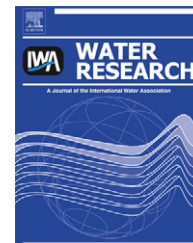


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Storage temperature affects distribution of carbon, VFA, ammonia, phosphorus, copper and zinc in raw pig slurry and its separated liquid fraction

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ABSTRACT

Chemical–mechanical separation of pig slurry into a solid fraction rich in dry matter, P, Cu and Zn and a liquid fraction rich in inorganic N but poor in dry matter may allow farmers to manage surplus slurry by exporting the solid fraction to regions with no nutrient surplus. Pig slurry can be applied to arable land only in certain periods during the year, so it is commonly stored prior to field application. This study investigated the effect of storage duration and temperature on chemical characteristics and P, Cu and Zn distribution between particle size classes of raw slurry and its liquid separation fraction. Dry matter, VFA, total N and ammonium content of both slurry products decreased during storage and were affected by temperature, showing higher losses at higher storage temperatures. In both products, total P, Cu and Zn concentrations were not significantly affected by storage duration or temperature. Particle size distribution was affected by slurry separation, storage duration and temperature. In raw slurry, particles larger than 1 mm decreased, whereas particles 250 μm –1 mm increased. The liquid fraction produced was free of particles $>500 \mu\text{m}$, with the highest proportions of P, Cu and Zn in the smallest particle size class ($<25 \mu\text{m}$). The proportion of particles $<25 \mu\text{m}$ increased when the liquid fraction was stored at 5 °C, but decreased at 25 °C. Regardless of temperature, distribution of P, Cu and Zn over particle size classes followed a similar pattern to dry matter.

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1. Introduction

Production and land application of slurry in areas with specialized and intensified pig farming often exceeds crop demands for nutrients. This poses a risk of nitrate and phosphorus (P) leaching and runoff, accumulation of trace metals in the topsoil and other severe environmental problems (Kronvang et al., 2005). In areas with intensive livestock production, animal slurry is one of the major sources of P

input to soils (Dao and Schwartz, 2010). When compared to other types of animal manure (e.g. dairy and beef cattle manure) pig slurry may contain high concentrations of certain trace metals (Møller et al., 2007a; Nicholson et al., 1999). It is a consequence of Cu and Zn being added to pig feed at high concentrations as additives, and pigs excrete 80–90% of Cu and Zn supplied in feed (Brumm, 1998), so approximately 260–800 $\mu\text{g Cu g}^{-1}$ DM and 500–1900 $\mu\text{g Zn g}^{-1}$ DM end up in slurry.

Abbreviations: DM, dry matter; w.w., wet weight; wt, weight; VS, volatile solids; EC₂₅, electrical conductivity; TSS, total suspended solids; VFA, volatile fatty acids.

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Legislative restrictions on slurry application rate cause a shortage of land for slurry application in livestock-intensive regions, so slurry separation into a dry matter- and P-rich solid fraction and inorganic N-rich liquid fraction provides a possible solution for farmers to manage surplus slurry by export to regions with no nutrient surplus. The number of slurry separation systems installed on commercial farm operation in Denmark is increasing in recent years, with approximately 1 million tons of animal slurry (3% of total amount of slurry produced in Denmark) being separated in over 50 separation plants (Birkmose, 2010).

In order to synchronise nutrient supply from animal manures with crop requirements, which vary throughout the year and are typically largest in spring and early summer, animal manure commonly needs to be stored prior to field application (Sommer, 2001). Storage duration is usually determined by differences in cropping season, manure application strategy and regulation of livestock production (Burton and Turner, 2003). The average storage capacity for slurry is around 6 months, but is longer in Scandinavian countries (9–12 months) (Burton and Turner, 2003). Both liquid and solid fractions from slurry separation are commonly used as a crop fertiliser applied directly to arable land, and therefore both fractions need to be stored before application for a similar period of time. Liquid separation fraction is commonly used as nitrogen fertilizer, whereas the end uses of solid fraction can be many (land application, biogas, composting, incineration etc.). This study focuses only on storage of raw slurry and its liquid separated fraction, as in Denmark, about 80% of solid fraction from separated pig slurry are used in the biogas (Birkmose, 2010) thus it is taken away from the farm without prior long-term storage. Storage conditions (temperature, degree of aeration etc.) can be expected to affect raw slurry and its liquid and solid fractions differently due to its different chemical, physical and biological characteristics.

The composition of slurry and the liquid separated fraction changes during storage due to turnover of organic matter and nutrients (Petersen and Sørensen, 2008). Microbial processes (anaerobic bacteria) lead to a decrease in total suspended solids (TSS) (Zhu et al., 2001). Nitrogen and P can be transferred between different fractions and chemical forms in slurry due to biological decomposition during storage (Henze et al., 1996). Microbial decomposition may also change the pH and chemical form of salts and metals (Henze et al., 1996; Sommer and Husted, 1995). The chemical nature and speciation of P, Cu and Zn govern their association to different particles in slurry and liquid separation fractions. Rather than particle size or the volume that they occupy, the contact surface can play a dominant role in the processes of P and metal adsorption. Therefore, it is important to know whether these elements are associated with particles or are dissolved in the liquid phase.

The awareness of slurry separation as method that can potentially contribute to reduce environmental impact of animal slurry increased recently, so more farmers choose slurry separation as environmentally friendly way to manage their slurry surplus. There are several works reported in the literature in which storage duration and temperature effects on chemical characteristics of raw slurry were studied

(Sommer et al., 2007; Møller et al., 2004), yet much less have been published for its separated liquid fraction.

The objectives of the present study were to investigate the effect of storage of raw slurry and its separated liquid fraction at different temperature on chemical characteristics (changes in pH, concentrations of ammonium, VFA, and C) and on the distribution of P and trace metals (Cu and Zn) between different particle sizes.

2. Materials and methods

2.1. Sampling and experimental set-up

Fresh pig (sow and suckling piglet) slurry and the liquid fraction after separation of the slurry with a commercial full-scale KEMIRA separator (Flocculation + belt press + screw press) (Møller et al., 2007a) were collected from one commercial farm operation in Denmark. Sampling was done in May 2010, when raw slurry (around 150 L) was collected from the pre-tank (short-term store connected directly to the animal house), while the same amount of liquid fraction was collected directly from the outlet of the separation plant in operation. Raw slurry and liquid fraction were collected in 6 plastic barrels (40–60 L each), transported at ambient temperature by car (15–17 °C) to the laboratory within 8 h and stored overnight at room temperature. The samples were carefully mixed with a rod for 2 min and divided into 1-L blue cap bottles (up to 700 ml) (for more details on sub-sampling procedures for best reproducibility, see Jørgensen and Jensen, 2009).

The experiment was carried out at two temperature treatments for 43 weeks. The blue cap bottles were covered with paraffin film (Parafilm® M) during the whole experiment. Parafilm® M is permeable to oxygen and carbon dioxide, but resistant to ammonia, and with low water permeability (highly insensitive to moisture loss and moisture adsorption). One sample series including both raw slurry and liquid fraction were stored at 5 ± 1 °C under controlled temperature conditions, while the other sample series was stored at room temperature (25 ± 5 °C) with temperature logged during the whole duration of the experiment for both treatments. The experiment was organised with 11 sub-sampling times and the zero sub-sampling was performed on the day of experiment set-up. At each sub-sampling time, destructive samples were taken as 3 replicate bottles from each series, after vigorous stirring and mixing of sample, split into 250-mL containers and frozen at -18 °C for further analyses.

2.2. Particle size distribution

Samples from two sub-sampling times (zero and 16 weeks) were analysed for particle size distribution. All raw slurry and liquid fraction samples were analysed in triplicate for particle size distribution by serial wet sieving through metal (1000, 500 and 250 µm), nylon (100 µm) and polyethylene (50 and 25 µm) mesh filters. Wet sieving was performed using pure (distilled) water. All water used for wet sieving of samples, together with particles smaller than 25 µm, was collected in a bucket below the smallest sieve. The cut-off at 25 µm was chosen due to the practical limitation of the sieving processing time. Material

from each sieve was collected after sieving, dried and weighed. The total amount of particles smaller than 25 μm was determined by taking two sub-samples from the bucket after the contents had been thoroughly mixed (magnetic stirrer equipment) to bring all particles into suspension. Sub-samples were dried and weighed, and the total mass of this fraction was calculated based on the dry matter content of sub-samples and the total mass of wet fraction. Recovery was calculated based on the dry matter content and was found to be 101% and 98% for raw slurry and liquid fraction, respectively.

2.3. Chemical analyses

Dry matter content was determined by drying fresh samples to constant weight (24 h) at 105 °C and volatile solids content was measured on dried samples as loss on ignition at 550 °C for 3 h (Clesceri et al., 1989). The pH was measured in 1:5 (wt:wt) wet samples to de-ionised water ratio for all samples (Jørgensen and Jensen, 2009). Electrical conductivity (EC_{25}) was measured in the same suspension but at different dilutions with distilled water (1:10 wt:wt) on a CMD 210 Meter laboratory conductivity meter (Radiometer, Denmark) and conductivity for the undiluted sample was calculated. Total N and ammonium were measured by the Kjeldahl method by distillation and titration. The concentration of volatile fatty acids $\text{C}_2\text{--C}_5$ (VFA; acetic, propionic, isobutyric, butyric, methylbutyric and valeric acid) was determined by gas chromatography (Møller et al., 2002). Total P and trace metals in raw slurry and solid and liquid separation fractions were determined in dry samples (0.25 g d.w.) digested in 5 mL 35% HNO_3 and 4.5 mL H_2O_2 at 120 °C on a graphite heating block (MOD block, CPI International, Amsterdam, Holland) digestion system. The analytical accuracy was evaluated using 2781 Domestic Sludge standard reference material (U.S. Department of Commerce National Institute of Standards and Technology, Gaithersburg, MD 20899). Phosphorus and trace metal concentrations in digestate were measured on an ICP-OES system (Optima 5300 DV, PerkinElmer, USA) equipped with a Meinhard nebuliser and cyclonic spray chamber. For different particle size fractions, total P and trace metals were determined in dry samples (0.25 g) using the same digestion procedure as for non-fractionated samples, and the concentrations were measured by ICP-OES. All chemical analyses were performed in triplicate.

2.4. Phosphorus, copper and zinc distribution among particle size classes

Distributions of P, Cu and Zn in the particle size fractions were calculated as the percentage of the total content of the compound in the recovered sample normalised to 100%, including the DM content from each fraction. Total dry matter recoveries ranged between 98 and 101%. Recovery for P, Cu and Zn in raw slurry corresponded to 115%, 104% and 111% of total concentration in the whole sample, respectively, while the corresponding values for the liquid fraction were 119%, 111% and 125%. Overestimation of P, Cu and Zn recovery may be potentially caused by sampling error. The particle size class with the highest impact on P, Cu and Zn total recovery is the

smallest particle size class (<25 μm), as it contains the highest concentration (based on dry matter) of P, Cu and Zn. This measurement is based on drying of approximately 200 ml subsample sampled from between 4 and 5 L of water and nonrepresentative sub-sampling may potentially be a source of error. Recoveries for dry matter, P, Cu and Zn did not go below 95% which indicates that dry matter was not lost during the fractionation procedure.

2.5. Statistical analyses

Differences in chemical characteristics of the two slurry products individually and between sub-samples were tested by one-way ANOVA. Student's t test was used at first and last sub-sampling when differences between two slurry types were tested. Correlation analyses were performed using Spearman's rank correlation coefficient (r).

3. Results

3.1. Chemical characterisation of raw slurry and liquid fraction at sub-sampling time zero

The measured initial (week 0) chemical composition of the raw fresh pig (sow and suckling piglets) slurry (Table 1.) was similar to that reported for commercial pig farms in Denmark (Popovic et al., 2011; Møller et al., 2007b; Christensen et al., 2009). The initial chemical characteristics of the liquid fraction were in line with previous findings (Popovic et al., 2011; Jørgensen and Jensen, 2009) for liquid fractions produced after KEMIRA separation (chemical pretreatment with flocculants and screw press). Dry matter and volatile solids content were significantly higher ($p < 0.01$) in raw slurry than in the liquid fraction. Total N content (on a wet weight basis) was significantly higher (by 30%; $p < 0.01$) in raw slurry than in the liquid fraction (Table 1). Other separator types including pretreatment (e.g. coagulation, ozonation) and also when only mechanical separation (e.g. centrifugation, screw press, sedimentation) was performed showed similar findings as for KEMIRA separator (Møller et al., 2007b; Popovic et al., 2012). However, the efficiency in reducing dry matter, volatile solids and total N in liquid fraction when compared to raw slurry vary, being higher for separation systems including chemical pretreatments. In the liquid fraction, ammonium ($\text{NH}_4\text{-N}$) comprised about 89% of total N, while in raw slurry the proportion of ammonium was 77%. Total VFA concentration was slightly (but not significantly) higher in raw slurry than in the liquid fraction (Fig. 4), and values were in line with previous findings (Christensen et al., 2009; Zhu et al., 1999). The largest component of VFA was acetic acid, comprising 65% of total VFA acids measured in raw slurry and 70% in the liquid fraction. Total P, Cu and Zn concentrations in the liquid fraction (on a wet weight basis) were significantly lower than in raw slurry (Table 2). Expressed on a dry matter basis, total P, Cu and Zn concentrations in raw slurry (21.3 mg g^{-1} , 346.1 $\mu\text{g g}^{-1}$ and 1308 $\mu\text{g g}^{-1}$ DM, respectively) were similar to those in the liquid fraction (23.2 mg g^{-1} , 390.1 $\mu\text{g g}^{-1}$ and 1399 $\mu\text{g g}^{-1}$ DM, respectively).

Table 1 – Chemical characteristics of two slurry products at the start (sampling time zero) and end (week 43) of the storage period. Means ($n = 3$), standard deviation in brackets.

Slurry product	Storage temp.	Storage duration (weeks)	DM (mg g^{-1} w.w.)	VS (g g^{-1} DM)	EC ₂₅ (Sm^{-1})	Total N (mg g^{-1} w.w.)	NH ₄ -N (mg g^{-1} w.w.)
Raw slurry		0	51.4a (3.61)	0.80a (0.02)	2.85a (0.06)	4.48a (0.06)	3.47a (0.04)
	5 °C	43	41.8b (0.58)	0.72b (0.05)	2.55b (0.09)	4.35a (0.14)	3.34a (0.02)
	25 °C	43	29.4c (0.57)	0.67c (0.02)	1.28b (0.03)	1.47b (0.22)	0.76b (0.07)
		0	16.3d (0.35)	0.62d (0.01)	2.24c (0.05)	3.41c (0.03)	3.02c (0.03)
Liquid fraction	5 °C	43	12.5e (0.15)	0.49e (0.01)	2.39d (0.03)	3.53d (0.11)	3.03c (0.01)
	25 °C	43	10.9f (0.45)	0.47f (0.02)	1.29e(0.02)	0.84e (0.02)	0.57d (0.12)

Means followed by different letters (a, b, c, d, e, f) are significantly different from each other ($p < 0.01$).

3.2. Changes in dry matter, pH, total N, NH₄-N and VFA content during storage

Dry matter content in raw slurry and the liquid fraction decreased significantly ($p < 0.01$) during storage at both temperatures tested (5 °C and 25 °C) (Fig. 1), with the largest decrease at 25 °C (43% and 32% decrease in dry matter content for raw slurry and liquid fraction, respectively). Changes in volatile solids followed a similar pattern to dry matter. For the liquid fraction, the decrease in volatile solids as a proportion of dry matter was significantly larger at the end of the experiment (week 43) at both temperatures than it was for the raw slurry (Table 1).

From the initial value of approximately 8, the pH in raw slurry and the liquid fraction increased slightly (0.1–0.2 units) during the first 8 weeks of storage at both temperatures (Fig. 2), but then the treatments digressed. The pH in the liquid fraction declined to below 8 at 5 °C (although at the last sampling it had risen to almost 8.3 again), while at 25 °C it continued to increase, with a final value of 8.45. The raw slurry behaved similarly at both 5 °C and 25 °C, with only a slight further increase to around 8.2 to 8.3 towards the end of storage (week 43).

Total N and NH₄-N content (based on wet weight) decreased slightly after storage of raw slurry fraction at 5 °C (by approximately 3% and 4%, respectively), while in liquid fraction the concentrations were unchanged (Table 1, Fig. 3). Significant

losses of total N (68% for raw slurry and 76% for liquid fraction) and NH₄-N (78% for raw slurry and 81% for liquid fraction) were found after storage at 25 °C (Table 1, Fig. 3).

Total VFA concentration decreased significantly ($p < 0.01$) during storage at both temperatures in raw slurry and the liquid fraction (Fig. 4), with the most rapid losses at 25 °C. After 16 weeks of storage at 5 °C, only acetic acid was detected in raw slurry, whereas all measured VFA had been lost from the liquid fraction. In raw slurry total carbon concentration was 24 g kg^{-1} w.w. and it was reduced during 43 weeks of storage to 17 and 11 g kg^{-1} w.w. at 5 °C and 25 °C, respectively (Table 3). VFA-C constituted about 10% of total carbon in freshly collected slurry, and losses of total carbon via VFA losses accounted for 34% and 20% at 5 °C and 25 °C, respectively. In the liquid fraction total carbon concentration decreased from 5.8 g kg^{-1} w.w. to 3.6 and 3 g kg^{-1} w.w. at 5 °C and 25 °C, respectively (Table 3). VFA-C constituted about 37% of total carbon in freshly collected liquid fraction, and losses of total carbon via VFA losses during storage were much higher (96 and 76% at 5 °C and 25 °C, respectively) than in raw slurry.

In both slurry products, concentrations of P, Cu and Zn did not change significantly during storage at either temperature (Table 2). The only exception was Cu concentration, which was significantly lower in the liquid fraction after 43 weeks of storage at 25 °C.

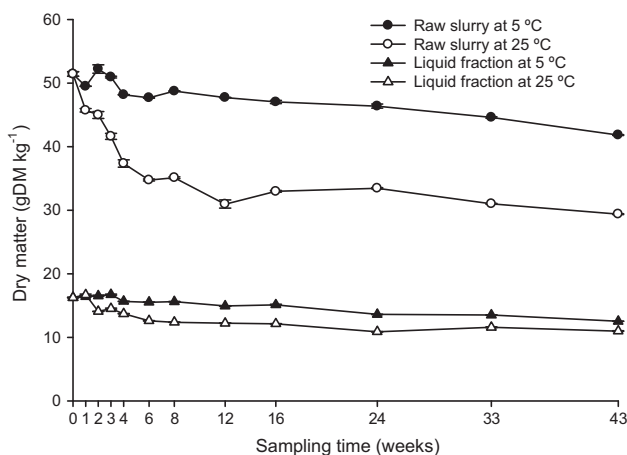


Fig. 1 – Changes in dry matter content during storage of pig slurry and liquid fraction at 5 °C and 25 °C. Means ($n = 3$) and standard deviation.

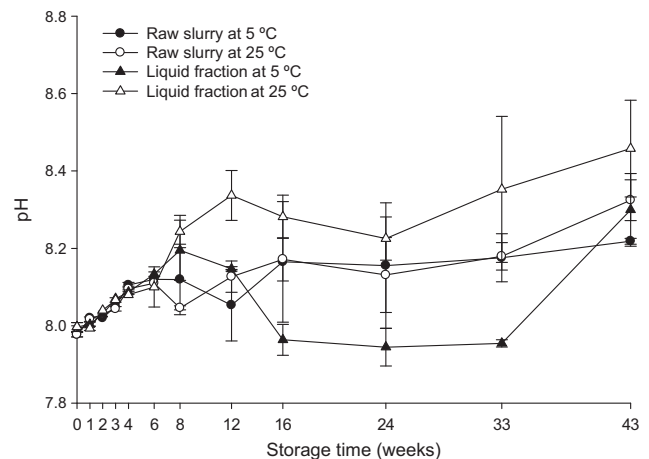


Fig. 2 – Changes in pH during storage of pig slurry and liquid fraction at 5 °C and 25 °C. Means ($n = 3$) and standard deviation.

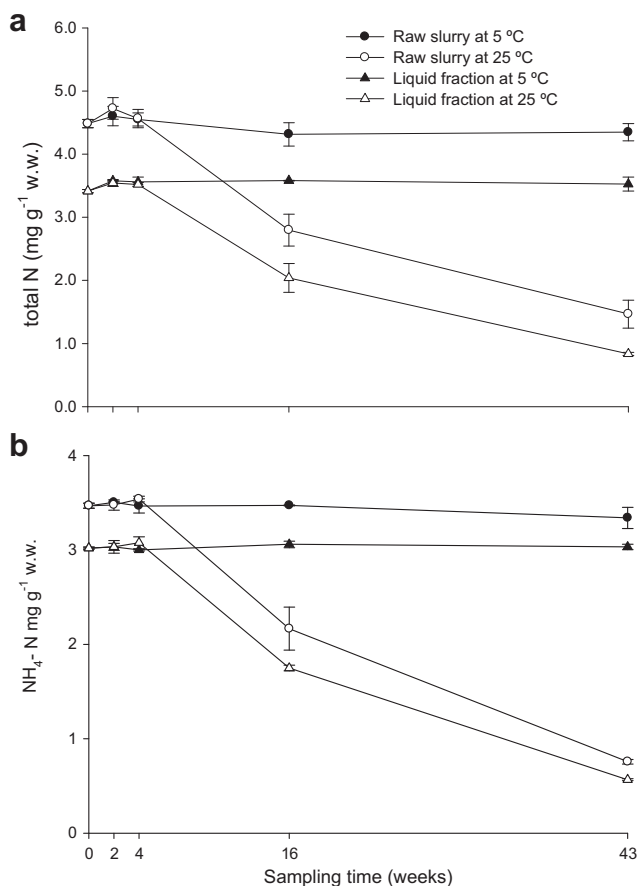


Fig. 3 – Changes in total N (a) and ammonium N (b) concentration during storage of pig slurry and liquid fraction at 5 °C and 25 °C. Means ($n = 3$) and standard deviation.

In raw slurry stored at 5 °C, the P concentration was positively correlated to both Cu ($r = 0.886$; $p = 0.02$) and Zn ($r = 0.943$; $p = 0.01$). No correlation was observed between P and metals in raw slurry stored at 25 °C. When the liquid

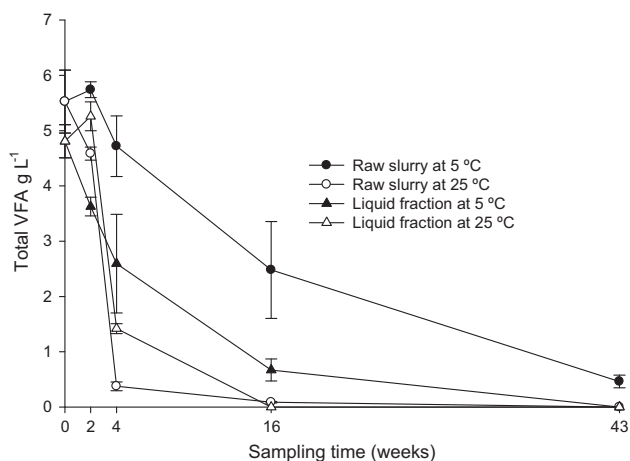


Fig. 4 – Changes in total VFA concentration during storage of pig slurry and liquid fraction at 5 °C and 25 °C. Means ($n = 3$) and standard deviation.

fraction was stored at 25 °C, P was positively correlated to Cu ($r = 0.829$; $p = 0.04$) while at 5 °C a positive correlation was observed between P and Zn ($r = 0.943$; $p = 0.01$).

3.3. Changes in P, Cu and Zn distribution and concentrations at different particle sizes over time in two temperature treatments

In raw slurry, regardless of the temperature during storage, the proportion of particles larger than 1 mm decreased, whereas the proportion of particles between 500 μm and 1 mm increased compared with the distribution in initial raw slurry (Fig. 5). The proportions of other particle sizes were unaffected by storage.

In the liquid fraction, regardless of the temperature during storage, the proportion of particles larger than 100 μm decreased compared with the initial distribution (Fig. 5). When the liquid fraction was stored at 5 °C, the proportion of particles in the size range 25–100 μm remained unchanged and the majority of dry matter (91%) was found in particles smaller than 25 μm . When the liquid fraction was stored at 25 °C, the proportion of particles in the size range 25–100 μm increased and the proportion (73%) of the smallest particles (>25 μm) decreased compared with the initial distribution.

Most of the P, Cu and Zn in raw slurry (49%, 57% and 57%, respectively) were found in particles smaller than 25 μm (Fig. 5). Medium-sized particles (25–250 μm) in raw slurry contained 37% of P, 32% of Cu and 33% of Zn, whereas the largest particles (>250 μm) contained the lowest concentrations (14% P, 11% Cu and 10% Zn). In raw slurry, an effect of storage temperature was not observed for P distribution among particle size classes, while the distribution of Cu and Zn was affected by both storage temperatures. After 16 weeks of storage at both temperatures, the proportions of Cu and Zn increased in the smallest particle size (<25 μm). The distribution of P, Cu and Zn among particle size classes in the liquid fraction was similar to that in raw slurry. After storage of the liquid fraction at 5 °C, the proportion of P, Cu and Zn in particles smaller than 25 μm increased (by 27%, 68% and 63%, respectively). Storage at 25 °C did not affect P, Cu and Zn proportions in the smallest particle size class (<25 μm), but the proportion of all three elements increased in the particle size class 25–50 μm .

4. Discussion

4.1. Chemical composition of freshly collected raw slurry and liquid fraction

The significantly higher content ($p < 0.01$) of dry matter, total N, P, Cu and Zn in raw slurry than in the liquid fraction (Tables 1 and 2) confirms that the separation method involving flocculation and screw press transferred a considerable amount (when compared to total amount in slurry) of these into the solid fraction (Popovic et al., 2011, 2012; Peters et al., 2011). The higher content of ammonium (calculated as % of total N) in the liquid fraction than in the raw slurry confirmed previous findings (Peters et al., 2011) that even though chemical-mechanical separators often have high efficiency for

Table 2 – P, Cu and Zn concentration during storage of two slurry products at 5 °C and 25 °C. Means (n = 3), standard deviation in brackets.

Slurry product	Storage temperature	Storage duration (weeks)	P (mg g ⁻¹ w.w.)	Cu (µg g ⁻¹ w.w.)	Zn (µg g ⁻¹ w.w.)
Raw slurry	5 °C	0	1.09a (0.05)	17.7a (0.31)	66.9a (1.00)
		16	0.86a (0.11)	17.2a (1.34)	61.5a (5.00)
		43	1.20a (0.27)	18.4a (1.23)	68.4a(7.68)
	25 °C	0	1.09 a (0.05)	17.8 a (0.31)	66.9 a (1.00)
		16	1.08 a (0.04)	18.5 a (1.04)	66.8 a (3.73)
		43	1.03 a (0.09)	18.9 a (0.95)	68.2 a (3.28)
Liquid fraction	5 °C	0	0.38b (0.04)	6.34b (0.59)	22.8b (2.01)
		16	0.39b (0.02)	6.78b (0.41)	23.7b (1.83)
		43	0.40b (0.02)	6.95b (0.24)	24.2b (0.75)
	25 °C	0	0.38 b (0.04)	6.34 b (0.59)	22.8 b (2.01)
		16	0.29 b (0.05)	4.64 b (1.13)	15.9 b (4.05)
		43	0.30 b (0.03)	4.27 c (0.31)	18.8 b (2.36)

Means followed by different letters (a, b, c, d, e, f) are significantly different from each other ($p < 0.01$).

transferring organic N to the solid fraction, dissolved NH₄⁺ accompanies the liquid fraction. A previous study (Christensen et al., 2009) showed that most slurry VFA can be found in the colloidal and dissolved fractions and thus VFA can be expected to accompany the liquid fraction during separation. As the liquid fraction after chemical-mechanical separation mainly contains particles smaller than 25 µm (Fig. 5), the concentrations of VFA in raw slurry and the liquid fraction did not differ significantly (Fig. 4).

4.2. Changes in chemical parameters during storage at two different temperatures

During storage of pig slurry and the liquid fraction, the dry matter content decreased (Fig. 1) due to degradation of organic matter, a process mainly based on transformation of organic carbon into methane (CH₄) and carbon dioxide (CO₂) (Møller et al., 2002). Carbon losses during storage via CH₄ and CO₂ emissions depend on slurry type, storage temperature, type of

storage (storage tanks with and without different covers; heaps; lagoons etc.) and presence of an adapted microbial community in pre-stored slurry (Sommer et al., 2007). During anaerobic storage CH₄ production is also controlled by type and content of organic compounds in manure so methane may be produced as a consequence of the microbial degradation of soluble lipids, carbohydrates, organic acids and proteins present in slurry (Chadwick, 2005). Significant amounts of CO₂ are produced at the slurry (or slurry crust)–air interface by aerobic microbial degradation processes (Møller et al., 2004).

Temperature plays a key role for carbon turnover during storage (Petersen et al., 1997) as it has been shown that temperatures around 25 °C increase CH₄ (Dinuccio et al., 2008; Husted, 1994) and CO₂ production and thus their losses (Dinuccio et al., 2008). Previous study (Sommer et al., 2007) showed at lower storage temperature (15–20 °C) proportion of methane production to be insignificant when compared to CO₂ emission, and it became significant to CO₂ production at

Table 3 – Losses of C (% of total C) from two slurry products due to VFA degradation during storage at 5 °C and 25 °C.

Slurry product	Storage temperature	Storage duration (weeks)	Total C (g C kg ⁻¹ w.w.)	VFA-C (% of total C)	Losses of C via VFA-C (%)
Raw slurry	5 °C	0	24.0	10	
		2	24.2	10	
		4	21.9	11	
		16	21.3	6	
		43	17.4	2	34
	25 °C	2	20.7	11	
		4	15.9	1	
		16	15.4	0	
		43	11.4	0	20
		0	5.82	37	
Liquid fraction	5 °C	2	7.48	24	
		4	5.48	26	
		16	5.30	6	
		43	3.56	0	96
		0	5.54	48	
	25 °C	2	4.55	17	
		4	3.44	0	
		16	3.44	0	
		43	2.97	0	76

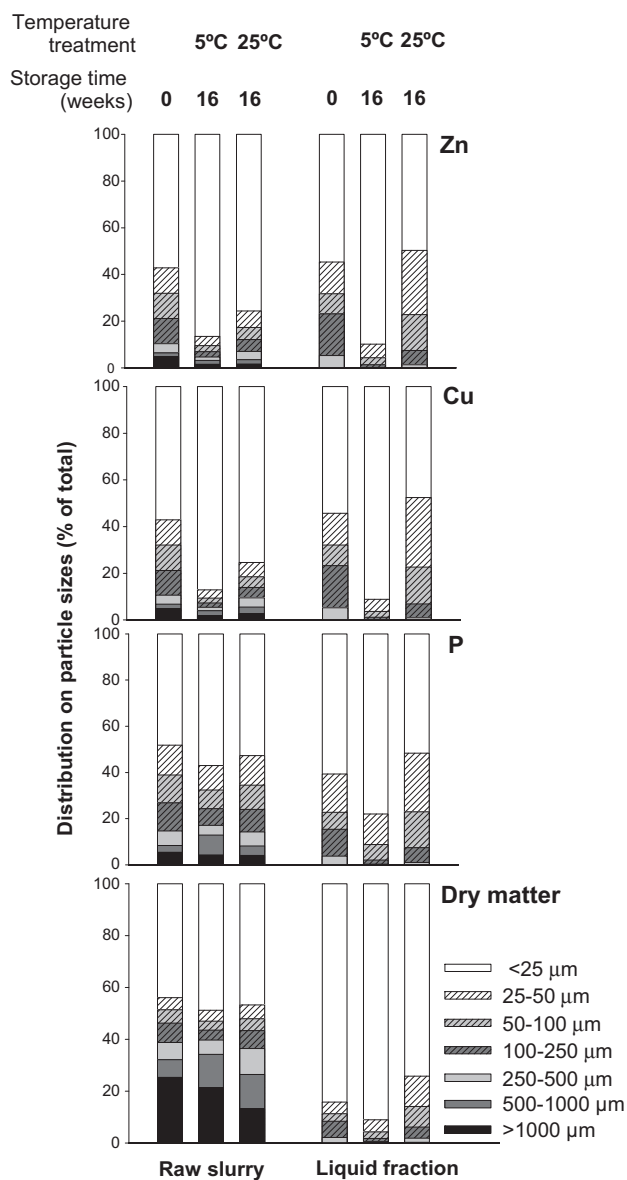


Fig. 5 – Distribution of dry matter, P, Cu and Zn between particle size classes in raw slurry and in the liquid fraction.

temperatures above 20 °C. Therefore, higher losses of dry matter at higher storage temperature (Fig. 1) were recorded for both slurry products (raw slurry and liquid fraction).

Another source of carbon loss during storage of raw slurry and liquid fraction is through microbial decomposition of VFA. The amount of VFA that can be lost from slurry during storage depends on slurry pH and concentration of VFA in slurry. The lower the pH the higher the proportion of VFA would be found in volatile non-ionized form (e.g. acetic acids) (Conn et al., 2005). Majority of VFA are produced during the first weeks after excretion from pigs (Miller and Varel, 2003). Data from this study showed that regardless of storage temperature, in raw slurry during the first 4 weeks of experiment, little of the total C was lost due to VFA-C losses, even though VFA-C constituted around 10% of total C. The reason can be formation of VFA due to microbiological degradation of

easily degradable material being faster than VFA losses due to degradation. The losses of total C in the first 4 weeks of the experiment can be due to methanogenesis (producing CH_4) at higher storage temperatures (above 20 °C) and some other degradation pathways producing CO_2 (fermentation, aerobic microbial activity etc.). In the liquid fraction, the high losses of total carbon via VFA-C losses (Table 3) show that only a small percentage of total carbon in the liquid fraction occurs in the form of stable organic compounds (lignin, humic substances, fat etc.). Results from this study showed, in both slurry products, the highest losses of total C due to net VFA degradation observed between 4 and 16 weeks of storage (at 5 °C) and these losses were affected by storage temperature (Table 3). The storage temperature might affect VFA degradation intensity by affecting microbes activity and survival (higher survival rate at lower temperatures when compared to higher temperatures).

Nitrogen losses during storage of animal manure typically range from 10 to 40% (Eghball et al., 1997) and can reduce the fertiliser value of the manure and have negative effects on the environment. Great variation in nitrogen losses can differ between animal type (cattle, pig etc.), manure chemical composition (pH, manure temperature, concentration of N, etc.) storage conditions (with or without cover) and storage temperature (Conn et al., 2007; Blanes-Vidal et al., 2012). However, in Denmark nitrogen losses are expected to be lower (15–20%) due to strict regulation for storage conditions (e.g. coverage on the tanks). The amount of NH_3 that can volatilise from manure is highly affected by the $\text{NH}_4\text{-N}$ content of the manure (Conn et al., 2007). Ammonia emissions from pig manure also depend on pH value of manure at its surface and the temperature (Conn et al., 2007). The higher the pH value of manure the larger proportion of $\text{NH}_4\text{-N}$ is in the volatile non-ionized form (NH_3) when compared to non-volatile ionized form ($\text{NH}_4\text{-N}$) (Arogo et al., 2003). Manure temperature affects the dissociation and Henry's constant and air temperature affects the diffusivity of gases in the air phase (Blanes-Vidal et al., 2009). Increase in temperature alters the $\text{NH}_4^+/\text{NH}_3$ balance in favour of the latter. Temperature also increases the rate of mineralisation of organic N in manure, leading to an increasing concentration of NH_4^+ . These processes increase the concentration and potential emissions of NH_3 . It is therefore likely that our findings of significant losses of total N and $\text{NH}_4\text{-N}$ at the higher storage temperature (25 °C) and no significant losses at the lower storage temperatures (5 °C) can be explained by these processes (Table 1 and Fig. 3).

The pH value of slurry is controlled by a complex buffering system, mainly total inorganic carbon (CO_2 , HCO_3^- and CO_3^{2-}), total ammonium nitrogen (NH_3 and NH_4^+) and volatile fatty acids ($\text{C}_2\text{-C}_5$ acids) (Sommer and Husted, 1995). During manure storage the pH value changes, mainly due to microbial transformation and NH_3 and CO_2 volatilisation (Blanes-Vidal et al., 2009). As volatilisation of CO_2 (acidic gas) is faster than that of NH_3 (alkaline gas), the pH initially increases over the storage period (Blanes-Vidal et al., 2009). Degradation or emissions of VFA during storage can also bring about pH changes over time, with e.g. decreasing concentrations of VFA (at constant total inorganic carbon concentrations) increasing pH (Sommer and Husted, 1995). This could explain the rapid increase in pH values observed in the first 6 weeks of storage

in this study at both temperatures (Fig. 2). Previous studies (Blanes-Vidal et al., 2009; Sommer and Sherlock, 1996) showed that pH increase slow down over time, because the pH increase favoured the emission of alkaline components and hindered the emission of acidic components, which limits the pH increase. Thus subsequent decrease in pH observed for the liquid fraction at 16 weeks (at both temperatures) (Fig. 2) could be explained by most VFA having been lost at that time, leaving NH_3 emissions to dominate. After 24 weeks of storage the pH again increased (Fig. 2), most probably due to CO_2 volatilisation resulting from exhaustion of the ammonium pool, at least at 25 °C. This increase in pH value was slower for raw manure stored at 5 °C than at 25 °C, as NH_3 volatilisation at lower temperatures was slower.

The positive correlation between total P and total Cu and Zn observed in this study for the liquid fraction at different storage temperatures may be explained by the fact that most P, Cu and Zn is associated with the smallest particles (<25 μm) and thus accompanies these particles during the separation process. Previous studies (L'Herroux et al., 1997; Legros et al., 2010a, 2010b) have shown that in raw pig slurry, 66% and 49% of Cu and Zn, respectively, is bound to organic matter. There, Cu and Zn can bind to carboxyl, aldehyde, hydroxyl, sulphhydryl, phosphoryl and amine groups (Sarret et al., 1998). Thus, precipitation of Cu and Zn by phosphate (Mohan and Sreelakshmi, 2008; Perez-Novo et al., 2011) could also be a reason for observing the positive correlation between P and the Cu and Zn concentration.

4.3. Storage effects on dry matter, P, Cu and Zn distribution between particle size classes

In raw slurry, reduction in the proportion of particles larger than 1 mm and a concomitant increase in the proportion of particles 250 μm –1 mm (Fig. 5), may be a consequence of microbial degradation of organic matter during storage (Møller et al., 2002). The liquid fraction contained no particles larger than 500 μm , with most of its dry matter (84%) in particles larger than 25 μm (Fig. 5) which shows that the separation method involving flocculation and screw press has a high efficiency in retaining large particles in the solid fraction (Popovic et al., 2011; Peters et al., 2011). During storage particles smaller than 25 μm are the first to be consumed by microbes due to their higher degradability. However, at the same time microbes hydrolyse and convert larger particles into particles smaller than 25 μm in order to obtain a continuous food supply for their growth (Zhu et al., 2000). This leads to an increase in particles <25 μm and a decrease in larger particles in the stored material. These processes may explain the increase in particles smaller than 25 μm in the liquid fraction stored at 5 °C relative to the distribution before storage. When the liquid fraction was stored at 25 °C, survival of microbes should be shorter than at lower temperatures and therefore the pattern of dry matter distribution between particle size classes should not be as obvious as for liquid fraction stored at 5 °C. Information on bacteria distribution between particles in liquid separation fractions is largely lacking. However, the literature provides data on bacterial attachment to different particle size classes in stormwater and some of the mechanisms involved can be assumed to be

similar in liquid separation fractions of slurry. In stormwater the majority of the bacteria are attached to small particles (<75 μm diameter) or present as planktonic cells (Popovic et al., 2011; Jeng et al., 2005) and their survival is dependent on storage temperature and time, as well as on pH, NH_3 and VFA concentration (Patni and Jui, 1985; Nicholson et al., 2004). Spore-forming bacteria can survive for many years in resistant dormant state in the soil (Gyles and Thoen, 1993) and when growth conditions become more favourable, they germinate to vegetative cells. The spores are tolerant to heat and lack of oxygen (*Clostridium* spp. grow only under anaerobic conditions, while *Bacillus* spp. are facultatively aerobic) (Quinn et al., 1994). After storage for 16 weeks at 25 °C, when VFA were lost in the liquid fraction and ammonium concentration was low, *Clostridium* spp. and *Bacillus* spp. could germinate into vegetative cells (>25 μm), which can lead to an increase in the proportion of particles in the 25–100 μm size class.

In raw slurry distribution of P followed a similar pattern to dry matter, while Cu and Zn re-distribution towards smaller particles was more intensive (Fig. 5). Decomposition of organic matter and thus changes in manure pH values during storage can contribute to and can affect partitioning of nutrients (e.g. N and P) and metals (e.g. Cu and Zn) between different fractions and chemical forms (Møller et al., 2002; Henze et al., 1996). During organic matter decomposition orthophosphates are produced as result of polyphosphate hydrolyses and organic phosphates degradation. Previous studies (L'Herroux et al., 1997; Legros et al., 2010b) showed most of Cu and Zn to be bound to organic matter that strongly retains metals. During storage, degradation of organic matter would shift Cu and Zn fraction associated with organic matter towards more stable fractions and its chemical forms (Marcato et al., 2009). In this study Cu and Zn in raw slurry and liquid fraction were found to be mainly in particles <25 μm , indicating that they were in either dissolved or colloidal form (Westerman and Bicudo, 2000). Marcato et al., 2008 showed 85% of Cu and Zn to be bound in particles between 3 and 25 μm , and only 8% being in particles between 0.45 and 3 μm . This indicates that most of metals in raw slurry and liquid fraction stored are probably bound to solids and thus will not be easily plant available.

Changes in pH and chemical forms of salts and metals may affect the amount of suspended phosphates as a result of precipitation processes. Copper and Zn are linked to solid particles at neutral to alkaline pH values, while at pH level lower than 6 Zn would pass gradually into solution whereas Cu would remained associated to the particles (Marcato et al., 2009). However, pH value of both manure types in this study did not change significantly, so we believe pH was not the major driving force causing partitioning of Cu and Zn between particles.

5. Conclusions

The highest losses of dry matter were observed at a storage temperature of 25 °C (43% and 32% for raw slurry and liquid fraction, respectively). Regardless of the temperature, during the first 8 weeks of storage the pH increased slightly (0.1–0.4 units). At 5 °C total N and $\text{NH}_4\text{-N}$ content (based on wet

weight) in both slurry products decreased slightly. Significant losses of total N (68% for raw slurry and 76% for liquid fraction) and $\text{NH}_4\text{-N}$ (78% for raw slurry and 81% for liquid fraction) were found after storage of these slurry products at 25 °C.

Total VFA concentration decreased significantly during storage at both temperatures for both slurry products, with most rapid losses at 25 °C. In raw slurry, the carbon fraction lost due to VFA losses was around 34% at 5 °C and 20% at 25 °C at all sampling times, while for the liquid fraction the losses were higher (96% at 5 °C and 76% at 25 °C).

In both manures total P, Cu and Zn concentrations were not significantly affected by storage duration or temperature.

Particle size distribution was affected by slurry separation, storage duration and temperature. In raw slurry, the proportion of particles larger than 1 mm decreased, whereas the proportion of particles 500 μm –1 mm increased. The liquid fraction was free of particles >500 μm , with the highest proportion of dry matter, P, Cu and Zn in the smallest particle size class (<25 μm). The proportion of particles <25 μm increased when the liquid fraction was stored at 5 °C, while it decreased at 25 °C. Regardless of storage temperature, the distribution of P, Cu and Zn over particle size classes in the liquid fraction followed a similar pattern to dry matter.

An understanding of storage duration and temperature effects on chemical characteristics of slurry and its separated liquid fraction is useful in order to recommend a maximum period of storage for both manure types to prevent losses of C and N and to decrease environmental risk posed by P, Cu and Zn loads to arable land. Our results recommend winter time storage (5 °C) in order to reduce emission of ammonia and carbon losses. Summer storage of liquid fraction would be recommended for decrease in ammonia and carbon losses, as initial concentration of total N, ammonia and total C were lower in liquid fraction when compared to raw slurry.

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