA compared with the non-AD manure, separation of solids from the effluent further significantly reduced the total VFA concentrations ( $169 \pm 80 \text{ mg l}^{-1}$ ) compared with the effluent without solid separation ( $286 \pm 98 \text{ mg l}^{-1}$ ,  $P < 0.05$ ). However, due to the limitation of only five VFA in this study, future investigations are needed to determine the effect of AD and separation of effluent solid on other VFA that exist in dairy manure.



**Fig. 7 – Comparison of butyric acid concentrations in the four manure sources. Top Left: Top layer of non-AD. Top Right: Top layer of AD-treated. Bottom Left: Bottom layer of non-AD. Bottom Right: Bottom layer of AD-treated.**

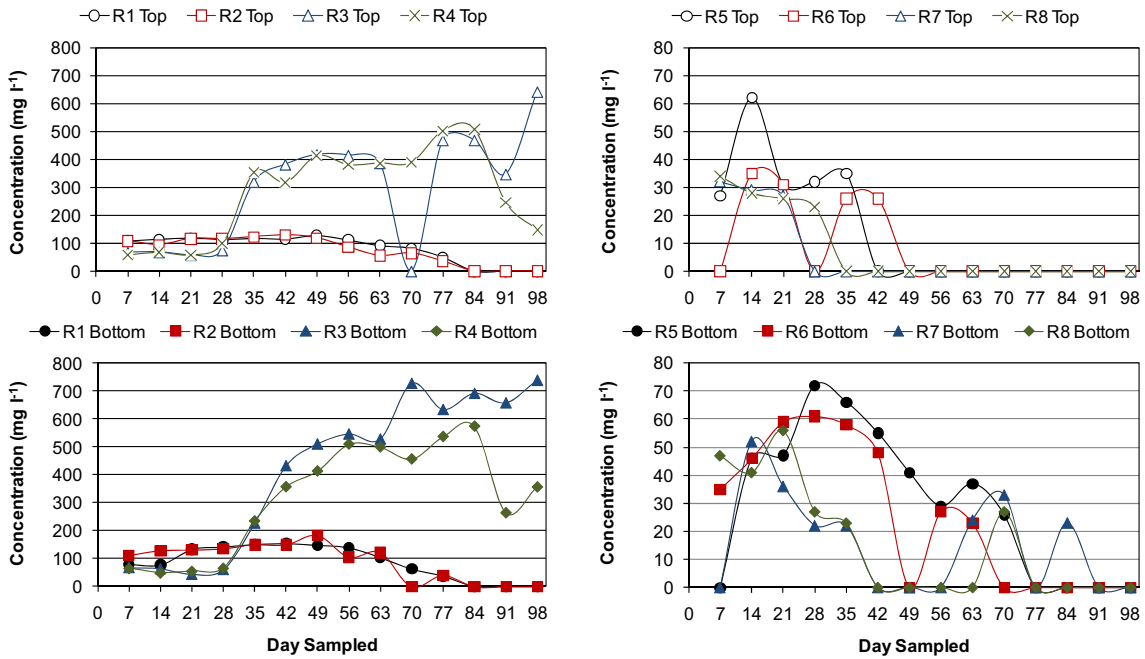


Fig. 8 – Comparison of 2-methylbutyric acid concentrations in the four manure sources. Top Left: Top layer of non-AD. Top Right: Top layer of AD-treated. Bottom Left: Bottom layer of non-AD. Bottom Right: Bottom layer of AD-treated.

3.4. Comparison with reported dairy manure volatile fatty acids

3.4.1. Comparison of volatile fatty acid concentration variations

Limited data exist on VFA in dairy manure, and few present actual concentrations. El-Mashad et al. (2011) collected raw

dairy manure from a dairy barn and diluted it to 2%, 4%, and 9% TS to test at temperatures of 15°, 25°, and 35 °C under complete anaerobic conditions. The VFA measured by El-Mashad et al. (2011) included acetic, propionic, iso butyric, butyric, and valeric acids. The authors concluded that higher manure TS content and higher temperature resulted in higher VFA concentrations (Table 5).

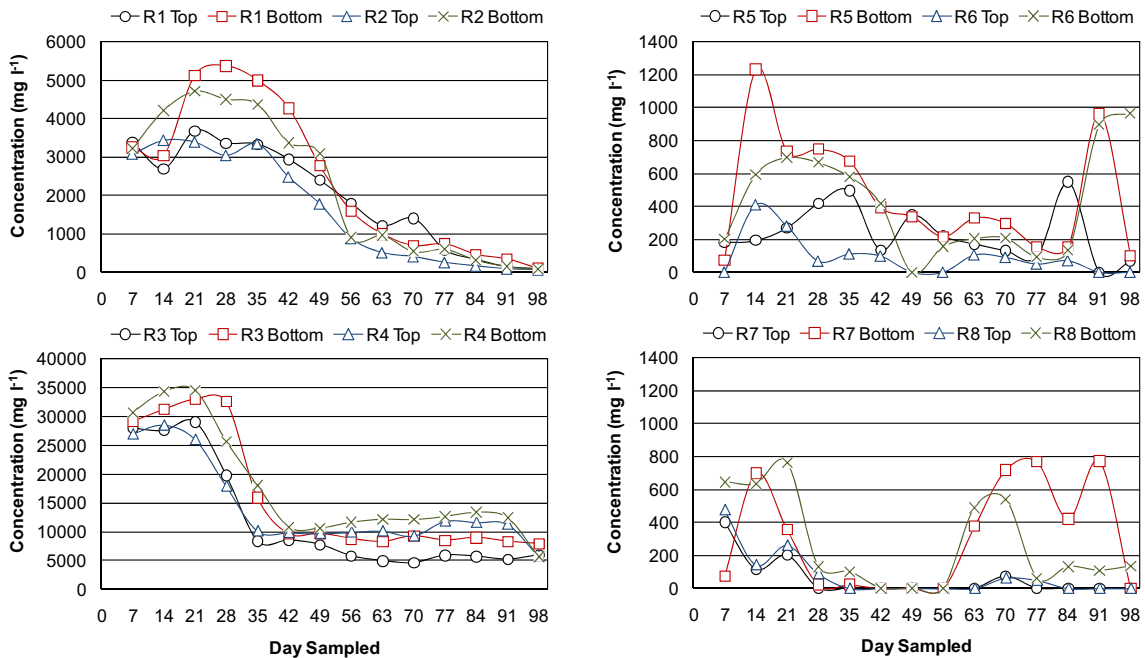


Fig. 9 – Variations of the total VFA concentrations in top and bottom layers in eight reactors. Top Left: Raw manure. Top Right: AD-treated (effluent). Bottom Left: Influent manure. Bottom Right: AD-treated after solid separation (effluent SS).

**Table 5 – Comparison of VFA concentrations in dairy manure.**

Data source	TS, % <sup>a</sup>	Maximum concentration		Acetic acid/total VFA, %
		Total VFA	Acetic acid	
<i>This study</i>				
R1 top at 20 °C on day 21	2.8	3677 mg l <sup>-1</sup>	2595 mg l <sup>-1</sup>	71
R1 bottom at 20 °C on day 28	2.8	5365 mg l <sup>-1</sup>	3383 mg l <sup>-1</sup>	63
R2 top at 20 °C on day 14	2.8	3432 mg l <sup>-1</sup>	Not maximum	N/A
R2 top at 20 °C on day 21	2.8	Not maximum	2312 mg l <sup>-1</sup>	N/A
R2 bottom at 20 °C on day 21	2.8	4704 mg l <sup>-1</sup>	2976 mg l <sup>-1</sup>	63
<i>El-Mashad et al. (2011)<sup>b</sup></i>				
At 25 °C on day 17	2	7930 mg [COD] l <sup>-1</sup>	3569 mg [COD] l <sup>-1</sup>	45
At 35 °C on day 6	2	7200 mg [COD] l <sup>-1</sup>	3600 mg [COD] l <sup>-1</sup>	50
At 15 °C on day 24	4	8600 mg [COD] l <sup>-1</sup>	N/A	N/A
At 35 °C after day 30	4	16,500 mg [COD] l <sup>-1</sup>	6930 mg [COD] l <sup>-1</sup>	42
At 35 °C on day 10	9	23,000 mg [COD] l <sup>-1</sup>	8000 mg [COD] l <sup>-1</sup>	35

<sup>a</sup> TS in initial manure source.

<sup>b</sup> Concentrations were not described numerically for all tested temperatures. Total VFA included acetic, propionic, iso-butyric, butyric, and valeric acids.

The maximum total VFA concentration was 7930 mg [COD] l<sup>-1</sup> at 2% TS and 25 °C from the study of [El-Mashad et al. \(2011\)](#). It was 48% and 59% higher compared with the raw manure in R1 (5365 mg l<sup>-1</sup>) and R2 (4704 mg l<sup>-1</sup>) of this study, respectively, at 2.8% initial TS and 20 °C in the bottom layer, where anaerobic conditions should persist. The differences were larger when compared with the top layers in R1 and R2. Moreover, the percentages of the maximum acetic acid in the maximum total VFA by [El-Mashad et al. \(2011\)](#), which ranged from 35 to 50%, were lower than observed in this study, which ranged from 63 to 71%, at different test conditions ([Table 5](#)). These variations may be explained by differences in manure characteristics, individual VFA measured, and test conditions between the two studies, but also could have been due to some yet unknown factors that affected the microbial eco-systems in different manure reactors as demonstrated by the differences between paired reactors in this study. Nevertheless, the maximum concentrations of individual VFA in both studies occurred on different test days, showing some similarities of the complex dynamics in VFA in dairy manure.

#### 3.4.2. Comparison of spatial and temporal variations in volatile fatty acid concentrations

In the study of [Patni and Jui \(1985\)](#), in which concentrations of six VFA were determined in dairy manure in four 12.3 m × 7.2 m concrete tanks of 3.0 m depth at the beginning and end of periods of 146 or 285 storage days, the authors revealed that in all four tanks and for all VFA except iso-valeric acid, concentrations were significantly lower at the 0.3 m depth than at greater depths after about 50 days of storage. This top-low and bottom-high trend of spatial VFA concentration variation largely agreed with the results in this study as presented in the previous sections.

Additionally, [Patni and Jui \(1985\)](#) reported various patterns of individual VFA concentration changes over time in different tanks. Although the changes in VFA concentrations were very different in this study compared with those by [Patni and Jui \(1985\)](#) and the test conditions were very different (laboratory vs. field), both studies confirmed that there existed profound

temporal VFA concentration variations in stored dairy manure.

## 4. Conclusions

The following conclusions were drawn from the results of this study:

1. Formic acid was dominant in the influent manure source. Formic acid degraded rapidly in influent manure to about 200 mg l<sup>-1</sup> in 6 weeks. However, its concentrations were more sporadic in AD-treated manure.
2. Acetic acid was dominant in raw, effluent, and effluent SS. Acetic acid accounted for between 60% and 75% of the total VFA in these three manure sources, but was only 21% of the total VFA in the influent manure reactors. Except for the raw dairy manure where it demonstrated a general decrease during the study, the pattern of acetic acid concentration changes in other manure sources was irregular.
3. Propionic acid accounted for 24% of the total VFA in raw manure and with lower concentrations in other manure sources.
4. Butyric acid was the second most dominant VFA and accounted for 23% of the total VFA in influent manure, but was only <6% in other manure sources. Concentrations of butyric acid and formic acid were highly correlated (correlation coefficients < -0.969) in the influent reactors, suggesting possible conversion of one to the other or concomitant competition.
5. Concentrations of 2-methylbutyric acid were the lowest among the five VFA in the non-AD manure, but were similar to propionic and butyric acids in AD-treated manure. Changes in 2-methylbutyric acid were generally decreasing in raw manure but were random in other manure sources.
6. The pre-consumer wastes mixed with dairy manure not only increased the total VFA by more than 600% of the total VFA, compared with the raw dairy manure, but also changed in the proportions of different VFA.

7. Concentrations of the total VFA in non-AD treated manure exhibited a general decreasing trend over the three months of storage. However, changes in VFA concentration in the AD-treated manure were more inconsistent and unpredictable.
8. Because VFA concentrations were significantly lower in the group of AD-treated manure than in the group of non-AD manure, this study demonstrated that AD significantly reduced VFA from dairy manure and pre-consumer wastes.
9. Most of the five VFA in the four different manure sources exhibited highly variable temporal and spatial variations. The characteristics of VFA revealed in this study were more complex than previously reported. This complexity makes it difficult to reliably model and predict the concentrations and compositions of VFA in dairy manure.

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