Effects of Applied Biogas Slurry Continuously for several years on Soil Chemical Characteristics

Zhang Chang-ai¹, Renhua Sun²*, Mengfei Ying³, Shaohua Ding², Shan Shengdao¹※

¹Zhejiang University of Science and Technology, Hangzhou Zhejiang 310023, China
²Agricultural ecology and resource protection station, Ministry of Agriculture and Rural Affairs, Beijing, 010023, People’s Republic of China;
³The technology promotion center of grain and oil crop in Shaoxing city, Shaoxing Zhejiang, 312000.
※Corresponding author’s e-mail: shengd shan@sinavip.com

Abstract: The objective of this study was to predict the potential influence of applying biogas slurry (BS) continuously for several years on soil chemical characteristics. Five kinds of Farmland which have been irrigated using BS respectively for 0, 1, 2, 4, 6 years were chosen as the research objects, and soil characteristics and cabbage growth in the different farmlands were analyzed, so can to provide practical basis for scientific application of BS. The results of the experiment indicated that soil pH value enhanced, soil exchangeable H⁺ and exchangeable Al³⁺ descend by applied BS, the acid-alkali balance of soil could been easier keep stable if BS been used for more years; the contents of reductive material(RM), activity reductive material(ARM), and ratio of ARM are all increased with the age added by applied BS, so the redox balance of soil have been broken because of applied BS; Soil water-soluble K⁺, Na⁺, Ca²⁺, Mg²⁺, SO₄²⁻, HCO₃⁻, Cl⁻ were been affected obviously by applied BS, the contents of water-soluble K⁺, Na⁺, Cl⁻, SO₄²⁻ are all increased, and the contents of soil water-soluble Ca²⁺, Mg²⁺, HCO₃⁻ are all decreased with the age added by applied BS.

1. Introduction
Biogas slurry (BS) as an important production from anaerobic digestion of livestock manure, is a kind of organic fertilizer resource will be beneficial to yield-increasing[1]. Therefore, BS returning to the field is an important link between planting and breeding recycling [2]. Other people's research showed that BS can enhance the output of many crops such as maize, vegetable, grain, fruit[3,4], In the meantime, returning BS to the fields is also conducive to the improvement of soil fertility and soil quality[5]. And the use of BS as organic fertilizer resources to replace fertilizer has been more and more important in China[6]. With the development of biogas in China, the research on BS returning to the field has gradually become one of the research focus[7].

Concurrently, The salt content, viscosity, heavy metal content of BS are all more higher than water, and BS redox potential is lower than water;therefore there have more indeterminacy risks if returning BS to the fields, and it is necessary to develop advantages and eliminate disadvantages, especially to analyze the effect of long-term BS applid. [8]. If we want to study the effect of long-term BS used on farmland, we not only need long-term positioning test, but also supervise the details such as BS properties changing, rotation, types of crops and the amount of fertilizer application and so on. At
present, there are few reports on the research of long-term BS applied due to the lack of positioning experiment in China.

Zhejiang Yijing Ecological Animal Husbandry Co., Ltd. is a dairy cattle farming enterprise. It has perfected the planting and breeding recycling system linked by biogas project. With the stable operation of the biogas project, the area of land that BS has been used is increased year by year in its planting park since 2011. Therefore, it can be realized that the plots with different years of BS applied can be found in the park as research object. On the basis of investigation and analyzing, 5 field plots which have been irrigated using BS respectively for 0, 1, 2, 4, 6 years were selected as the research object in the park. The effects on soil properties and growth of cabbage were studied in them during the cabbage production season.

2. MATERIAL AND METHODS:

The experiment was set in the planting area of Yijing Ecological Animal Husbandry Co., Ltd, ZheJiang. Five plots with different years of BS using have been determined as research and analysis specimens. The experiment have 5 treatments, that's: ① the plot without BS applied (treatment code is CK); ② the plot there have been irrigated using BS for 1 year (treatment code is Y1); ③ the plot there have been irrigated using BS for 2 years (treatment code is Y2); ④ the plot there have been irrigated using BS for 4 years (treatment code is Y3); ⑤ the plot there have been irrigated using BS for 6 years (treatment code is Y4);

In the experimental area, The BS was conveyed by pipes and pump, and the rotation mode were as "corn + maize + cabbage". According to 300 kg (15-15-15) compound fertilizer ha⁻¹ of basic fertilizer was applied after receipt, and the soil is mechanically tilled after raking. The soil is loamy tidal soil. The basic physical and chemical properties of the tested original soil are shown in Table 1.

| Indexes                  | Estimated value |
|-------------------------|-----------------|
| OM/(g·kg⁻¹)             | 17.64           |
| Available N/(mg·kg⁻¹)   | 106.72          |
| Available P/(mg·kg⁻¹)   | 46.45           |
| Available K/(mg·kg⁻¹)   | 186.32          |
| pH value                | 5.53            |
| EC/(μS·cm⁻¹)            | 72.1            |
| Sand/(g·kg⁻¹)           | 244             |
| Silt/(g·kg⁻¹)           | 253             |
| Clay/(g·kg⁻¹)           | 503             |

The annual amount of biogas slurry is about 1500-1800t·ha⁻². The amount of washing water used in dairy cattle farming is different in different seasons. Therefore, the nutrient content of biogas slurry in summer and autumn is different from that in winter and spring. The basic physical and chemical properties are shown in Table 2.

| Indexes                      | Biogas Slurry in Winter or Spring | Biogas Slurry in Summer or Autumn |
|------------------------------|----------------------------------|----------------------------------|
| Redox Potential/mV           | -45.32                           | -25.37                           |
| pH Value                     | 7.85                             | 7.62                             |
| Water-soluble Salt Content/ (%) | 0.975                           | 0.712                           |
In the process of cabbage production, the management measures of fertilization, watering, medication and tillage by the agricultural technology working group in the park are basically the same. 10 representative cabbage plants were harvested and soil samples were collected in harvested. Soil pH was determined by 1:5 soil-water ratio, pHSJ-3F acidity potentiometry, plant total nitrogen, phosphorus and potassium were digested by H₂SO₄-H₂O₂ digestion method, nitrogen was determined by Kjeldahl method, phosphorus was determined by colorimetry, potassium was determined by water bath evaporation-weighting method, and calcium and magnesium ions were determined by flame photometry, and atomic absorption spectrometry. Spectrophotometric method, barium chromate colorimetric method for determination of sulfate, FIA-4 ORP instrument for in situ determination of redox potential and pH value of biogas slurry, formaldehyde method for determination of ammonium nitrogen content, and conventional analysis method for determination of other items. Data are processed and analyzed by SAS software.

3. Results and Discussion

3.1 Effect of biogas slurry returning to field on soil acid-base balance system

3.1.1 Effect of biogas slurry returning to field on soil pH

Before the experiment, the pH value of the soil treated with no biogas slurry was 5.53 (Table 1), but changed to 5.41 (Figure 1) after cabbage planting. The results showed that under the condition of normal cultivation of cabbage, the soil acidified gradually, and the soil pH was significantly affected by the return of biogas slurry to the field. The results showed that under the condition of normal cultivation of cabbage, the soil acidified gradually, and soil pH was significantly affected by the return of biogas slurry to the field. The soil pH of unused biogas slurry plot was the lowest, and it continued to increase with the increase of the years of biogas slurry returning to the field. In addition to 1 years of biogas slurry plots, other treatment plots of soil pH increase greatly, compared with the control reached a significant level; But the difference of soil pH 2 years of returning and returning for 4 years did not reach significant level, with the increase of the utilization years of biogas slurry, the disturbance of soil pH caused by biogas slurry decreased, which indicated that biogas slurry had obvious buffer effect on soil pH. It has been proved that returning biogas slurry to the field can significantly increase the pH of acidic soil. Although the organic matter in the biogas slurry can also produce some organic acids in the mineralization process, the biogas slurry itself has a higher pH value and contains a higher content of cations, so the increase of salt-based ions will slow down the acidification of soil. The use of biogas slurry on soil pH effect can not be simply to rise or fall as a judge, In fact, the disturbance of soil acid-base balance caused by biogas slurry is more complex, which requires further or more in-depth study.
3.1.2 Effect of biogas slurry returning to field on soil exchangeable acid

Exchange acidity in soil exchangeable base not saturated, instead of the position of the excha ngeable H⁺ and exchangeable Al³⁺. The results showed that the exchangeable Al³⁺ in soil decre ased significantly after adding biogas slurry. The order of exchangeable aluminium content in e ach treatment was as follows: CK > Y1 > Y2 > Y3 > Y4. From the point of view of soil acidi fication, the existence and increase of exchangeable Al³⁺ is not the cause of soil acidificat i on, but the result of soil acidification [9]. Therefore, the addition of biogas slurry to soil af fects the acid-base balance of soil and alleviates the problem of soil acidification. But it is no teworthy that there is no significant difference between the exchangeable aluminum content of 2 - 6 years of soil slurry returning, the acidity of the soil to reduce the visible without limit extension. On the one hand, soil acidification is difficult to recover in time. On the other ha nd, the organic matter in the biogas slurry increases soil acid-base buffer performance, which is beneficial to the stability of soil acid-base buffer system.

Fig.1 Effects of biogas slurry applied on soil pH

![Fig.1 Effects of biogas slurry applied on soil pH](image)

3.1.2 Effect of biogas slurry returning to field on soil exchangeable acid

The order of exchangeable hydrogen ion content in different treatments was as follows: CK> Y1>Y2>Y3>Y4. The results showed that the content of exchangeable H⁺ in soil decreased wi th the increase of the application years of biogas slurry, but there was no significant difference between Y3, Y4 and Y2 treatments. The potential acidity of soil is affected by exchangeable H⁺ and exchangeable Al³⁺, which reflects the trend of soil acidification. The ratio of exchangeable hydrogen ion to exchangeable acid in soil reflects the composition of exchangeable acid in soil. The smaller the value that the activation of aluminum in soil is more obvious, affect soil acid-base balance in the fierce. The order of the proportion of exchangeable H⁺ to exchangeable acids in each treatment was as follows: Y4>Y2>Y3>Y1>CK. The is indicated that the application of biogas slurry not only increased the soil pH, but also stabilized the soil acid-base balance system with the increase of the application years of biogas slurry. Therefore, returning biogas slurry to field is beneficial to the stability of soil acid-base balance system.

Fig.2 Changes of exchangeable H⁺ and exchangeable Al³⁺ among all treatments

![Fig.2 Changes of exchangeable H⁺ and exchangeable Al³⁺ among all treatments](image)
3.2 Effect of biogas slurry returning to field on reducing substances in soil

The content of reducing substances in soil not only reflects the redox state of soil, but also shows the effect of different treatments on the redox system of soil.[10] The total reducing substances of each treatment in the order: Y4>Y3>Y2>Y1>CK. The total amount of reducing substances in Y4, Y3, Y2 and Y1 treatments increased by 39.22%, 32.35%, 22.55% and 10.78%, respectively. It has significant difference compared with control group. Compared with Y3, Y 3 and Y4 treatments, there was no significant difference in the total amount of soil reducing substances, which indicated that the effect of biogas slurry application mainly changed the redox environment of soil, rather than the introduction of reducing substances. Although NH4+-N is an important reducing substance, NH4+-N in soil has been transformed or leaked during the harvest period.

The sequence of active reducing substances in accordance with reducing amount of material, the proportion of active reduce showed a similar trend. What accounts for the low proportion of active reducing substances, generally in the 11.17% ~ 17.61%.

3.3 Effect of biogas slurry returning to field on soil soluble salt content

3.3.1 Effect of biogas slurry returning to field on anions in soil aqueous solution

The order of HCO3- content in soil is as follows: CK>Y1>Y2>Y3>Y4. After applying biogas slurry, the content of HCO3- in soil tended to decrease. Compared with CK, HCO3- content in soil decreased by 3.21% after one year of application of biogas slurry, but the difference was not significant. When the biogas slurry was applied for more than 2 years, there was a significant difference in the redox environment of soil, rather than the transformation of reducing substances. The main reason is that the pH of biogas slurry is high, which is not conducive to the existence of HCO3- in biogas slurry. The Cl- content in soil increased with the age of biogas slurry increased, compared with CK, Cl- content of Y4 increases the maximum, reaching 50.61% (Fig.4). Biogas slurry contains high content of soluble organic matter.
The order of SO$_4^{2-}$-content was $Y_4 > Y_3 > Y_2 > Y_1 > CK$. Compared with CK, the SO$_4^{2-}$-content of $Y_1$, $Y_2$, $Y_3$ and $Y_4$ increased by 5.50%, 11.64%, 17.36% and 51.33%, respectively. Except for $Y_1$, SO$_4^{2-}$-content in other treatments was significantly different from CK. Overall, the biogas slurry caused by soil SO$_4^{2-}$ and Cl$^-$ content changes and reasons is very similar. Therefore, the accumulation of SO$_4^{2-}$ and Cl$^-$ in plough layer soil caused by long-term returning of biogas slurry to field deserves attention and further study.

3.3.2 The effect of biogas slurry on the cation content of soil solution in water

After the harvest of cabbage, the contents of water-soluble K$^+$, Na$^+$, Ca$^{2+}$, Mg$^{2+}$ in the soil without biogas slurry treatment were shown in Fig.5. Among them, the content of Ca$^{2+}$ was higher, accounting for 36.78% of the total four cations.

The content of water-soluble K$^+$ in soil with biogas slurry increased with the application of biogas slurry (Fig.5). Compared with CK, $Y_1$, $Y_2$, $Y_3$ and $Y_4$ of soil water soluble K$^+$ content increased by 20.22%, 39.11%, 73.08% and 95.64%, the difference was significant; Compared with $Y_1$, the content of water-soluble K$^+$ increased by 15.72% in $Y_2$, and the difference reached a significant level. While the difference reached a significant level in different years of application of biogas slurry. Therefore, under the existing management model, the water soluble K$^+$ content in the plough layer soil has accumulated. In fact, the presence of NH$_4^+$-N will lead to the increase of K$^+$ content in soil extract[12], but whether it is an important reason needs further study and analysis. From the production point of view, although biogas slurry promoted the increase of cabbage biomass (Fig. 6), the content of water soluble K$^+$ in soil increased year by year, which indicated that the absorption of plant potassium was in a state of l
uxury absorption. Therefore, the consumption of potassium fertilizer should be reduced on this basis in production.

The soil changes of water soluble Na\(^+\) and K\(^+\) content also showed a similar situation, with the increase of the number of biogas slurry phenomenon. Except Y1 and Y2, other treatments reached significant levels. The content of water soluble Na\(^-\) in Y4 treatment was 38.09% higher than CK. The Na\(^-\) content of biogas slurry is high. Because of the application of biogas slurry, the ability of water storage and fertilizer conservation of soil tillage layer has been significantly enhanced [13]. Therefore, the increase of K\(^-\) and Na\(^-\) in soil tillage layer is understandable.

The soil Ca\(^{2+}\) and Mg\(^{2+}\) content of the same order, are: CK > Y1 > Y2 > Y3 > Y4. It can be seen that the content of Ca \(^{2+}\) and Mg \(^{2+}\) in soil decreased gradually with the extension of the application years of biogas slurry. The reason is that the application of biogas slurry not only does not bring in a high amount of ions, but also promotes the activation of these two ions by increasing soil acidity. Moreover, the application of biogas slurry promotes the growth and biomass of plants, which will inevitably promote the absorption of Ca\(^{2+}\) and Mg\(^{2+}\) by plants, thus showing a downward trend year by year. The reason is that the biogas slurry returning to the field does not bring in a high amount of ions, but it promotes the activation of these two ions by increasing soil acidity, and the application of biogas slurry promotes the growth and biomass of plants, which will inevitably promote the absorption of Ca\(^{2+}\) and Mg\(^{2+}\) by plants, thus showing a downward trend year by year.

4. conclusion

1) Returning biogas slurry to field in acidic soil can improve soil pH and slow down soil acidification. Soil acid-base balance system is more stable with the increase of the application years of biogas slurry. Specifically, with the increase of different years of biogas slurry returning to the field, soil pH increased significantly, exchangeable hydrogen ions and exchangeable chloride ions decreased, and the proportion of exchangeable hydrogen ions in exchangeable acid increased.

2) After applying biogas slurry to soil, the total amount of soil reducible substances and the total amount of soil active reducible substances will be increased, and the proportion of active reducible substances to the total amount of reducible substances will also be increased. Therefore, the long-term return of biogas slurry to field has a significant disturbance on the balance of soil redox.

Acknowledgements

This research was supported by the Key Research and Development Program of Zhejiang Province (Grant number: 2019C02053).

Reference

[1] Garg R N, Pathak H, Das D K, Tomar R K. Use of flyash and biogas slurry for improving wheat yield and physical properties of soil[J]. Environ Monit. Assess, 2005, 107(1 /3): 1-9.

[2] Zhong Zhenmei, Huang Qinlou, Weng Boqi, et al. Energy analysis on planting-breeding circulating agriculture ecosystem linked by biogas[J]. Transactions of the Chinese Society of Agricultural Engineering (Transactions of the CSAE), 2012, 28(14): 196-200. (in Chinese with English abstract).

[3] Wen Ke Liu, Qi Chang Yang, Lian Feng Du, Rui Feng Cheng & Wan Lai Zhou (2011): Nutrientsupplementation increased growth and nitrate concentration of lettuce cultivated hydroponically with biogas slurry, Acta Agriculturae Scandinavica, Section B - Soil & Plant Science, 61:5, 391-394.
[4] Fang-Bo Yu, Xi-Ping Luo, Cheng-Fang Song, et al. Concentrated biogas slurry enhanced soil fertility and tomato quality, Acta Agriculturae Scandinavica, Section B - Soil & Plant Science, 2010, 60(3), 262-268.

[5] DAUDEN A, QUILEZ D. Pig slurry versus mineral fertilization on corn yield and nitrate leaching in a Mediterranean irrigated environment[J]. European Journal of Agronomy, 2004, 21(1):7-19.

[6] WANG Jing-Quan, GU duan-yin, YU xiao-dong, et al. Effects of Biogas Slurry Replacing Nitrogen Fertilizer on Yield, Quality and Growth and Development of Winter Wheat[J]. Journal of Applied Ecology. 2019, 30(01): 246-253.

[7] T.K. Enock, C.K. King’ondu, A. Pogrebnoi, Effect of biogas-slurry pyrolysis temperature on specific capacitance, Mater. Today Proc. 5 (2018) 10611-10620.

[8] Han Min, Liu Kefeng, Wang Shunli, et al. Definition, Ingredient, Approaches and Risks for Reuse in Biogas Slurry[J]. Journal of Agriculture. 2014, 4(10): 54-57.

[9] Xu W B. Advance in study on soil acidification. Advance in Earth Sciences (In Chinese). 1996, 11(4): 378-401.

[10] HUANG Hong -ying, CAO Jin -liu, CHANG Zhi -zhou, et al. Influence of application of digested pig slurry on nitrous oxide emission under rice-wheat rotation system [J]. Journal of Agro-Environment Science, 2011, 30(11): 2353-2361.

[11] JIN Hong -mei, CHANG Zhi -zhou, YE Xiao -mei, et al. Physical and chemical characteristics of anaerobically digested slurry from large scale biogas project in Jiangsu Province[J]. Transactions of the CSAE, 2011, 27(1): 291-296.

[12] Zhang F S. ed. Plant Nutrition: Ecophysiology and Genetics. Beijing: China Agricultural Science and Technology Press, 1993.

[13] Yu Weiwei, Zhang Zhi, Luo Surong, et al. Characteristics of purple vegetable soil under biogas slurry irrigation[J]. Transactions of the Chinese Society of Agricultural Engineering (Transactions of the CSAE), 2012, 28(16): 178-184. (in Chinese with English abstract)