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ACIDIFICATION OF SLURRY WITH DIFFERENT PRETREATMENTS AND THEIR EFFECTS ON BUFFER CAPACITY AND ACID CONSUMPTION

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ABSTRACT Slurry acidification is a well-known method for reducing methane and ammonia emissions. Since there are different buffers in the slurry, the acid addition must be adapted to the different buffer capacities. In the acidic range, fatty acid buffer and the carbonate buffer are relevant. The objective of the present study was to investigate slurries with different pretreatments (storage conditions, separation) with regard to their acid consumption for defined pH values. Titration experiments were carried out with samples of fresh dairy cow slurry, fattening pig slurry and sow slurry, which were stored over a period of 12 weeks at 4.7 °C and 23.6 °C. Additionally, the liquid phase was observed immediately after separation and after 8 weeks. The slurries were titrated weekly with HCl to pH value 2.5 by using a titrator. The acid consumption up to pH values 5.5 and 3.0 of the various treatments were compared with each other. Results showed a lower acid consumption for the liquid phase compared to the non-separated slurry when titrating up to pH value 3.0. Furthermore, different storage temperatures affected the acid consumption. Within storage time the acid consumption for achieving the pH value 3.0 from 5.5 changes in all slurries. This effect could be an indicator for changes between the fatty acid buffer and carbonate buffer over the storage period. The slurry pretreatment and the condition and duration of storage have an influence on the buffer capacity and amount of acid for targeted pH value. This influences the current costs of acidification technologies.

Keywords: manure treatment, slurry acidification, ammonia emission, methane emission, slurry storage conditions

INTRODUCTION Acidification of slurry to minimize NH_3 emissions is a well-established method in Denmark (Fangueiro et al., 2015; Jacobsen, 2017; Kaupenjohann et al., 2019). There are different possibilities of acidification such as in-house, during storage and during field application (Kaupenjohann et al., 2019; Fangueiro et al., 2015). The addition

of acids such as sulfuric acid (H_2SO_4) affects the equilibrium between $NH_4^+ \rightleftharpoons NH_3 + H^+$. By reducing the pH value, the volatile and non-ionized form NH_3 shifts towards the nonvolatile ionized form NH_4^+ (Conn et al., 2007; Arogo et al., 2003). The adjustment of the pH value is influenced by buffers such as the volatile fatty acid (VFA) buffer, carbonic acid-bicarbonate buffers (H_2CO_3/HCO_3^- and HCO_3^-/CO_3^{2-}) and ammonia buffer (NH_4^+/NH_3) which are all present in slurries (Georgacakis et al., 1982; Patni and Jui, 1985). The buffers that are important for acidification are in particular the HCO_3^- buffer (pH 7.0 to 5.5) and the VFA buffer (pH 5.5 to 3.0) as shown in Figure 1.

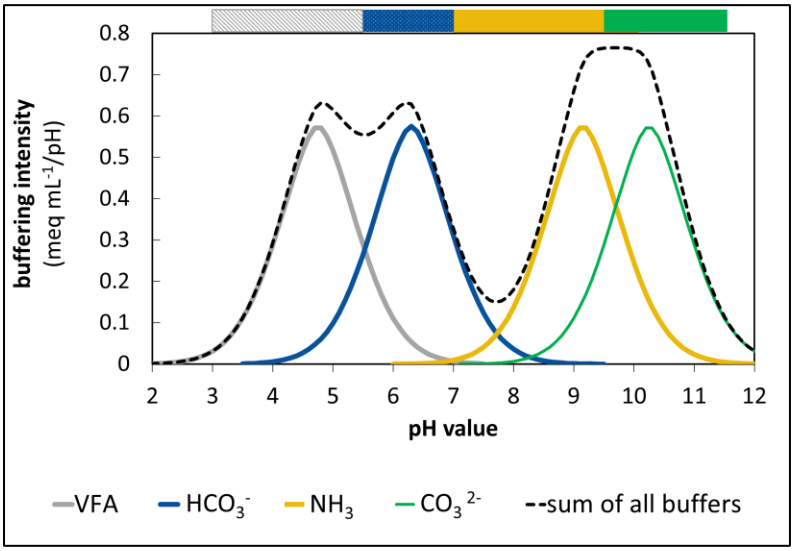

Figure 1: Dynamics in buffering intensity with pH for different buffers commonly found in anaerobic digesters; vertical bars indicate the boundaries between the buffer areas (modified according to Georgacakis et al., 1985).

The pH value in the slurry and the amount of acid required to adjust a certain pH value may vary due to changes in the different buffer capacities during storage and due to the different pretreatments. The objective of the present study was to investigate slurries with different pretreatments (storage under warm and cold conditions, separation at different times) with regard to their amount of acid for defined pH values and buffer capacities. Therefore, samples of fresh slurry (dairy cow, fattening pig and sow) were titrated weekly. These results can be used to optimize acidification technologies, as it allows faster, more precise and efficient timing of pH adjustment with lower acid consumption.

MATERIALS AND METHODS In order to investigate the dynamics of the buffer capacity over storage time, the different slurries were titrated weekly with 0.5 M HCl to a pH of 2.5. The titration of the slurry (50 g slurry diluted with 50 g deionized water) was performed with a titrator ('TitroLine 7000', SI Analytics®, 55122 Mainz, Germany). In the summer of 2019, one slurry sample each of fattening pig, dairy cow and sow, which were not older than three days, were collected. The samples were stored for 12 weeks under cold (4.7 ± 1.1 °C) and warm (23.6 ± 2.1 °C) conditions. Further information can be found in Overmeyer et al., 2020. The influence of separation on the buffer capacity of the slurry

should also be considered. A part of the slurry was centrifuged 10 min at 4,650 G by Avanti™ J-20 Centrifuge (Beckman Coulter GmbH, Krefeld, Germany) twice and the supernatant was sieved (0.9 mm pore size) for separating floating components. Afterwards the liquid phase was titrated. The part of the liquid phase was re-sampled during the eighth week of investigation. To see how the buffer capacity is influenced by the time of separation, the raw slurry was stored under warm and aerobic conditions until the eighth week and then separated and titrated. The separation was carried out using the same method as previously explained. The storage of the liquid phase, as well as the raw slurry required for separation in week 8 was carried out under warm storage conditions. In the following, the liquid phase is called separated slurry. The different variants are shown in Table 1.

Table 1: Overview of the different variants of pretreatments (separation, storage condition, storage time)

Name	Separation	Storage Condition	Titration
Raw TitW0	no	No storage	Week 0
Raw Cold TitW8	no	Cold	Week 8
Raw Warm TitW8	no	Warm	Week 8
SepW0TitW0	Week 0	No storage	Week 0
SepW0TitW8	Week 0	Warm	Week 8
SepW8TitW8	Week 8	Warm	Week 8

To characterize the respective buffers within the slurry the amounts of acid in the pH range 7.0 to 5.5 (HCO_3^- buffer) and 5.5 to 3.0 (VFA buffer) were considered. The statistical analysis was done with an one-way analysis (ANOVA) and Tukey's Honestly Significance Difference (HSD) to describe the differences in pH value and the amount of acid (level of significance $p < 0.05$).

RESULTS

Storage time and temperature The influence of storage time and temperature is shown using the example of fattening pig slurry (Figure 2). The individual values and significant differences are shown in Overmeyer et al., 2020. At the beginning of storage, the VFA buffer (pH range 5.5 to 3.0) increases under warm storage conditions until week 2. With the reduction of the VFA buffer, the carbonate buffer (pH 7.0 to 5.5) increases after week 2 until week 6. Then this buffer decreased until the end of the storage period (week 12). In the coldly stored slurry, the amount of acid and thus the total buffer capacity hardly changes, but there is a small decrease in the VFA buffer and a small increase in the HCO_3^- buffer. The pH value initially drops readily regardless of the storage temperature and then rises continuously until the end of the measurement.

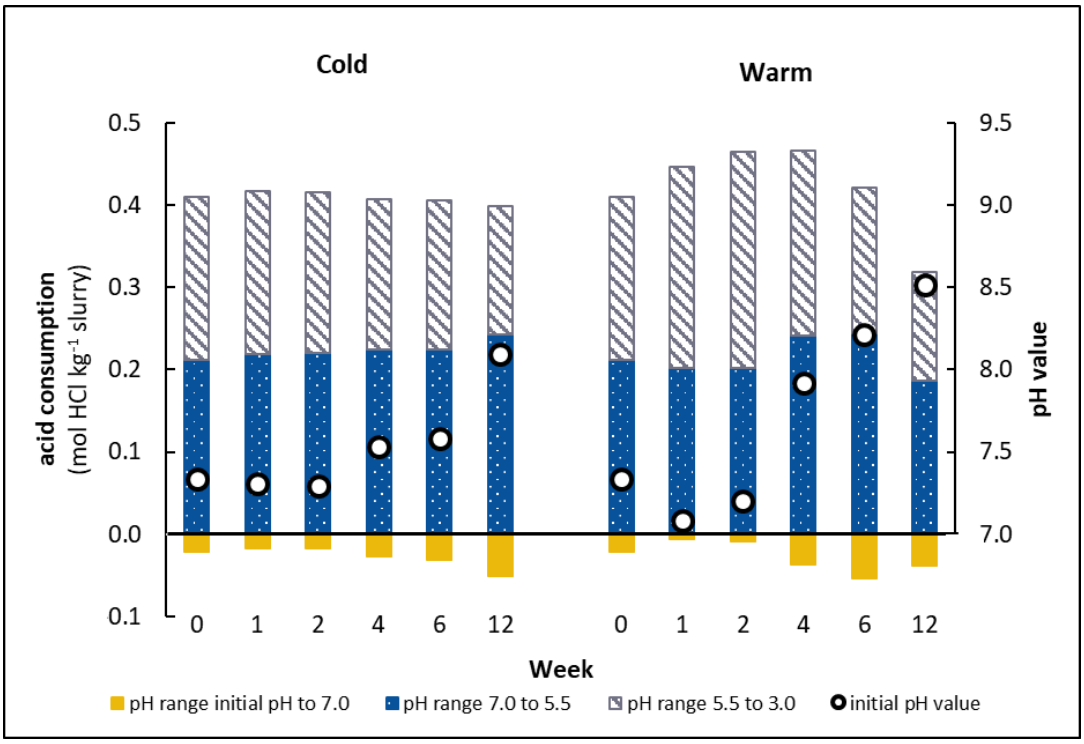

Figure 2: Initial pH value of fattening pig slurry as well as the amount of acid under cold (4.7 ± 1.1 °C) and warm (23.6 ± 2.1 °C) storage conditions in the pH range initial to pH 7.0, 7.0 to 5.5 and 5.5 to 3.0 over a storage period of 12 weeks; for better visualization, the amount of acid in the pH range initial to 7.0 is shown below the black line (modified to Overmeyer et al., 2020)

Different separation times Table 2 shows all individual values as well as the significant differences. The separation reduces the buffer capacity and thus the amount of acid in all slurries regardless of the animal species (Raw TitW0 and SepW0TitW0). Both, the VFA and HCO_3^- buffer are reduced equally.

SepW0TitW8 (fattening pigs) resulted in a significant degradation of the VFA buffer and increase in carbonate buffer compared to SepW0TitW0 (Figure 3). The slurry, which was separated and titrated in week 8 has a similarly high carbonate buffer as SepW0TitW8. However, the VFA buffer is significantly increased compared to SepW0TitW8. The buffer capacity of warmly stored raw slurry is almost twice as large as SepW8TitW8.

Table 2: Initial pH value of fattening pig, dairy cow and sow slurry as well as the amount of acid under cold (4.7 ± 1.1 °C) and warm (23.6 ± 2.1 °C) storage conditions and different separation times in the pH range initial pH value to 7.0, 7.0 to 5.5 and 5.5 to 3.0 (means (SEM)), same letters within rows indicate no significant differences among the variants.

		Raw Tit W0	Raw Cold TitW8	Raw Warm TitW8	SepW0 TitW0	SepW0 TitW8	SepW8 TitW8
Fattening pig slurry							
Initial pH value		7.33 (0.049) [a]	7.35 (0.031) [a]	7.96 (0.011) [b]	7.44 (0.012) [a]	8.85 (0.016) [c]	7.96 (0.016) [b]
Initial to 7.0	mol HCl kg^{-1}	0.021 (0.004) [a]	0.020 (0.002) [a]	0.042 (0.001) [b]	0.020 (0.001) [a]	0.080 (0.001) [c]	0.036 (0.002) [b]
7.0 to 5.5	mol HCl kg^{-1}	0.211 (0.010) [cd]	0.222 (0.002) [d]	0.239 (0.003) [d]	0.119 (0.001) [a]	0.146 (0.001) [bc]	0.144 (0.008) [ab]
5.5 to 3.0	mol HCl kg^{-1}	0.199 (0.005) [c]	0.194 (0.004) [c]	0.206 (0.006) [c]	0.118 (0.001) [b]	0.033 (0.001) [a]	0.114 (0.003) [b]
Dairy cow slurry							
Initial pH value		7.74 (0.032) [b]	7.46 (0.038) [a]	7.45 (0.024) [a]	7.79 (0.014) [b]	7.82 (0.062) [b]	7.50 (0.049) [a]
Initial to 7.0	mol HCl kg^{-1}	0.029 (0.001) [b]	0.020 (0.001) [a]	0.018 (0.001) [a]	0.028 (0.000) [b]	0.035 (0.002) [b]	0.019 (0.002) [a]
7.0 to 5.5	mol HCl kg^{-1}	0.152 (0.002) [bc]	0.174 (0.007) [c]	0.166 (0.009) [c]	0.134 (0.000) [ab]	0.162 (0.006) [bc]	0.119 (0.002) [a]
5.5 to 3.0	mol HCl kg^{-1}	0.193 (0.001) [b]	0.190 (0.003) [b]	0.247 (0.007) [c]	0.148 (0.001) [a]	0.138 (0.003) [a]	0.205 (0.004) [b]
Sow slurry							
Initial pH value		8.89 (0.051) [ab]	9.31 (0.055) [c]	9.06 (0.016) [b]	8.86 (0.060) [ab]	9.30 (0.023) [c]	8.82 (0.044) [a]
Initial to 7.0	mol HCl kg^{-1}	0.064 (0.009) [a]	0.152 (0.006) [c]	0.131 (0.011) [bc]	0.059 (0.008) [a]	0.159 (0.003) [c]	0.114 (0.004) [b]
7.0 to 5.5	mol HCl kg^{-1}	0.085 (0.079) [ab]	0.171 (0.004) [cd]	0.187 (0.024) [d]	0.068 (0.005) [a]	0.131 (0.005) [bc]	0.197 (0.007) [d]
5.5 to 3.0	mol HCl kg^{-1}	0.066 (0.002) [ab]	0.084 (0.003) [b]	0.081 (0.012) [ab]	0.052 (0.001) [a]	0.060 (0.003) [ab]	0.075 (0.007) [ab]

In the dairy cow slurry, similar tendencies can be observed as in the fattening pig slurry (Figure 4). Also, in this case the separation reduces the buffer capacity, although the effect is not as strong as it was observed in fattening pig slurry. It is also noticeable that the VFA buffer in the SepW8TitW8 is twice as large as the carbonate buffer. Both, the fattening pig slurry and the dairy cow slurry have very high pH values in SepW0TitW8. Whereas, the pH value in SepW8TitW8 showed similar levels compared to the stored raw slurries.

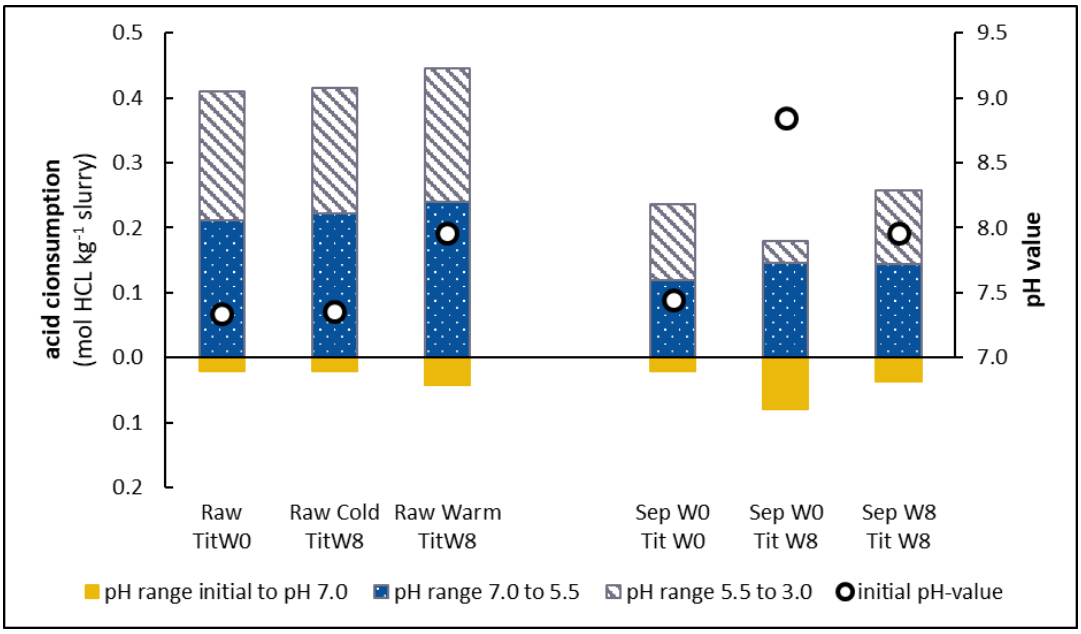

Figure 3: Initial pH value of fattening pig slurry as well as the amount of acid under cold (4.7 ± 1.1 °C) and warm (23.6 ± 2.1 °C) storage conditions and different separation times in the pH range initial to pH 7.0, 7.0 to 5.5 and 5.5 to 3.0; for better visualization, the amount of acid in the pH range initial to 7.0 is shown below the black line.

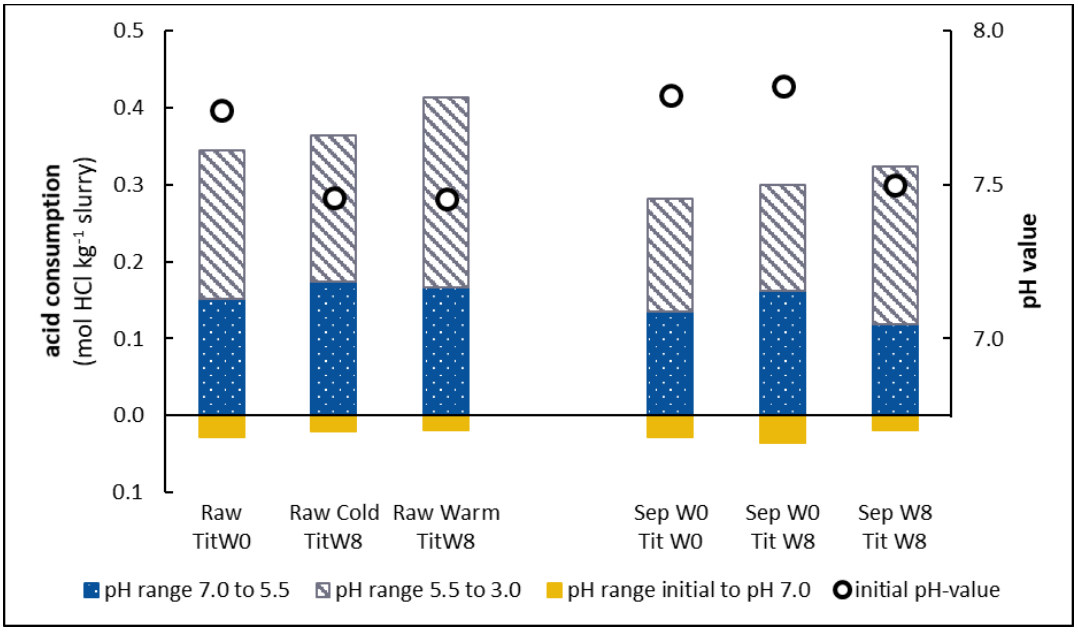

Figure 4: Initial pH value of dairy cow slurry as well as the amount of acid under cold (4.7 ± 1.1 °C) and warm (23.6 ± 2.1 °C) storage conditions and different separation times in the pH range initial to pH 7.0, 7.0 to 5.5 and 5.5 to 3.0; for better visualization, the amount of acid in the pH range initial to 7.0 is shown below the black line.

The VFA buffer was very small in all sow slurry samples (Figure 5). In addition, the carbonate buffer is very small for raw and separated slurry in week 0. The HCO_3^- buffer increased clearly during storage of raw and separated slurry, while the VFA buffer remained at a similar level. Remarkable, a separation in W8 had no effect on the buffer capacity compared to the warmly stored sow slurry in week 8. In addition, the sow slurry needs most acid from pH range initial to pH 7.0 in comparison to the slurry of the other animal species.

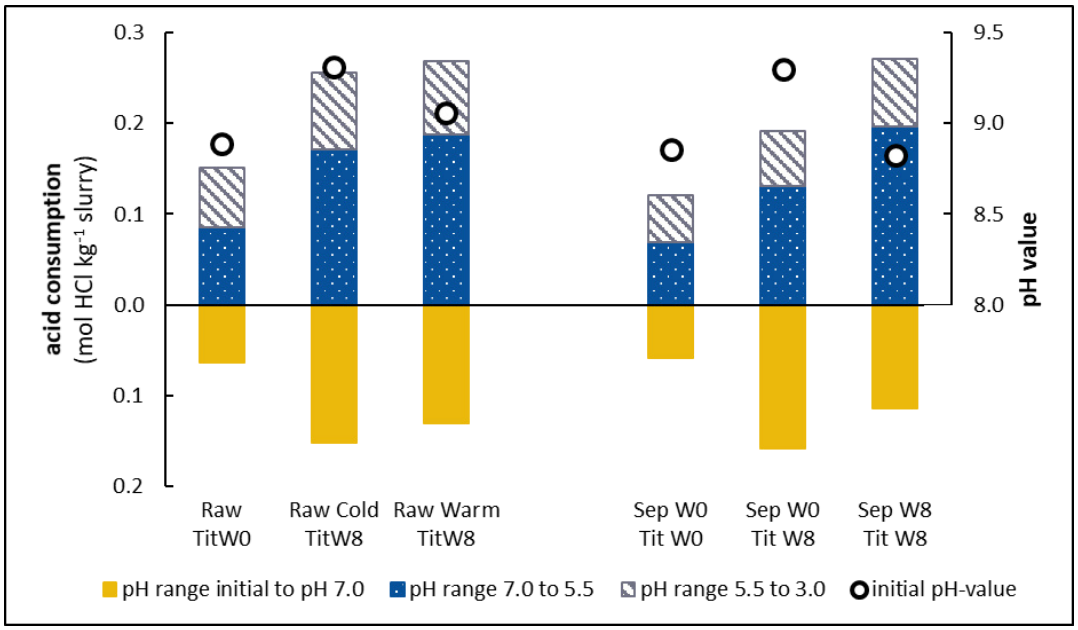

Figure 5: Initial pH value of sow slurry as well as the amount of acid under cold (4.7 ± 1.1 °C) and warm (23.6 ± 2.1 °C) storage conditions and different separation times in the pH range initial to pH 7.0, 7.0 to 5.5 and 5.5 to 3.0; for better visualization, the amount of acid in the pH range initial to 7.0 is shown below the black line.

Characteristics of fattening pig, dairy cow, and sow slurry depending on storage conditions as well as the separated variants are shown in Table A1 in the appendix.

DISCUSSION As the VFA buffer increased, the pH value decreased, while the degradation of VFA buffer led to a rise in the pH value. In further investigations, a strong dependency between VFA buffer and initial pH value was found (Overmeyer et al., 2020). VFAs are metabolized under aerobic conditions leading to the formation of CO_2 (Sommer and Husted, 1995). This is shown in the increase of the HCO_3^- buffer in our investigation (Figure 2). As a result of naturally occurring volatilization processes, CO_2 is emitted during storage (Dinuccio et al., 2008). Therefore, from week 6 until the end of the storage period the carbonate buffer decreases as shown in Figure 2. McGill and Jackson (1977) described, that the higher the storage temperature, the more VFA are reduced compared to coldly stored slurry. Thus, microbial conversion processes are slower at cold temperatures, resulting in a delay in the dynamics of the individual buffers in our investigation. The separation led to a reduction but not complete elimination of the VFA buffer in the

fattening pig and dairy cow slurry. The carbonate buffer was also reduced due to the separation. This could be explained by the strong mechanical stress to which the slurry was subjected during centrifugation, which in turn resulted in CO_2 being expelled from the slurry.

VFA formation was reduced during storage of separated slurry compared to raw slurry. Since there is more organic material in the raw slurry that can be degraded to VFA, the VFA buffer in SepW8TitW8 is higher compared to the slurry separated in week 0 and titrated in week 8. Because the dry matter content was lower in the sow slurry, the VFA buffer was quite low compared to the other two types of slurry. Thus, hardly any solid phase could be separated from sow slurry with the already low amount of organic substance. Therefore, there were no differences with regard to the VFA buffer for sow slurry (raw slurry compared to separated slurry in week 0). The carbonate buffer in SepW8TitW8 is similar as high as the stored raw slurry (independent of storage temperature) and clearly increased compared to SepW0TitW8. This could be caused by urea degradation processes, which releases carbonate (Sigurdarson et al., 2018). The degradation of urea is complete 30 hours after mixing feces and urine (Dai and Karring, 2014). Since there was a short storage period slurry between collection and first titration (four hours) of sow slurry, there was no complete urea degradation. Because of the rapid separation of liquid (urine) and solid (faeces) components of the slurry, the urea present in the urine was hardly degraded by the enzymes from the faeces. Therefore, urea degradation was also reduced in the further storage process of the separated slurry. This may be a reason why the carbonate buffer in SepW0TitW8 is lower compared to SepW8TitW8.

CONCLUSION Our investigation shows that there is a strong dynamic (increase and degradation) of VFA and carbonate buffer in the acidic range during storage of raw fattening pig, dairy cow and sow slurry. Storing the slurry under cold conditions delays the build-up and breakdown of buffers. Therefore, during cold storage the time of acidification has hardly any influence on the amount of acid required for the targeted pH value. The situation is different when considering warmly stored slurry. Immediate acidification of slurry has a positive effect on the amount of acid used to set a target pH, as microbial conversions of organic material, which increase the buffer capacity, may not yet have taken place. In general, it can be shown that a previous separation reduces the amount of acid. The earlier the separation is carried out, the more acid can be reduced. In this way the acid costs and thus the current costs can be lowered.

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APPENDIX

Table A1: Characteristics of fattening pig, dairy cow, and sow slurry (fresh material) in week 0 and 8 depending on cold (4.7 ± 1.1 °C) and warm storage conditions (23.6 ± 2.1 °C) as well as the separated variants.

		Fattening pig slurry						Dairy cow slurry						Sow slurry					
Ingredients		**Raw Tit W0**	**Raw Cold TitW8**	**Raw Warm TitW8**	**SepW0 TitW0**	**SepW0 TitW8**	**SepW8 TitW8**	**Raw Tit W0**	**Raw Cold TitW8**	**Raw Warm TitW8**	**SepW0 TitW0**	**SepW0 TitW8**	**SepW8 TitW8**	**Raw Tit W0**	**Raw Cold TitW8**	**Raw Warm TitW8**	**SepW0 TitW0**	**SepW0 TitW8**	**SepW8 TitW8**
Dry residue	*%*	8.30	8.27	7.23	2.30	1.77	2.27	9.80	10.03	8.90	4.00	3.53	3.83	2.50	2.37	2.20	0.80	0.70	0.70
N	*kg m^{-3}*	4.81	4.92	5.02	2.11	2.21	2.81	4.20	4.22	4.11	3.17	3.04	3.28	5.37	5.41	5.03	5.14	4.55	5.17
NH_4-N	*kg m^{-3}*	2.88	2.99	3.17	1.97	1.88	2.57	2.42	2.37	2.51	2.36	2.13	2.39	4.97	4.20	4.37	4.67	4.00	4.78
P_2O_5	*kg m^{-3}*	2.56	2.94	3.36	0.15	0.12	0.07	1.16	1.53	1.58	0.61	0.68	0.43	0.92	0.87	0.93	0.02	0.03	0.06
K_2O	*kg m^{-3}*	4.14	4.72	5.03	4.47	4.57	4.85	4.14	5.31	5.36	4.70	5.66	5.18	1.70	1.72	1.78	1.58	1.78	1.78
MgO	*kg m^{-3}*	2.01	2.22	2.51	0.72	0.72	0.50	0.81	1.03	1.02	0.64	0.74	0.42	0.62	0.61	0.64	0.19	0.19	0.09
CaO	*kg m^{-3}*	3.63	3.72	4.30	0.32	0.30	0.16	3.13	4.03	3.96	0.91	1.01	1.12	0.89	0.77	0.86	0.06	0.05	0.03
S	*kg m^{-3}*	0.55	0.65	0.69	0.18	0.25	0.20	0.53	0.67	0.60	0.49	0.50	0.33	0.35	0.36	0.35	0.29	0.31	0.25
Cu	*g m^{-3}*	15.00	16.10	18.47	0.76	0.73	0.80	3.50	4.48	4.47	1.92	2.12	2.08	2.87	2.75	2.93	<0.30	<0.30	<0.30
Zn	*g m^{-3}*	80.40	90.87	102.40	2.97	2.76	3.27	17.40	22.10	21.97	8.39	8.43	8.44	16.20	15.47	16.47	0.61	0.75	0.95
Acetic acid	*g kg^{-1}*	7.00	5.83	2.67	5.00	0.07	3.20	6.20	5.83	6.87	5.50	4.93	7.77	2.70	2.77	2.50	1.70	2.33	3.33
Propionic acid	*g kg^{-1}*	1.60	1.53	2.17	0.88	<0.05	2.57	1.20	1.17	1.97	1.10	0.82	2.13	0.14	0.15	0.29	0.10	0.21	0.30
Acetic acid equivalent	*g kg^{-1}*	9.30	8.10	4.90	6.30	<0.10	5.93	7.70	7.27	9.03	6.80	5.73	10.27	2.90	3.00	2.93	1.80	2.53	3.77