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Article

Simple Management Changes Drastically Reduce Pig House Methane Emission in Combined Experimental and Modeling Study

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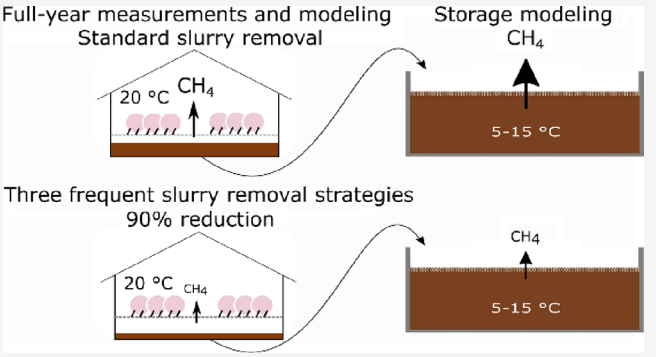
ABSTRACT: Reducing methane from livestock slurry is one of the quickest ways to counteract global warming. A straightforward strategy is to reduce slurry retention time inside pig houses by frequent transfer to outside storages, where temperature and therefore microbial activity are lower. We demonstrate three frequent slurry removal strategies in pig houses in a year-round continuous measurement campaign. Slurry funnels, slurry trays, and weekly flushing reduced slurry methane emission by 89, 81, and 53%, respectively. Slurry funnels and slurry trays reduced ammonia emission by 25−30%. An extended version of the anaerobic biodegradation model (ABM) was fitted and validated using barn measurements. It was then applied for predicting storage emission and shows that there is a risk of negating barn methane reductions due to increased emission from outside storage. Therefore, we recommend combining the removal strategies with anaerobic digestion pre-storage or storage mitigation technologies such as slurry acidification. However, even without storage mitigation technologies, predicted net methane reduction from pig houses and following outside storage was at least 30% for all slurry removal strategies.



KEYWORDS: *methane, modeling, management, emission, pigs, slurry*

INTRODUCTION

Slurry from livestock animals is a considerable source of global methane emission. In many regions with intensive livestock production, manure from pigs and cattle is managed as the liquid slurry in pits and channels underneath the barn floor. In such systems, the slurry environment is anaerobic, and anaerobic microbes transform organic matter to methane and carbon dioxide.[1,2] The biological processes driving organic matter transformation depend strongly on temperature.[3−5] Therefore, strategic removal of slurry from pig houses with a temperature around 20 °C to cold outside storages or anaerobic digesters can reduce net methane emission from the whole management chain. In Danish finisher pig houses, slurry pits underneath the floor are typically 40−60 cm deep, and the slurry is removed with a vacuum flushing system when the pit is nearly full (after 5−6 weeks). However, removing slurry more frequently on a weekly basis was reported by Jørgensen et al.[6] to reduce in-house slurry methane emission by 45%. Methane emission rate is not directly proportional to slurry mass because slurry residence time is crucial for the development of a methanogenic community, and effects of methanogenic adaptation on methane emission have been reported in multiple studies.[7−9] The complexity associated with a dynamic methanogen inoculum makes emission prediction difficult but presents an opportunity for reducing emission through simple management changes. To avoid growth and adaptation of a methanogen community, it is necessary to remove the slurry frequently and reduce the amount of residual slurry in the pits. Vacuum flushing systems in conventional pig houses leave a significant fraction of slurry behind (5−15%), and therefore new slurry removal techniques must be developed. These should be tested and documented experimentally, but it is of increasing importance to also use modeling tools for (i) designing management strategies and (ii) integrating knowledge on methane production from animal slurry. These management changes may increase methane emission from outside storage due to increased transfer of organic matter from the barn. To ensure a reduction in overall emission, the effects of this transfer must be considered.

With a higher slurry removal frequency, the methanogen growth rate becomes the limiting factor for methane emission

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but most currently available models do not explicitly account for this. Instead, most current models assume a fixed methanogenic community, for which the activity is determined by temperature through an Arrhenius equation.[10,11] The anaerobic biodegradation model (ABM)[1] was developed to fill this gap, taking into account a dynamic community of methanogens and a separate step for conversion of organic matter to methanogen substrates (volatile fatty acids). The model processes respond to changes in temperature, chemical environment, and management practices. However, reducing uncertainty in parameter estimates is essential and requires a large data set with repeated slurry filling-emptying cycles.

The objectives of this work were to (i) evaluate three types of slurry handling systems with frequent removal of slurry for effectiveness in reducing methane, ammonia, and odor emission using full-scale experiments and (ii) refine, test, and apply a mechanistic model of slurry methane emission (ABM) to experiments and use it for predicting emission reduction effects in the complete manure management chain (in-house and outside storage). The hypotheses of the study were that (i) new slurry removal techniques focusing on increased removal frequency and removal of residual slurry can reduce in-house slurry methane emission by at least 50%, and (ii) a model that explicitly considers microbial growth can accurately predict reductions in methane emission from barn systems with frequent slurry removal. We consider an agreement in the overall emission reduction within ±10% of reference (control) emission to be accurate.

Here, we report in situ continuous and year-around emissions of methane, ammonia, carbon dioxide, hydrogen sulfide, and odor from four pig sections with (i) weekly vacuum flushing, (ii) slurry trays, (iii) slurry funnels, and (iv) standard vacuum flushing. A best-fit parameter set of the ABM model was developed and used to evaluate the model as well as extrapolate results of the manure removal strategy effects in barns and outside storages.

MATERIALS AND METHODS

Animals and Diets. Four measurement campaigns each 77 days long were conducted from May 2020 to May 2021. Period 1 was from May 28 to Aug 13, period 2 was from Aug 20 to Nov 5, period 3 was from Nov 12 to Jan 28, and period 4 was from Feb 25 to May 13. In each period, 120 crossbred growing-finishing pigs [Duroc × (Danish Landrace × Yorkshire)] with an initial body weight (BW) of ca. 30 kg were used. The pigs were weighed at the beginning of the study and before they were slaughtered at ca. 110 kg. They were fed a standard diet for growing pigs from 30 to 55 kg and a diet for finishing pigs from 55 to 110 kg with crude protein contents of 155 and 152 g kg^{-1}, respectively (see the Supporting Information, Table S1).

Experimental Setup. Four experimental pig sections at Aarhus University, Foulum, were used in the study (Figure 1). Each section contained two pens with 15 pigs in each. The ventilation system in the sections was a negative pressure system with a diffuse air inlet through the ceiling and with a supplementary ceiling inlet for each pen. The ventilation rate was controlled according to a set temperature between 18 and 21 °C. The ceiling inlets were set to open at an outside temperature higher than 19 °C. The pen area was 11 m^2 (2.4 × 4.6 m), the wall height was 2.6 m, and the floors were 1/3 drained floor and 2/3 slatted floor. In the four sections, four different slurry removal strategies were applied: (i) slurry

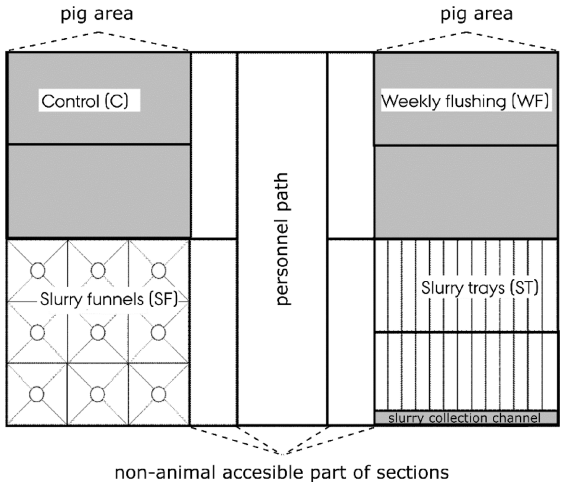

Figure 1. Schematic drawing of control and three experimental sections. Slurry funnels and slurry trays were installed underneath the drained and slatted floor (floor not shown).

funnels (SF), slurry trays (ST), weekly vacuum flushing (WF), and a control section (C). The same physical sections were used for the same removal strategy during all four measuring periods as it was not practicable to switch removal technologies between the batch periods. Between the batches of pigs, 7 days were used to clean and prepare for the next batch of pigs, except between batch periods 3 and 4 with a break of 28 days due to a delay in delivery of pigs.

Section C had a 60 cm deep slurry pit beneath the floor, and the slurry was removed with a vacuum flushing system to a slurry height of ca. 5 cm at days 40 and 77. The WF section was physically identical to section C, but the slurry was removed weekly instead. Section SF had nine connected slurry funnels (width: 1500 mm; length: 1580 mm; height: 979 mm; bottom diameter: 178 mm; slope: 60°) beneath the slatted floor (Figure 1). The funnels were connected with a tube below the funnel bottoms, and a slurry pump (PL200, Börger GmbH, Borken-Weseke, Germany) was used for mixing by recirculation followed by emptying three times per week. In section ST, the slurry was collected in 13 cross-sectional trays underneath the floor with a slight tilt toward a collection channel at the end of the trays (Figure 1). The collection channel in the ST section was emptied weekly after back-flushing the slurry tray channels with mixed slurry. In between the weekly emptying, the channels in the slurry trays were back-flushed in sets of three if needed to keep the slurry liquid enough to ensure drain-off to the collection channel (0−9 of 13 tray channels 0−3 times a week with more channels and at a higher frequency in the end of the batch).

Slurry Sampling and Analysis. For section C, slurry samples were collected when the slurry pit was emptied at days 40 and 77. In the experimental sections, slurry samples were taken weekly when the slurry was removed from the sections. In sections C and WF, representative subsamples taken during emptying were mixed before sampling from this mixed slurry pool. In section SF, representative subsamples taken from a tap during recirculation were mixed before sampling from this mixed slurry pool. In section ST, samples were collected from the recirculation tap in the collection channel after thorough homogenization of the slurry by recirculation. Slurry samples were analyzed for Kjeldahl-N, total ammoniacal nitrogen (TAN), pH, dry matter (DM), volatile solids (VS), and

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volatile fatty acids (VFA). The slurry analysis methods have been described before.[12] Feces and urine samples were taken weekly during period 2 from section C by sampling directly after feces excretion to the floor or collecting urine directly in a cup upon urination. Feces and urine were analyzed for Kjeldahl-N, TAN, DM, and VS. In addition, elemental composition (C, H, N, S, and O) (feces and urine), fiber contents (feces), and crude fats (feces) were determined. Fibers were analyzed according to the Van Soest method[13] using a Fibertec M6 system (Foss Analytical, Hillerød, Denmark), crude fats were analyzed using the blight and dyer method,[14] and elemental composition analysis was done using a vario MacroCube organic elemental analyzer (Elementar, Langenselbold, Germany).

Emission Measurement. Heated and insulated sample tubes of PTFE (outer diameter: 8 mm, inner diameter: 6 mm, Mikrolab A/S, Aarhus Denmark) for the venting outlet in each section and the common fresh air supply were flushed continuously (ca. 5 L $min^{-1)}$ by a pump with a PTFE membrane (Capex L2, Charles Austen Pumps Ltd., Byfleet, UK) placed in an insulated room next to the sections. The concentrations of methane, carbon dioxide, and ammonia was measured by cavity-ring down spectroscopy (CRDS) using G2201-i, G4301, and G2103 analyzer models (Picarro Inc., Santa Clara, CA, USA). The VOCs and hydrogen sulfide were measured by proton-transfer reaction mass spectrometry (HS-PTR-MS, Ionicon Analytik, Innsbruck, Austria) during periods 1 and 4. The CRDS analyzers were connected to the outlet from the Teflon pump using a 10-way PEEK valve (VICI, Houston, TX, USA) and PTR-MS with a five-way PEEK valve (Bio-Chem Valve Incorporated, Boonton, NJ). Measurements were performed in a continuous cycle with two measurements per hour for each outlet for methane, carbon dioxide, and ammonia and one measurement per hour for VOCs and hydrogen sulfide. The VOCs measured were methanethiol, trimethylamine, acetic acid, propanoic acid, butanoic acid, pentanoic acid, 4-methylphenol, and skatole. These VOCs together with hydrogen sulfide were chosen as they are found in high concentrations in air from pig sections and/or have low odor threshold values.[15−17] The PTR-MS was operated with standard drift tube conditions: a voltage of 600 V, a pressure between 2.1 and 2.2 mbar, and a temperature of 75 °C. The inlet temperature was 75 °C. The rate constants used were based on previously reported values,[15,18] and the hydrogen sulfide concentration was corrected for humidity dependence.[15]

Temperature, relative humidity, airflow rate in each section, and the temperature outside were recorded every minute by a log system (VengSystem A/S, Roslev, Denmark). Calibrated measuring fans were used to estimate the airflow rate (Reventa, Horstmar, Germany). In-house air temperature was measured 1.7 m above the floor over the pen partitioning and ca. 1/3 from the back end of the section using a calibrated temperature sensor of the ventilation control. Slurry temperature (PT100, Campell Scientific, Logan, UT, USA) was measured in sections C and WF in the bottom of the slurry pits.

Data Analysis. *Emission Calculations.* Gas emission was estimated according to eq 1, where E is the emission rate (g h^{-1}), M is the molar mass (g mol^{-1}), C_{out} is the concentration (atm) measured in the air outlet from the sections, C_{in} is the concentration (atm) measured in the air inlet for the sections, Q is the ventilation rate (m^3 h^{-1}), R is the gas constant ($m^3 \cdot atm \cdot K^{-1} \cdot mol^{-1}$), and T is the temperature (K).

$$E = (M \cdot (C_{out} - C_{in}) \cdot Q)/(R \cdot T) \quad (1)$$

Odor was assessed as the odorant concentration and estimated as the sum of odor activity values (SOAV) for hydrogen sulfide and the eight VOCs according to eq 2 in which SOAV is calculated as the concentration measured by PTR-MS divided by the odor threshold value (OTV, units of ppb_v) for each of the nine odorants.

$$\text{SOAV} = \sum_{i=1}^{9} \text{odorant concentration}_i\ (ppb_v)/\text{OTV}_i\ (ppb_v) \quad (2)$$

Odor emission was estimated according to eq 3, where E_{odor} is the emission (SOAV s^{-1}), SOAV is the sum of odor activity values expressed per m^3 (SOAV m^{-3}), and Q is the ventilation rate (m^3 h^{-1}).

$$E_{odor} = \text{SOAV} \cdot Q/3600 \quad (3)$$

Enteric methane emission was calculated on a daily basis according to eq 4,[10] where $E_{CH4\ enteric}$ (g pig^{-1} d^{-1}) is the enteric methane emission, GE is the gross energy consumption (MJ d^{-1} pig^{-1}), Y_m is the fraction of gross energy intake being converted to methane (%), n is the number of pigs in the section, and 0.005565 is the energy content of methane (MJ g^{-1}).

$$E_{CH4\ enteric} = \text{GE} \cdot Y_m/100 \cdot n/0.05565 \quad (4)$$

Y_m was set to 0.24% based on an average of four studies.[19−22] Slurry methane emission was estimated by subtracting enteric methane emission from eq 4 from the measured total methane emission.

Enteric carbon dioxide emission, $E_{CO2\ enteric}$ (g pig^{-1} d^{-1}), was calculated using the empirical relationship in eq 5,[23] where BW is the pig body weight (kg). The constants in eq 5 were derived from fitting to multiple datasets.[23]

$$E_{CO2\ enteric} = 0.136 \cdot \text{BW}^{0.573} \quad (5)$$

The average daily body weight of pigs was calculated by linear interpolation between in and outgoing weights of the pigs. Linear growth is a realistic assumption for pigs that are between 100 and 200 days old (as in this study).[24]

Processing and Statistics. The data were initially processed and sorted according to the valve position using MS Excel (Microsoft, MS Excel 2016). The sorted data was then analyzed using R (v4.1.2; R Core Team 2022). Raw data files and code for creating figures, tables, optimization algorithms, and statistical analysis are provided in a public online repository at: https://github.com/AU-BCE-EE/Dalby-2023-FrequentSlurryTransfer-Paper.

Statistical analysis was done using R (v4.2.1; R Core Team 2022). For each compound (or odor value), a linear model was applied using the aov() function with period means as observations (n = 4 periods) and both the manure management system (C, WF, SF, and ST) and period as categorical predictors. The response variable of period mean emission rate in g pig^{-1} d^{-1} was $\log_{10}$-transformed to deal with expected relative (not absolute) effects and a log-normal error distribution common for environmental concentrations and emission rates. Confidence intervals were back-transformed to relative reductions with $1 - 10^c$ where c is the model coefficient for comparison of a manure management system to the reference C. Effect size was quantified as average

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Table 1. Period-Averaged and Overall Mean Emission Rates

	Control (C)		Weekly flushing (WF)		Slurry funnels (SF)		Slurry trays (ST)	
CH_4, g d^{-1} pig^{-1}	barn	slurry	barn	slurry	barn	slurry	barn	slurry
Period 1	7.18	5.33	3.65	1.74	2.87	1.08	3.80	1.90
Period 2	9.35	7.16	4.41	2.27	2.75	0.34	3.00	0.78
Period 3	6.55	4.50	4.69	2.69	2.45	0.46	2.54	0.54
Period 4	4.85	2.90	4.65	2.68	2.13	0.26	2.63	0.66
Mean [a]	6.98	4.98	4.35	2.35	2.55	0.54	2.99	0.97
s [b]	1.86	1.77	0.48	0.45	0.33	0.37	0.57	0.63
Reduction, %			38	53	64	89	57	81
Reduction 95% CI, %			16–52	2.1–76	51–72	81–95	43–67	61–91
p-value [c]			0.0048	0.044	$2 \cdot 10^{-5}$	$3 \cdot 10^{-6}$	$7 \cdot 10^{-5}$	$3 \cdot 10^{-4}$
NH_3, g d^{-1} pig^{-1}	barn		barn		barn		barn	
Period 1	6.06		6.84		4.80		6.38	
Period 2	5.52		6.47		3.75		3.03	
Period 3	3.64		5.36		2.71		2.11	
Period 4	4.18		5.84		2.54		2.72	
Mean [a]	4.85		6.13		3.45		3.56	
s [b]	1.13		0.66		1.05		1.92	
Reduction, %			-26		29		27	
Reduction 95% CI, %			-70–3.0		6.9–47		9.6–48	
p-value [c]			0.07		0.020		0.013	
CO_2, kg d^{-1} pig^{-1}	barn	slurry	barn	slurry	barn	slurry	barn	slurry
Period 1	1.95	0.42	1.90	0.37	1.82	0.29	2.08	0.53
Period 2	1.80	0.24	1.78	0.24	1.79	0.24	1.73	0.18
Period 3	1.73	0.17	2.01	0.45	1.71	0.16	1.53	-0.01
Period 4	1.80	0.24	2.18	0.61	1.70	0.16	1.80	0.23
Mean [a]	1.82	0.27	1.97	0.42	1.76	0.21	1.78	0.23
s [b]	0.09	0.10	0.17	0.15	0.06	0.06	0.23	0.23
Reduction, %			-8.3	-56	3.3	20	2	14
Reduction 95% CI, %			-22–4.5	-170–12	-9.3–15	-44–54	-10–14	-95–45
p-value [c]			0.19	0.12	0.55	0.42	0.66	0.89
Odor, SOAV s^{-1}	barn		barn		barn		barn	
Period 1	1110		933		729		921	
Period 4	918		1190		709		649	
Mean [a]	1020		1060		719		785	
s [b]	137		181		14.1		192	
Reduction, %			-4.5		29		23	
H_2S, g d^{-1} pig^{-1}	barn		barn		barn		barn	
Period 1	1.14		0.59		0.12		0.45	
Period 4	0.81		0.45		0.10		0.15	
Mean [a]	0.98		0.52		0.11		0.30	
s [b]	0.23		0.10		0.01		0.21	
Reduction, %			47		89		69	

[a]Values are based on $n = 4$ periods except for odor and H_2S ($n = 2$). [b]s is the sample standard deviation. [c]P-values are from the t-test of differences in period-averaged emissions between individual treatments and the control section from a linear model, and confidence intervals are from the same model. Statistical tests were omitted for H_2S and odor due to the insufficient number of replicates.

reductions, calculated by directly comparing mean emission during the entire measuring campaign (including all periods). Model assumptions were qualitatively evaluated using plots of residuals from the plot.lm() function. Comparison of treatment groups with the control group was based on a two-tailed t-test from the summary.lm() function ($n = 4$ periods per treatment/management strategy). Pearson's correlation coefficient (r) was used to evaluate correlation between variables. P-values were reported in the text where relevant and in tables with statistical significance assessed according to $\alpha = 0.05$.

Modeling. The anaerobic biodegradation model (ABM)[1] was used to model methane emission from the slurry present in each of the pig house sections and for extrapolation of emissions from the slurry in outside storage. The ABM predicts organic matter transformation to methane and carbon dioxide by simulating (i) initial disintegration, hydrolysis, and

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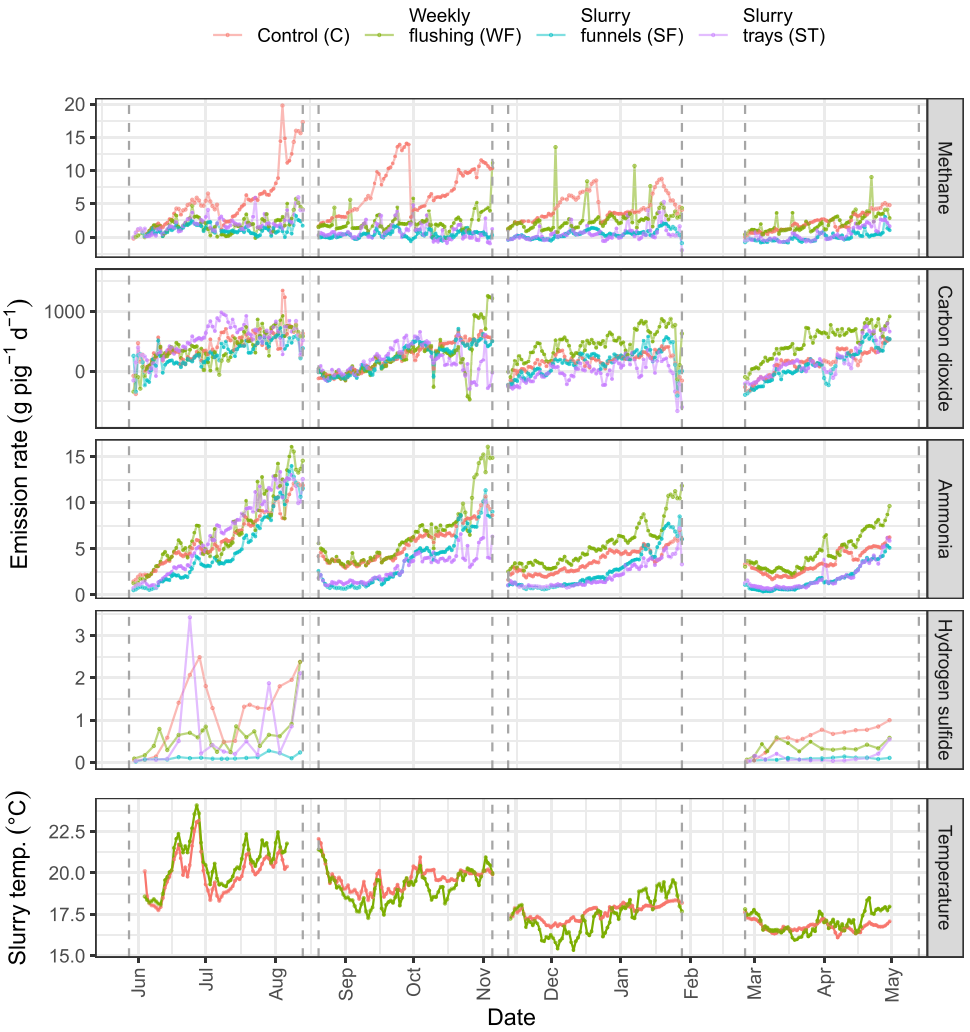

Figure 2. Emission dynamics of four gases for four different slurry removal systems over four production periods, along with slurry temperature (bottom panel). For slurry temperature, only measurements from the control (C) and weekly flushing (WF) sections are shown. Methane and carbon dioxide emissions are corrected for enteric contributions and represent emission from the slurry only. The start and end of the periods are indicated with gray dashed lines. Hydrogen sulfide rates were averaged over 5 days and other gases over 1 day.

fermentation of degradable volatile solids (VSd) to VFA through a single first-order reaction and (ii) methanogenesis using Monod kinetics for describing VFA conversion by active methanogens, resulting in the production of methane and carbon dioxide. The ABM explicitly simulates development of a methanogen community and by default includes five methanogen populations,[1] which are active in different temperature ranges. These default settings were initially chosen based on fitting to methane productivity at varying temperatures as reported by Elsgaard et al.[25] Here, the numbers of methanogen groups were reduced to three (m0, m1, and m2) to decrease computation time and complexity during parameter estimation. In light of recent studies on methanogen activity at low temperatures,[3,26] VFA substrate conversion rates ($q_{max,opt}$) at low temperatures were reduced taking into consideration measured methane potential curves[3] and implementing of a new methanogen group (m0) (Supporting Information, Table S2 and Figure S1).

Enrichment of VSd in the residual slurry remaining after slurry removal (from pig houses as well as from outside storages) was implemented in a similar fashion as for methanogens, which has previously been described.[1] Washing of the pig sections between batches of pigs was simulated by the initial removal of slurry, leaving only the residual mass, which was then diluted with water (70 kg pig^{-1}), and finally removal of diluted slurry to the slurry level before washing (but after the initial removal of slurry). This simulation would have the net effect of reducing the amount of VSd and methanogens present in the pit before the next batch of pigs enters the section. Substrate (VFA) inhibition was implemented in the ABM using a modified version of the model published by Zhang et al.,[27] see the Supporting Information, Text S1.

Parameter Estimation and Model Validation. As described previously,[1] there is significant uncertainty (and probably high variability between locations) in the values of ABM parameters related to hydrolysis and microbial kinetics. New estimates were developed here using only measurements from section C. For parameter estimation, slurry production (inferred from slurry heights during batches) and slurry temperatures were fixed to measured values from section C. The composition of the produced slurry was calculated based on the fresh feces and urine composition, assuming that urine and feces were excreted in a ratio of 3:1 w/w %.[28] Degradable VS was calculated as 70% of VS,[29,30] and a factor of 1.54 gCOD gVSd^{-1} was used for conversion to COD.[1] The ratio between $q_{max,opt}$ for the three methanogen populations (m0:m1:m2) was fixed at

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1:2.4:3.73 during optimization. Optimization was performed with a quasi-Newton method[31] using the optim() function in base R (stats package, v4.2.1) (R core team, 2022) and specifying method argument as "L-BFGS-B" with parameter boundaries. Optimization minimized the absolute difference between measured and ABM-calculated daily methane emission rates (g d^{-1}) and concentrations of VFA (gCOD kg^{-1}_{slurry}). The methane emission rate and VFA concentration were equally weighted by centering and scaling to a mean of 0 and standard deviation of 1 in measurements. Period 4 was excluded from the optimization and validation due to uncertainty in the washing procedure and a 1 month delay in delivery of piglets for the fourth batch period.

The optimized parameter values were used for validation of the model. Sections WF, SF, and ST during periods 1−3 were used as validation datasets. Slurry temperature was not measured in sections SF and ST, and instead the slurry temperature from section WF was used as the model input. Temperature data from section WF rather than from section C was used because the retained slurry mass in section WF better represented slurry masses in sections ST and SF. Hence, slurry temperatures were expected to respond similarly to heat transfer from the air and surroundings. The slurry production rate in ST was set to the rate in the control section since slurry production measurements were systematically underestimated in the ST section.

Modeling Implications of Management in the Barn and Storage Scenarios. The relative effect of the different manure removal strategies was modeled in scenarios with significantly higher and lower base methane emission. Multiple barn and outside storage simulations were run by applying the optimized ABM parameter set and varying the hydrolysis rate (α_{opt}) and substrate conversion rate of methanogens ($q_{max,opt}$) to force various levels of base methane emission levels. The two parameter values spanned from 20 to 500% of the optimized parameter values, covering reported methane emission levels in pig houses (Supporting Information, Table S3). Input variables and parameters for barn simulations were similar to those described for model validation (but with changes in α_{opt} and $q_{max,opt}$). When calculating averaged methane emission on a yearly basis, predicted emissions between the batch periods (7 days) were included. The slurry mass effluents and slurry effluent concentrations of degradable VS and methanogens from the barn simulations were used as the input for outside storage simulations. The slurry temperature was altered in monthly intervals according to Danish weather conditions (Supporting Information, Table S4). In the storage simulations, the slurry was completely removed once a year in March and 10% of the slurry was removed for field application in September. The enrichment factor (resid_enrich) was set to zero due to assumed vigorous agitation of the slurry tank before field application. The simulated storage was scaled to fit the slurry from 30 pigs by setting the surface area to 20 m^2, thereby achieving an average slurry height of ca. 2 m over a 1 year simulation. The pH in the storage was set to 7 for all treatments (slightly higher than in-barn slurry pH) as pH tends to increase slightly during storage.[32] Predicted methane emission was normalized to slurry volume to correct for differences in slurry production between the sections.

RESULTS AND DISCUSSION

Emissions of Methane, Ammonia, Carbon Dioxide, and Odor. Table 1 shows that in-house methane emission from the slurry was reduced considerably in all experimental sections compared to the control (C) section: 89% ($p = 3 \times 10^{-6}$) for slurry funnels (SF), 81% ($p = 3 \times 10^{-4}$) for slurry trays (ST), and 53% ($p = 0.044$) for weekly flushing (WF). It is important to recognize that these reductions could be negated in the outside storage due to increased transfer of organic matter, and this dilemma is addressed below. The dynamic emission rates in Figure 2 show that while emission peaks are higher in section C than in other sections, the first methane emission peak during period 1 was comparatively low, although it occurred simultaneously with the highest slurry temperatures (in July). Temperature is a key factor controlling methane emission, which is inconsistent with this observation. It is likely that during this period, the microbial inoculum was still not established as the pig house had been absent of pigs and fresh manure 1 year prior to this measuring campaign. During period 4, the slurry temperature was consistently higher in section WF than in section C, possibly explaining the similarity in methane emission during this period. Consequently, a Dunnett test finds no significant effect of WF (Dunnett test, $p = 0.106$), and the effect of WF is less clear than the others. Jørgensen et al.[6] reported a 45% reduction in slurry methane emission with weekly slurry removal, but this was with manure removal in weeks 5 and 9 in the reference scenario, which could explain the small discrepancy from the present study. The simple model applied here for enteric methane production was at least slightly inaccurate as evidenced by periodic negative slurry methane emission (Figure 2). Therefore, measured methane emission including enteric emission is included in Table 1. Ammonia emission was reduced to the highest extent in section SF, by 29% ($p = 0.035$), and measurements may suggest a reduction in hydrogen sulfide and odor as well. Effects on individual VOCs that contribute to odor are available in the Supporting Information, Table S5. For ammonia, the reductions in sections SF and ST (27%, $p = 0.025$) can be attributed to the larger fraction of emitting surfaces being either dried out or urine running off the funnel and tray surfaces, thereby reducing net urea hydrolysis and release of ammonia. Unlike the other manure removal strategies, WF did not provide a reduction in ammonia emission compared to C, and the overall mean was actually 26% higher ($p = 0.12$). Ammonia emission depends on the emitting surface area,[33] and pit dimensions and flooring were nearly identical for the WF and C sections. Crust formation on the slurry surface was less pronounced for the WF section compared to the C section, and this could contribute to higher ammonia emission. Reduced crust formation probably resulted from the more frequent disturbance and mixing of slurry during flushing.

The fact that simple changes in slurry management drastically reduce methane emission and simultaneously reduce emission of ammonia is an important and promising result, providing hope for low climate impact pig production. These systems would be relatively simple to incorporate in new and some existing pig houses. Methane emission from outside slurry storages is expected to increase by the in-house treatments presented here as they increase the transfer of degradable organic matter to outside storage. In northern regions, microbial activity may be much lower in outside storages than in the pig house due to lower temperatures, partially counteracting increases in substrate transfer. In Denmark, the estimated yearly average temperature of an outside stored slurry is 9−10 °C,[34] which is substantially lower

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than within pig houses where available measurements show temperatures of 16−22 °C with an average of ∼19 °C.[34] VanderZaag et al.[26] measured methane emission rates from cold stored pig slurry in Canada that were lower than the current IPCC algorithms predict.[35] A reduced methanogenic activity could, however, be outweighed by a much longer storage time, which may also change the chemical slurry properties drastically. Downstream methane emission scenarios resulting from frequent slurry transfer are therefore important to consider in this context, and we address these scenarios using the ABM below.

Danish slurry methane emission from finisher pigs is estimated to 1.3 kg CH_4 $pig^{-1}_{produced}$ (including housing and storage emissions), which is 0.91 kg CH_4 $pig^{-1}_{produced}$ from housing only (assuming that 70% comes from the barn).[34] Here, we measured 0.38 kg CH_4 $pig^{-1}_{produced}$ from in-house slurry in section C. Slurry methane emission from dirty washing water remaining in the pits between the batches of pigs was not measured but assessed to have only a minor effect on emission estimates. The difference between measured emission and the Danish emission factor may be due to inaccurate emission factors and good management practices at the test facility (e.g., thorough washing of the pig houses) or because the slurry was more effectively drained with one plug per pen versus one plug per two to four pens at commercial farms. Regardless, the poor correlation highlights the need for improving models and conducting farm scale emission measurements for understanding drivers of methane emission from livestock slurry. A literature survey of reported methane emission from reference pig houses clearly indicates high variation in methane emission and that the current study had relatively low methane emission levels (Supporting Information, Table S3). The treatment effect in cases with the low or high baseline methane emission level is discussed below. Ammonia emission levels were 1.90 kg NH_3-N m^{-2} $year^{-1}$ in section C (calculated from the full year emission value in Table 1, pig count in Table 2, and an area of 22 m^2), which is slightly below a Danish normative system reference value for partly slatted floor of 2.2 kg NH_3-N m^{-2} $year^{-1}$.[36]

The molar $CH_4/(CH_4 + CO_2)$ fraction from the slurry increased with the average amount of slurry present in the sections. In section SF, the fraction was 0.7 ± 0.3%, and in section ST, it was 1.0 ± 0.2% (omitting period 3 for section ST due to the negative carbon dioxide emission resulting from uncertainty in estimation of enteric carbon dioxide production, see Table 1). In section WF, the fraction was 1.6 ± 0.6%, and in C, it was 5.2 ± 2.2%. Stoichiometry dictates that methanogenesis of pig manure with elemental composition $C_{13.2}H_{22.2}O_{6.5}N$ produces a $CH_4/(CH_4 + CO_2)$ fraction of at least 60%, suggesting that the main source of carbon dioxide from the manure was instead fermentation, surface respiration, or urea hydrolysis. Carbon dioxide emission from the manure was not significantly different in any of the sections, and differences in $CH_4/(CH_4 + CO_2)$ fractions between treatments hence reflect primarily differences in methanogenic activity. A $CH_4/(CH_4 + CO_2)$ fraction in the range of 20−40% was recently reported from the slurry sampled from the same measuring campaign as this study.[4] In that study, an assay eliminated slurry surface respiration by incubation of the slurry with nitrogen in the headspace,[4] explaining the large difference from our in situ measurements.

Experimental Conditions and Slurry Composition. The DM, VS, and Kjeldahl-N contents of the slurries were on average lower in section C followed by WF, ST, and SF, monotonically increasing with the estimated average slurry retention time in these sections (Table 2) and hence increased time for organic matter transformation to occur. Notice that the average slurry retention times are higher than half of the emptying interval due to the residual slurry being carried over in the next filling/emptying interval. These transformation trends are partially consistent with the average emission, i.e., higher loss of VS in section C is consistent with higher methane emission, but this could not be confirmed for carbon dioxide due to the larger uncertainty in measured emission. Conversely, TAN was slightly higher in section C, which could indicate more conversion of organic nitrogen to TAN. Kjeldahl-N and TAN consistently increased during each batch and for all treatments (Figure 3) with increases of 0.028 g Kjeldahl-N kg^{-1}_{slurry} d^{-1} ($p \leq 2 \times 10^{-16}$, $r = 0.69$) and 0.028 g TAN kg^{-1}_{slurry} d^{-1} ($p \leq 2 \times 10^{-16}$, $r = 0.78$). The pig diet was changed at a body weight of 60 kg (around 40 days), but the N increase in the slurry was continuous and shows that the N excretion increases as the pigs grow.[37] Ammonia

Table 2. Experimental Conditions, Animal Growth, and Slurry Characteristics

[a]	control (C)	weekly flushing (WF)	slurry funnels (SF)	slurry trays (ST)
	Temperature and ventilation			
air temperature, °C	20.1 ± 1.2	20.3 ± 1.2	20.0 ± 1.2	20.0 ± 1.2
slurry temperature, °C	18.5 ± 1.5	18.6 ± 1.5		
ventilation rate, m^3 h^{-1} pig^{-1}	60.2 ± 24.2	63.7 ± 24.7	57.7 ± 24.8	57.0 ± 25.3
	Growth			
pigs in section	28.8 ± 0.8	28.8 ± 1.5	29.5 ± 0.6	28.8 ± 0.4
daily growth, kg d^{-1} pig^{-1}	1.10 ± 0.02	1.08 ± 0.06	1.07 ± 0.03	1.08 ± 0.02
feed consumption, kg d^{-1} pig^{-1}	2.84 ± 0.19	2.85 ± 0.15	2.87 ± 0.34	2.86 ± 0.19
N ingested, g d^{-1} pig^{-1}	156 ± 15	157 ± 15	162 ± 20	158 ± 11
N excreted, g d^{-1} pig^{-1}	87 ± 11	86 ± 10	89 ± 18	86 ± 11
	Slurry			
slurry production, kg pig^{-1}	418 ± 25	411 ± 22	459 ± 43	NA[b]
average slurry mass in section, ton	4.37 ± 1.19	1.27 ± 0.12	0.59 ± 0.02	0.78 ± 0.07
average slurry retention time in section, d[c]	19.2 ± 2.3	4.79 ± 0.33	1.77 ± 0.07	3.67 ± 0.20
DM, g kg^{-1}	69.6 ± 10.9	81.5 ± 5.1	86.3 ± 8.9	85.1 ± 9.8
VS, g $kgDM^{-1}$	768 ± 21	787 ± 10	794 ± 12	796 ± 15
pH	6.88 ± 0.15	6.82 ± 0.09	6.75 ± 0.09	6.83 ± 0.04
Kjeldahl-N, g kg^{-1}	4.63 ± 0.54	4.85 ± 0.22	5.19 ± 0.23	5.04 ± 0.20
NH_4-N, g kg^{-1}	3.37 ± 0.26	2.88 ± 0.10	3.15 ± 0.21	3.09 ± 0.17
VFA, g L^{-1}	13.2 ± 1.6	11.2 ± 1.6	12.4 ± 1.4	11.8 ± 1.4

[a]Data given as mean ± standard deviation of periods ($n = 4$). [b]Not available due to systematic incorrect measurements. [c]Calculated as the average time the slurry spends in the pit before being removed.

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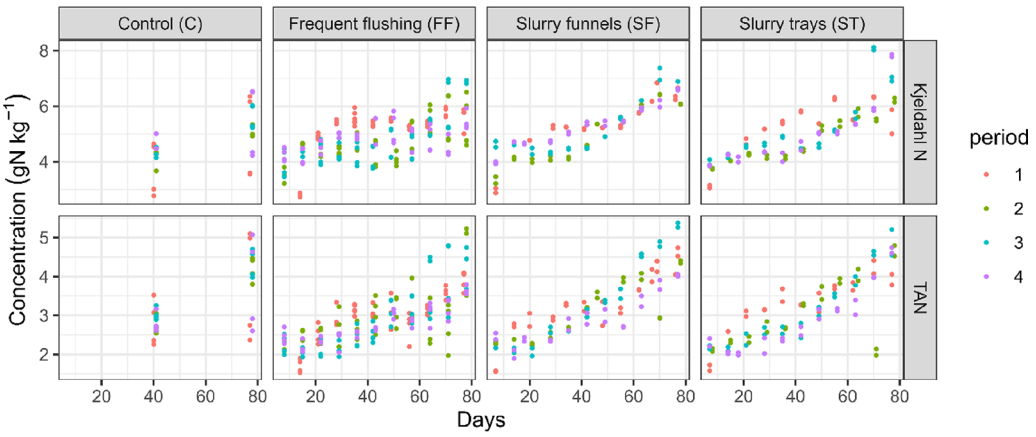

Figure 3. Concentration of nitrogen in slurry samples. TAN is the total ammoniacal nitrogen, and Kjeldahl-N is the total nitrogen as by the Kjeldahl method.

emission increased during each period and for periods 2−4 with an exponential increase toward the end. Ammonia emission responds linearly to the TAN concentration, and the exponential behavior could therefore be attributed to increasing ventilation rate (data not shown) that affects mass transfer of ammonia across the slurry−air interface. Another explanation could be increased fouling on the slatted floor or depositing of urine puddles on the solid floor toward the end of the batches, leading to an increased surface ammonia emitting area.[33,38] Slurry production by the pigs (Table 2) was lower than national estimates for finisher pigs of 0.50 ton $pig^{-1}_{produced}$.[36] Since slurry production in this study was inferred from slurry levels in the pits, water evaporation may have reduced apparent slurry production rates by perhaps 5−15%. Slurry production in section ST is omitted as it was systematically underestimated (during all periods) due to incorrect accounting of the slurry in the piping system during slurry removals.

Model Parameter Estimation and Validation. A model sensitivity analysis was conducted with different α_{opt} and $q_{max,opt}$ reference values. With a low α_{opt} reference value, the model was most sensitive to $q_{max,opt}$ and vice versa. This shows that the rate-limiting parameter depends on other parameter settings. The sensitivity analysis results are shown in the Supporting Information, Figure S3. From previous performance tests,[1] the $q_{max,opt}$ fit was best at 40% of the reference values and therefore the parameter selection for optimization was based on the model sensitivity analysis with $q_{max,opt}$ = 40% of reference values (equivalent to $q_{max,opt}$ of 0.6, 1.44, and 2.24 $g_{COD\text{-}S}\ g_{COD\text{-}B}^{-1}\ d^{-1}$ for methanogen groups m0, m1, and m2, respectively) and α_{opt} = 0.02 d^{-1}. Model sensitivity analysis suggested that methanogenesis (mainly controlled by $q_{max,opt}$) will be rate-limiting for methane production, and $q_{max,opt}$, α_{opt}, K_{Scoef}, and $C_{Xi,in}$ were chosen as optimization parameters.

Other model input variables are shown in Table 3. The VFA and VSd inputs were calculated from the composition of the fresh slurry (Supporting Information, Table S6), whereas TAN and SO4 inputs were default ABM values. The mass of the slurry in the sections and the slurry temperature changed over time and was different for the four sections.

As expected, the model showed good performance for section C, which was used for parameter estimation. Model-predicted methane emission reductions were accurate within ±10% of measured emission reductions (Table 4). The predicted average methane emission rates were similar to

Table 3. Model Input Variables for Control and Experimental Sections

ABM input	description	unit	value[a]
VSd	degradable VS in fresh slurry	gCOD kg^{-1}	73.8[b]
VFA	conc. VFA in excreted slurry	gCOD kg^{-1}	2.83
TAN	conc. total ammonia in excreted slurry	gN kg^{-1}	3.0
SO4	conc. sulfate in excreted slurry	gS kg^{-1}	0.2
pH	pH in the slurry		6.88, 6.82, 6.75, 6.83
area	surface area of the slurry	m^2	22
resid_enrich	enrichment factor		0.9, 0.9, 0[c], 0.9
slurry_prod_rate	slurry production rate	kg d^{-1}	Var[d]
temp_C	slurry temperature	°C	Var[d]

[a]Multiple values indicate values for different sections in the order of control (C), weekly flushing (WF), slurry funnels (SF), and slurry trays (ST). [b]Calculated from the fresh slurry composition (Supporting Information, Table S6). [c]The enrichment factor (resid_enrich) of SF was set to 0 as the slurry was exclusively handled in a piping system with high turbulence. [d]The model input was given as a vector of actual observations rather than a fixed value.

Table 4. Model Results and Comparison for Periods 1−3

target parameters	parameter values			
	$q_{max,opt}$	$K_{S,coef}$	α_{opt}	$C_{XI,fresh}$
best-fit values	0.47, 1.13, 1.75 (m0, m1, m2)	1.17	0.049	0.063
	performance			
	control (C)	weekly flushing (WF)	slurry funnels (SF)	slurry trays (ST)
CH_4 measured, g d^{-1}	162.3	63.6	18.1	31.5
CH_4 modeled, g d^{-1}	157.9	65.6	16.9	24.8
CH_4 reduction measured, %		60.8	88.8	80.6
CH_4 reduction modeled, %		58.5	89.2	84.3
VFA conc. measured, gCOD kg^{-1}_{slurry}	10.8	10.3	11.7	11.1
VFA modeled, gCOD kg^{-1}_{slurry}	13.6	9.2	5.0	5.3

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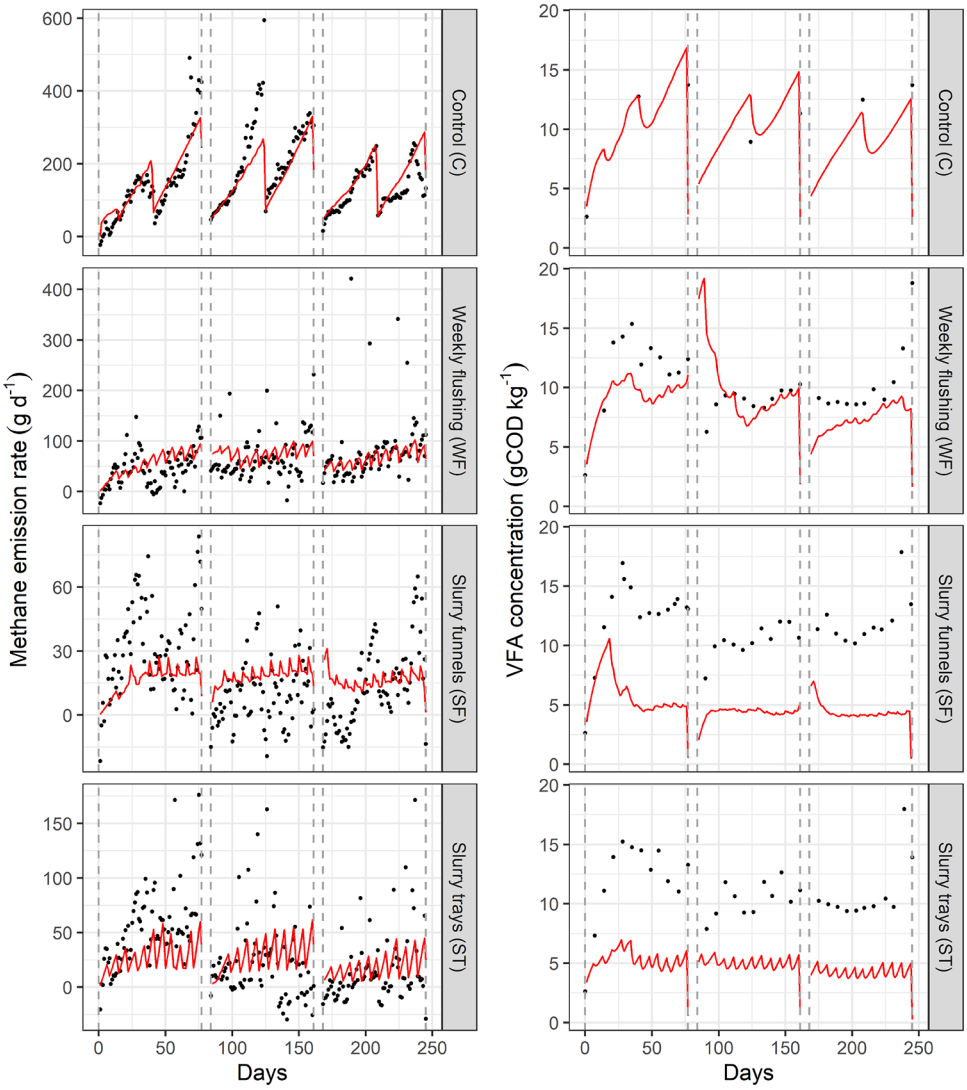

Figure 4. Measured (black dots) and predicted (red lines) methane emission rates (to the left) and VFA concentration (to the right) of the different treatments. Dashed gray lines indicate measuring periods and breaks in between. *Y*-axis scales vary for methane emission rates.

measured emissions, but the model did not always capture emission rate dynamics, particularly for sections SF and ST (Figure 4). The measured changes in emission rates over time are likely associated with more frequent slurry disturbances and methane releases through ebullition, and they become increasingly apparent with lower methane emission and different scaling of the *Y* axis in Figure 4. This transport mechanism does not affect methane production and is not included in the model. As previously mentioned, measurements periodically resulted in negative slurry methane emissions due to the subtraction of estimated contribution from enteric methane production (Figures 1 and 3) and obviously this affects the performance of the model, which cannot predict production below 0. Further, the model algorithms for removal of slurry and enrichment of the residual slurry do not account for non-flat surfaces or spatial differences in slurry levels throughout the pit and piping system. The VFA dynamics matched well in section WF but with poor performance in sections SF and ST (Figure 4). The high VFA measurements in sections SF and ST, with short slurry retention times, suggest that hydrolysis rates of some organic matter components are considerably larger than the average hydrolysis rate of degradable VS. Hence, improvements to the model should focus on segregating degradable VS into smaller VS pools with considerable differences in hydrolysis kinetics. In fact, multiple VS pools with different degradability might be the key to understanding the high variability in reported methane emissions (Figure 5A), together with the methanogenic adaptation rate. In turn, VS pools and degradability are linked to feed composition and feed digestibility in the pig, implying that an integrated analysis must be conducted to truly understand variation in reported emissions.

To increase certainty in parameter estimates, the objective function should be based on more output variables, i.e., carbon dioxide emission rate, and concentration of organic matter components in the slurry but that would require a more complex algorithm for prediction of carbon dioxide from fermentation processes. Using concentrations of organic matter components would on the other hand require intensive slurry sampling at multiple depths, which could disturb slurry processes or trigger the release of trapped methane. Measurement of individual parameters in separate experiments would reduce the number of variables to be optimized but introduce

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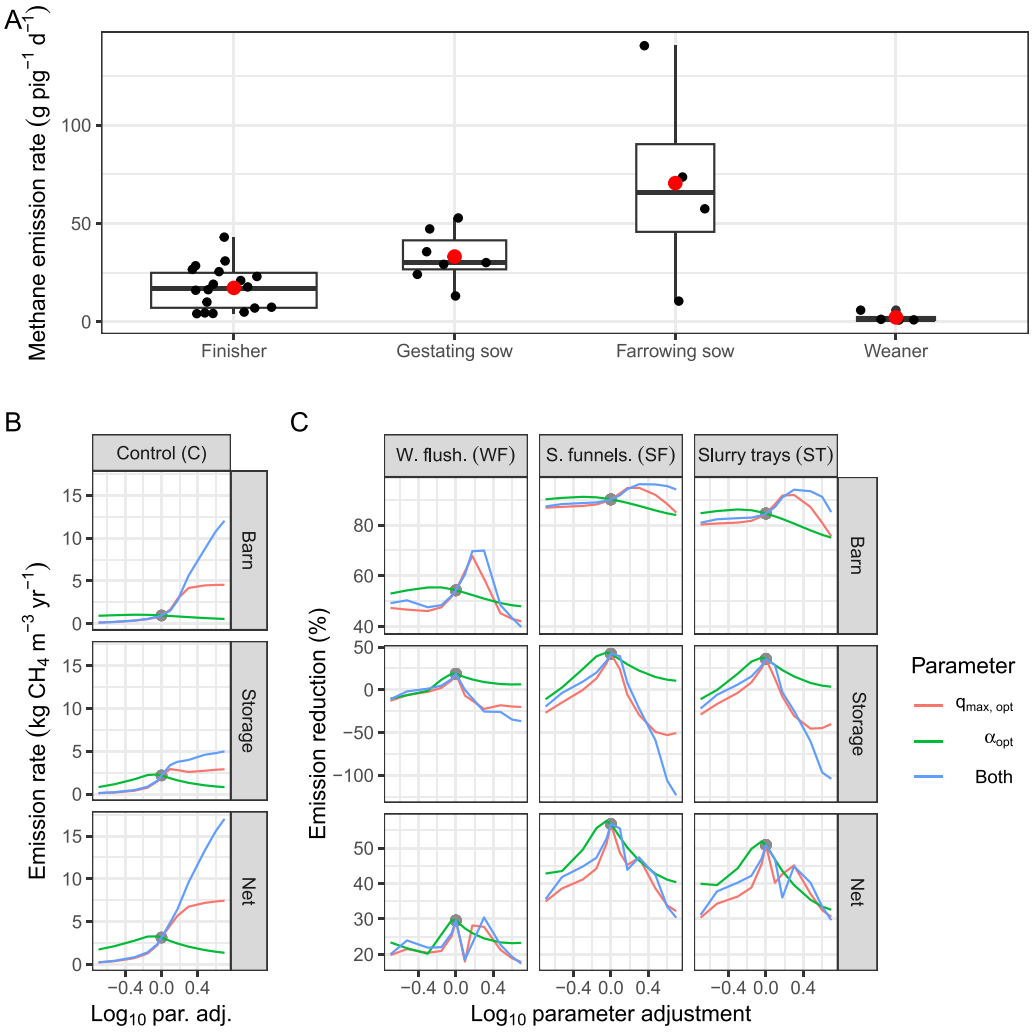

Figure 5. (A) In situ measured methane emission from pig houses (enteric emission + slurry emission) as gathered from a literature survey and from different pig categories. Red dots indicate averages. (B) ABM-predicted emission of methane emission from the control (C) section in the barn, storage, and total (Net) with high and low baseline methane emissions as inferred by changing the hydrolysis rate (α_{opt}) and substrate conversion rate by methanogens ($q_{max,opt}$). In the storage, the exported slurry volume is including washing water, whereas slurry volume in the barn is as excreted by the pigs and therefore excluding washing water. (C) Emission reduction of methane emission with the treatments, weekly flushing (W. flush. (WF)), slurry funnels (S. funnels. (SF)), and slurry trays (ST), in the barn, storage, and total (Net), when changing parameter values of hydrolysis rate (α_{opt}) and substrate conversion rate by methanogens ($q_{max,opt}$). Emission reduction was calculated as (1 − emission$_{treatment}$/emission$_{control}$) × 100%; thus, negative reductions reflect higher emission from the treatment than the control.

uncertainty due to differences in slurry properties between in-lab and in situ slurry.

In general, the ABM model successfully captured methane emission dynamics from frequent slurry removal systems but had more difficulties in capturing emission dynamics from the unconventional slurry management systems where slurry disturbances and transport phenomena affect measured methane emission peaks relatively more. Recalling that large variations in methane emissions have been reported (Supporting Information, Table S3), model parameterization would benefit from not only multiple large measuring campaigns at pig houses with differences in management practice (including feeding, cleaning, and animal type) but also from outside storage so that the effect of temperature can be accurately tuned.

Modeling of Management Implications in the Barn and Storage Scenarios. Measurements made in this single facility cannot definitively show that similar reductions would be observed in other locations. A literature survey on methane emission from pig houses (Supporting Information, Table S3) showed a mean of 17.2 ± 11.1 g pig^{-1} d^{-1} for finisher pigs including enteric- and slurry-derived methane emission (Figure 5A), and such large variation implies that factors controlling the production of methane vary substantially among facilities. The potential relative reductions from changes in slurry management may similarly vary. This uncertainty was partially assessed by predicting reductions in methane emission with high and low baseline methane emission, inferred by changing the two rate-limiting processes: methanogenic activity (through changes in $q_{max,opt}$) and hydrolysis rate (through changes in α_{opt}) (Figure 5B,C). Predicted slurry methane emission reductions from the barn (upper Figure 5C) match well with 95% CI reported in Table 1. For the three treatments, the barn-predicted ranges of reductions were WF (40−70%), SF (84−96%), and ST (75−94%), strengthening confidence in measured reduction effects of the treatments in the barn. In all cases, considerably higher $q_{max,opt}$ and α_{opt} values reduced the treatment effects due to the depletion of

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degradable VS in the control section and rapid substrate consumption in the treatment sections, despite short slurry retention times. Increasing α_{opt}, while keeping $q_{max,opt}$ fixed, did not increase methane emission due to the VFA inhibition of the methanogens—a phenomenon also observed in anaerobic digestion studies.[27,39,40] The values of $q_{max,opt}$ and α_{opt} applied in Figure 5B,C are extreme but could theoretically result from changes in pig diet that are known to significantly affect the intestine microbiome[41] as well as chemical composition of excreted manure.[42]

As previously discussed, storage methane emission could be significantly affected by the frequent slurry removal due to increased organic matter transfer to the outside storage. In the model simulations, it is important to recognize that the hydrolysis rate of VSd in barn simulations may not represent average hydrolysis rates in the storage, with an expected larger fraction of recalcitrant but still degradable VS remaining. Nevertheless, simulations of storage emissions (Figure 5B,C) suggest that storage methane emissions from section C contribute significantly more than barn emission with 2.17 kg CH_4 m^{-3}_{slurry} (exported from barn) versus 0.96 kg m^{-3}_{slurry} (excreted by animal) with the best-fit parameter set (Figure 5B, gray circles). The average retention time of slurry in the simulated storage was ∼4.8 months, equivalent to 5.4 kg CH_4 m^{-3}_{slurry} (present in storage) $year^{-1}$, which is close to a baseline emission of 6 kg CH_4 m^{-3}_{slurry} (present in storage) $year^{-1}$ that Kupper et al.[43] reported in a recent review on storage emissions. Husted[44] measured year-around storage methane emission at a Danish farm of 8.9 kg CH_4 pig^{-1} $year^{-1}$ and with emissions ranging from 0.15 to 13.1 kg CH_4 m^{-3}_{slurry} (present in storage) $year^{-1}$ during cold and warm seasons. This is roughly equivalent to ∼3.9 kg CH_4 m^{-3}_{slurry} (exported from barn). Petersen et al.[45] measured methane emission from Danish pilot storages with pig slurry during winter time at 0.11−0.23 kg CH_4 m^{-3}_{slurry} (present in storage) $year^{-1}$ and during summer time at 14.0−17.4 kg CH_4 m^{-3}_{slurry} (present in storage) $year^{-1}$, which are consistent with the range of emissions reported by Husted.[44] These figures suggest that the simulations underestimate storage emissions from section C, but on the contrary, Danish emission inventories predict 0.57 kg CH_4 m^{-3}_{slurry} (exported from barn),[46] being considerably lower than model simulations presented here. This further suggests that storage methane emissions are associated with considerable uncertainty and that more continuous measuring campaigns are needed.

Figure 5B indicates that in the case of extremely high methanogenesis and hydrolysis activity, barn slurry-methane emission will dominate due to the substrate depletion in the storage (flat curve in the storage plot). The simulations indicate that there is a risk of losing reduction gains from the barn in the storage when frequent slurry removal is applied, with higher risks for sections SF and ST than WF (negative reductions in Figure 5C, storage plots). However, simulations suggest that with some parameter values, including the best-fit parameter set, there is no increase or even reduction of methane emission from the storage (Figure 5B, storage plots), despite more organic matter being transferred to the outside storage. This results from multiple mechanisms being triggered or enhanced with more frequent slurry removal: (i) lower concentrations of the dominant m1 methanogen in the slurry exported to the storage due to a limited growth period in the barn, which is consistent with Feng et al.,[4] measuring lower specific methanogenesis activity in the frequently removed slurry; (ii) hydrolysis of degradable VS is not rate-limiting and hence increased transfer of organic matter has little influence on methane emission; (iii) stronger inhibition of methanogens in the storage, due to increased concentrations of hydrogen sulfide, but reductions were also estimated without inhibition from hydrogen sulfide (not shown). One should be cautious with model interpretations from storage simulations since the datasets used for obtaining the best-fit parameter estimates did not change much in temperature and therefore do not reflect well the temperature effect on microbial activity at low temperatures. With these reservations in mind, simulations (using optimized α_{opt} and $q_{max,opt}$) predict net methane reductions of all the treatments of 48% for scenario SF (range, 25−52%) and 44% for scenario ST (range, 24−48%). The net effect of WF was smaller at 32% emission reduction and ranging from 26 to 41% depending on the rate-limiting parameters (Figure 5B,C). Further model development will benefit from full-scale measuring campaigns focusing on outside storages at a representative temperature range to adjust and increase confidence in parameter values under these conditions.

Combining Frequent Slurry Removal with Storage Mitigation Technology. The risk of increasing emission from outside storages emphasizes the importance of combining in-house frequent slurry removal with storage mitigation technologies. Anaerobic digestion is an obvious choice of technology since the frequently removed slurry contains more VS, potentially increasing biogas output from anaerobic digestion. Møller et al.[47] assumed that 90% of degradable VS is converted by anaerobic digestion, and Baldé et al.[48] reported 88% reduction in methane emission from degassed slurry compared to normal storage. When neglecting fugitive methane emissions, which can be minimized by proper plant maintenance,[49] an ∼90% reduction in methane emissions from the digestate storage as compared to normal outside slurry storage is a reasonable estimate.[48] Therefore, combining slurry funnels, which we here show to reduce in-house slurry-methane emission by 89%, with subsequent anaerobic digestion, a net methane reduction of ∼90% from the total manure management chain (sum of in-house and outside storage emission), is realistic. Early summer acidification with sulfuric acid was reported to reduce slurry methane emission from the storage of pig slurry by 95%[50] and is an alternative to anaerobic digestion. Ma et al.[51] also reduced methane emission by >95% using low-dose acidification with 6 kg sulfuric acid m^{-3}_{slurry}. However, Ma et al. discussed that the inhibition effect might be overcome by the methanogenic community at such low doses of sulfuric acid and it is unclear whether the slurry needs to be repeatedly acidified multiple times during a season to sustain the inhibitive effect.[51] By combining slurry funnels with acidification methods that reduce methane by >95% in the storage, net methane emission reduction (in-house and storage emission) could exceed 90%. Net methane reductions may vary slightly from the mentioned figures, depending on how methane emissions distribute between barn and outside storage in a baseline emission scenario, as suggested in Figure 5B,C, but these management combinations clearly show a large potential for reducing pig production's climate impact.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.2c08891.

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Table S1: Feed analysis; Table S2: Changes to default settings of the ABM; Table S3: Literature review of methane emission from pig houses; Table S4: Slurry temperature used in storage simulations; Table S5: VOC emissions contributing to odor; Table S6: Characteristics of fresh feces and urine from period 2; Figure S1: Changes to default microbial settings of the ABM; Figure S2: Sensitivity analysis; Text S1: Inhibition by protonated VFAs on microbial activity (PDF)

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Author Contributions

A.F., M.J.H., L.B.G., S.D.H., and F.R.D. were involved with the conception of the project. M.J.H., L.B.G., and F.R.D. collected the data from measurement campaigns and for model parameters. F.R.D., S.D.H., M.J.H., and L.B.G. processed and analyzed the data. F.R.D. and S.D.H. developed and applied the model. S.D.H. and F.R.D. made the statistical analyses. F.R.D. wrote the draft of the manuscript, and all authors contributed to editing of the manuscript. A.F. acquired funding to conduct the work.

Notes

The authors declare no competing financial interest.

The data and analysis presented in this work are publicly available at https://github.com/AU-BCE-EE/Dalby-2023-FrequentSlurryTransfer-Paper.

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REFERENCES

(1) Dalby, F. R.; Hafner, S. D.; Petersen, S. O.; Vanderzaag, A.; Habtewold, J.; Dunfield, K.; Chantigny, M.; Sommer, S. G. A Mechanistic Model of Methane Emission from Animal Slurry with a Focus on Microbial Groups. *PLoS One* **2021**, *16*, No. e0252881.

(2) Dalby, F. R.; Hafner, S. D.; Petersen, S. O.; VanderZaag, A. C.; Habtewold, J.; Dunfield, K.; Chantigny, M. H.; Sommer, S. G. Understanding Methane Emission from Stored Animal Manure: A Review to Guide Model Development. *J. Environ. Qual.* **2021**, *50*, 817−835.

(3) Hilgert, J. E.; Amon, B.; Amon, T.; Belik, V.; Dragoni, F.; Ammon, C.; Cárdenas, A.; Petersen, S. O.; Herrmann, C. Methane Emissions from Livestock Slurry: Effects of Storage Temperature and Changes in Chemical Composition. *Sustainability* **2022**, *14*, 9934.

(4) Feng, L.; Guldberg, L. B.; Hansen, M. J.; Ma, C.; Ohrt, R. V.; Møller, H. B. Impact of Slurry Removal Frequency on CH_4 Emission and Subsequent Biogas Production; a One-Year Case Study. *Waste Manage.* **2022**, *149*, 199−206.

(5) Kariyapperuma, K. A.; Johannesson, G.; Maldaner, L.; VanderZaag, A.; Gordon, R.; Wagner-Riddle, C. Year-Round Methane Emissions from Liquid Dairy Manure in a Cold Climate Reveal Hysteretic Pattern. *Agric. For. Meteorol.* **2018**, *258*, 56−65.

(6) Jørgensen, M.; Bache, J. K.; Granath, S. W. Y. *Meddelelse Nr. 1253. Gylleudslusning Ugentligt Samt Hver 14. Dag i En Slagtegrisestald Med Drænet Gulv*; Samt Drænet Gulv 2022.

(7) Haeussermann, A.; Hartung, E.; Gallmann, E.; Jungbluth, T. Influence of Season, Ventilation Strategy, and Slurry Removal on Methane Emissions from Pig Houses. *Agric. Ecosyst. Environ.* **2006**, *112*, 115−121.

(8) Sokolov, V.; VanderZaag, A.; Habtewold, J.; Dunfield, K.; Tambong, J. T.; Wagner-Riddle, C.; Venkiteswaran, J. J.; Gordon, R. Acidification of Residual Manure in Liquid Dairy Manure Storages and Its Effect on Greenhouse Gas Emissions. *Front. Sustain. food Syst.* **2020**, *4*, No. 568648.

(9) Massé, D. I.; Jarret, G.; Hassanat, F.; Benchaar, C.; Saady, N. M. C. Effect of Increasing Levels of Corn Silage in an Alfalfa-Based Dairy Cow Diet and of Manure Management Practices on Manure Fugitive Methane Emissions. *Agric. Ecosyst. Environ.* **2016**, *221*, 109−114.

(10) Gavrilova, O.; Leip, A.; Dong, H.; MacDonald, J. D.; Gomez, C. A. B.; Amon, B.; Rosales, R. B.; del Prado, A.; de Lima, M. A.; Oyhantçabal, W.; van der Weerden, T. J.; Widiawati, Y. Emissions from Livestock and Manure Management. In *2019 Refinement to the 2006 IPCC Guidelines for National Greenhouse Gas Inventories: Agriculture, Forestry and Other Land Use*; IPCC, 2019.

(11) Mangino, J.; Bartram, D.; Brazy, A. Development of a Methane Conversion Factor to Estimate Emissions from Animal Waste Lagoons. *11th Int. Emiss. Invent. Conf.*; US EPA 2001.

(12) Hansen, M. J.; Kamp, J. N.; Adamsen, A. P. S.; Feilberg, A. Low-Emission Slurry Pits for Pig Houses with Straw Application. *Biosyst. Eng.* **2020**, *197*, 56−63.

(13) Van Soest, P. J.; Robertson, J. B.; Lewis, B. A. Methods for Dietary Fiber, Neutral Detergent Fiber, and Nonstarch Polysaccharides in Relation to Animal Nutrition. *J. Dairy Sci.* **1991**, *74*, 3583−3597.

(14) Jensen, S. K. Improved Bligh and Dyer Extraction Procedure. *Lipid Technol.* **2008**, *20*, 280−281.

(15) Feilberg, A.; Liu, D.; Adamsen, A. P. S.; Hansen, M. J.; Jonassen, K. E. N. Odorant Emissions from Intensive Pig Production Measured by Online Proton-Transfer-Reaction Mass Spectrometry. *Environ. Sci. Technol.* **2010**, *44*, 5894−5900.

(16) Hansen, M. J.; Jonassen, K. E. N.; Løkke, M. M.; Adamsen, A. P. S.; Feilberg, A. Multivariate Prediction of Odor from Pig Production Based on In-Situ Measurement of Odorants. *Atmos. Environ.* **2016**, *135*, 50−58.

(17) Hansen, M.; Kasper, P.; Adamsen, A.; Feilberg, A. Key Odorants from Pig Production Based on Improved Measurements of Odor Threshold Values Combining Olfactometry and Proton-Transfer-Reaction Mass Spectrometry (PTR-MS). *Sensors* **2018**, *18*, 788.

(18) Cappellin, L.; Karl, T.; Probst, M.; Ismailova, O.; Winkler, P. M.; Soukoulis, C.; Aprea, E.; Märk, T. D.; Gasperi, F.; Biasioli, F. On Quantitative Determination of Volatile Organic Compound Concentrations Using Proton Transfer Reaction Time-of-Flight Mass Spectrometry. *Environ. Sci. Technol.* **2012**, *46*, 2283−2290.

(19) Jørgensen, H.; Zhao, X.-Q.; Knudsen, K. E. B.; Eggum, B. O. The Influence of Dietary Fibre Source and Level on the Development

of the Gastrointestinal Tract, Digestibility and Energy Metabolism in Broiler Chickens. *J. Geophys. Res. Oceans* **1996**, *75*, 379−395.
(20) Jørgensen, H.; Larsen, T.; Zhao, X.-Q.; Eggum, B. O. The Energy Value of Short-Chain Fatty Acids Infused into the Caecum of Pigs. *J. Geophys. Res. Oceans* **1997**, *77*, 745−756.
(21) Schrama, J. W.; Bosch, M. W.; Verstegen, M. W.; Vorselaars, A. H.; Haaksma, J.; Heetkamp, M. J. The Energetic Value of Nonstarch Polysaccharides in Relation to Physical Activity in Group-Housed, Growing Pigs. *J. Anim. Sci.* **1998**, *76*, 3016−3023.
(22) Wang, J. F.; Zhu, Y. H.; Li, D. F.; Jørgensen, H.; Jensen, B. B. The Influence of Different Fiber and Starch Types on Nutrient Balance and Energy Metabolism in Growing Pigs. *Asian-Australas. J. Anim. Sci.* **2004**, *17*, 263−270.
(23) Philippe, F.-X.; Nicks, B. Review on Greenhouse Gas Emissions from Pig Houses: Production of Carbon Dioxide, Methane and Nitrous Oxide by Animals and Manure. *Agric. Ecosyst. Environ.* **2015**, *199*, 10−25.
(24) Strathe, A. B.; Danfær, A.; Sørensen, H.; Kebreab, E. A Multilevel Nonlinear Mixed-Effects Approach to Model Growth in Pigs. *J. Anim. Sci.* **2010**, *88*, 638−649.
(25) Elsgaard, L.; Olsen, A. B.; Petersen, S. O. Temperature Response of Methane Production in Liquid Manures and Co-Digestates. *Sci. Total Environ.* **2016**, *539*, 78−84.
(26) VanderZaag, A. C.; Glenn, A.; Balde, H. Manure Methane Emissions over Three Years at a Swine Farm in Western Canada. *J. Environ. Qual.* **2022**, *51*, 301−311.
(27) Zhang, W.; Dai, K.; Xia, X. Y.; Wang, H. J.; Chen, Y.; Lu, Y. Z.; Zhang, F.; Zeng, R. J. Free Acetic Acid as the Key Factor for the Inhibition of Hydrogenotrophic Methanogenesis in Mesophilic Mixed Culture Fermentation. *Bioresour. Technol.* **2018**, *264*, 17−23.
(28) Dalby, F. R.; Svane, S.; Sigurdarson, J. J.; Sørensen, M. K.; Hansen, M. J.; Karring, H.; Feilberg, A. Synergistic Tannic Acid-Fluoride Inhibition of Ammonia Emissions and Simultaneous Reduction of Methane and Odor Emissions from Livestock Waste. *Environ. Sci. Technol.* **2020**, *54*, 7639−7650.
(29) Møller, H. B.; Sommer, S. G.; Ahring, B. K. Methane Productivity of Manure, Straw and Solid Fractions of Manure. *Biomass Bioenergy* **2004**, *26*, 485−495.
(30) Møller, H. B.; Sommer, S. G.; Ahring, B. K. Biological Degradation and Greenhouse Gas Emissions during Pre-Storage of Liquid Animal Manure. *J. Environ. Qual.* **2004**, *33*, 27−36.
(31) Byrd, R. H.; Lu, P.; Nocedal, J.; Zhu, C. A Limited Memory Algorithm for Bound Constrained Optimization. *J. Sci. Comput.* **1995**, *16*, 1190−1208.
(32) Blanes-Vidal, V.; Sommer, S. G.; Nadimi, E. S. Modelling Surface PH and Emissions of Hydrogen Sulphide, Ammonia, Acetic Acid and Carbon Dioxide from a Pig Waste Lagoon. *Biosyst. Eng.* **2009**, *104*, 510−521.
(33) Aarnink, A. J. A.; Elzing, A. Dynamic Model for Ammonia Volatilization in Housing with Partially Slatted Floors, for Fattening Pigs. *Livest. Prod. Sci.* **1998**, *53*, 153−169.
(34) Albrektsen, R.; Mikkelsen, M. H.; Gyldenkærne, S. *Danish Emission Inventories for Agriculture*; Danish Centre for Environment and Energy 2021.
(35) Dong, H.; MacDonald, J. D.; Ogle, S. M.; Sanz, M. J. S.; Rocha, M. T. Agriculture, Forestry and Other Land Use. In 2019 *Refinement to the 2006 IPCC Guidelines for National Greenhouse Gas Inventories*; IPCC: Ottawa, Canada, 2019.
(36) Børsting, C. F.; Frydendahl, A. L. *Normtal for Husdyrgødning 2022/23*; 2022.
(37) Fernández, J. A.; Poulsen, H. D.; Boisen, S.; Rom, H. B. Nitrogen and Phosphorus Consumption, Utilisation and Losses in Pig Production: Denmark. *Livest. Prod. Sci.* **1999**, *58*, 225−242.
(38) Aarnink, A. J. A.; Swierstra, D.; Van Den Berg, A. J.; Speelman, L. Effect of Type of Slatted Floor and Degree of Fouling of Solid Floor on Ammonia Emission Rates from Fattening Piggeries. *J. Agric. Eng. Res.* **1997**, *66*, 93−102.
(39) Ahring, B. K.; Sandberg, M.; Angelidaki, I. Volatile Fatty Acids as Indicators of Process Imbalance in Anaerobic Digestors. *Appl. Microbiol. Biotechnol.* **1995**, *43*, 559−565.
(40) Maurus, K.; Kremmeter, N.; Ahmed, S.; Kazda, M. High-Resolution Monitoring of VFA Dynamics Reveals Process Failure and Exponential Decrease of Biogas Production. *Biomass Convers. Biorefin.* **2021**, No. 0123456789.
(41) Hăbeanu, M.; Lefter, N. A.; Toma, S. M.; Dumitru, M.; Cismileanu, A.; Surdu, I.; Gheorghe, A.; Dragomir, C.; Untea, A. Changes in Ileum and Cecum Volatile Fatty Acids and Their Relationship with Microflora and Enteric Methane in Pigs Fed Different Fiber Levels. *Agriculture* **2022**, *12*, 451.
(42) Le Dinh, P.; van der Peet-Schwering, C. M. C.; Ogink, N. W. M.; Aarnink, A. J. A. Effect of Diet Composition on Excreta Composition and Ammonia Emissions from Growing-Finishing Pigs. *Animals* 2022, 12, 229. *Animals* **2022**, *12*, 902.
(43) Kupper, T.; Häni, C.; Neftel, A.; Kincaid, C.; Bühler, M.; Amon, B.; VanderZaag, A. Ammonia and Greenhouse Gas Emissions from Slurry Storage - A Review. *Agric. Ecosyst. Environ.* **2020**, *300*, No. 106963.
(44) Husted, S. Seasonal Variation in Methane Emission from Stored Slurry and Solid Manures. *J. Environ. Qual.* **1994**, *23*, 585−592.
(45) Petersen, S. O.; Dorno, N.; Lindholst, S.; Feilberg, A.; Eriksen, J. Emissions of CH_4, N_2O, NH_3 and Odorants from Pig Slurry during Winter and Summer Storage. *Nutr. Cycling Agroecosyst.* **2013**, *95*, 103−113.
(46) Petersen, S. O.; Gyldenkærne, S. *Redegørelse Omkring Forventede Justeringer i Beregning Af Metanemission Fra Husdyrgødning*; Nationalt Center for Fødevarer og Jordbrug 2020.
(47) Møller, H. B.; Sørensen, P.; Olesen, J. E.; Petersen, S. O.; Nyord, T.; Sommer, S. G. Agricultural Biogas Production-Climate and Environmental Impacts. *Sustainability* **2022**, *14*, 1849.
(48) Baldé, H.; VanderZaag, A. C.; Burtt, S. D.; Wagner-Riddle, C.; Crolla, A.; Desjardins, R. L.; MacDonald, D. J. Methane Emissions from Digestate at an Agricultural Biogas Plant. *Bioresour. Technol.* **2016**, *216*, 914−922.
(49) Baldé, H.; Wagner-Riddle, C.; MacDonald, D.; VanderZaag, A. Fugitive Methane Emissions from Two Agricultural Biogas Plants. *Waste Manage.* **2022**, *151*, 123−130.
(50) Lemes, Y. M.; Garcia, P.; Nyord, T.; Feilberg, A.; Kamp, J. N. Full-Scale Investigation of Methane and Ammonia Mitigation by Early Single-Dose Slurry Storage Acidification. *ACS Agric. Sci. Technol.* **2022**, *2*, 1196−1205.
(51) Ma, C.; Dalby, F. R.; Feilberg, A.; Jacobsen, B. H.; Petersen, S. O. Low-Dose Acidification as a Methane Mitigation Strategy for Manure Management. *ACS Agric. Sci. Technol.* **2022**, *2*, 437−442.

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