Measurement and analysis of biogas fertilizer use efficiency, nutrient distribution and influencing factors of biogas residues and slurry on pig farms

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Abstract: Although the effects of biogas residues and slurry returning to farmland are good, they still cannot be used widely in China. In this study, the biogas fertilizer use efficiency, nutrient distribution and influencing factors of fertilizer use efficiency of biogas residues and slurry in 20 biogas projects in Chongming County, Shanghai, China were measured and analyzed. The correlation and a linear regression fit of parts of test indicators were also analyzed. The results show that pig farm biogas residues and slurry mixture are nutrient-rich and can be used as a high-quality organic fertilizer, while its fertilizer use efficiency is unstable because of the differences among area, raw materials, fermentation technology and operation management. Nutrients are not evenly distributed in biogas residues and slurry. Higher levels of organic matters, P and trace elements were detected in biogas residues and higher levels of water-soluble N and K were detected in biogas slurry. The correlations between some test indicators of biogas residues and slurry mixture are significant, especially between total K and conductivity. Linear regression model fitting results of parts of test indicators are satisfactory. Hence, the values of the other test indicators can be estimated by one known indicator which can effectively reduce the determination workload under some limited situations.

Keywords: biogas residues and slurry, biogas fertilizer, fertilizer use efficiency, nutrients, influence factors, environmental protection, pollution control, supernatant

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1 Introduction

The development of the livestock industry in China has its particularity, such as intensification, large quantities, and high-density rearing. Mechanical desludging and flush are main ways to clean manure and slurry. As a result, large quantities of manure and sewage which are high turbid, rich in nitrogen (N) and phosphorus (P), with high moisture content and difficult to transport are produced, and caused a lot of environmental pollutions[1]. In the processing of livestock manure, biogas anaerobic fermentation can help farmers to solve the manure pollution problems in large-scale livestock industry and the solid and liquid mixture residues (biogas residues and slurry) after fermentation are a kind of widely used fertilizer[2]. Research shows that biogas residues and slurry are a kind of quickly decayed and effective fertilizer, rich in organic matters, humic acid, N, P, K, amino acids, vitamins, enzymes, trace elements and other vital active substances[3]. These high available nutrients can be quickly absorbed by crops and the organic matters and small molecule humus contained in biogas residues and slurry can be used to improve soil structure, increase soil

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fertility[4] and effectively reduce crop diseases and insect pests[5]. Therefore, it is an effective way to use biogas residues and slurry by returning them to farmland[6,7].

However, according to production practices and scientific experience, biogas residues and slurry still have not been fully utilized despite their good effects in China. Biogas residues are typically used for directly composting or returning to farmland; the fertilization mode of biogas slurry is generally irrigation, furrow irrigation, and topdressing, which can easily lead to N loss by NH_3 volatilization[6,7], greenhouse gas emissions[8] and leaching[9]. These could greatly reduce the biogas fertilizer use efficiency. Drip irrigation, subsurface irrigation, deep application and other methods can effectively improve the use efficiency of biogas residues and slurry[6,7], and reduce environmental pollution, but the higher pre-treatment technology and equipment are required when biogas slurry is applied onto farmland because it contains a lot of particulate matters and easily blocks nozzles[10,11]. In addition, many Chinese regions are facing the situation like dual-constrains of land tension and lack of breeding scale and facilities, biogas slurry often fails to use in farmland and needs treatments to meet the national standards[12] before discharge[13]. Biogas residues and slurry after anaerobic fermentation are complicated organic complexes. There are large differences of their compositions and traits depending on different raw materials[14,15], therefore, the fertilizer effects of biogas residues and slurry on biogas engineering are unstable, and there are no reliable measurement standards. Besides, many farmers, lack of the necessary theoretical guidance, do not know about the fertilizer use efficiency of purchased biogas manure, thus they are unable to determine how to apply fertilizer scientifically, leading to the current more rough application ways of biogas fertilizer[16]. In order to explore the biogas fertilizer use efficiency and the causes of its instability, 20 biogas projects of small and medium-sized individual pig farms distributed in Chongming county, Shanghai, China, are surveyed in this study, and the fertilizer use efficiency, distribution of nutrients and the impact factors of fertilizer use efficiency of biogas residues and slurry were analyzed at the same time. Correlation analysis and linear regression fit of parts of measurement indicators were also conducted, which provided theoretical basis for applying biogas fertilizer more efficiently and rationally in rural areas.

2 Materials and methods

2.1 Test materials

Test samples were collected from 20 biogas projects of small and medium sized individual pig farms distributed in Chongming County, Shanghai, China. Test time is from March to June, 2013.

2.2 Test set and content

The samples were divided into two batches, one batch was the mixture of biogas residues and slurry, of which organic matter, major elements and trace elements were measured; the other was the supernatant of the mixture after centrifugation, of which major elements and trace elements were measured.

2.3 Test index and analysis

Fertilizer use efficiency analysis test: The pH-value and conductivity were measured in the sample within 24 h after collection, pH meter and conductivity meter models were PHS-3C and DDS-307A, respectively. Total solid (TS) was measured by drying samples at 103°C to constant weight; total N (TN) was determined by the Kjeldahl method; total P (TP) was determined by ammonium molybdate spectrophotometry; total K (TK) was determined by flame spectrophotometry; organic matters were determined with potassium dichromate method; trace elements were measured by inductively coupled plasma (ICP) instrument.

Nutrient distribution test: Major elements and trace elements measured results of two batches of samples were compared. The water-soluble N, P and K contents are the ratio percentages between N, P, K content in the supernatant fluid and mixture.

Influence factors analysis: Test index correlation and regression analysis are determined by using data processing software.

2.4 Data processing

IBM SPSS statistics software 19.0 was used for result analysis, including descriptive statistics of data, correlation analysis of factors and regression.

3 Results and analysis

3.1 Analysis of biogas fertilizer use efficiency and distribution of nutrients

3.1.1 Basic physicochemical properties and nutrient content of first batch of samples

The result (Figure 1) showed that the first batch of samples are neutral to slightly alkaline basically, this is consistent with the other reported results[2,17]. The full amount of N, P and K content and the average content of individual sampling were both shown as K > N > P, and the contents of N and P are close. Phosphorus has the maximum variation among the total nutrients, and coefficient of variation (C.V.) reaches 95.2%. Table 1 shows the average content of trace elements in biogas residues and slurry mixture as Mg > Fe > Zn > Cu > Mn. Except Mg, the variation of the rest trace elements content is more significant, and C.V. values are all higher than 100%. Distribution of organic matters is similar with the distribution of TS, but their contents vary remarkably. The conductivity variation is significant and the mean value is high.

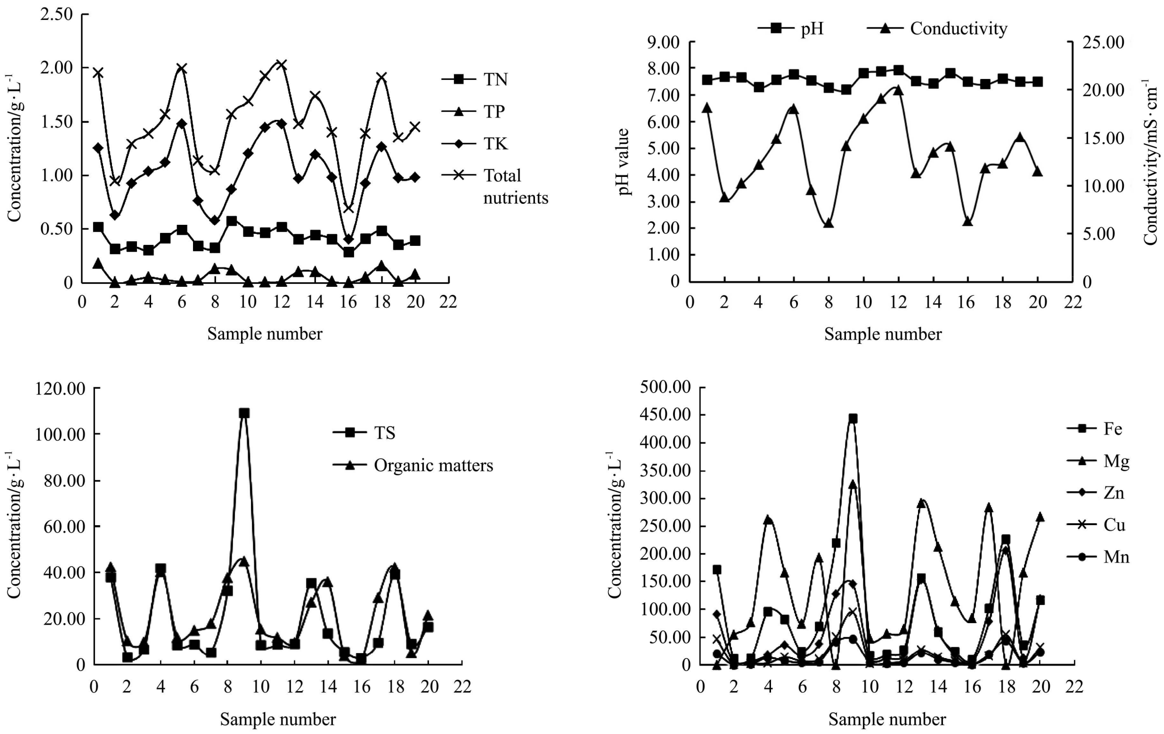

Figure 1 Component contents of the first batch of samples

Table 1 Descriptive statistics of component content for the first batch of samples

	Minimum	Maximum	Mean	Standard deviation	C.V. /%
TS/g·L-1	2.96	108.93	20.54	24.62	119.9
Organic matters/g·L-1	2.27	44.70	21.61	14.39	66.6
Total nutrients/g·L-1	0.70	2.02	1.50	0.37	24.5
TN/g·L-1	0.29	0.58	0.41	0.08	19.8
TP/g·L-1	0.00	0.18	0.06	0.06	95.2
TK/g·L-1	0.41	1.48	1.02	0.29	28.6
pH	7.19	7.92	7.56	0.20	2.7
Conductivity/mS·cm	6.11	19.92	13.19	3.96	30.0
Fe/mg·L-1	9.92	443.41	96.28	106.88	111.0
Mg/mg·L-1	48.17	325.41	161.17	97.08	60.2
Zn/mg·L-1	3.01	205.43	58.92	60.74	103.1
Cu/mg·L-1	0.36	94.84	20.12	24.52	121.9
Mn/mg·L-1	0.18	46.44	14.19	14.84	104.6

3.1.2 Nutrient distribution analysis

The second batch of samples (supernatant) were measured and compared with the first batch of samples. The result (Figure 2) shows that except TK contents in samples 1, 4 and 5 in the supernatant fluid are higher than those in mixture, the rest of the samples that TN, TP, TK contents in supernatant fluid are lower than those in mixture. Water-soluble N and K, representing the ratios of TN and TK in mixture, which are 30.4% and 92.9%, respectively, are greater than the proportion of water-soluble P of TP in mixture which is 6.0%. The trace element content in supernatant is significantly lower after centrifugation, the rest of trace elements almost distributes in solid waste except Mg, and the average contents of trace elements are ranked as Mg > Fe > Zn > Cu > Mn, which is consistent with the characteristics of trace elements content in the mixture (Table 2).

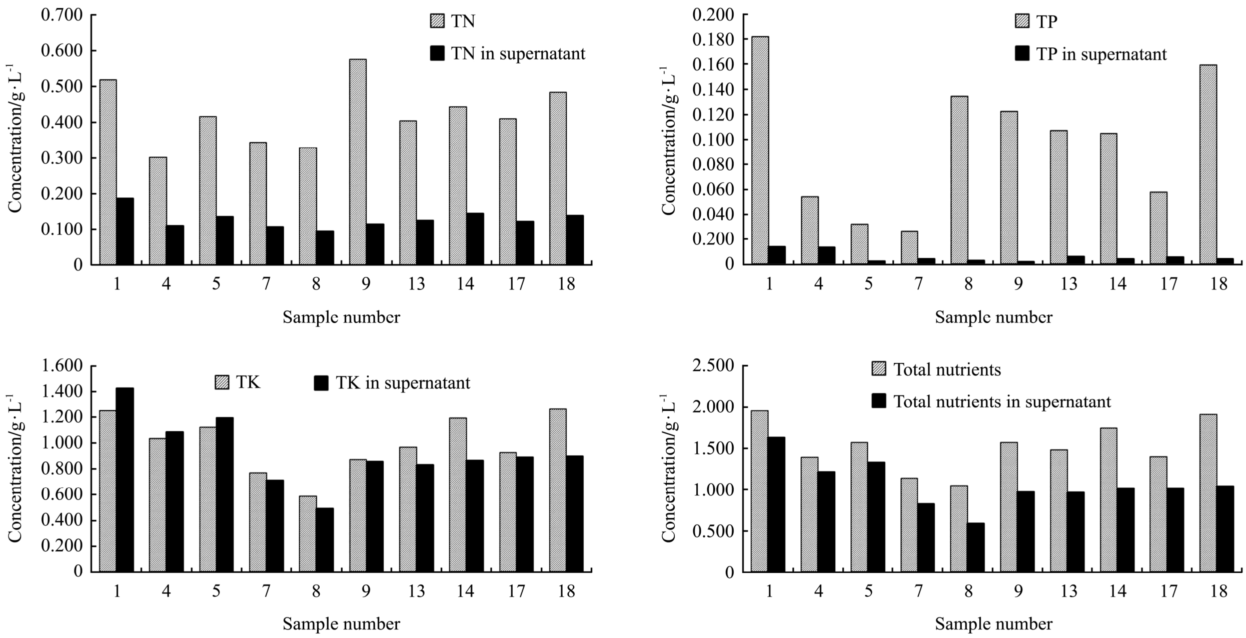

Figure 2 Comparison of the nutrients content in mixture and supernatant

Table 2 Comparison of the trace element content in mixture and supernatant

	Fe	Mg	Zn	Cu	Mn
Mixture/mg·L^{-1}	162.66	247.61	95.34	33.39	23.27
Supernatant/mg·L^{-1}	9.97	60.03	4.81	1.30	0.60
Ratio (supernatant/mixture)/%	6.13	24.24	5.05	3.90	2.58

3.2 Analysis of influencing factors of pig biogas residues and slurry

3.2.1 Correlation analysis

The result (Table 3) shows that at 0.01 level (bilateral), in biogas residues and slurry mixture, the total nutrients and TK, total nutrients and TN, total nutrients and conductivity, TK and conductivity, organic matters and TP, showed a strong correlation for the Pearson coefficient between 0.8 and 1.0[18]. Total nutrients and TK, TK and conductivity exhibited evident correlation particularly for the Pearson coefficient of 0.964 and 0.905, respectively.

Table 4 shows that at 0.01 level (bilateral), the conductivity of mixture and the conductivity of supernatant, total molar content of ammonia nitrogen (NH_4-N) and K in supernatant and the conductivity of mixture all show high correlation for the Pearson coefficient of 0.982 and 0.924, respectively. Total molar contents of NH_4-N and K in both supernatant and mixture exhibited evident correlation with their conductivity and the Pearson coefficients were 0.871 and 0.872, respectively. These results fully show the strong correlation between the test indicators, and a test index changes is likely to affect another test indicators.

Table 3 Correlation between the test indicators in mixture

Pearson coefficient	TS	Organic matters	Total nutrients	TN	TP	TK	Conductivity
TS	1	0.741**	0.168	0.446*	0.646**	-0.039	0.018
Organic matters	0.741**	1	0.265	0.325	0.875**	0.071	-0.065
Total nutrients	0.168	0.265	1	0.846**	0.261	0.964**	0.880**
TN	0.446*	0.325	0.846**	1	0.349	0.712**	0.763**
TP	0.646**	0.875**	0.261	0.349	1	0.037	-0.088
TK	-0.039	0.071	0.964**	0.712**	0.037	1	0.905**
Conductivity	0.018	-0.065	0.880**	0.763**	-0.088	0.905**	1

Note: ** Means correlation at the 0.01 level (bilateral); * Means correlation at the 0.05 level (bilateral).

Table 4 Correlation between the test indicators in both mixture and supernatant

Pearson coefficient	Total molar content of NH_4-N and K in mixture	Conductivity of mixture	Total molar content of NH_4-N and K in supernatant	Conductivity of supernatant
Total molar content of NH_4-N and K in mixture	1	0.871**	0.738*	0.869**
Conductivity of mixture	0.871**	1	0.924**	0.982**
Total molar content of NH_4-N and K in supernatant	0.738*	0.924**	1	0.872**
Conductivity of supernatant	0.869**	0.982**	0.872**	1

Note: ** Means correlation at the 0.01 level (bilateral); * Means correlation at the 0.05 level (bilateral).

3.2.2 Regression analysis

(1) Total nutrients and TK in biogas residues and slurry mixture

Table 5 shows the total nutrients and TK unary linear regression model fitting result from which we can see R^2 and adjusted R^2 are both above 0.9, which means the model fitting effect is good[19], the explanatory power of independent variables (TK content) to dependent variable (total nutrients) is very high.

Table 5 Model summary b

Model	1
R	0.964a
R^2	0.929
Adjusted R^2	0.925
The standard estimate error	0.1

Note: "a" means predicting variables: (constant), TK content (g/L); "b" means dependent variable (total nutrients, g/L).

Table 6 shows the significance in F test of regression equation, the statistic is of 236.986, the corresponding confidence level is 0.000, far smaller than the commonly used confidence level of 0.05, so the regression equation is very significant.

Table 6 Regression model from ANOVA b

Model		Quadratic sum	df	Mean square	F	Sig
1	Regression	2.371	1	2.371	236.986	0.000a
	Residual	0.180	18	0.010		
	Total	2.551	19			

Note: "a" means predicting variables: (constant), TK content (g/L); "b" means dependent variable (total nutrients, g/L).

Table 7 shows the coefficient of TK content in the model is significantly different from zero at the 1% significant level (Tables 5 and 6), therefore, the coefficient of TK content can be used as its marginal effect, which means once the TK content of 1 g/L is improved, total nutrients will increase by 1.206 g/L.

Table 7 Coefficient a

Model		Quadratic sum	Unstandardized coefficients	Standardized coefficients	t	Sig
		B	Standard deviation			
1	Constant	0.262	0.083		3.138	0.006
	TK content	1.206	0.078	0.964	15.394	0

Note: "a" means dependent variable (total nutrients, g/L).

Figure 3 is the histogram of standardized residuals used to show the distribution of residuals. The normal distribution showed in Figure 4 is used to observe whether the distribution of standardized residuals conform to normal distribution.

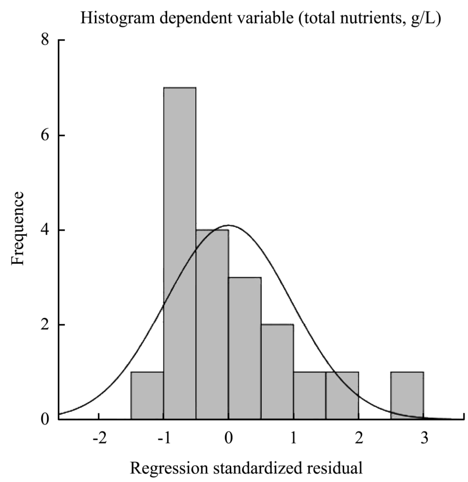

Figure 3 Standardized residuals for total nutrient

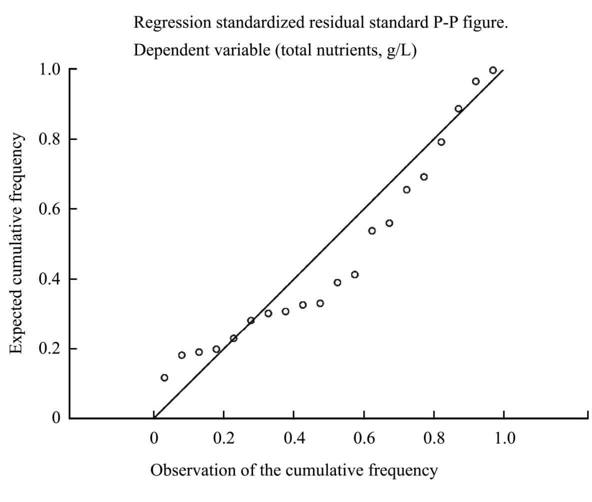

Figure 4 Normal distribution for total nutrient

Considering that the total nutrients and TK content unary linear regression model fitting effect is ideal, we got the linear regression equation as:

Total nutrients (g/L) = 0.262+1.206×TK (g/L) (1)

(2) Total molar content of NH_4-N and K in biogas residues and slurry mixture and the mixture conductivity

By R^2 and adjusted R^2 which are 0.759 and 0.729 respectively (Table 8), molar content of NH_4-N and K in the mixture and mixture conductivity linear fitting effect is ideal, the explanatory power of independent variables (mixture conductivity) to dependent variable (molar content of NH_4-N and K in the mixture) is very big.

Table 8 Model summary [b]

Model	1
R	0.871[a]
R^2	0.759
Adjusted R^2	0.729
The standard estimate error	0.004

Note: "a" means predicting variables: (constant), mixture conductivity (mS/cm); "b" means dependent variable (molar content of NH_4-N and K in the mixture, mol).

Combined the results of Tables 9 and 10, Figures 5 and 6, we got the linear regression equation between total molar contents of NH_4-N and K in biogas residues and slurry mixture and the mixture conductivity:

Total (NH_4-NK+K) in mixture / mol =

0.014+0.002× mixture conductivity / (mS/cm) (2)

Table 9 Regression model from ANOVA [b]

Model		Quadratic sum	df	Mean square	F	Sig
1	Regression	0	1	0	25.206	0.001[a]
	Residual	0	8	0		
	Total	0	9			

Note: "a" means predicting variables: (constant), mixture conductivity (mS/cm); "b" means dependent variable (molar content of NH_4-N and K in the mixture, mol).

Table 10 Coefficient [a]

Model		Quadratic sum	Unstandardized coefficients	Standardized coefficients	t	Sig
		B	Standard Deviation			
1	Constant	0.014	0.005		2.984	0.018
	Mixture conductivity	0.002	0.000	0.871	5.021	0.001

Note: "a" means dependent variable (molar content of NH_4-N and K in the mixture, mol).

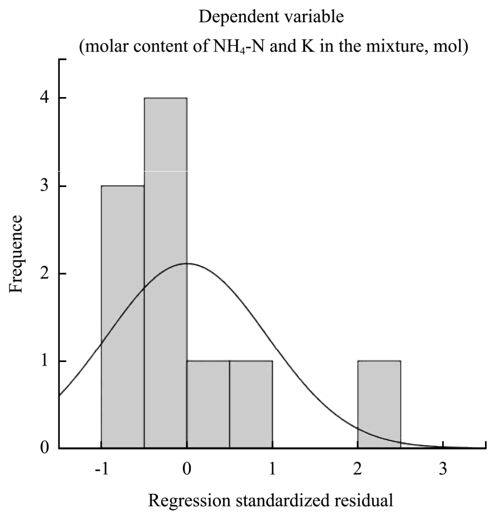

Figure 5 Standardized residuals for molar contents of NH_4-N and K in the mixture

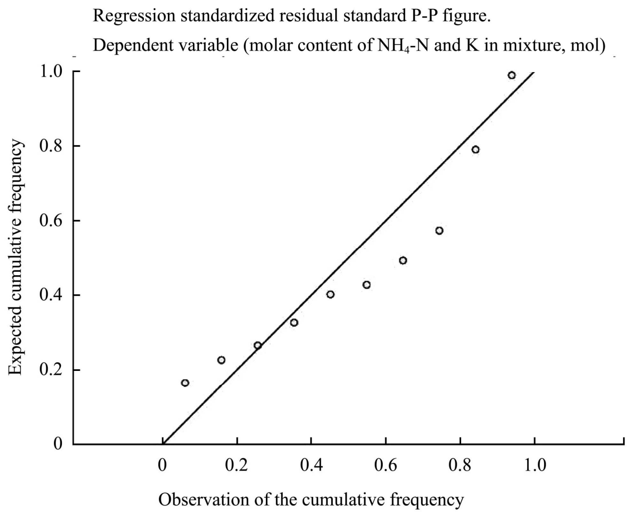

Figure 6 Normal distribution for molar contents of NH_4-N and K in the mixture

Using the same analysis method, the linear regression equation between total molar content of NH_4-N and K in supernatant and the mixture conductivity is given as follows:

Total (NH_4-NK+K) in supernatant / mol =

0.002×mixture conductivity / (mS/cm) (3)

(3) Other test indicators

Table 11 shows the rest of the several groups of indicators for linear regression model fitting results by using the same analysis method as shown above.

4 Discussion

4.1 Biogas fertilizer use efficiency and the influencing factors of biogas residues and slurry

The results of basic physicochemical properties and

Table 11 Other indicators linear regression fitting results

Dependent variable	TK	Total nutrients	Total nutrients	TP
Independent variable	Mixture conductivity	Mixture conductivity	TN	Organic matters
R^2	0.986	0.775	0.985	0.882
Adjusted R^2	0.985	0.763	0.984	0.875
F value	1301.929	62.097	1219.726	141.623
Sig corresponding with F value	0.000	0.000	0.000	0.000
t value corresponding with constant	Constants ignored	2.966	Constants ignored	Constants ignored
Sig corresponding with t (constant)	Constants ignored	0.000	Constants ignored	Constants ignored
t value corresponding with independent variables	36.082	7.880	34.925	11.901
Sig corresponding with t (independent variables)	0.000	0.000	0.000	0.000
Unstandardized coefficients-constant	-	0.422	-	-
Unstandardized coefficients-B	0.077	0.082	3.625	0.003
Linear regression equation	TK (g/L) = 0.077* mixture conductivity (mS/cm)	Total nutrients (g/L) = 0.422+0.082* mixture conductivity (mS/cm)	Total nutrients (g/L) = 3.625*TN (g/L)	TP (g/L) = 0.003* organic matters (g/L)

nutrients content of biogas residues and slurry mixture in chapter 3.1.1 showed that the average content (in dry basis) of TN, TP, TK and organic matters are 3.1%, 1.0%, 10.3% and 58.8%, respectively. Lv et al.[17] determined biogas residues of cattle manure and goat manure in Bozhou region of China, and analyzed the content of organic matters, TN, TP, TK, pH, total Cu, Fe, Zn and Mn etc., indicators. Zhang et al.[16] collected biogas residues of four different kinds of fermenting materials in Shandong Province of China and analyzed the nutrients content etc., indicators. It is determined that biogas manure contains 30% to 50% organic matters, 10% to 25% humic acid, 0.8% to 1.5% N, 0.4% to 0.6% P and 0.6% to 1.2% K[2]. Comparing the test result, it is easy to find that the average content of TN, TP, TK and organic matters of the samples are all higher than those in the existing research results, especially the organic matters and TK, which indicates the nutrient elements content in biogas residues and slurry is very rich and it can be used as a kind of high quality organic fertilizer. The coefficient of variation column in Table 1 reflects that although the nutrients content of overall sample is rich, but there is a significant difference among the samples, which actually reflects the difference among sampling points. Due to the practical operations of the biogas projects differ in thousands ways, different feed concentration, different type of fermentation tank, different fermentation time and fermentation temperature and different inoculum will affect the final nutrients content of biogas residues and slurry[20]. Zhang et al.[21] used biogas residues under different fermentation temperatures of household biogas digester in Shanxi Province of China for the study, the results showed that the contents of TN, TP and TK in biogas residues of same raw materials were the highest at the medium temperature. Jin et al.[22] analyzed physical and chemical properties for biogas slurry of large-scale biogas projects of livestock industry in Jiangsu Province of China and found running time of biogas projects had a great effect on the physical and chemical properties of biogas slurry. The longer the running time is, the more stable the system would be. Therefore, biogas residues and slurry of biogas projects of pig farms can be used as a high-quality organic fertilizer, but it would have some greater instability as an organic fertilizer due to the differences in region, raw materials and the nutrients content difference caused by fermentation technology and operational management.

4.2 Distribution of nutrients in pig biogas residues and slurry

The results in section 3.1.2 showed that major nutrients in both biogas residues and slurry mixture and supernatant of pig manure as K > N > P, this is in accordance with the research results of biogas manure in Chongqing region of China by Zhong et al[2]. P has the maximum variation among the total nutrients, this is accordance with the physicochemical properties analysis results of biogas slurry in Jiangsu Province of China by Jin et al[22]. Water-soluble N and K representing the ratios of TN, TK in mixture which are 30.4% and 92.9%, respectively, are greater than the proportion (5.98%) of water-soluble P of the TP in mixture. This shows that the N, K are given priority to inorganic state in biogas residues and slurry, which is very conducive to plant uptake. The distribution of trace elements in biogas residues and slurry mixture is consistent with supernatant, for Mg>Fe>Zn>Cu>Mn, and the trace elements content in supernatant is significantly lower after centrifugation, especially for Mn and Cu. This is consistent with the analysis results of research for biogas residues of cattle manure, goat manure and pig manure in Bozhou region in China by Lv et al.[17], and this may be because there are a lot of carbonates and sulfides in biogas slurry which can form precipitates with metal elements, then their concentration in the slurry is greatly reduced, and biogas slurry may also contain a lot of organic matters which may have a strong complexing ability on copper and various fatty acids, amino acids and other functional groups are also there for the copper complexation. The effectiveness of Mn decreases with the increase of pH value; generally, when the pH value is close to 7, the exchangeable Mn in soil is very little[17]; while the pH value of biogas slurry that is above 7 may affect the release of Mn in soil. Therefore, very few trace elements can get into the slurry. Xu et al.[23] analyzed biogas residues of five different kinds of fermentation raw materials and found the nutrients content in biogas residues are higher than that in biogas slurry. Huang et al.[24] got the same results after the analysis of biogas manure of different kinds of biogas projects. In conclusion, in terms of pig manure, nutrients are unevenly distributed in biogas residues and slurry; the content of organic matters, P and trace elements are higher in biogas residues; the contents of water-soluble N and K are higher in biogas slurry, this also determines the different fertilizer effects and application methods between biogas residues and slurry.

4.3 Factor analysis of test indicators of pig biogas residues and slurry

The linear fitting results between test indicators of the two batches of samples show that there is a great correlation between some test indicators, particularly between the total nutrient content and TK, TK content and electrical conductivity, and the unary linear regression fitting result is ideal between the most indicators. By fitting out of the equations, such as TK (g/L) = 0.077 × mixture conductivity (mS/cm), shows the contribution of TK content to electrical conductivity in biogas mixture is very big. The initial TK content of biogas manure can be simply determined by measuring the conductivity of the mixture under limited conditions, which can greatly reduce the workload and improve work efficiency. Similarly, we can indirectly know the other nutrient contents of biogas manure by fitting out the equations between the rests of indicators, this also provides an effective approach to obtain the fertilizer use efficiency of biogas manure quickly.

5 Conclusions and suggestions

5.1 Conclusions

(1) The biogas residues and slurry of biogas projects of pig farms rich in nutrients, can be used as a high-quality organic fertilizer, but due to the differences in region, raw materials and the nutrients content difference caused by fermentation technology and operational management, have some greater instability as an organic fertilizer.

(2) In terms of pig manure, nutrients are unevenly distributed in biogas residues and slurry; the contents of organic matters, P and trace elements are higher in biogas residues, the contents of water-soluble N and K are higher in biogas slurry.

(3) Parts of test indicators of biogas residues and slurry mixture are significantly correlated, the unary linear regression fitting result is ideal between most indicators, can accurately estimate the value of other test indicators by one known indicator, by which can reduce the workload effectively.

5.2 Suggestions

(1) In terms of pig manure, nutrients are unevenly distributed in biogas residues and slurry, it should be applied according to the actual situations. It can be solid-liquid separated before applying to the farmland. Biogas slurry should be applied to the farmland which needs more water-soluble N and K, and biogas residues should be applied to the farmland which is lack of organic matters.

(2) The fertilizer use efficiency of biogas residues and slurry is unstable for many different reasons; biogas residues and slurry should be stabilized before applying to the farmland.

(3) In addition to the major elements, the biogas residues and slurry also contain heavy metals, pathogenic bacteria and other materials which are harmful to the environment and human health. In order to avoid its enrichment in the crops and pollution of groundwater, these harmful materials should be removed before use.

(4) This study selected only the pig manure of different regions as the research objects. If more different kinds of livestock manure can be studied and the test results can be analyzed, a set of rapid determination method could be summarized which is very significant for applying biogas residues and slurry from livestock industries.

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