Volatile Fatty Acids in Stored Dairy-Cattle Slurry*

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ABSTRACT

Changes in the volatile fatty acids (VFA) content of dairy-cattle liquid manure slurry during its storage in covered concrete tanks, 12·3 x 7·2 x 3·0 m deep, were studied. Slurry was stored from January to October (285 days) in two tanks and, similarly, from June to November (146 days). Slurry samples were collected at regular intervals from each of the tanks at two locations at depths of 0·3, 1·0, 1·8 and 2·5 m below the slurry surface. A centrifuged supernatant of the slurry was analysed for VFA. The temperature history of the stored slurry greatly influenced the VFA concentrations. In all four tanks, for all VFA except iso-valeric acid, concentrations were significantly lower at the 0·3m depth than at greater depths after about 50 days of storage. Concentrations increased during storage in all tanks except that in one of the two winter-filled tanks, total VFA concentration decreased at all depths (luring the last two months of storage, probably due to a shift in microbial activity. The mean concentrations of VFA in all the tanks were substantially in excess of those normally associated with steadily operating methane digesters. Acetic acid was the dominant VFA in every tank, and changes in its concentration set the trend for changes in the concentration of total VFA in the slurry stored in that tank. On a molar basis, concentrations decreased in the order of acetic, propionic, butyric, iso-valeric, isobutyric and valeric acid in all the four tanks. The last three acids accounted for only 6 to 8 of the total VFA.

INTRODUCTION

Animal wastes produced at confined-animal operations are frequently handled in the `liquid' or slurry form. This slurry is usually stored at the farm for some time, with or without additions of fresh slurry, prior to its utilization or disposal. The stored slurry, unless aerated, undergoes anaerobic biodegradation with the production of a number of organic compounds including short-chain volatile fatty acids (VFA). VFA are important intermediates in the production of methane (CH_4) by anaerobic digestion, and their concentration is one of the most important control tests for detecting instability in the anaerobic digestion process (McCarty, 1964; Stafford, 1982). It has been suggested (Asinari Di San Marzano *et al.,* 1981) that controlled storage of manure could act as the first stage of anaerobic digestion systems in which the hydrolysis/ acidogenic phase and the methanogenic phase are separated in two different digesters (Ghosh & Klass, 1978). The VFA content of the wastes from different animal species has been used to characterize substrates in the study of the kinetics of methane fermentation of animal wastes (Hill, 1983; Hill *et al.,* 1983). VFA have been implicated in the malodours associated with manure slurries (Burnett, 1969; Barth *et al.,* 1974; Roustan *et al.,* 1977; Guenzi & Beard, 1981), and the VFA concentration has been suggested as a possible non-sensorial indicator of the odour potential of such slurries (Spoelstra, 1980). Utilization of manures for crop production can be affected by VFA because of their inhibitory effect on the germination of seeds and growth of plants (Takijima, 1964; Clarke& Humphreys, 1970; Schuman & McCalla, 1976). VFA contribute significantly to the biochemical oxygen demand of manure slurries (Williams, 1983). Thus, land application of slurries at high rates could cause phytotoxic effects due to deoxygenation of the soil, and lead to pollution of drainage water.

For better handling and utilization of manures, it is therefore important to know about the changes in VFA concentrations that occur in slurries during farm storage. Most of the present knowledge in this respect appears to be derived from laboratory and small-scale studies, mostly with piggery slurries. The objective of this work was to study the changes in VFA concentrations in dairy-cattle slurry during undisturbed storage in farm-size covered concrete tanks. To assess and compare seasonal effects, slurry characteristics were studied during storage through winter followed by summer, as well as through summer only.

METHODS

The study was conducted at the Research Farm of the Animal Research Centre of Agriculture Canada, near Ottawa, Ontario, Canada.

Manure storage tanks

Slurry was stored in outdoor reinforced-concrete covered tanks. For details of construction, see Turnbull *et a/.* (1971). The tanks were below ground except for the top 0.2 m. The storage site consisted of six separate but adjacent tanks, each 12.3 x 7.2 x 3.0 m deep (Fig. 1). Only tanks 7, 9,10 and 12 were studied. They were washed and cleaned prior to filling. During the study period all six tanks were further covered with 0.15 mm-thick black polyethylene film to prevent entry of rain and snow through ventilation slots in the concrete cover. As the wall-to-floor and wall-to-wall joints in the concrete were not sealed, liquid level recorders were installed on each tank to monitor any seepage into or out of the tanks.

Manure source

Slurry for each tank was obtained from one of the two wings of a 240-cow free-stall barn. Manure accumulated under slotted floors in the barn for six weeks before it was transferred to the storage
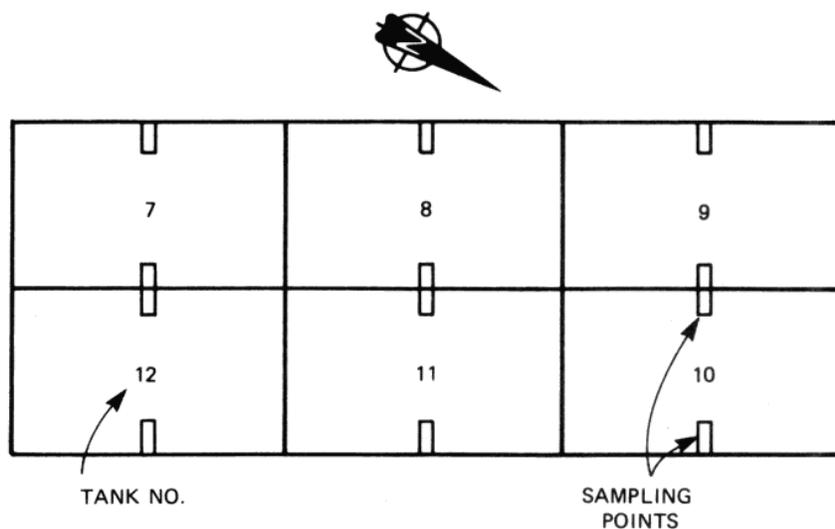

Fig. 1. Diagram of the relative location of covered manure slurry storage tanks, 12.3 x 7.2 x 3.0 m deep each.

tanks, using the minimum necessary dilution water. Tanks 9 and 10 were filled in winter, on 6 January and left undisturbed until 18 October (285 days). Tanks 7 and 12 were filled in the summer, on 9 June, and left undisturbed until 2 November (146 days). The filling and emptying of tanks 8 and 11 were not controlled, and were left to the operational requirements of the farm. A free space of about 0.3 m existed between the manure surface and the concrete cover. The total solids (TS) contents of the slurry transferred to tanks 9, 10, 7 and 12 were 9.8, 8.8, 10.0 and 10.0 %, respectively. Wood shavings, used as bedding in the barns, accounted for about 8 of the TS in the slurry. The cows were fed a combination of alfalfa silage, corn silage, with haylage and/or chopped hay.

Sample collection, processing and analysis

Samples were collected from each tank at two locations (Fig. 1). A long-handled sampler, with a 2-litre bottle equipped with a remotely operated stopper, was used to obtain slurry samples at depths of 0.3, 1.0, 1.8 and 2.5 m below the slurry surface, with minimum possible disturbance. Samples were collected at the time of tank filling, one week later, and at about monthly intervals after the date of filling. One final sample was collected after a thorough mixing of the contents of the tank, prior to hauling for land application. In all, twelve collections each were made from tanks 9 and 10, and seven each from tanks 7 and 12. Sixteen samples were obtained at each collection time (2 tanks x 2 locations x 4 depths).

The temperature of the slurry was determined immediately upon collection using a thermistor probe (Yellow Springs Instrument Co., Yellow Springs, Ohio). Preliminary tests demonstrated that the temperature of the slurry sample immediately upon collection was the same as that obtained by immersion of the thermistor probe to the depth at which the sample was collected.

About 1.5 litres of the slurry sample were blended for 45 s in a Waring blender to make the slurry homogeneous. A 750 ml sub-sample was used to obtain a supernatant by centrifuging at 13 700 g for 20 min at 15ºC. The supernatant pH (Radiometer Model 26 pH meter) was determined. Sub-samples of the supernatant were then frozen for determination of VFA later, as described by Ackman (1972). A 1: 5 aqueous dilution of the supernatant was injected directly on to a 3.6 m-long glass column packed with Chromosorb 101, in a Hewlett Packard Model 5840 gas chromatograph equipped with a flame ionization detector. Formic

acid was added to the carrier gas (helium) to reduce ghosting and tailing. The temperatures of the injection port, the column oven and the detector were 200, 180 and 350ºC, respectively. The analyses were done in triplicate. This method gave the concentrations of acetic, propionic, iso-butyric, butyric, valeric and iso-valeric acids with an accuracy of ±2 % or 10 mg/litre, whichever was greater.

Data were statistically analysed separately for each tank because the slurry used to fill the different tanks was not identical in composition. The least-square significant difference test (t-test) was used to compare the mean concentrations of VFA at the beginning and end of the storage period. Single degrees-of-freedom comparisons were made for VFA concentrations at different depths.

RESULTS

Manure level changes in storage tanks

Continuous recording of slurry levels in the tanks indicated that these did not vary by more than 4 cm above or below the initial filling level. Some of the apparent fluctuations in the manure levels may have resulted from a buoyancy effect of rising gas bubbles on the level-sensing float at the surface. The maximum observed change represented a volume change of less than 1.5 %, indicating that seepage into or out of the tanks was minimal, and the slurry volume was considered to be constant.

Slurry temperature

Variation of the temperature of the slurry with time and depth was much greater in tanks 9 and 10 than in tanks 7 and 12 (Fig. 2) in response to seasonal changes in ambient temperature shown in Table 1. The change of slurry temperature was largest near the surface and smallest near the bottom. In the winter-filled tanks, temperatures started to decrease immediately after filling, and started to increase in April (Fig. 2). In August, the temperature at the 1.0 m depth and below was still rising when the temperature at the 0.3 m depth had started to fall because of falling ambient temperature. The temperature of the slurry at the time of filling was
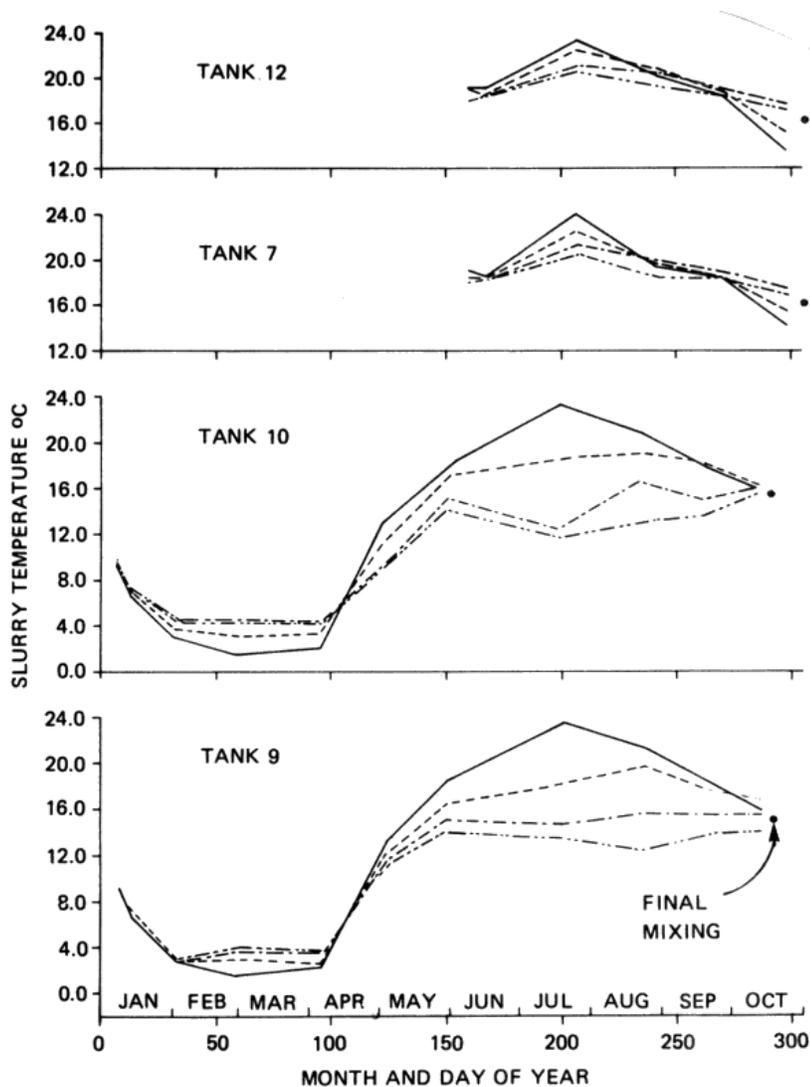
Fig. 2. Changes in slurry temperature with time at depths of 0·3 m (———), 1·0 m (– – – –), 1·8 m (– · – · –), and 2·5 m (– ·· – ·· –) below the surface. Tanks 12 and 7 were filled in summer, tanks 10 and 9 in winter.

higher in tanks 7 and 12 than in the winter-filled tanks (9 and 10). The spread of temperature between different depths was narrower in tanks 7 and 12 than in tanks 9 and 10. The mean temperatures of the slurry on sample collection days in tanks 9, 10, 7 and 12 ranged from 3.0 - 17.5. 3.3 - 17.3, 16.1 - 22.1 and 15.9 - 21.8 °C, respectively. Final mixing resulted in a uniform temperature throughout the slurry.

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TABLE 1

TABLE 1

Monthly Mean Temperatures Recorded at a Weather Station 8 km from the Study Site

Month	Monthly temperature (°C)		
	Mean maximum	Mean	Mean minimum
January	-10.5	- 15.4	- 20.3
February	-5.1	-9.8	-14.4
March	1.5	-3.7	-8.8
April	9.5	4.5	-0.6
May	21.0	15.2	9.4
June	21.9	16.9	11.8
July	27.3	20.6	13.8
August	22.8	17.4	11.9
September	19.9	14.9	9.8
October	14.1	9.2	4.2

Supernatant pH

Variation in the supernatant pH with depth below surface and with time is shown in Fig. 3. The pH tended to be lower in tanks 7 and 12 than in tanks9 and 10. It initially dropped at all depths in all the tanks (for about 50 days), after which it was significantly (P < 0.01) higher at the 0.3 m depth than at greater depths. The trend of pH variation was similar in tanks 7 and 12, and tanks 9 and 10 were similar until late August. In September and October the pH increased at depths of 1 m or more in tank 10 but remained relatively steady in tank 9. After final mixing the mean pH in tanks 9, 7 and 12 was significantly (P < 0.01) lower than that at the time of filling, but in tank 10 it was significantly (P < 0.01) higher. The ranges of mean pH values in tanks 9, 10, 7 and 12 were 6.67–7.24, 6.54–7.31, 6.35–6.74 and 6.34–6.68, respectively.

V FA concentrations

Variation in concentration with depth

In both the summer- and winter-filled tanks, after about 50 days of storage, the concentrations of all VFA except iso-valeric were significantly (P < 0.01) lower at the 0.3 m depth than at greater depths. For the straight-chain acids, concentrations at 0.3 m were as much as 20 to 30 % lower than at greater depths. Typical variation in the mean concentration at each depth
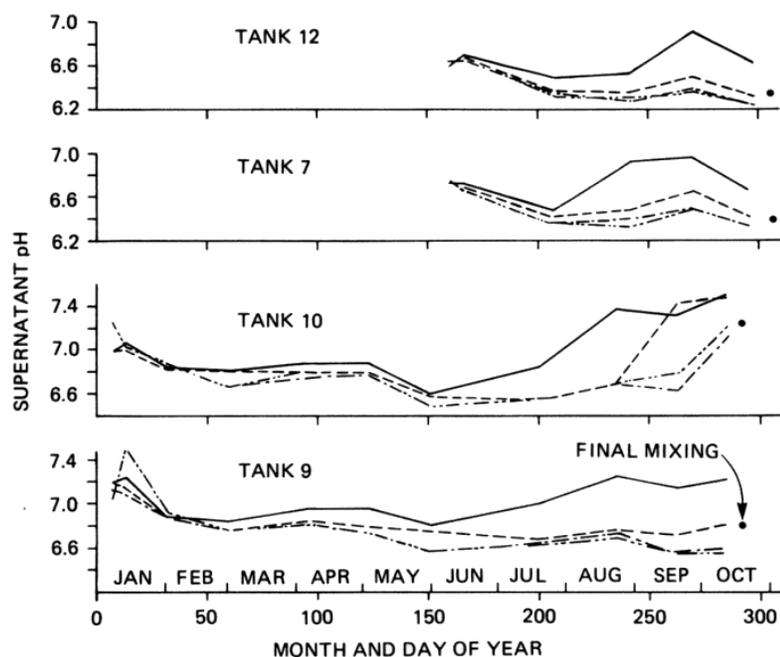
Fig. 3. Changes in supernatant pH with time at depths of 0·3 m (———), 1·0 m (–––––), 1·8 m (–·–·–), and 2·5 m (–··–··–) below the surface.

in different tanks is shown in Fig. 4 for acetic acid. The trends of concentration changes were similar in each pair of tanks until about late August. In September and October a substantial drop in concentration occurred at all depths in tank 10, which corresponded with the increase in pH noted above.

Change in mean concentration with time

The mean (of eight observations per tank) molar concentrations of the total and individual VFA during the storage period are shown in Figs 5-8.The predominant acid was acetic acid, and changes in its concentration set the trend for changes in the total VFA concentrations. Increases in the concentration of all acids occurred in tanks 9 and 10 (Figs 5 and 6) until about 50 days after filling, when the slurry temperatures had reached near-minimum values. Acid concentrations in both tanks then remained relatively steady until about mid-July when another increase occurred lasting until late August. In September and October VFA concentrations tended to remain steady in tank 9, but in tank 10 total VFA, and acetic,
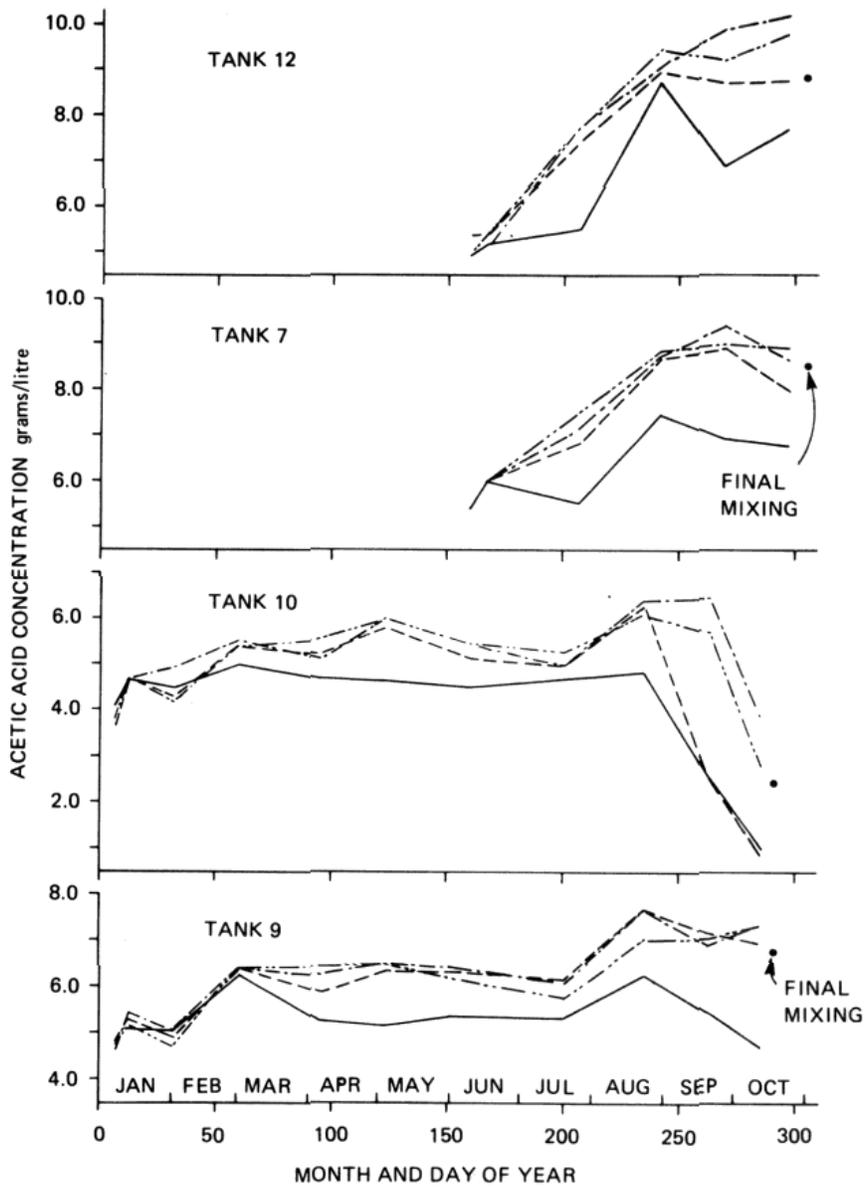
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Fig. 4. Changes in concentration of acetic acid with time at depths of 0·3 m (———),
1·0 m (– – – –), 1·8 m (– · – · –), and 2·5 m (– ·· – ·· –) below the surface.

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Fig. 5. Changes in mean concentration of VFA in tank 9. A = acetic, P = propionic, B = butyric, i-V = *iso*-valeric, i-B = *iso*-butyric and V = valeric acid. Dotted lines indicate final mixing.
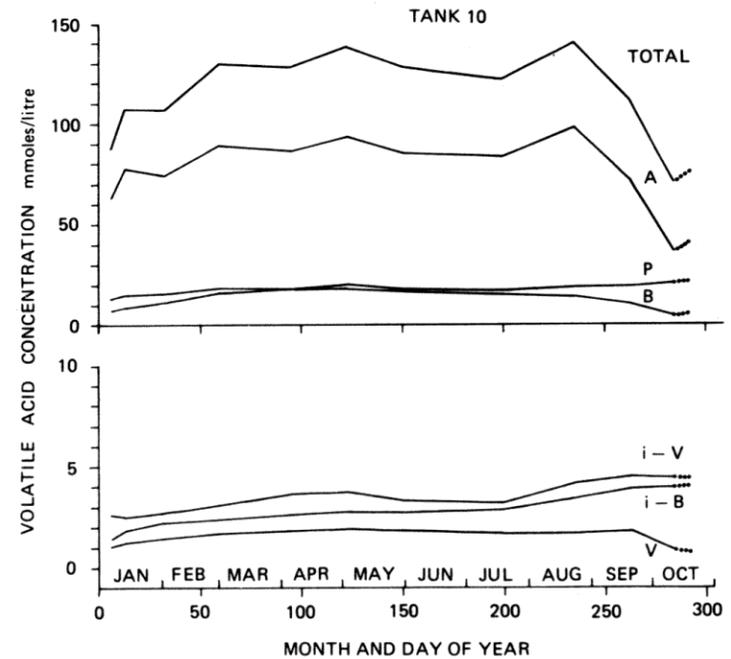
Fig. 6. Changes in mean concentration of VFA in tank 10. A = acetic, P = propionic, B = butyric, i-V = *iso*-valeric, i-B = *iso*-butyric and V = valeric acid. Dotted lines indicate final mixing.
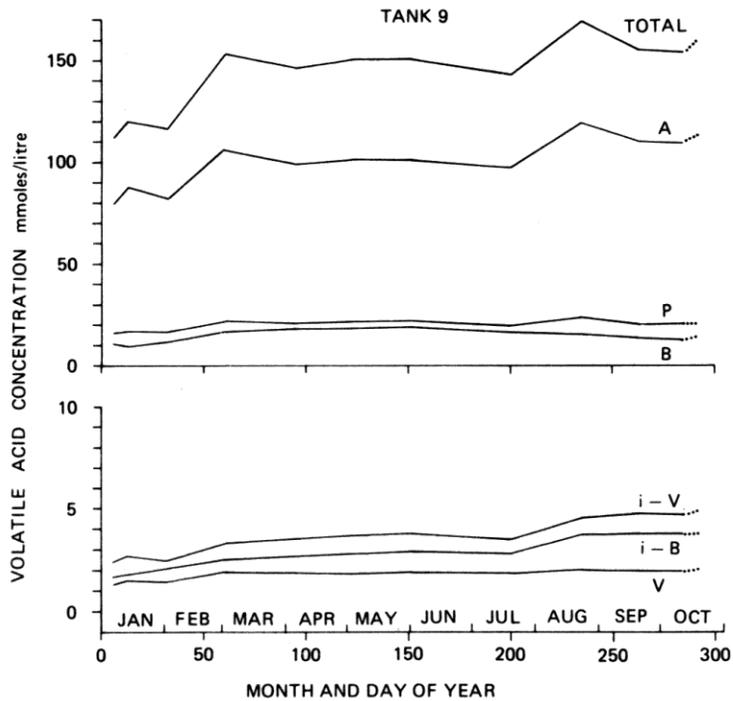
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Fig. 7. Changes in mean concentration of VFA in tank 7. A = acetic, P = propionic, B = butyric, i-V = *iso*-valeric, i-B = *iso*-butyric and V = valeric acid. Dotted lines indicate final mixing.

Fig. 8. Changes in mean concentration of VFA in tank 12. A = acetic, P = propionic, B = butyric, i-V = *iso*-valeric, i-B = *iso*-butyric and V = valeric acid. Dotted lines indicate final mixing.
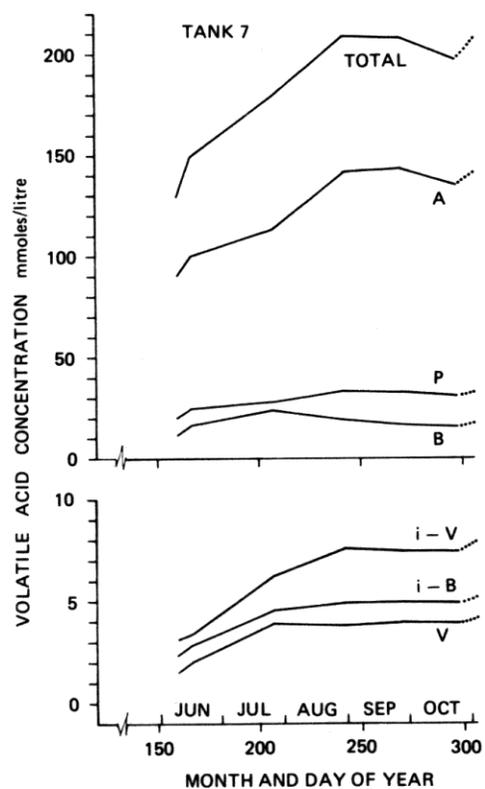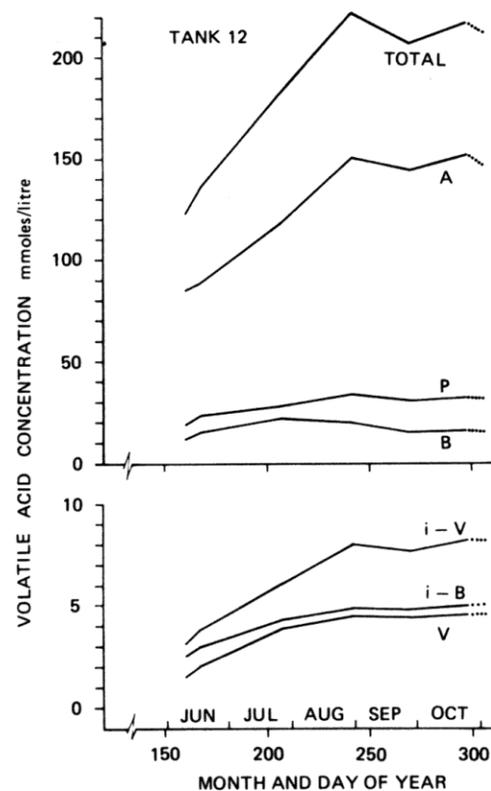
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TABLE 2

Mean Concentrations of VFA in the Stored Dairy Manure Slurry, Initially and After Mixing at the End of the Storage Period

Volatile acid	Mean concentration and standard deviation (mmoles/litre)			
	(285-day storage)		(146-day storage)	
	Tank 9	Tank 10	Tank 7	Tank 12
Total VFA				
Initial	112.2 ± 3.5	87.5 ± 8.9	128.6 ± 5.0	122.5± 11.3
Final	1599 ± 2.2	75.2 ± 3.4	207.6 ± 5.2	2125 ± 4.3
Acetic acid				
Initial	79.5 ± 2.7	63.0 ± 7.2	89.9 ± 4.0	85.0 ± 8.1
Final	113.1 ± 1.6	40.2± 2.3	141.4±3.8	147.2±3.1
Propionic acid				
Initial	16.3± 0.5	12.8± 0.4	20.4± 1.0	18.9± 1.9
Final	21.1± 0.3	20.8± 0.6	32.3±0.7	31.6± 0.7
Butyric acid				
Initial	10.9 ± 0.3	6.67 ± 1.3	11-4 ± 0.6	11.5 ± 2.1
Final	14.6 ± 0.3	5.05 ± 0.3	16.8 ± 0.6	15.7 ± 0.6
iso-Butyric acid				
Initial	1.73±0.10	1.45±0.19	2.31 ±0.12	2.45±0.35
Final	3.99 ± 0.04	3.99 ± 0.25	5.17 ± 0.09	5.19 ± 0.08
Valeric acid				
Initial	1.31 ± 0.15	1.05 ± 0.19	1.47 ± 0.00	1.53 ± 0.17
Final	2.17 ± 0.03	0.82 ± 0.07	4.09 ± 0.13	463 ± 0.09
iso-Valeric acid				
Initial	2.45±0.20	2.57±0.24	3.12±0.15	3.10±0.23
Final	4.97± 0.13	4.43± 0.19	7.87± 0.13	8.19±0.20

Differences between the initial and final values are highly significant (P < 0.01) in all cases.
Each mean value is derived from 8 observations (2 locations, 4 depths).

butyric and valeric acids dropped below the initial concentration (Figs 4 and 6). In the tanks 7 and 12 (Figs 7 and 8), concentrations of all VFA increased for the initial 80 days at a much greater rate than in the winter-filled tanks and then remained relatively steady.

Initial and final concentrations

Slurry in the tanks was well-mixed at the time of filling and after final mixing. Concentrations of all the VFA increased significantly (P < 0.01) in tanks 9, 7 and 12 from the time of filling to final mixing,

TABLE 3

Distribution of Individual VFA as Percentage of Total VFA Molar Basis

Volatile acid	Percentage of total volatile fatty acids			
	(285-day storage)		*(146-day storage)*	
	Tank 9	*Tank 10*	*Tank 7*	*Tank 12*
Acetic				
Mean [a]	69.8	65.3	67.5	68.1
Range	66.9-72.9	46.7-72.6	62.5-69.9	646-69.9
Propionic				
Mean	14.1	17.3	15.8	15.3
Range	13.2-14.9	13.6-34.2	15.5-16.4	14.7-16.9
Butyric				
Mean	10.3	9.8	9.4	9.1
Range	8.0-12.7	4.3 - 13.1	7.8- 13.3	7.2-12.1
iso-Butyric				
Mean	2.0	2.8	2.3	2.3
Range	1.5-2.5	1.6-6.5	1.8-2.6	2.0-2.4
Valeric				
Mean	1.3	1.3	1.8	1.9
Range	1.2-1.4	1.1-1.8	1.1-2.2	1-3-2.2
iso-Valeric				
Mean	2-6	3-5	3.3	3.4
Range	2.2 - 3.1	2.3-7.3	2.3-3.8	2.6-3.9

[a] Values for the mean and range are for 12 sample collections each for tanks 9 and 10, and 7 sample collections each for tanks 7 and 12.

but in tank 10 concentrations of acetic, butyric and valeric acids decreased significantly (Table 2). The total VFA concentrations at the end of the storage period in tanks 9, 10, 7 and 12 were 143, 86, 161 and 173% and the highest concentrations were 151, 161, 162 and 181%, respectively, of the initial concentrations (Figs 5 - 8).

Relative proportions of different acids

The distribution of individual VFA as a percentage of the total remained nearly the same in all tanks during the storage period (Table 3). During September and October in tank 10, the proportion of propionic acid increased while the proportions of acetic and butyric acids decreased. On the average, acetic acid constituted 65-70% of the total VFA, while iso-butyric, valeric and iso-valeric acids together accounted for only 6 - 8%.

No major differences between summer- or winter-filling of the tanks were evident.

DISCUSSION

Slurry temperature

The higher temperature of slurry at the time of filling, and of the ground during the summer kept the slurry at a consistently higher temperature in tanks 7 and 12 than in tanks 9 and 10. In these latter tanks, slurry temperatures were close to the lower limit of the mesophilic range from the time of filling to mid-April (Fig. 2). The slurry temperatures did not exceed 24ºC at any time, and were considerably below the recommended optimum of 35–37ºC for methanogenic cultures (Mah, 1981). During anaerobic digestion of piggery wastes, Van Velsen (1979) found that gas production fell off rapidly below 25ºC and was almost zero at 15ºC. It would appear that the present slurry temperatures would not promote active methane production.

pH

The pH of manure slurries is largely determined by the strength and equilibrium of carbonic acid–bicarbonate buffers, VFA and ammonia. Protein-derived ammonia plays a major role and acts to neutralize the acids produced from the fermentations occurring in manures. In deep storage tanks for slurries, pH would also be a function of depth because of an increasing solubility of carbon dioxide under increasing hydrostatic pressure. Decreasing VFA concentrations would, of course, tend to increase the pH. High pH at the 0.3 m depth than at greater depths in our study (Fig. 3) resulted from lower concentrations of VFA rather than higher concentrations of ammonia. In all four tanks, ammonia concentrations in the slurry after the initial 50 days were, in fact, significantly ($P < 0.01$) lower at the 0.3 m depth than at greater depths (Patni & Jui, unpublished). Slurry ammonia concentration increases of 14, 21, 29 and 29 mmoles/litre in tanks 9, 10, 7 and 12, respectively, were not sufficient to neutralize the increases in VFA concentrations (Table 2, Figs 5–8). The absence of drastic changes in the pH (Fig. 3) indicates that the slurry in the four tanks was well-buffered. The relatively

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rapid increase of pH in tank 10 in September and October was caused mainly by a drop in the concentration of acetic acid (Figs 4 and 6).

Methanogenic bacteria are seriously inhibited at pH below 6.5 (Sawyer& McCarty, 1978) and a pH close to 7.0 is recommended for methanogenic media (Mah, 1981). In two-phase anaerobic digestion of sewage sludge and glucose in the laboratory, Ghosh & Klass (1978) found the optimum pH to be 5.7–5.9 for the fermentative acidification stage and 7.2 for the methanogenic stage. The optimum pH for breakdown of cellulose and other fibres in the rumen is about 6.5 and for cellulolytic enzymes from a variety of sources is 6.7 (Hobson *et al.,* 1981).From these considerations it appears that the pH values in our study (Fig. 3) were generally more favourable for acid than methane production.

VFA concentrations

VFA production and persistence in the slurry (Figs 4–8) would be the result of a dynamic equilibrium between acid production and consumption by oxidation and/or methane formation.

Variation in concentration with depth below surface
The effects of dilution of the slurry due to rain, snow or seepage into or out of the tanks on the concentrations of VFA during storage were, here, practically eliminated. In slurry samples collected at six different piggeries, Spoelstra (1979) found that more diluted wastes tended to have lower VFA concentrations. The lower concentrations of VFA at the 0.3 m depth than at greater depths (Fig. 4), could have been due to a loss of VFA by volatilization at the slurry surface, or to dissimilation by aerobic, facultatively anaerobic or methanogenic bacteria. A significant loss due to volatilization was unlikely because of the low to insignificant amounts of unionized VFA that would exist at the prevailing pH (Fig. 3). Loss due to dissimilation by methanogenic bacteria was probably not important because of unfavourable pH and/or unfavourable temperature most of the time in all tanks. The most reasonable explanation appears to be increased consumption of VFA by aerobic and facultatively anaerobic bacteria at the 0.3 m depth. Faecal wastes contain large numbers of such bacteria (Hobson *et al.,* 1981). Laboratory studies have demonstrated that VFA in manure slurries are lost within a few weeks when the surface of stored slurry is in contact with air (Barth & Polkowski, 1974;

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Stevens &Cornforth, 1974; Cooper & Cornforth, 1978). In the present tanks, air movement was restricted but not absent in the 0.3 m of free space over the slurry surface. Waves of trapped air moving between the concrete and plastic covers on the tanks were often visible. A flotation effect caused by rising gas bubbles may have provided for some mixing of the slurry near the surface in each tank.

It appears that for representative sampling of unmixed slurry from covered farm-size storage tanks, samples for VFA analysis should be collected at depths of about 1 m or more below the surface. Caution is advisable when results from storage studies using small containers are extrapolated to large, farm-size storage tanks. McGill & Jackson (1977) reported that the concentration of VFA in stored piggery slurry tended to be higher as the size of the stored slurry sample increased from 100 to 500 to 1000 mL.

Change in concentration of VFA with time of storage
The initial total VFA concentrations in tanks 9, 10, 7 and 12 (Figs 5 to 8) were 6.0, 7.0, 7.7 and 7.4 g (as acetic acid) per 100 g of TS, respectively. These values are considerably higher than 1.5 g per 100 g of TS in rectal samples of ingesta in cattle (Phillipson, 1970), and 3.2 g per 100 g of TS indairy-cattle manure slurries (Hart & Turner, 1965). Cooper & Cornforth (1978) found the mean concentration of total VFA (as individual acids) in cow manure slurry at ten farms in N. Ireland to be 4.65 g/litre. Higher initial VFA concentrations in our study than in these other studies suggest that the VFA were being produced in the slurry during its storage in the barn for six weeks prior to its transfer to the tanks. Continued acid production until the end of February in tanks 9 and 10 (Figs 5 and 6) indicated that acid-forming bacteria were not completely inhibited for about 30 days after the slurry temperature had dropped below 5 ºC (Fig. 2).Relatively constant VFA concentrations in these tanks from March to mid-July could have been due to near-equal rates of VFA production and consumption. The drastic drop in the total VFA concentration in tank 10 in September and October could have been caused by a spontaneous shift in microbial activity which increased the rate of consumption, mainly of acetic acid, at all depths (Figs 4 and 6). Relatively high VFA concentrations (as acetic acid) of 10,000 to 13,000 mg/litre in tanks 9, 7 and 12 compared to 8400 mg/litre in tank 10 by late August, and other unknown factors, may have inhibited microbial acid consumption in tanks 9, 7 and 12. As methane fermentation in stored farm

wastes is usually not a quantitatively important process (Spoelstra, 1979), carbon dioxide was probably the main product of the increased acid consumption in tank 10.

In the summer-filled tanks 7 and 12 VFA concentrations continued to increase for about 80 days after filling (Figs 7 and 8) and remained nearly constant thereafter. At that time either the acid-forming bacteria were inhibited or acid production and consumption rates were nearly equal. It is also possible that a depletion of easily-fermentable substrate in the slurry stopped further acid production in these tanks.

Both the initial VFA concentrations and their rates of increases were higher in the summer-filled tanks than in the winter-filled tanks, as would be expected. These results are consistent with those of Spoelstra (1979) from laboratory studies with pig manure slurry, in which the rate of increase in the concentration of VFA in the slurry was higher at 25 ºC than at 15 ºC during about 100 h of incubation.

Initial and final concentrations

The maximum increases in VFA concentrations of 151-181 % observed (Table 2) were considerably smaller than increases of 400 in 150 days (Spoelstra, 1979) and 300-900 % in about 200 days (Williams & Evans, 1981) in stored pig manure slurry. This is reasonable because of the relatively less easily fermentable material that is normally present in cattle manures than in pig manures, and also because the slurry in our study had been partly fermented while it was being collected in the barn for six weeks before its transfer to the outdoor tanks.

The VFA concentration in the stored slurry (Table 2) was much higher than the 50-250 mg/litre (as acetic acid) that is common in well-balanced, steadily operating, sludge digesters (Sawyer & McCarty, 1978). It therefore appears that controlled storage of manure slurries might provide the hydrolysis/acidification step in two-phase digestion for methane production as suggested by Asinari Di San Marzano *et al.* (1981). Kennedy & van den Berg (1982) have shown that the hydrolysis/acidification step is the rate-limiting step in anaerobic digestion of piggery wastes. The same should be true for cattle wastes. Because of this limitation, for two-phase systems for livestock wastes to be feasible, hydrolysis/acidification may have to be a batch process while the methanogenic process could be continuous. While controlled storage of livestock manure for near-complete hydrolysis/acidification may be of benefit for methane production, increase of VFA in slurry during storage would tend to increase the

potential for odour nuisance, runoff water pollution, and inhibition of seed germination and/or plant growth when such slurry is applied at high rates on land.

Relative proportions of different acids

Results in Table 3 are consistent with those from studies with pig manure slurries (McGill & Jackson, 1977; Cooper & Cornforth, 1978; Spoelstra, 1979; Williams & Evans, 1981). Even though the relative proportions of individual VFA in the slurry remained fairly constant during storage (Table 3), it appears that uncontrollable shifts in microbial activity can substantially change these proportions in a matter of weeks, as appears to have happened in tank 10 in September and October (Fig. 6). Interestingly, the mean relative proportion of 72.8, 16.8 and 10.4% for acetic, propionic and butyric acids, respectively, in the four tanks (Table 3) was close to the corresponding values of 69.0, 17.7 and 13.3 % reported for the cattle rumen (Hill, 1970).

ACKNOWLEDGEMENTS

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