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Changes in the properties of pig manure slurry*

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The paper presents the results of analyses of samples of manure from a pig farm located near Piła, Poland performed between June 2011 and May 2012 using a single sampling system. The statistical analyses of the average content of chemical and biological oxide demands, nitrogen, phosphorus, potassium, calcium and dry mass in the slurry in various seasons allowed us to draw conclusions concerning the changes in the chemical composition of the manure in specific seasons and to determine the correlations between the chemical parameters. The average content of N, BOD, P, and dry mass content tended to decrease systematically from the spring until the winter. The highest correlation coefficient, which indicates significant interdependency among the variables tested, was consistently found for COD and BOD, whereas the smallest correlation coefficient was found consistently for K and Ca and once for Ca and N.

Key words: pig slurry, swine/pigs, chemical composition, fertilizer components

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INTRODUCTION

Industrial pig breeding in Poland produces large amounts of pig manure slurry that according to the Polsh law (Act, 2007) is defined as fertilizer. The arable land fertilized with slurry, however, is diminishing, and the management of this waste is getting more and more problematic (Oudendag & Luesink, 1998). On the average, 100 pigs produce daily 2846 kg of manure. In pig slurry, which is a mixture of urine, excrement, and water, two fractions can be distinguished: the liquid one , that consists primarily of nitrogen compounds, and the solid one , that consists of phosphorus and organic compounds (Kowalski *et al.*, 2012; Lens *et al.*, 2004). The amount of slurry produced is strictly associated with the size and age of the pigs as well as the method of keeping the animals. The total amount of slurry produced in the USA is assessed to be 1Gt per annum. This slurry contains approximately 5Mt of nitrogen, 3Mt of potassium, and 1.5Mt of phosphorus (Troeh & Thompson, 1993; Taylor, 1994).

Intensive pig breeding contributes to changes in the natural environment due to acidification, eutrophication and an increasing greenhouse effect (the emission of CO_2, CH_4, and NO_x).

The chemical composition of pig manure depends on many factors, including the type and age of animals and a feeding method. Nitrogen is the component that determines the value of the specific slurry as a fertilizer. One-half of the nitrogen in pig slurry occurs in the form of easily soluble ammonium nitrogen. The amount of nitrogen in slurry decreases with time, and the difference between its total amount in fresh pig slurry and in pig slurry that has been stored for 90 days may be approximately 60%. The total amount of phosphorus in slurry increases gradually and subsequently decreases to a value lower than that in fresh feces. Density of pig feces ranges between 900 and 1100 g/dm³ (Hus & Kutera, 1998). This density was analyzed by Czop (Czop, 2011) and it was equal to 886–889 g/dm³, and the total nitrogen content ranged between 4.04 and 5.01 g/dm³. These values are similar to the data presented elsewhere (Magrel, 2004; Krawczyk & Walczak, 2010; Prapaspongsa, 2010).

Nitrogen in pig slurry occurs in organic and inorganic forms. The forms of nitrogen in slurry include ammonia, ammonium compounds, nitrates, nitric oxides, and organic matter (Rulkens *et al.*, 1998; Bertora *et al.*, 2008). Nitrogen in slurry is composed primarily of inorganic compounds, which constitute approximately 75% of the total amount of N (Prapaspongsa, 2010). A fertilizer derived from nursing or pregnant sows differs in composition from the slurry derived from the other specimens. Determination of the nitrogen content for different groups of pigs (Table 1) was investigated elsewhere(Sánchez & González, 2005). Nursing and pregnant sows, together with piglets belonged to Group 1. Group 2 contained all the other specimens (both adult pigs and piglets). Pigs weighing between 14 and 16 kg (grower) and raised for slaughter were classified as Group 3.

Phosphorus compounds in the manure mainly occur in inorganic form (74–87% of the total P content). The phosphorus content depends on the physiology of the animals from which the slurry is derived (Sánchez & González, 2005).

Storage of manure is associated with the generation of odors produced due to anaerobic degradation of materials present in manure. Pig manure contains approximately 400 volatile organic and inorganic compounds of unpleasant odor, including hydrocarbons, aldehydes, ketones, alcohols, mercaptans, esters, phenols, cyclic amines, hydrogen sulfide, ammonia, and nitric oxides. The main sources of the odors are proteins, which are subjected to anaerobic decomposition resulting from the activity of putrefactive bacteria (Cotta *et al.*, 2003; Hus & Kutera, 1998; Pawełczyk & Muraviev, 2003; Szynkowska & Zwoździak, 2010) include *Pseudomonas fluorescens*, *Bacil-*

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Abbreviations: COD, chemical oxygen demand; TKN, total nitrogen determined with Kjeldahl's method; BOD5, biochemical oxygen demand

lus subtilis, and *Bacillus cereus*, as well as *Clostridium sporogenes* and *Clostridium butyricum*. The decomposition process resulting in the emission of malodorous gases applies, apart from proteins, to saccharides and lipids. Decomposition of lipids produces an increased amount of volatile fatty acids (from C_4 to C_{12}) (Kuczyński, 2002; Libudzisz, 2008).

Harmful microorganisms growing in pig manure slurry include bacteria, viruses, and other pathogens. The most common pathogenic bacteria include gram-negative anaerobic bacilli of the genera *Enterobacter, Escherichia, Salmonella*, and *Proteus*. Soils that are fertilized with manure containing solid parts cannot be deemed free from pathogens and indicatory organisms, including *E-coli* group bacteria, fecal streptococci, and *Salmonella*, for at least one year after fertilization (Rufete *et al.*, 2006; Sorensen & Amato, 2001). Low temperatures, high air humidity, and neutral soil generally contribute to the development and survival of enteric bacteria. The soil texture may also be changed (Głąb & Gondek, 2008). Composting of separated pig manure resulted in organic matter transformation (Hsu & Lo, 1999).

In the other study (Moral *et al.*, 2005), slurry samples were collected from 36 commercial farms in Southeast Spain. Samples were analyzed for pH, electrical conductivity (EC), redox potential, specific density, total solids, sedimentable solids, biological oxygen demand, chemical oxygen demand, total nitrogen, ammonium nitrogen (AN), organic nitrogen, and total contents of phosphorus, potassium, calcium and magnesium. Relationships between major nutrient levels of pig slurries and a range of physical and chemical properties were investigated. TKN, AN and K were closely related to EC. The P content in slurries was related more closely to solids-derived parameters. Pig manure could be a source of pollutants. The work (De la Torre *et al.*, 2000) estimates the environmental risk in nine samples from different farm treatment systems based on the evaluation of their effects in Daphnia magna acute test, and on the assessment of Cu, Zn and ammonia as main contributors.

This paper presents the results of tests conducted on the pig manure slurry obtained from a pig farm located near Piła, Poland. The analyses of the slurry were performed between June 2011 and May 2012 using a single sampling system. The tests performed throughout one year enabled us to determine changes in the slurry's chemical composition at different seasons of the year.

MATERIALS AND METHODS

The pig slurry collected between June 2011 and May 2012 at a pig farm located near the town of Piła, Poland was analyzed. The farm produces piglets intended for fattening at other pig farms, as well as sows for renewing the stock. The average monthly livestock statistics, by a pig type, were as follows: 1 101 sows, 64 gilts, 2 536 sucking piglets, 140 weaned piglets, 200 shoats, and 160 porkers. The total number of pigs was 4 201.

Pig manure samples were taken from drainpipe carrying the slurry from the pig farm to a lagoon according to the PN-B-12098:1997 standard. The same system and sample source were used throughout the study. Preparation and measurements of the samples were performed according to the proper polish standards (Kowalski *et al.*, 2012) to determine the content of nitrogen, the biochemical oxygen demand, the chemical oxygen demand, and the content of phosphorus, potassium, calcium, and dry mass. To determine Kjeldahl nitrogen a DK6 digester and a steam distillation unit produced by VELP were used. Phosphorus was determined with a Nanocolor UV/VIS spectrophotometer produced by Machery-Nagel. A WSL M-9 digester produced by WSL was used to mineralize the samples to determine COD. Potassium and calcium were determined by flame atomic absorption spectroscopy (FAAS) using a Perkin Elmer OPTIMA 7300 DV apparatus. Microbiological tests were performed to identify *Salmonella* bacilli (according to the PN-Z-19000-1:2001P norm) and live parasite eggs.

Quantitative variables were characterized by the average value and standard deviation. The equality of average values in independent groups was tested using an analysis of variance (ANOVA). The correlation among quantitative variables was identified using a Pearson correlation coefficient and multiple regression, and $p<0.05$ was considered statistically significant. The analysis was conducted using a previously described program (R Development Core Team, 2010).

RESULTS AND DISCUSSINON

The properties of the pig manure analyzed in the long-term tests revealed changes in the chemical composition of slurry throughout the whole year. Because of the chemical composition being changed significantly, the average values of all determinations were calculated for slurry samples obtained in prescribed time intervals. All interpretations of the results were compared with the average values for a specific season.

The test results of all of samples of the pig manure are presented in Table 2. Table 3 presents the descriptive statistics of the variables tested (average and standard deviation). The matrix of the Pearson linear correlation coefficients is given in Table 4, and Table 5 shows the results of the data analysis using the multiple regression model.

Figure 1 shows a series of charts presenting the changes in the content of a given parameter depending on the date of collection of the pig slurry sample. Because the samples were obtained between June 2011 and May 2012, the results are arranged in chronological order, to present changes in the slurry's properties from summer through autumn and winter to spring. The average results of the parameter determination at given time of year are identified using black line segments.

The analyses of the average values of nitrogen, biochemical oxygen demand, phosphorus, and dry mass show that the highest average values tended to occur in the spring, whereas the lowest average results were found in winter. The lowest average values were as follows: N 4.18 g/kg, BOD 14.98 g/kg, P 0.81 g/kg, and dry mass 39.05 g/kg. The highest average values were as follows: N 7.14 g/kg, BOD 25.48 g/kg, P 1.52 g/kg, and dry mass 83.07 g/kg. A systematic decrease in N, BOD, P, and dry mass occurred between spring and

Table 1. Average nitrogen content in pig manure from different specimens (Sánchez & González 2005).

Nitrogen content (g /kg of slurry)	Group 1	Group 2	Group 3
Ammonium (NH_4^+)	1.50	1.69	2.43
Inorganic	2.07	2.47	3.31
Organic	0.67	0.70	0.88
Total	2.61	3.07	4.08

Table 2. Results of pig manure analysis.

Batch No.	Season of the year	Sampling date	Parameter determined (g/kg)							Microbiological tests	
			N	BOD_5	COD	P	K	Ca	Dry mass	*Salmonella*	Live eggs of parasites
1	Summer	06.06.11	4.69	19.7	43.1	1.27	2.09	1.46	83.3	absent	absent
2		13.06.11	7.69	34.1	67.5	1.67	3.16	1.61	86.1	absent	absent
3		20.06.11	2.97	6.75	17.45	0.77	2.02	1.26	84.4	present	present
4		04.07.11	6.71	37.2	91	2.18	1.45	1.94	78.4	absent	absent
5		11.07.11	6.82	20.1	75.4	2.35	2.86	1.33	118	absent	absent
6		18.07.11	12.9	16.7	43	1.89	1.71	1.67	80.1	present	absent
7		25.07.11	4.4	10.4	38.6	0.83	1.43	1.98	60.2	absent	absent
8		01.08.11	1.5	6.45	19.65	0.52	0.16	0.78	30	absent	absent
9		08.08.11	3.11	10.5	20.8	0.64	1.31	2.04	68	absent	absent
10		16.08.11	6.18	28.1	58	1.96	2.4	4.63	81.5	absent	absent
11		22.08.11	4.37	25.25	53.4	0.91	1.92	1.32	40.5	absent	absent
12		29.08.11	7.75	44.7	100.7	1.99	3.68	3.78	119	absent	absent
13	Autumn	05.09.11	3.97	13.8	36.7	1.13	1.32	2.3	45	absent	absent
14		12.09.11	5.39	14.5	29.6	0.55	2.41	1.13	33	absent	absent
15		19.09.11	2.33	7.7	18.4	0.85	0.9	1.62	34	absent	absent
16		26.09.11	3.23	7.05	14.95	0.22	1.09	1.51	29	absent	absent
17		03.10.11	7.65	50.8	125.2	2.04	2.76	6.32	106	absent	absent
18		10.10.11	7.65	32.2	118	1.52	3.26	1.57	109	absent	absent
19		17.10.11	8.8	31.7	115.1	1.73	3.74	5.77	103	absent	absent
20		24.10.11	5.15	13.75	32.65	0.27	2.12	0.75	25	absent	absent
21		31.10.11	5.45	8.9	40.5	1,35	2.68	1.68	53	absent	absent
22		14.11.11	8.73	36.9	87.9	1.66	2.13	2.44	109	absent	absent
23		28.11.11	3.94	18.1	39.3	0.57	0.29	3.85	39	absent	absent
24	Winter	12.12.11	3.68	9.62	20	0.46	0.71	1.11	21	absent	absent
25		27.12.11	3.05	10.4	29	0.64	0.94	2.27	48.5	absent	absent
26		09.01.12	7.97	41.4	98.3	1.81	6.56	2.18	94.8	absent	absent
27		23.01.12	2.96	2.62	8.76	0.22	1.18	0.23	10	absent	absent
28		13.02.12	3.48	13.6	29.2	0.96	1.55	1.05	43	absent	absent
29		20.02.12	3.96	12.24	36.88	0.78	1.16	0.57	17	absent	absent
30	Spring	19.03.12	9.18	18.8	60.9	1.77	2.27	1.88	80	absent	absent
31		02.04.12	7.31	21	109	1.62	1.57	3.5	111	absent	absent
32		16.04.12	6.31	38.2	112.8	1.59	2.22	2.27	82.4	absent	absent
33		30.04.12	8.08	28.4	123.1	1.79	2.03	2.82	98	absent	absent
34		14.05.12	4.315	9.4	23.65	0.79	1	1.54	39	absent	absent
35		28.05.12	7.635	37.1	82.1	1.54	2.46	1.86	88	present	absent

winter (Table 5). The average values of N and BOD remained relatively constant in summer and autumn: 5.76 g/kg in summer and 5.66 g/kg in autumn for N and 21.66 g/kg in summer and 21.40 g/kg in autumn for BOD. The average COD values ranged between 37.02 and 85.26 g/kg (Table 2). As in the case of N, BOD, P, and dry mass, the lowest average values were found in winter and the highest in spring (Fig. 1).

The average Ca values ranged between 1.24 and 2.63 g/kg. As in the case of N, BOD, P, and dry mass, the lowest average values were found in winter and the highest in spring.

Only in the case of potassium the average values remained at nearly the same level throughout the year (Fig. 1). The segments shown in Fig. 1 fall nearly on a straight line. The average K values (Table 2) ranged between 1.92 and 2.02 g/kg. Throughout the year, the highest values were observed for dry mass (67.06 g/kg) and COD (57.73 g/kg), whereas the lowest values were observed for P (1.22 g/kg); a somewhat higher but rela-

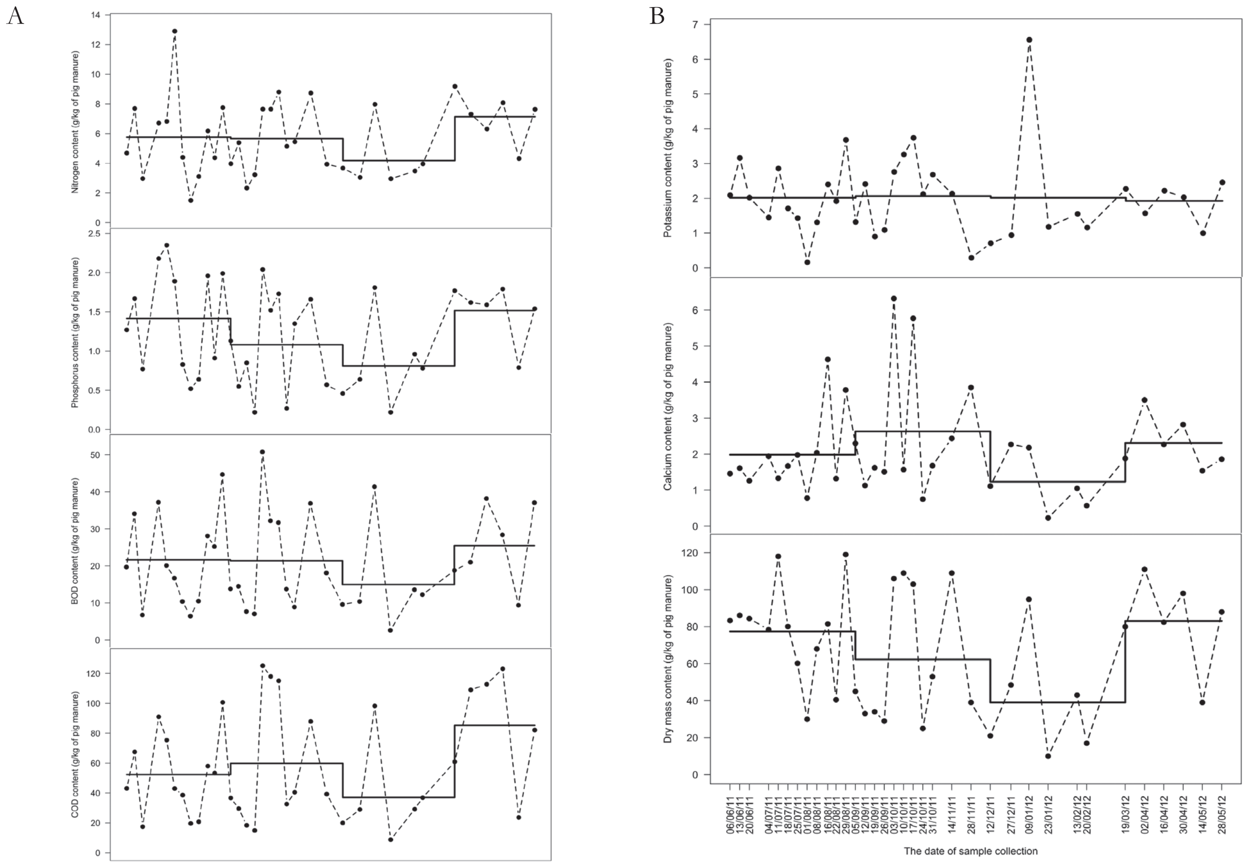

Figure 1. Changes in:
(**A**) nitrogen, BOD_5, COD, phosphorus, (**B**) potassium, calcium and dry mass content according to the date of slurry collection

tively comparable level was observed for K (2.02 g/kg) and Ca (2.11 g/kg).

The microbiological analysis identified *Salmonella* bacilli in three samples only and live parasite eggs in one sample.

The results of the variance analysis for the individual parameters are shown in the last column of Table 3. The null hypothesis of the variance analysis test assumes that the average parameter values are equal throughout the year. None of the cases analyzed contradicted the null hypothesis. The parameters of COD, P, and dry mass, for which the p-values were 0.133, 0.124, and 0.054, respectively, were the closest to statistical significance.

The Pearson linear correlation coefficient was used in the next stage of the analysis (Table 4). All correlations except the one with smallest correlation coefficient (i.e., the correlation between Ca and K) were statistically significant.

The highest correlation coefficient was found between COD and BOD (0.88). A strong interdependence also occurred between dry mass and P (0.86), dry mass and COD (0.82), P and N (0.79), P and COD (0.79), P and BOD (0.76), and BOD and dry mass (0.74). A moderately strong correlation occurred between BOD and N (0.66), BOD and K (0.66), dry mass and K (0.62), COD and Ca (0.61), COD and K (0.60), P and K (0.59), and K and N (0.58). Ca and N as well as K and Ca displayed weak correlations: 0.40 and 0.29, respectively.

These analyses identified increasing or decreasing tendencies linking pairs of parameters. The COD and BOD parameters can be used to determine the purity of the slurry. The strong interdependence between these two parameters was demonstrated by their high correlation coefficient (0.88). Additionally, the strong correlations between dry mass and P, dry mass and COD, and dry mass and BOD provide important information. These correlations allow us to hypothesize that a higher dry mass content is associated with a higher level of BOD, COD, as well as a higher level of phosphorus, which is a valuable constituent of fertilizers. The strong correlations between phosphorus and COD, BOD, and N help to identify tendencies in the content of other constituents. Specifically, a higher P content is associated with higher levels of COD, BOD, and N.

Table 5 shows the regression coefficients for statistically significant independent variables in the regression models created for the dependent variables given in the first column of the table. The last two columns of Table 5 contain measures of the goodness of fit, i.e., the coefficient of determination and the standard deviation of the residuals. It can be assumed that the regression models created for BOD, COD, P and dry mass indicate a relatively good fit. In the case of the remaining parameters, the fit is unsatisfactory.

The regression models for BOD, COD, P and dry mass enable us to predict the value of a given parameter based on knowledge about other parameters. For example, it is possible to predict the value of BOD_5 by determining COD.

The analysis of the average values of N, BOD, P and dry mass in different seasons has shown that these parameters tend to decrease systematically between spring

Table 3. Descriptive statistics of the variables (average, standard deviation) and analysis of variance results.

Variable	Total	Season				p-value
		Summer	Autumn	Winter	Spring	
	Number of measurements					
	35	12	11	6	6	
N	5.69 (2.47)	5.76 (3.00)	5.66 (2.24)	4.18 (1.89)	7.14 (1.67)	0.234
BOD	21.09 (12.89)	21.66 (12.49)	21.40 (14.32)	14.98 (13.49)	25.48 (11.21)	0.576
COD	57.73 (36.83)	52.38 (27.42)	59.85 (42.68)	37.02 (31.52)	85.26 (37.82)	0.133
P	1.22 (0.62)	1.42 (0.66)	1.08 (0.63)	0.81 (0.55)	1.52 (0.37)	0.124
K	2.02 (1.18)	2.02 (0.94)	2.06 (1.06)	2.02 (2.24)	1.92 (0.54)	0.997
Ca	2.11 (1.36)	1.98 (1.11)	2.63 (1.88)	1.24 (0.83)	2.31 (0.73)	0.232
Dry mass	67.06 (32.64)	77.46 (26.21)	62.27 (36.08)	39.05 (31.21)	83.07 (24.41)	0.054

Table 4. Matrix of the Pearson linear correlation coefficients.

Variable tested	N	BOD	COD	P	K	Ca	Dry mass
N		0.66	0.70	0.79	0.58	0.40	0.71
BOD	0.66		0.88	0.76	0.65	0.59	0.74
COD	0.70	0.88		0.79	0.60	0.61	0.82
P	0.79	0.76	0.79		0.59	0.51	0.86
K	0.58	0.65	0.60	0.59		0.29	0.62
Ca	0.40	0.59	0.61	0.51	0.29		0.55
Dry mass	0.71	0.74	0.82	0.86	0.62	0.55	

Table 5. Results of multiple regression modeling.

Dependent variable	Intercept	Regression coefficients for independent variables (x - not significant)							R^2(%)	Root Mean Squared Error
		N	BOD	COD	P	K	Ca	Dry mass		
N	1.872	x	x	X	3.123	x	x	x	62	1.55
BOD	1.447	x	x	0.267	x	2.087	x	x	80	6
COD	-6.78	x	1,734	X	x	x	x	0.417	84	15.4
P	-0.046	0.0759	0.0096	X	x	x	x	0.0095	82	0.28
K	0.4506	x	0.0396	X	x	x	x	0.0109	47	0.89
Ca	0.795	x	0.063	X	x	x	x	x	35	1.11
Dry mass	11.862	x	x	0.324	29.823	x	x	x	79	15.5

and winter. An analogous situation occurred in the case of COD and calcium, where the lowest values were also recorded in winter. Time at which the highest values occur represents a somewhat different situation because the highest content of COD was observed in spring, whereas the highest content of Ca was recorded in autumn. The values of potassium remained stable throughout the year.

The results have shown a strong interdependence between the variables tested, consistently occurred between COD and BOD, whereas the lowest occurred consistently between K and Ca and once between Ca and N.

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