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Changes of Physico–Chemical Properties of Pig Slurry During Storage

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ABSTRAK

Tujuan penelitian ini untuk mempelajari perubahan sifat limbah cair kotoran babi sebagai pupuk organik pada berbagai waktu penyimpanan. Rancangan acak lengkap digunakan pada penelitian ini. Perlakuan yang diberikan adalah waktu penyimpanan, yaitu 0, 15, 30, 45, dan 60 hari. Peubah yang diamati meliputi kehilangan limbah cair, derajat keasaman (pH), konduktivitas elektrik (electrical conductivity, EC), kandungan bahan kering (total solid, TS), bahan kering teruapkan (volatile solid, VS), kandungan *total chemical oxygen demand total* (tCOD), kandungan *soluble chemical oxygen demand total* (sCOD), kandungan nitrogen total (total nitrogen, TN), kandungan ammonia-nitrogen (NH_3-N), kandungan nitrat–nitrogen (NO_3–N), Kandungan fosfat total (total phosphate, TP), dan kandungan fosfat terlarut (dissolve reactive phosphate, DRP). Hasil penelitian menunjukkan bahwa waktu penyimpanan berpengaruh nyata terhadap seluruh peubah yang diamati, kecuali terhadap kandungan nitrat–nitrogen dan kandungan fosfat total. Derajat keasaman, TS, VS, DRP, dan kehilangan limbah cair meningkat selama penyimpanan, sedangkan EC, TN, NH_3-N, tCOD, dan sCOD mengalami penurunan selama penyimpanan. Sifat fisik dan kimia limbah cair kotoran babi mengalami perubahan selama penyimpanan sebagai hasil perombakan bahan organik yang dikandungnya.

Kata kunci: sifat fisik dan kimia, limbah cair, waktu penyimpanan

ABSTRACT

This study was aimed to determine changes of the characteristics of raw pig slurry as liquid organic fertilizer at various storage times. A completely randomized design was used in this research. The treatments were storage times, i.e.: 0, 15, 30, 45, and 60 days. Variables observed were loss of the slurry, degree of acidity (pH), electrical conductivity (EC), total solid (TS), volatile solid (VS), total chemical oxygen demand (tCOD), soluble chemical oxygen demand (sCOD), total nitrogen (TN), ammonia-nitrogen (NH_3-N), nitrate–nitrogen (NO_3-N), total phosphate (TP), and dissolve reactive phosphate (DRP). The results showed that storage time significantly affected all the observed variables, except the concentration of NO_3-N and total phosphate content. The pH, TS, VS, DRP, and losses of slurry lost during storage times increased, while EC, TN, NH_3-N, tCOD, and sCOD decreased. Physico-chemical properties of slurry during storage times changed, as a result of organic matter breakdown.

Key words: physico-chemical properties, slurry, storage times

INTRODUCTION

There is no doubt that livestock manure has benefits as a source of organic fertilizer. Slurry is an important source of organic matter, macro and micronutrients, and also heavy metals and pathogens (Araji *et al.*, 2001; Baloda *et al.*, 2001; Barker & Overcash, 2007; Suresh *et al.*, 2009a). Bulluck *et al.* (2002) measured a greater improvement in physical properties, chemical, and biological soil, and the increased crop production, when applied organic fertilizer compared to chemical fertilizer. The manure is a good nutrient source for crop production. Several studies have shown that utilization of manure in liquid form support plant growth better than solid form

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(Zhang *et al.*, 2006), because liquid form has higher nitrogen availability than in solid form (Sutton *et al.*, 1986).

Liquid manure usually cannot be directly applied to the land, but they must be collected and stored in storage ponds. Application manure as a liquid fertilizer is usually given after harvesting or before planting. The slurry occur microbiological process (Peu *et. al.*, 2006) and mechanical process during storage, which can change physico-chemical characteristics of the liquid manure. Therefore, the objective of this research was to determine the effect of storage times on physico-chemical properties of pig slurry.

MATERIALS AND METHODS

Materials

The pig slurry was collected from pig houses of University Farm, Animal Environment and Bio-engineering Laboratory, Seoul National University, located in Suwon, South Korea. The slurry from storage tank (tank volume around 20,000 l) was mixed (10 min using electric pump) and then 160 l slurry was collected, and they were divided into 16 containers, each container was filled 10 l of slurry, then slurry was stored and kept in aerobic condition for 2 mo at the laboratory. The room temperature ranged from 12-18 ^{o}C, with relative humidity ranged between 65%-70%.

Sampling and Analysis of Slurry

The physico–chemical properties were observed for 2 mo, and the samples were collected every 15 days. Each period, samples were taken from four containers. The slurry were stirred and followed by sampling. Fifty ml samples were taken from each container periodically, and samples were kept in temperature of 4 ^{o}C until they were analyzed.

The collected samples were analyzed for loss of slurry, the degree of acidity (pH), electrical conductivity (EC), total solid (TS), volatile solid (VS), total chemical oxygen demand (tCOD), soluble chemical oxygen demand (sCOD), total nitrogen (TN), ammonia nitrogen (NH_3-N), nitrate nitrogen (NO_3-N), total phosphate (TP), and dissolved reactive phosphate (DRP). The samples were pH adjusted (pH<2) either with H_2SO_4 for COD, TN, NH_3-N, NO_3-N, TP, and DRP analyzed.

A loss of slurry was measured by a change of volumes. EC and pH were measured using EC214 conductivity meter (Hana Instruments, Ltd., Sarmeola di aarubano, Italy) and pH meter (Inolab, WTW GmbH, Weilheim, Germany) with a 0.01 pH resolution over the pH range 0–14. TS, VS, tCOD, sCOD, TN, NH_3-N, NO_3-N, TP, and DRP were analyzed per standard method for water and waste water (Eaton *et al.*, 2005). The total solid and volatile solid were analyzed by gravity method. The tCOD, sCOD, TN, NH_3-N, NO_3-N, TP, and DRP were analyzed using a DR 5000 UV-vis Spectrophotometer (Hach Co., Loveland, Colo) per manufacturer's protocol. Reactor Digestion Method was used to observe tCOD, and sCOD. Persulfate Digestion Method was used to observe TN. Salicylate Method was used to observe NH_3-N. Chromotropic Acid Method was used to observe NO_3–N. Acid Persulfate Digestion Method was used to observe TP. Molybdovanadate Method was used to observe DRP.

Statistical Analysis

A completely randomized design was used in this research. Microsoft Office Excel 2007 was used to analyze the experimental data. Data were analyzed by variants analysis, and different mean between treatments were analyzed by Duncans multiple range test (P<0.05). Person product–moment correlation coefficient were calculated by choosing bivariate with two tailed option to show the relationship between the observed variables.

RESULTS AND DISCUSSION

Losses of slurry were as a result of evaporation. Mean of losses varied from 0–1.38 l and the rate of losses was 25 ml/day (Table 1). There were increased in losses of slurry to storage times. Mean of losses at each storage times were significantly different. The amount of evaporation was affected by humidity, and temperature. Evaporation did not evaporate only water, but also evaporated some compounds, as result of organic materials degradation of slurry. Losses of slurry had a close correlation and affected the other properties, such as pH, EC, TS, VS, tCOD, sCOD, TN, NH_3-N, and DRP (Table 2).

The EC values ranged from 17.33–19.47 mS/m. The highest EC at 0 day storage times, and the lowest EC at 45 days storage times. There was a change of EC values of slurry. EC values during storage times decreased (Table 1). The change of EC values showed that there were changes of ion composition in the slurry, because EC described as a result of measurement of ion transfer between the anode and cathode in the solution. EC was normally considered to measure the solubility of salt in the solution (Motsara & Roy, 2008), its correlation to concentration of dissolved ions in a solution (Provolo & Martinez-Suller, 2007). The changes of EC values were as a result of organic compounds degradation and or inorganic compounds to simple molecules or ions. Therefore, EC had a very close relationship with the other properties of slurry (Table 2). The EC had a positive correlation with the ammonia nitrogen (NH_3-N), TN, specific gravity (SG), TS, VS, fixed solids (FS), and total dissolved solids (TDS) (Suresh *et. al.*, 2009b).

The pH values ranged from 7.18 to 7.82. The pH slurry significantly increased. The pH increased gradually during storage periods, and moved from neutral to alkali. It was caused by degradation of some intermediate compound and emitted to the atmosphere. The slurry pH will become more alkaline in aerobic storage system (Fentonet *et al.*, 1983). On the other hand, increasing acidity would be associated with losses of ammonia. In this study, loss of ammonia continued to rise, because pH of slurry was higher than 7. It is supported by Zhang & Lau (2007) that ammonia emission will increase dramatically, when pH value is higher than 7. Furthermore, there were negative correlation between pH and NH_3-N concentration of slurry (Table 2). It means that pH was affected by ammonia emission to atmosphere. When pH was low, losses of ammonia from slurry can be reduced.

The mean of TS concentration varied from 16.65–20.21 g/l. The mean of VS ranged from 10.66 to 12.99 g/l. Concentration of TS and VS increased during storage times (Table 1). Increased concentration of TS and VS in slurry was influenced by the loss of water due to evaporation. Although there were degradation of organic matter, but these did not reduce the concentration of TS and VS, because the rate of water loss through evaporation was greater than the rate of degradation of organic material. Beside that, TS concentrations affected and had a correlation to the other properties such as pH, EC, VS, tCOD, sCOD, TN, NH_3-N, DRP, and losses of slurry (Table 2).

The mean of tCOD ranged from 25.50–29.35 g/l, while the mean of sCOD varied from 12.75 to 18.70 g/l (Table 1). There were decreased of tCOD and sCOD during storage periods. Decreasing of tCOD were significantly different at 0–15 days storage times and 30 to 45 days storage times, while 15 to 30 days and 45 to 60 days were not significant change. The content of soluble COD decreased during increasing storage times. The COD described the organic substrate in the solution. The tCOD and sCOD decreased during storage periods

Table 1. Physico-chemical properties of pig slurry at various storage times

Observed variables	Storage times (days)					Significant
	0	15	30	45	60	
Losses of slurry (ml)	0.00±0.00[e]	400.06±0.05[d]	874.11±45.03[c]	1101.47±65.44[b]	1389.50±105.08[a]	**
pH	7.18±0.01[d]	7.58±0.05[c]	7.64±0.03[bc]	7.71±0.08[ab]	7.77±0.04[a]	**
EC (mS/m)	19.47±1.02[a]	19.33±0.21[ab]	18.17±0.11[bc]	17.33±1.00[c]	17.83±0.25[c]	**
TS (g/l)	16.65±0.15[c]	17.66±0.12[c]	19.07±0.08[b]	20.21±1.24[a]	19.58±0.13[ab]	**
VS (g/l)	10.66±0.12[b]	11.04±0.12[b]	11.98±1.09[ab]	12.99±1.29[a]	12.65±0.13[a]	*
tCOD (g/l)	29.35±0.15[a]	27.85±0.15[b]	28.05±0.75[b]	26.20±0.20[c]	25.50±1.00[c]	**
sCOD (g/l)	18.70±0.10[a]	16.65±0.15[b]	15.85±0.25[c]	15.05±0.35[d]	12.75±0.55[e]	**
TN (g/l)	3.90±0.61[a]	3.57±0.34[a]	3.20±0.41[ab]	3.23±0.48[ab]	2.60±0.12[b]	*
NH_3-N (g/l)	1.35±0.05[a]	1.25±0.04[b]	1.18±0.02[b]	1.08±0.05[c]	1.09±0.04[c]	**
NO_3-N (g/l)	0.64±0.30	0.56±0.02	0.60±0.09	0.78±0.05	0.77±0.04	NS
TP (g/l)	0.41±0.06	0.42±0.06	0.42±0.07	0.44±0.03	0.45±0.04	NS
DRP (g/l)	0.28±0.03[b]	0.28±0.02[b]	0.40±0.002[a]	0.38±0.003[a]	0.37±0.02[a]	**

Note: *= P<0.05, **= P<0.01, NS= non significant. Values with different superscript of the same row are significantly different (P<0.05).
EC= electrical conductivity, TS= total solid, VS= volatile solid, tCOD= total chemical oxygen demand, sCOD= soluble chemical oxygen demand, TN= total nitrogen, NH_3-N= ammonium nitrogen, NO_3-N= nitrate nitrogen, TP= total phosphate, DRP= dissolve reactive phosphate.

Table 2. Pearson correlation between the observed variables

	pH	EC	TS	VS	tCOD	sCOD	TN	NO_3-N	NH_3-N	TP	DRP	LS
pH	1.00											
EC	-0.47	1.00										
TS	0.74**	-0.85 **	1.00									
VS	0.51	-0.80 **	0.85**	1.00								
tCOD	-0.51	0.64 *	-0.64*	-0.69**	1.00							
sCOD	-0.57*	0.69 **	-0.67**	-0.69**	0.91**	1.00						
TN	-0.42	0.65 **	-0.60*	-0.73**	0.63*	0.77**	1.00					
NO_3-N	0.028	-0.17	0.30	0.29	-0.50	-0.40	0.08	1.00				
NH_3-N	-0.69 **	0.75 **	-0.83**	-0.80**	0.87**	0.861**	0.78**	-0.27	1.00			
TP	-0.03	-0.21	0.28	0.06	-0.02	0.04	0.17	0.45	-0.05	1.00		
DRP	0.65 **	-0.80 **	0.85**	0.69**	-0.53*	-0.65**	-0.57 *	0.20	-0.74**	0.38	1.00	
LS	0.66 **	-0.78 **	0.82**	0.79**	-0.88**	-0.95**	-0.75**	0.40	-0.93**	0.13	0.81**	1

Note: *= P<0.05, **= P<0.01. EC= electrical conductivity, TS= total solid, VS= volatile solid, tCOD= total chemical oxygen demand, sCOD= soluble chemical oxygen demand, TN= total nitrogen, NH_3-N= ammonium nitrogen, NO_3-N= nitrate nitrogen, TP= total phosphate, DRP= dissolve reactive phosphate, LS= losses of slurry.

showed there was degradation of COD, or occurred degradation of organic material. At storage periods, there were activity of microorganisms to break down organic matter, and produced some organic compounds, such as ammonia, volatile fatty acids, organic acids, alcohols, phenolics, sulfides, and so forth. The organic matters are found in slurry are carbohydrates, fat, protein, and NPN. Carbohydrates and fats will be released into the atmosphere in gaseous form, while protein and NPN will be degraded to be simple nitrogen molecules, namely NH_3, N_2, N_2O, NO, and emitted to the atmosphere (Oenema *et al*., 2007). Furthermore, ammonia is a gas that indirectly affects to the enhanced greenhouse effect through physical and chemical processes in the atmosphere and soil (Seidl, 1999). Changed of sCOD could be used as indicator for other properties, because sCOD have correlation to pH, EC, TS, VS, tCOD, NH_3-N, DRP, and losses of slurry (Table 2).

The concentration of TN ranged from 2.49 to 3.80 g/l (Table 1). The TN concentration during storage periods decreased. The mean concentrations of TN at 60 days were significantly different compared to 0–15 days storage times. The decrease was due to nitrogen emissions to the atmosphere. These gases were products from decomposition of urine and undigested proteins in slurry.

The concentration of NH_3-N varied from 1.03 to 1.40 g/l (Table 1). It trends to decrease when storage times increased. Decreasing of NH_3-N concentration indicated losses of nitrogen in the ammonia form, ammonia in the solution will be evaporated easier. It is supported by many studies. Approximately 50% losses of nitrogen in slurry are ammonia (Harper *et al*., 2000), the others are N_2, and only a small portion are N_2O (Rotz, 2004). The release of ammonia from the manure is a slow process which governed by factors as ammonia concentration, pH, temperature, air velocity, and emitting surface area (Aarnink & Verstegen, 2007). The ammonium ion (NH_4) will be converted to ammonia (NH_3) when the degree of acidity increased (Karakashev *et al*., 2008). In addition, emission of NH_3 will be higher if there were increased of temperature and ammonium ion concentration, and the wind will accelerate the emission of NH_3 into the atmosphere.

The concentration of NO_3-N ranged from 0.64 to 0.77 g/l (Table 1). There were not different of NO_3-N concentration, it means that N-NO_3 concentrations were not affected by storage times. It indicated that nitrification process is equal to denitrification process. Nitrate is the end product of nitrification process, converse of ammonium to nitrate by bacterial activity. Nitrate can not be directly emitted into the atmosphere, but it must be conversed to NO, N_2O, and N_2 through denitrification process. Moreover, NO_3-N concentration did not have correlation to other properties (Table 2)

The mean concentration of TP varied from 0.41 to 0.45 g/l (Table 1). There were no different of TP concentration, it means that TP concentrations were not affected by storage times. Losses of phosphates during storage period by evaporation are extremely rare, because losses of phosphates occur more frequently when slurry is applied to land, through the mechanism of run off and leaching. Losses of phosphates when applied as organic fertilizer has been widely studied (Tabbara, 2003; Daverede *et al*., 2004).

The mean concentration of DRP varied between from 0.28 to 0.40 g/l (Table 1). The DRP concentration increased during storage times. The concentration of DRP dramatically increased after 15 days, increased almost 100 mg/l. During storage, there was a change of organic matter to be simple organic compounds or inorganic forms (Fontenot *et al*., 1983). Although total phosphates concentration did not change, but the composition of phosphates changed, namely from organic phosphate to inorganic phosphates through decomposition process by microorganism. In this study, comparison TP concentration to DRP concentration ranged from 66% to 89%. According to Sharpley and Moyer (2000), pig slurry contains 80%-90% DRP from TP. The increasing of DRP concentration will increase the availability of phosphor for plant nutrient, while phosphor will be the easiest to uptake by plant. If it is applied to agricultural lands in the form of animal slurry has the potential source of pollution on surface waters, leading to eutrophication.

CONCLUSION

Physico-chemical properties of pig slurry changed during storage. Losses of slurry, pH, TS, VS, and DRP concentration increased, but EC, tCOD, sCOD, TN, and NH_3-N concentration decreased during storage period, while concentration of NO_3-N and TP did not change. Losses of slurry, sCOD and NH_3-N concentration had a close correlation to other properties, except to NO_3–N, and TP. The pig slurry as a source of liquid organic fertilizer must be treated to minimize nutrient loss and pollution.

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