

Changes in Solids and Carbon Content of Dairy-Cattle Slurry in Farm Tanks*

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(Received 18 June 1986; accepted 7 July 1986)

ABSTRACT

Changes in Total Solids by weight and volume (TS_w and TS_v), Fixed and Volatile Solids (FS and VS) and Total Carbon (TC) in dairy-cattle liquid manure slurry during undisturbed storage in covered concrete tanks, 12.3 x 7.2 x 3.0 m deep, were studied. Slurry with nearly 10% TS_w was stored, from January to October (285 days) in two tanks and, similarly, from June to November (146 days). Slurry samples were periodically collected from each of the tanks at two locations at depths of 0.3, 1.0, 1.8 and 2.5 m below the surface. Slurry TS, were determined by high-speed centrifuging.

Substantial spatial and temporal concentration variations occurred in slurry TS_w , TS_v , FS and VS. Most of the concentration change and loss of TS_w , TS_v and VS was limited to the top 1 m of the slurry. Settling of solids did not appear to be an important process in the stored slurry. Large concentration changes were limited to the top 0.3 m only for about 6 months after winter and 3 months after summer-filling of the tanks. Thus, most of the initial organic matter and biogas generation potential was probably retained in the slurry at depths of 1 m or more. The rate and location of TS_w concentration decreases suggested that VS biodegradation occurred mainly due to aerobic processes, starting near the surface and progressing downwards with time. Mass balances indicated that about one quarter of the initial TS_w , VS and TC were lost by the end of the storage period in all tanks. Correlations between TS_w and TS_v and between wet-basis TC and TS_w or TS_v were highly significant.

* Contribution No. 1402 from Animal Research Centre and 1-826 from Engineering and Statistical Research Centre, Research Branch, Agriculture Canada, Ottawa, Canada, K1A 0C6.

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INTRODUCTION

Animal wastes at confined-animal operations are often handled in the slurry form with little or no bedding added. The slurry is usually stored for some time prior to disposal or utilization. Slurry composition tends to change during storage because of fermentation. The extent of this change depends on several factors including the conditions and duration of the storage period. Loss of nutrients, and hence of the fertilizing value of manure during storage, has been of concern in the past (Vanderholm, 1975; Muck & Steenhuis, 1982; Midwest Plan Service, 1985). With the recent interest in manure utilization for crop and/or biogas production, it is useful to know the extent of changes in the Total and Volatile Solids (TS and VS) content of slurries during storage. Gilbertson *et al.* (1979) reviewed the literature and estimated the loss of VS in systems with pit storage of slurry to be 10% for dairy and beef cattle and sheep manure, and 20% for swine and poultry manure. For crop utilization, the loss of VS from manure represents a loss of organic matter (OM) which would otherwise have been added to the soil with resultant improvements in soil physical properties (Sweeten & Mathers, 1985). Application of organic wastes to the soil increases the soil organic carbon concentration (Khaleel *et al.*, 1981) which improves soil aggregation, water-holding capacity and hydraulic conductivity. Influent solids concentration and organic loading rates are important parameters in the operation of methane (CH₄) digesters (Merkel, 1981). In cold climatic regions, storage of manure slurry may actually be desirable to obtain a better balance between the demand and supply of biogas energy. For example, energy demand increases during the autumn and winter months, so storage of manure prior to digestion for CH₄ production may be advisable. Edelmann *et al.* (1981) compared gas production from stored and fresh manures and found that storage of dairy-cattle slurry at 15-19°C for 50 days resulted in a significant decrease in the production of biogas, apparently due to a destruction of digestible OM. While the loss of OM from stored slurry may lead to a loss in the potential for CH₄ production and for improvement in soil physical properties, the accompanying loss in slurry TS could be an advantage in terms of the ease of slurry handling. In general, the higher the TS concentration in slurry, the more difficult it is to keep slurry pumps operating (Hart *et al.*, 1966), and the greater is the frictional pressure drop in slurry pipelines (Rolfes *et al.*, 1977; Patni, 1981). Information is required on the transformations and losses of TS, VS and carbon (C) in stored slurries in order to develop guidelines for improved management and utilization of manure slurries.

The objectives of the work reported here were to determine the spatial and temporal changes in the Total Solids (by weight, TS_w as well as by volume, TS_v), Fixed Solids (FS), VS (= TS_w - FS),

and Total Carbon (TC) in dairy-cattle slurry during undisturbed storage in farm-sized, covered concrete tanks, and the loss of TS_w, FS, VS and TC from winter- and summer-filled tanks. Changes in slurry Volatile Fatty Acid (VFA) content during the same study were reported earlier (Patni & Jui, 1985).

METHODS

The study was conducted at the Research Farm of the Animal Research Centre, near Ottawa, Ontario, Canada. The slurry storage tanks had been in use for about thirteen years prior to this study.

Procedure

Slurry from a free-stall dairy-cattle barn was stored in outdoor, adjacent, covered concrete tanks, 12.3 x 7.2 x 3.0 m deep. The site consisted of six tanks that were built with their tops extending 0.2 m above ground. After prior cleaning, four of the six tanks were used in the study. The stored slurry was left undisturbed for 285 days (January 6 to October 18) in two tanks, identified as Tanks 9 and 10, and for 146 days (June 9 to November 2) in two additional tanks, identified as Tanks 7 and 12. Slurry samples were periodically collected from each tank at two locations at depths of 0.3, 1.0, 1.8 and 2.5 m below the surface (eight samples per collection per tank), twelve times from Tanks 9 and 10, and seven times from Tanks 7 and 12. This included samples collected immediately after filling of the tanks, and at the end of the storage period after a thorough mixing of the slurry by circulation using centrifugal pumps. Entry of rain and snow into the tanks was prevented by an additional cover of 0.15 mm thick polyethylene sheet on the tanks. Prior to its transfer to the outdoor tanks, manure collected in 1.3 m deep concrete trenches beneath slotted floors inside the barn for a 6-week period. About 8% of the TS in the slurry were from wood shavings used as bedding in the barns.

Sample and data processing and analysis

Two-litre samples of slurry were collected at each sampling point. Slurry temperature was determined immediately upon collection using a YSI thermistor probe. About 1.5 litres of the slurry sample was blended in a Waring blender for 45 s to make the slurry homogeneous. Subsamples of the blended slurry were used for the determination of TS_w in duplicate, by drying for 24 h at 103°C. The dry slurry solids from duplicate analyses were combined and ground to a 20 mesh size for FS

and TC analysis later. Fixed Solids were determined by ignition at 550°C in a muffle furnace for 2 h and TC was determined using a Coleman Model 33 carbon and hydrogen analyzer. To reduce the analytical requirements, FS were analyzed for ten out of the twelve sample collection days in Tanks 9 and 10, and five out of the seven sample collection days in Tanks 7 and 12. Total C was analyzed for seven sample collection days in Tanks 9 and 10, and five sample collection days in Tanks 7 and 12. Volatile Solids were determined as loss in TS_w upon ignition. Total Solids by volume in the slurry were determined by centrifuging a 750-ml subsample of the slurry at 13,700 g for 20 min at 15°C and decanting the supernatant.

Data were analyzed both separately for each tank, and for pairs of tanks based on winter- and summer-filling. An analysis of variance (ANOVA) was carried out for each variable. The mean concentrations at the beginning and end of the storage period were compared. Linear regressions were used to establish relationships amongst TS_w , TS_v and TC. Mass balances were made to determine losses during storage.

RESULTS

Slurry volume

Continuous records indicated that slurry levels in the tanks did not vary by more than 4 cm above or below the initial-filling level. The small fluctuations in the slurry levels were probably due to a buoyancy effect on the level-sensing float due to foam at the slurry surface. Slurry levels did not rise appreciably following rainstorms nor did they fall when the adjacent tanks were empty or during the summer when the water table was lower than the bottom of the tanks. This indicated that seepage into or out of the tanks was practically absent. Absence of a dry crust on the slurry surface suggested that evaporative losses from the covered tanks were relatively small. The volume of the slurry during storage was considered to be constant since it did not vary by more than 1.5% in any of the tanks.

Slurry temperature

Slurry temperatures at different depths during the storage period are shown in Fig. 1. The temperature changed in response to changes in the ambient temperature, with the greatest change occurring near the surface and the smallest near the bottom. The mean temperature of the slurry on

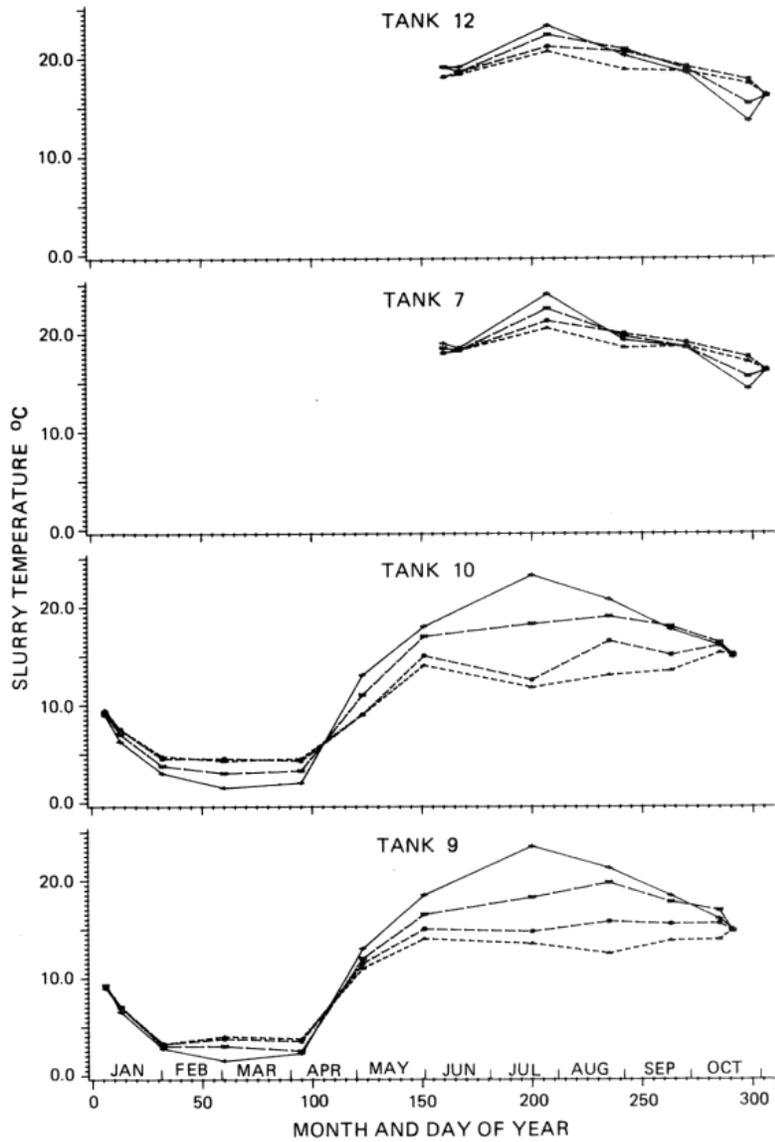


Fig. 1. Changes in slurry temperature at depths of 0.3 m (—), 1.0 m (---), 1.8 m (---) and 2.5 m (-----) below the surface. (Note: More broken the line, greater the depth below surface.) The slurry was mixed prior to the last sample collection.

the sampling days ranged from 3° to 17°C in Tanks 9 and 10, and from 16° to 22°C in Tanks 7 and 12. In Tanks 9 and 10 the slurry temperature was below 5°C at all depths from late January to early April. It did not exceed 16°C in the bottom half of these tanks at any time. Freezing of the slurry was absent in spite of subfreezing ambient temperatures because of the insulation provided by the snow cover on the tanks and the adjacent ground, the concrete and polyethylene covers, the free space of about 0.3 m below the covers, and the relatively stable foam on the slurry surface. In Tanks 7 and 12, the slurry temperature was always 18°C or more except in October.

TABLE 1
Analysis of Variance of TS_w , TS_v , FS and TC Concentrations in Winter- and Summer-filled Tanks ^a

Source of variation ^b	Slurry component, degrees of freedom (df) and mean square (ms)							
	TS_w		TS_v		FS		TC	
	df	ms	df	ms	df	ms	df	ms
Winter-filled tanks (9 and 10)								
T	1	24.91**	1	114.55**	1	0.38	1	0.10
C	11	13.70**	11	238.40**	9	34.30**	6	6.60**
D	3	86.19**	3	3051.47**	3	164.30**	3	9.79**
T x C	11	0.19	11	20.89**	9	0.84	6	1.85**
T x D	3	0.36	3	44.05**	3	1.42	3	0.55
C x D	33	5.30**	33	181.30**	27	17.06**	18	1.75**
T x C x D	33	0.39**	33	16.57*	27	2.11*	18	0.85**
Residual	96	0.18	96	10.22	80	1.26	56	0.37
Summer-filled Tanks (7 and 12)								
T	1	0.00	1	50.89**	1	10.59**	1	1.65
C	6	12.28**	6	163.60**	4	27.69**	4	3.38**
D	3	23.28	3	792.96**	3	38.44**	3	1.68*
T x C	6	0.03	6	2.25	4	0.38	4	0.53
T x D	3	0.05	3	2.10	3	0.11	3	0.69
C x D	18	4.73**	18	155.76**	12	21.43**	12	1.06*
T x C x D	18	0.06	18	2.98	12	0.31	12	0.41
Residual	56	0.09	56	4.75	40	0.34	40	0.44

^a TS_w = Total Solids by weight. TS_v = Total Solids by volume. FS = Fixed Solids. TC = Total Carbon.

^b T = tank, C = sample collection day, D = sampling depth.

** and * = significant at $P < 0.01$ and 0.05 , respectively.

Slurry composition changes

An analysis of variance (ANOVA) of TS_w, TS_v, FS and TC concentrations in the winter- and summer-filled tanks indicated that the sample collection day, sampling depth and collection day by depth interaction were the major sources of variation (Table 1). The observed concentration changes for these slurry components are shown in Figs 2 to 5.

Total solids

There was a significant ($P < 0.05$) overall decrease in both TS_w and TS_v from the time of filling to the final mixing at the end of the storage period (Table 2). Most of the decrease of TS_w (Fig. 2) and

TABLE 2
Mean Concentrations of Slurry Components, Initially and After Mixing
at the End of the Storage Period

Slurry component ^a	Mean and standard error ^b			
	285-days storage		146-days storage	
	Tank 9	Tank 10	Tank 7	Tank 12
TS _w (% w/w)	9.81	8.80	10.02	10.02
Initial				
Final	7.35	6.63	7.99	7.89
Std. error		0.21		0.15
TS _v (% v/v)	44.2	40.9	45.2	44.3
Initial				
Final	36.9	35.2	39.9	37.6
Std. error		1.60		1.09
FS (% TS _w)	13.94	13.73	13.48	14.28
Initial				
Final	15.44	15.46	15.60	16.17
Std. error		0.56		0.29
TC (% TS _w)	46.6	45.6	44.6	44.8
Initial				
Final	44.8	44.7	44.1	43.4
Std. error		0.30		0.33

^a TS_w = Total Solids by weight, TS_v = Total Solids by volume. FS = Fixed Solids (ash), TC = Total Carbon.

^b Differences between the initial and final values are significant at least at $P < 0.05$ for all variables in all tanks except for TC in Tank 7. Each mean value is derived from eight observations (two locations, four depths).

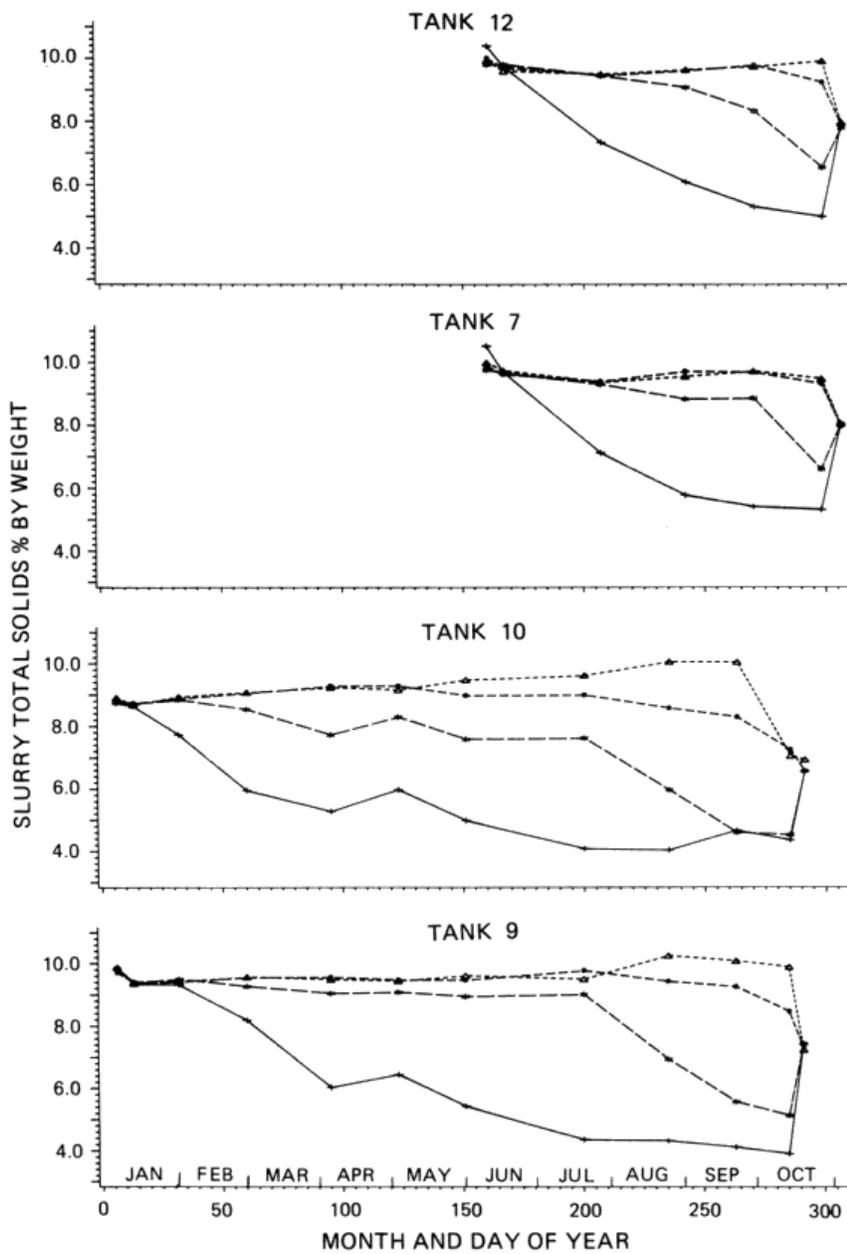


Fig. 2. Changes in slurry Total Solids by weight at depths of 0.3 m (—), 1.0 m (---), 1.8 m (---) and 2.5 m (----) below the surface.

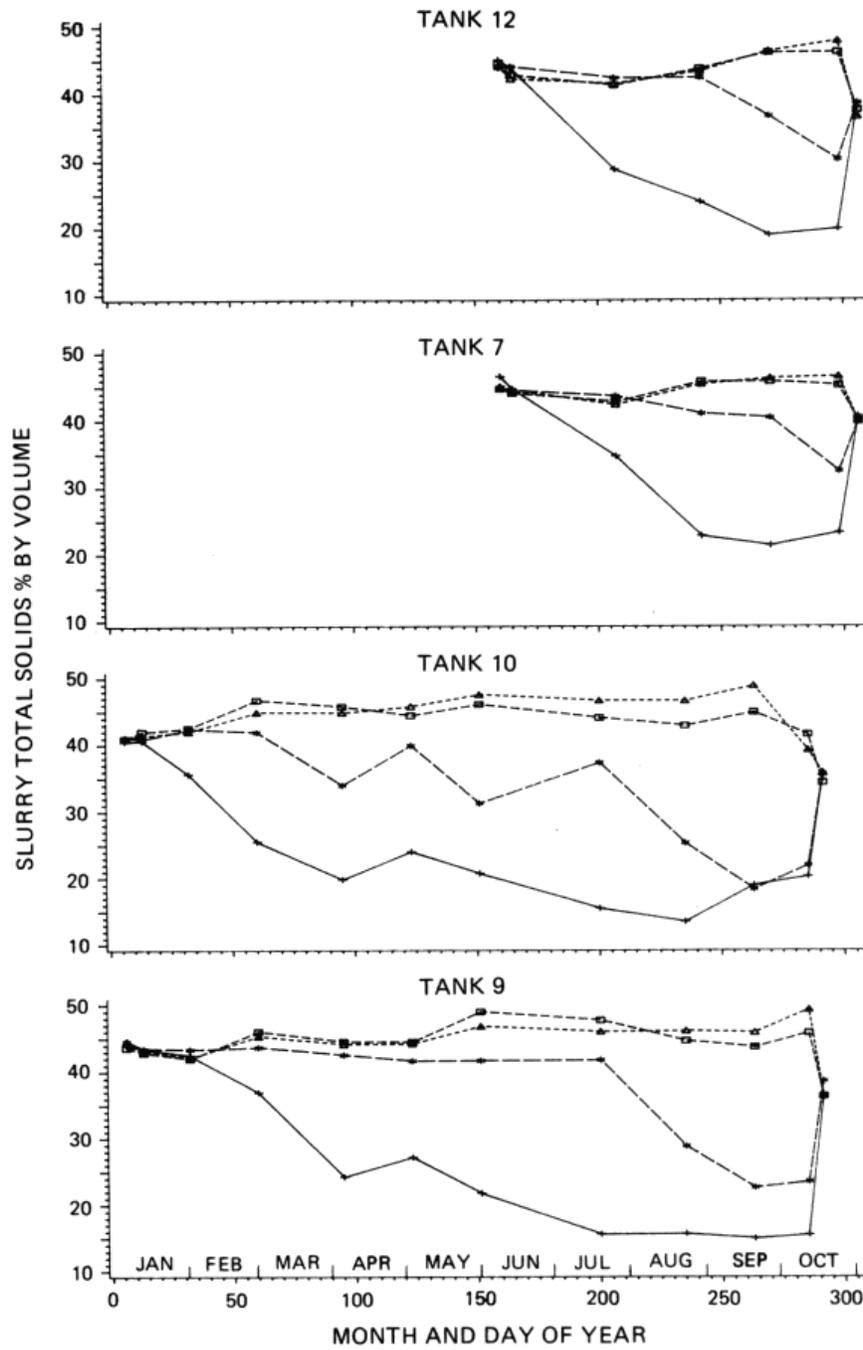


Fig. 3. Changes in slurry Total Solids by volume at depths of 0.3 m (—●—), 1.0 m (—■—), 1.8 m (—▲—) and 2.5 m (—◆—) below the surface.

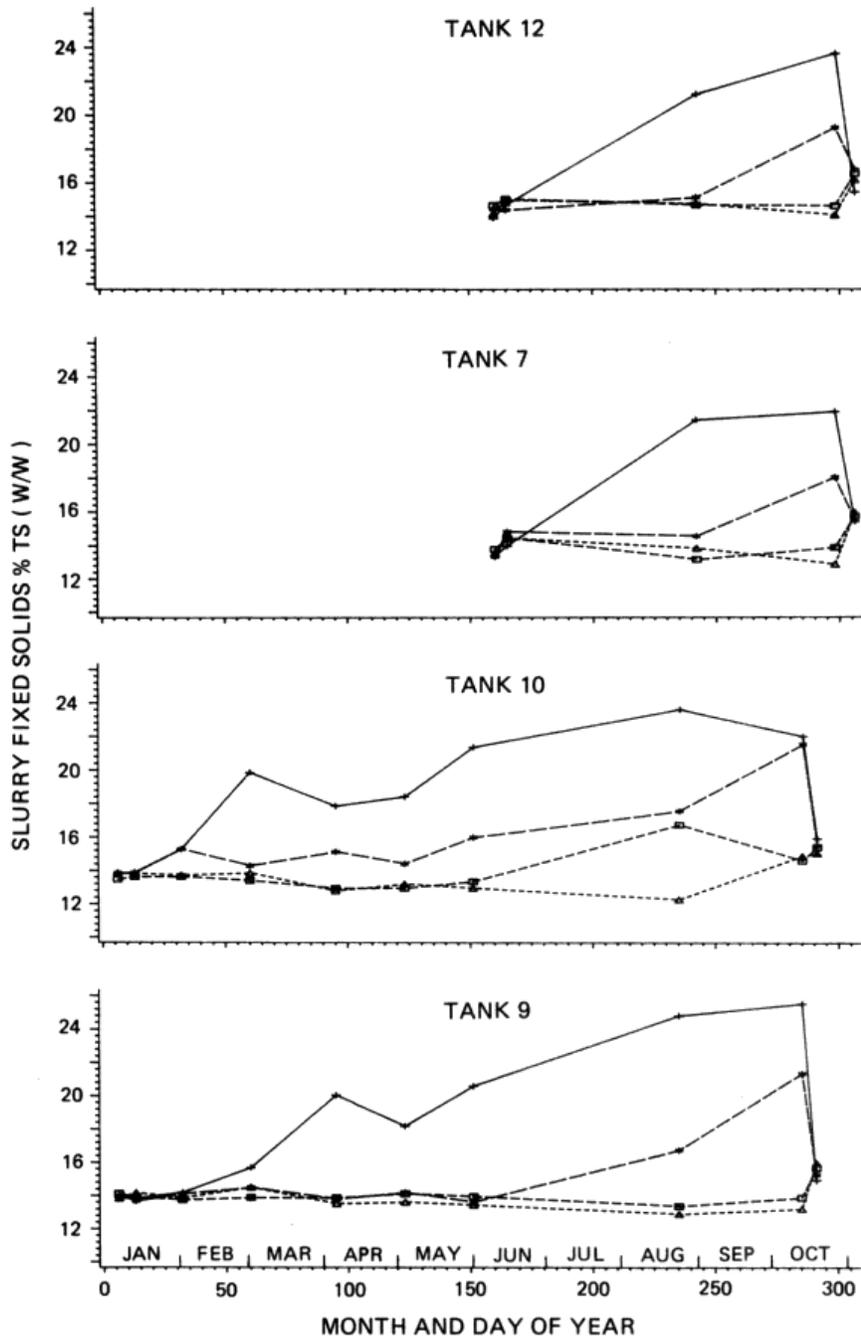


Fig. 4. Changes in slurry Fixed Solids (dry basis) at depths of 0.3 m (—●—), 1.0 m (—■—), 1.8 m (—▲—) and 2.5 m (—◆—) below the surface.

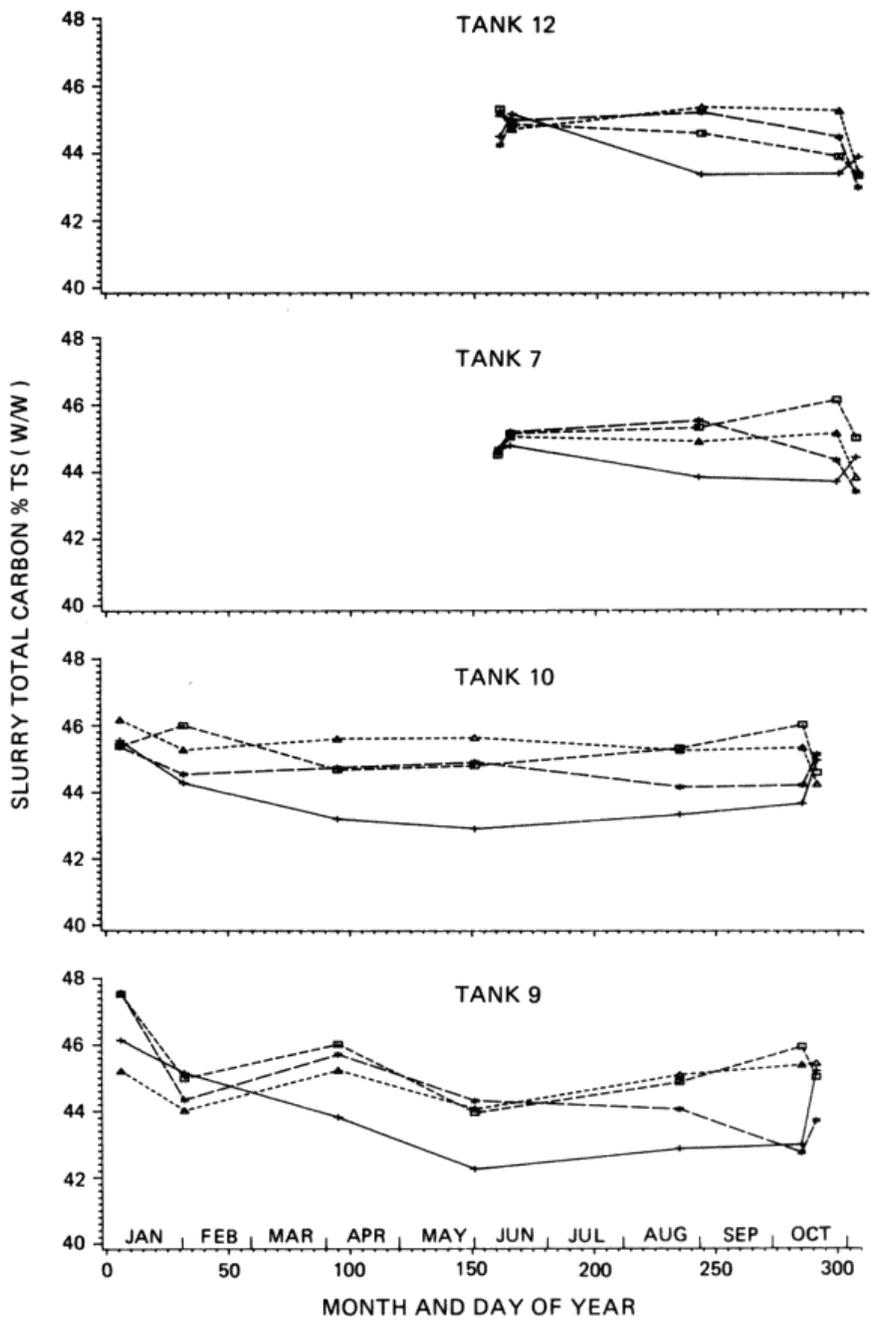


Fig. 5. Changes in slurry Total Carbon (dry basis) at depths of 0.3 m (—), 1.0 m (---), 1.8 m (· · ·) and 2.5 m (- - - -) below the surface.

TS_v (Fig. 3) in the undisturbed slurry occurred at the 0.3 and 1.0 m depths, and it was not accompanied by a corresponding increase at greater depths. Increase of TS_w and TS_v at the 1.8 and 2.5 m depths was relatively small, and it occurred mostly during late summer. In all tanks, within a few weeks after filling, TS at the 0.3 m depth were significantly ($P < 0.01$) lower than at greater depths. In Tanks 9 and 10, a small increase in TS at the 0.3 m depth was noticeable in April (Figs 2 and 3). This increase probably resulted from a flotation of slurry solids by dissolved gases released in the slurry because of a sharp rise in slurry temperature at that time (Fig. 1). The decrease in TS_w initially occurred at the 0.3 m depth only in all tanks (Fig. 2). After some time, a small decrease in TS_w occurred at the 1.0 m depth also, and it increased sharply when TS_w at the 0.3 m depth stabilized, by July in Tanks 9 and 10, and by August in Tanks 7 and 12. The rate of the sharp decrease at the 1.0 m depth was similar to that at the 0.3 m depth earlier, which is indicated by similar slopes of the TS_w lines at these two depths. Furthermore, in Tanks 9 and 10, there appeared to be a tendency for at the 1.8 m depth to decrease sharply as TS_w at the 1.0 m depth tended to stabilize. However, this was not sufficiently established by the time the study was terminated (to provide storage space for winter-produced slurry at the Farm). A mass balance for TS_w in the different tanks is shown in Table 3. An average 25% of the initial TS_w in Tanks 9 and 10, and 21%

TABLE 3
Mass Balance for Solids and Total Carbon in Slurry Stored in Tanks

<i>Slurry component^a</i>		<i>285-days storage</i>		<i>146-days storage</i>		
		<i>Tank 9</i>	<i>Tank 10</i>	<i>Tank 7</i>	<i>Tank 12</i>	
TS _w	— initial	(kg)	23,730	21,290	24,240	23,260
	— final	(kg)	17,780	16,040	19,330	18,320
	— loss	(%)	25.1	24.7	20.3	21.2
FS	— initial	(kg)	3,310	3,920	3,270	3,320
	— final	(kg)	2,750	2,480	3,020	2,960
	— loss	(%)	16.9	15.1	7.6	10.8
VS	— initial	(kg)	20,420	18,370	20,970	19,940
	— final	(kg)	15,030	13,560	16,310	15,360
	— loss	(%)	26.4	26.2	22.2	23.0
TC	— initial	(kg)	11,060	9,710	10,810	10,420
	— final	(kg)	7,970	7,170	8,520	7,950
	— loss	(%)	27.9	26.2	21.1	23.7

^a TS_w = Total Solids by weight. FS = Fixed Solids (ash).
VS = Volatile Solids (= TS_w - FS). TC = Total Carbon.

in Tanks 7 and 12, were lost during storage. The rate of loss per unit of time was greater in Tanks 7 and 12 than in Tanks 9 and 10.

Changes in TS_v (Fig. 3) closely followed the pattern of TS_w changes. Analysis of the data for TS_w and TS_v indicated a highly significant correlation between the two. The coefficients of the regression equation:

$$TS_w = a_1 + b_1 TS_v \quad (1)$$

were determined (Table 4) for TS_w ranging from nearly 4% to 10% by weight, and TS_v from 20% to 50% by volume. High values of the coefficient of determination (R^2) in all tanks suggest that TS_v determinations using high-speed centrifuging can be used to obtain reliable estimates of TS_w .

TABLE 4
Coefficients of Regression Equation (1) ^a

<i>Coefficient</i>	<i>Values of coefficients</i>				
	<i>285-days storage</i>		<i>146-days storage</i>		<i>All tanks</i>
	<i>Tank 9</i>	<i>Tank 10</i>	<i>Tank 7</i>	<i>Tank 12</i>	
a,	1.62	1.70	1.23	1.83	1.57
b,	0.176	0.162	0.185	0.175	0.174
R ²	0.908	0.905	0.919	0.859	0.887

^a Regression equation: $TS_w = a_1 + b_1 TS_v$
n = 96 for Tanks 9 and 10, 56 for Tanks 7 and 12 and 304 for all tanks.

rapidly. Figures 2 and 3 indicate that changes in TS_w and TS_v were a function of both the storage duration and the depth below the surface. The changing rate of decrease in TS_w at different depths has not been adequately recognized in previous farm-scale studies because of the confounding influence of other factors such as dilution by rain, loss by seepage, and periodic addition of fresh manure to stored manure. Slurry temperature would also affect changes in TS_w and TS_v because of the effect on biochemical reactions and gas solubility. The temperature effect was, at least in part, responsible for the longer time to reach relatively 'steady-state' TS values at the 0.3 m depth in Tanks 9 and 10 (200 days) than in Tanks 7 and 12 (100 days).

Analysis of data for TS_w at the 0.3 m depth during the period of decreasing TS ; that is, the 'non-steady state' transient period, revealed that the TS_w decrease was closely approximated by the expression for a first-order type of reaction:

$$TS_{w,t} = TS_{w,0} e^{-kt} \quad (2)$$

where $TS_{w,t}$ and $TS_{w,0} = TS_w$ at time t and initially, respectively, $k =$ rate constant (day^{-1}), and $t =$ time (day). Values of k were established from a least-squares analysis of the pooled, transient-period data for Tanks 9 and 10, and Tanks 7 and 12. Using Eqn (2), the value of k was determined to be 0.0041 day^{-1} for Tanks 9 and 10, and 0.0067 day^{-1} for Tanks 7 and 12, for corresponding mean slurry temperatures of 10.0°C and 20.6°C , respectively, which were established graphically. Equation (2) predicts TS_w reasonably well in all tanks (Table 5), in spite of the disturbing effects of temperature changes and the associated release of dissolved gases in the slurry.

TABLE 5
Difference between Predicted [Eqn (2)] and Observed Values of TS_w ,
at the 0.3 m Depth During the Transient Period ^a

<i>Winter-filled tanks, k = 0.0041</i>			<i>Summer-filled tanks, k = 0.0067</i>		
<i>Days after</i>	<i>Difference (%)</i>		<i>Days after</i>	<i>Difference (%)</i>	
<i>filling</i>	<i>Tank 9</i>	<i>Tank 10</i>	<i>filling</i>	<i>Tank 7</i>	<i>Tank 12</i>
7	2.29	-1.83	7	3.46	2.03
26	-5.10	1.62	47	7.24	4.42
54	-3.75	17.51	82	3.73	0.26
89	13.35	14.88	110	-8.60	-4.12
117	-5.27	-9.77			
145	0.42	-3.43			
194	2.24	-3.40			

^a Difference = $100.0 \times (TS_w \text{ predicted} - TS_w \text{ observed}) / TS_w \text{ observed}$. The mean temperature of the slurry during the transient period was 10.0°C in Tanks 9 and 10, and 20.6°C in Tanks 7 and 12.

Fixed solids

A small but significant ($P < 0.05$) overall increase in slurry FS, from 13-14% of TS_w initially to 15-16% at the end of the storage period, occurred in all tanks (Table 1). In the undisturbed slurry, the increase in the dry-basis FS occurred mainly at the 0.3 and 1.0 m depths (Fig. 4). As with TS_w and TS_v changes, this increase occurred initially at the 0.3 m depth only. After some time when FS at the 0.3 m depth began to stabilize, FS at the 1.0 m depth began to increase sharply. Near the end of the storage period, small increases in FS (Fig. 4) and decreases in TS_w and TS_v , (Figs 2 and 3) were noticeable at the 1.8 and 2.5 m depths in Tank 10 but not the other tanks. The dominant biochemical processes may have been different in Tank 10 from those in the other tanks at that time. This was suggested by a sharp decrease in the VFA concentrations at all depths in Tank 10 but not in

the other tanks (Patni & Jui, 1985).

A mass balance for FS in the slurry (Table 3) indicated that 7.6% to 16.9% of the FS initially present were lost during storage. This loss of FS, particularly in Tanks 9 and 10, is too large to be explained by the variability of FS concentrations in well-mixed slurry (Table 1) and/or analytical precision and accuracy. Possible explanations for the apparent decrease in FS are discussed later.

Volatile solids

Changes in slurry VS can be visualized from the FS changes in Table 2 and Fig. 4 since $VS = TS_w - FS$. A small overall decrease occurred in the VS concentration from 86 - 87% of TS_w initially to 84 - 85% finally (Table 2). In undisturbed slurry, the decrease in slurry VS occurred mainly at the 0.3 and 1.0 m depths. Lack of a substantial change in both TS_w and FS, and hence in VS at the 1.8 and 2.5 m depths in all tanks (Figs 2 and 4) suggests that VS loss from these depths was small, irrespective of winter- or summer-filling of the tanks. However, this did not mean that the lower part of the tanks acted merely as a holding pit for the slurry. Significant microbial activity at all depths in all tanks was indicated by substantial increases in VFA (Patni & Jui, 1985) as well as ammoniacal nitrogen concentrations (Patni & Jui, 1983). A mass balance for VS in each tank is given in Table 3. An average 26% VS in Tanks 9 and 10, and 23% in Tanks 7 and 12, were lost during storage. The VS mass balance is based on FS concentrations in oven-dried (103°C) slurry solids (TS_w). The

TABLE 6
Coefficients of Regression Equations (3) and (4)^a

<i>Coefficient</i>	<i>Values of coefficients</i>				
	<i>285-days storage</i>		<i>146-days storage</i>		<i>All tanks</i>
	<i>Tank 9</i>	<i>Tank 10</i>	<i>Tank 7</i>	<i>Tank 12</i>	
a_2	-0.227	-0.159	-0.176	-0.204	-0.165
b_2	0.477	0.471	0.468	0.469	0.468
R^2	0.989	0.996	0.993	0.963	0.987
a_3	0.401	0.475	0.180	0.322	0.348
b_3	0.086	0.081	0.091	0.090	0.087
R^2	0.910	0.888	0.903	0.874	0.894

^a Regression equations: $TC_{wb} = a_2 + b_2 TS_w$ and $TC_{wb} = a_3 + b_3 TS_v$; $n = 56$ for Tanks 9 and 10, 40 for Tanks 7 and 12, and 192 for all tanks.

proportion of slurry solids subject to volatilization at 103°C may have been different initially and at the end of the storage period.

Total carbon

Small but significant ($P < 0.05$) decreases in dry-basis TC concentrations were observed in all tanks except Tank 7 (Table 2, Fig. 5). There appeared to be a tendency for TC at the 0.3 m depth to be marginally lower than at greater depths. Changes in TS_w and TC at the different depths (Figs 2 and 5) suggest that TC losses paralleled TS_w losses in the slurry, so that there was little change in TC relative to TS_w . On average, 27% of the initial TC was lost in Tanks 9 and 10 compared with 22% in Tanks 7 and 12 (Table 3). It is noteworthy that percentage losses of TS_w , VS and TC were similar in each of the tanks. Conversion of the dry-basis concentrations of TC to wet-basis concentrations (TC_{wb}) indicated that changes in slurry TC_{wb} closely followed changes in slurry TS_w . Regression equations were developed relating TC_{wb} to TS_w , and also to TS_v since TS_v can be relatively rapidly determined.

$$TC_{wb} = a_2 + b_2 TS_w \quad (3)$$

$$TC_{wb} = a_3 + b_3 TS_v \quad (4)$$

The values of the regression coefficients are given in Table 6.

DISCUSSION

Slurry volume and temperature

Lack of a significant change in the volume of slurry stored in the tanks appeared to be due to a sealing of the non-watertight joints in the concrete and/or the soil immediately adjacent to the tanks. The ability of cattle manure to seal soils of different types has been demonstrated in several laboratory, as well as field, studies (Davis *et al.*, 1973; Chang *et al.*, 1974; Baier *et al.*, 1974; Hills, 1976; DeTaar, 1979; Barrington & Jutras, 1985; Miller *et al.*, 1985; Rowsell *et al.*, 1985). Sealing of soils can occur by physical, chemical or biological mechanisms (Davis *et al.*, 1973). Results from the studies of Chang *et al.*, Hills, Barrington and Jutras and Rowsell *et al.* suggest that a mat formation at the soil surface and physical clogging of the soil pores by manure particulate material is the main initial mechanism of soil sealing, and that biological sealing by microbial products such as polysaccharide and polyuronide gums becomes significant after a few months. Sealing due to

chemical mechanisms, such as soil deflocculation by sodium ions, does not appear to be important. The rate of physical sealing increases as the manure TS quantity and size increase and soil pore size decreases (Barrington & Jutras, 1985). The slurry used in our study contained about 10% TS_w compared with < 1 to 5% in the above studies. Coarse solids had been removed from the slurry in most of these other studies. The lack of a fall in slurry levels in full tanks adjacent to empty tanks suggests that the void spaces in the unsealed concrete were sealed by the slurry. Our results tend to support the observation of Jongebreur *et al.* (1979) that sealing of seams in above-ground, large concrete tanks built from prefabricated elements is necessary only for the storage of urine.

Slurry temperature in all tanks was considerably below the recommended optimum of 35-37°C for methanogenic cultures (Mah, 1981). The activity of methane bacteria tends to be limited at temperatures below 15°C whereas acid-producing bacteria can be active down to 4°C (Barth, 1985). Indeed, substantial increases in VFA concentration occurred in Tanks 9 and 10 during the winter when the slurry temperature was between about 2 and 5°C (Patni & Jui, 1985). The higher temperature of the slurry initially, and of the ground during the summer, kept the slurry at a consistently higher mean temperature in Tanks 7 and 12 than in Tanks 9 and 10. Temperature variation was, probably to a large extent, responsible for the major sources of variation indicated in Table 1.

Total solids

Changes in TS_w due to settling of solids

Lack of a significant increase in slurry TS_w at the 1.8 and 2.5 m depths, corresponding to the substantial decrease at the 0.3 and 1.0 m depths, suggests that either the settling of solids was not an important process during the undisturbed storage of slurry, or that increase in TS_w at the 1.8 and 2.5 m depths due to settling of solids was balanced by a nearly equivalent decrease due to settling out and/or volatilization of solids. Also, gases formed in the fermenting slurry at these depths may have prevented or reduced settling of solids by a flotation effect. However, these latter processes do not appear to have occurred to any large extent because almost all of the observed loss of TS_w in all the tanks at the end of the storage period could be accounted for by the loss at the 0.3 and 1.0 m depths. The decrease in TS_w at these depths therefore appears to have occurred mainly due to volatilization rather than settling of solids.

Settling of solids in suspension occurs under the influence of the gravitational force which is opposed by the buoyancy and drag forces (Fair *et al.*, 1968). Factors that affect settling include the size, shape, density and volumetric concentration of the suspended particles, and the density,

viscosity—and hence the temperature of the fluid in which the particles are suspended. The particle density of fresh dairy cattle manure is about 1.2 to 1.6 g cm⁻³ (Sobel, 1966). However, manure solids absorb water and swell substantially on exposure to water (Azevedo & Stout, 1974). This effect, and the inclusion of bedding and some spilled feed in the manure, would tend to reduce its effective particle density, and hence settling under the gravitational force. Settling of solids is hindered as the volumetric concentration of suspended particles increases, because of an increase in the drag force. Fair *et al.* (1968) give an approximate relationship for hindered and unhindered settling velocities (V_h and V_s , respectively) of particles in suspension as a function of the volume fraction of liquid (f_l) in the suspension as:

$$V_h = V_s f_l^4 \quad (5)$$

Assuming eqn (5) to be valid for manure slurries and $f_l = 0.55$, based on 45% TS, in the slurry (Fig. 3), the settling velocity of suspended particles in the tanks was only about 9% of that under unhindered conditions. This suggests that increased drag force on the manure solids may have substantially reduced or prevented settling in the tanks. Absence of settling in thick slurries in laboratory tests has been reported in previous studies. In highly diluted (< 1% TS_w) manure, settling of most solids occurs within minutes, and is clearly visible (Moore *et al.*, 1975). Sobel (1966) found that settling of solids in manure slurries decreased as dilution of manure decreased, and at 1:1 dilution of dairy-cattle manure, settling was practically absent. Bolke *et al.* (1982) were unable to observe settling in slurry stored for several days when the TS_w concentrations exceeded 6% in dairy-cattle slurries and 8% in pig slurries. Solids separation is usually not a problem in anaerobic digesters when influent solids concentration is above about 10% (Loehr, 1984). The slurry used in our study contained about 10% TS_w initially. It is not surprising, therefore, that settling of solids was not indicated to be an important process by the observed concentration changes and mass balances for TS_w in the tanks. It appears, therefore, that microbial reduction, rather than settling of solids, was the principal mechanism responsible for TS_w reduction in the tanks.

Changes in TS_w due to biodegradation

The requirements for microbial reduction of manure have been reviewed by Berry (1966). High concentrations of dissolved organic and mineral materials in slurry can produce plasmolysis in most bacterial cells and inhibit bacterial reduction of manure. Minimal dilution of manure in our study may have promoted such conditions. Since the rate at which oxygen (O₂) is consumed in bacterial reduction of manure exceeds the rate of supply, based on the solubility of atmospheric O₂ in water

(H₂O), aerobic degradation processes were likely to be confined to near the surface and anaerobic processes away from the surface. Results in Figs 2 to 4 suggest that the loss of TS in the slurry was initiated at, or near, the surface and progressed downwards as easily biodegradable material in the upper layers was depleted. In spite of the relatively long duration of slurry storage, most of the loss of TS was confined to the top 1 m. This suggests that aerobic processes, which would be limited by the rate of diffusion of atmospheric O₂ into the slurry, probably played a major role in the degradation of slurry solids. The observed first-order type of rate of decrease of TS_w at the 0.3 m depth (eqn (2), Table 5), and the similar rate at the 1.0 m depth subsequently (Fig. 2), supports this explanation because of the well-known first-order type of decrease of oxidizable organic matter during aerobic treatment of wastes (Sawyer & McCarty, 1978). The rate constant *k* is temperature dependent. The relationship of *k* at T°C to *k* at 20°C can be expressed as:

$$k_T = k_{20} \theta^{(T-20)} \quad (6)$$

where θ is usually constant over a limited temperature range, and has a commonly used value of 1.048 between 20° and 30°C (Loehr, 1984). Interestingly, our data yield a value of 1.047 for θ at 20°C. This appears to provide further support to the explanation that most of the solids, and hence VS and C reduction in the stored slurry, occurred due to aerobic biodegradation. The main end products of aerobic degradation of OM are CO₂ and H₂O. Water formation would tend to lower the concentration of dissolved materials and hence alleviate conditions promoting plasmolysis.

From the above considerations, it would seem that conservation of biodegradable OM or C in stored slurry may be enhanced under cool climatic conditions if access of atmospheric O₂ to the slurry surface is prevented or reduced. Further studies are required to confirm this. Air movement above the slurry surface was restricted in our study because of the concrete and plastic covers, but not entirely absent. Waves of trapped air moving between the concrete and the plastic sheet were often visible, and the plastic cover had to be held down by discarded tires. Gas bubbles, often observed bursting at the slurry surface, may have also caused some mixing and aeration near the surface. Presumably, the rate of OM degradation would have increased because of increased availability of atmospheric O₂, had the tanks been without covers. On the other hand, crust formation on the surface of the slurry in open tanks would tend to reduce O₂ transfer at the surface. Another factor affecting O₂ transfer and consumption in uncovered tanks would be a greater variation in slurry temperature compared with that in covered tanks.

Changes in TS_v

The highly significant linear relationship between TS_w and TS_v (Table 4) is in agreement with studies by Voorburg (1979) which showed that the volume of filtrate recovered from various dilutions of pig slurry decreased linearly as TS_w increased. In our study, the supernatant volume did not increase appreciably beyond a g force of 9000, so the limit of solid—liquid separation had probably been achieved. Results in Fig. 3 show that slurry with 10% TS_w yielded about 55% to 60% supernatant by volume. Commercial solid—liquid separators would yield a substantially smaller proportion of slurry in a liquid fraction. Therefore, the use of such separators for relatively thick manure slurries may be of limited use, at best. High speed centrifuging for rapid estimation of TS_w, would be useful when a 24 h waiting period for TS_w determination by oven-drying may be too long, such as in the monitoring of loading rates to anaerobic digestors, and in the estimation of slurry nutrient content based on its TS_w content (Tunney, 1979). Validity of eqn (1) for slurries from other animal species and for conditions different from those of this study needs to be established.

Fixed and Volatile Solids

Caution is necessary when representative samples of unmixed slurry are to be obtained from farm storage structures because of the substantial spatial and temporal variation in TS_w and FS, and hence in VS concentrations. Samples collected at depths of 1 m or more are more likely to be representative of unmixed slurry in deep storage tanks. Even if samples are obtained from well-mixed slurry, changes in the dry-basis concentrations of FS or VS would not adequately indicate the loss of VS from stored slurry because of the high proportion of VS in TS_w. This is indicated by the results in Tables 2 and 3. The dry-basis VS concentration in the slurry transferred from the barn to the tanks was 86% (Table 2, VS = TS_w - FS), which is the same as the mean value for fresh dairy-cattle manure, based on a literature review (Overcash *et al.*, 1983). This does not necessarily indicate that there was practically no loss of VS from manure during its 6 week collection in the barn.

Examination of Figs 2 and 4 indicates that loss of VS from slurry at depths of 1 m and more was small for almost 6 months after winter-filling, and three months after summer-filling, of the tanks. During this period, therefore, the OM content and the biogas generation potential probably remained largely unchanged in the slurry at 1 m and greater depths. Thus, tank storage of slurry for CH₄ generation during later, peak energy demand periods may be feasible provided the slurry used is obtained from depths of about 1 m or more.

A possible explanation for the apparent loss of FS from the stored slurry (Table 3) could be that the proportion of TS_w that was volatile at 550°C increased at the end of the storage period. For example, some of the non-volatile carbonates and sulfates present initially may have been transformed into volatile bicarbonates, CO_2 and sulfides. Substantial increases occurred in the slurry acetate and ammonium contents. At the end of the storage period, therefore, the slurry may have had increased concentrations of compounds which are stable at 103°C but not at 550°C, such as acetates of sodium, potassium and ammonium. Precipitation and settling of insoluble phosphates and sulfides could also, in part, account for the apparent decrease in FS. More information is required on the fate and transformation of FS in stored slurry. Conclusions in some of the published studies are based on the assumption that dry-basis FS in manure remain unchanged during storage. Our results suggest that this may not always be so.

Dairy-cattle manure contains a refractory or non-biodegradable organic portion ranging from 38% to 63% of the total (Loehr, 1984). Since nearly 86% of the initial TS_w were volatile, results in Fig. 2 suggest that biodegradable VS were essentially depleted at the 0.3 m depth in all tanks, and nearly depleted at the 1.0 m depth in Tanks 9 and 10.

Total carbon

About one-quarter of the initial TC present in the slurry was lost during storage (Table 3). The slurry temperature, pH, C:N ratio and VFA concentrations in all tanks were unfavourable for CH_4 production. The reduction of C by anaerobic processes was therefore probably limited to the production of organic acids, H_2 and CO_2 by facultative bacteria which are common in fecal wastes (Hobson *et al.*, 1981). Since CO_2 is also an end product of aerobic biodegradation of OM, it appears that the loss of C from the slurry occurred mainly as CO_2 , rather than CH_4 . Indeed, gas concentration measurements during storage and mixing of similar slurry subsequent to the present study indicated CO_2 to be the main C gas that was evolved (N. K. Patni, unpublished data). Janni *et al.* (1981) similarly found CO_2 to be the major gaseous component released from stored swine manure.

Results in Figs 2 and 5 suggest that TC_{wb} , rather than TC_{db} , concentrations should be used for estimating the TC content and possible biogas production potential of stored slurry. Equations (3) and (4) provide a rapid means of estimating TC_{wb} reliably. Validity of eqns (3) and (4) for slurry from other animal species and different types of slurry handling methods needs to be established.

ACKNOWLEDGEMENTS

The authors wish to thank L. van den Berg for helpful discussions, and D. Balchin and R. Arcand for technical assistance.

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