



Study on the Characteristics of Soil Irrigated by Biogas Slurry in the Southwest of China

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Biogas slurry as quality organic fertilizer is widely used in large scale livestock and poultry farms in the southwest of China. This research used the wastewater from a dairy farm in the southwest, including Grit Chamber wastewater, collection basin wastewater, anaerobic tank wastewater, aerobic effluent and clean water for parallel irrigation in the greenhouse. The results indicate that anaerobic tank wastewater contains the maximum ammonia nitrogen content of 860 mg/kg in 0-5 cm soil profile sample. In 0-5 cm soil profile samples, the content of nitrate nitrogen in anaerobic tank wastewater remains the highest 23.95 mg/kg. In 5-10 and 10-20 cm soil profile samples, the nitrate nitrogen content of the other four test groups increase and reach the final value of 23.67 mg/kg. In 0-5 cm from soil surface the phosphorus content of the five groups are less than 100 mg/kg. The phosphorus absorption coefficient of clean water reaches a peak value of 570 after a month. In the test of soil carrying capacity, the maximum content of ammonium nitrogen, nitrate and available phosphorus are 1355, 24.65 and 163.66 mg/kg, respectively. The phosphorus absorption coefficient within 21-25 days goes above 500. Scanning electron microscopy analysis shows that, after long-term biogas slurry irrigation, the soil porosity and microorganism adherent to the clusters increase, resulting in improvement of the stability of the soil.

Key Words: Biogas slurry irrigation, Soil nutrient, Longitudinal variation, SEM.

INTRODUCTION

Pollutant discharge in rural China has accounted for "half" of country's overall amount, which contains 43 % of chemical oxygen demand (COD), 57 % of total nitrogen (TN) and 67 % of total phosphorus (TP). Yang *et al.*^{1,2}, estimated that the production amount of animal manure in China was *ca.* 3.19 billion tons, more than the industrial solid waste, becoming the major source of environmental pollution in 2003. The amount of livestock and poultry manure of China reached 4.5 billion tons in 2010. The livestock dung was about 85.7 million tons in the southwest of China³. According to the US Environmental Protection Agency, in 2003 agricultural non-point source pollution is the largest pollution source of rivers and lakes, causing 40 % of the rivers and lakes to have poor water quality. The nonpoint pollution is also the third largest source of estuarine pollution and the main cause of ground-water contamination and wetlands degradation⁴. In European countries, the agricultural non-point pollution is the primary factor which causes water, particularly groundwater, contamination. It's the main cause of phosphorus enrichment in surface water, which accounts for 24-71 % of the surface water pollution⁵⁻⁷. According to the survey, the contribution rate of biogas slurry manure for the farmland to the nitrogen is 10-30 % and the phosphorus is 3 %⁸. How to make the effective disposal

and comprehensive utilization of the large scale livestock and poultry farm dung to protect ecological environment is one of the urgent issues at present.

Biogas slurry is one kind of quality organic fertilizer which contains the necessary organic matter and various ions helping the growth of plant. But biogas slurry irrigation technology, with regards to the soil carrying capacity, the fertilizing amount and cycle of dung, is not well developed, making it impractical in most part of China⁹. In the southwest area more attention is given to the efficiency of irrigation, making use of nutrient resources of the biogas slurry. The feasibility of biogas slurry irrigation is mainly affected by the chemical composition of raw wastewater and the treated wastewater¹⁰. Biogas slurry supplies the nitrogen and phosphorus, while its excessive irrigation may cause withering of seedlings and damage the soil environment. Especially rainfall leaching could cause eutrophication of surface water. Thus, the main concern of this research is to investigate accumulation and absorption of nitrogen and phosphorus and determine the optimum irrigation water quality and soil carrying capacity.

EXPERIMENTAL

Experiment station is located in Jiangbei district, Chongqing (29°61'N, 106°75'E) southwest China, which experiences a tropical monsoon climate with average annual

rainfall of 1085.3 mm. The annual average temperature is 17.5-18.7 °C and frost-free period is 296 days. The trial began in June 2010 and ended in August 2011. It used a completely random block design, which is divided into 5 block experiments, each with an area of 10 m². This was in accordance with local conventional agricultural practices. The research was separated into two parts with each part repeated three times.

Experiment design: Wastewater of different process treatment Grit Chamber wastewater (GCW), collection basin wastewater (CBW), anaerobic tank wastewater (ATW) and aerobic effluent (AE) from the farm sewage station is used for irrigation separately. Clean water (CW) is set as the control group and the five tests are made simultaneously. The trial cycling time is from sowing time to harvest time of plants (*ca.* 4 months). After continuous irrigation by biogas slurry for a few days, the carrying capacity of soil for each nutrient is obtained.

Material tested: The cabbage is used as the test crop (heat resistance to 605) and the soil is neutral purple layer, whose calcium carbonate content is less than 30 g/kg and the pH value is *ca.* 7.5. The wastewater samples come from the farm sewage station processing unit. The different process leads to different water quality. GCW is filtered by grid. The HRT (Hydraulic Retention Time) of CBW is 1d. The HRT of ATW and AE are 18d and 29.2 h, respectively. With the same amount of irrigation (500 mL applied simultaneously), the nutritional content of soil absorbed are different. The average concentration of the sewage is given in Table-1¹¹.

Sewage source	Ammonium nitrogen (mg/L)	Phosphate (mg/L)	Nitrogen (mg/L)	CODcr (mg/L)	pH
GCW	7.24	9.27	3.21	1482	7.23
CBW	10.47	10.81	4.27	1758	7.14
ATW	200.90	6.09	5.31	591	7.20
AE	7.26	0.71	15.89	72	7.11
Total input amount					
	Ammonium nitrogen (mg)	Phosphate (mg)	Nitrogen (mg)		
GCW	22.08	28.27	9.79		
CBW	31.93	32.97	13.02		
ATW	519.68	16.38	14.25		
AE	87.18	16.38	190.71		

Measurements: The fresh sample characterizes the natural state of the soil field, so the measurement of ammonium and nitrate is sampled from the fresh soil. The soil samples were collected with the Profile method. The soil is divided into three layers depth-wise from top to substrate, which are 0-5, 5-10 and 10-20 cm in depth. At the same depth of soil profile the layer exhibits plum-shaped distribution using Quartering Mixed method. Test the dried samples after crushing is filtered by 2, 1 or 0.25 mm sieve for the determination of effective nutrients, pH, enzyme activity and soil structure. The experimental indicators, methods and main instruments are according to the references¹²⁻¹⁴.

RESULTS AND DISCUSSION

Ammonium nitrogen: Nitrogen absorbed by the soil exists in the form of the simple compound. But most of them are in the form of ammonium nitrogen and nitrate nitrogen. They will undergo complete nitrification within 1 to 2 weeks under the proper condition. Soil colloid has two electric layers, one being the diffusion layer. In this layer, compensation ion and the ion with same charge in the soil solution make an equivalent exchange. This is known as the ion substitution absorption, which is primary way of preservation of effective nutrition in the soil. The soil colloid usually holds negative charge, which is attractive to the cation. The absorption of the ammonium ion depends on the specific surface area and clay mineral content¹⁵. Input ammonium nitrogen of ATW is 5.96 times of AE and the amount of nitrate in test AE is 13 times of ATW. The introduction of phosphate in both tests is almost the same but low. As Fig. 1 shows, in the 0-5 cm soil layer, ammonium nitrogen content of ATW is the highest, which is 860 mg/kg. The surface of soil colloid with negative charge absorb NH₄⁺ effectively. Ammonium nitrogen concentration of test groups GCW, CBW, CW and AE are 740, 708.35, 622 and 600 mg/kg, respectively. Furthermore, the ammonium content of the soil has a positive relationship with the quality of the irrigation water. In the 5-10 cm soil layer, ammonium nitrogen content of test ATW and CBW increases, especially the CBW increases by 13.4 %. Mineralization is completed by the interaction of a variety of microorganisms that are using the carbonate in organic matter as an energy source. When the temperature and pH value in the middle layer is optimum, CBW can provide more carbon, in which case the mineralization is more obvious, with an apparent increase in ammonium nitrogen content¹⁶. The ammonium nitrogen content of the tests ATW, AE, GCW and CBW in the 10-20 cm depth soil presents descending trend indicating that the roots of plants absorb more ammonium nitrogen. The total amount of ammonium nitrogen in the soil is the comprehensive result of soil organic nitrogen mineralization, plant uptake and other conversion processes.

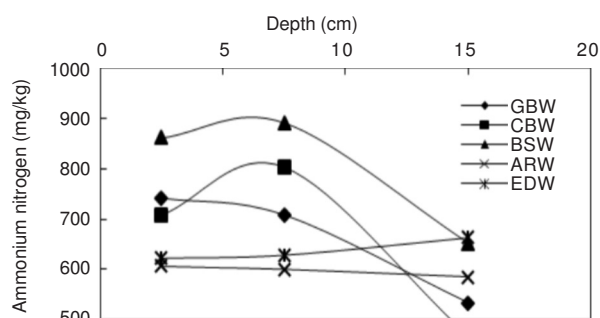


Fig. 1. Changes of soil ammonium nitrogen by different quality wastewater irrigation

Nitrate nitrogen: Quantitatively, the soil absorbs less anion than cation. But a majority of anions play important role in nutrition for plants, environmental protection and formation of minerals. Thus the soil absorption of anions is also relatively active. The content of nitrate in the test ATW in the 0-5 cm layer is the highest at 23.95 mg/kg compared to other four groups (Fig. 2). The test GCW, CBW, CW and AE

are 22.41, 19.59, 19.42 and 19.46 mg/kg, respectively and their content changes in a pattern similar to that of the ammonium nitrogen. In the tests GCW, CBW, AE and CW, nitrate at the 5-10 cm depth increases, especially almost a 9 % increase in CW. The nitrate content in the 10-20 cm soil layer increases for all GCW, CBW, ATW, AE and CW. In CBW, it is 21 % higher than the 5-10 cm soil layer. Overall, the average content of nitrate is just 3 % of the average content of ammonium nitrogen, which means nitrogen exists mainly in the form of ammonium nitrogen in soil. In term of quality of irrigation, the $\text{NO}_3^-/\text{NH}_4^+$ ratio of GCW, CBW, ATW and AE wastewater are 44, 41, 3 and 219 %, respectively. The average value of $\text{NO}_3^-/\text{NH}_4^+$ is only around 3 % in soil, indicating that nitrate conversion in the GCW, CBW and AE is not as expected. On one hand, due to the negative charge of NO_3^- , it is most susceptible to rainfall leaching and the soil suffers a greater loss of nitrate in moist rainy areas of the southwest. However, on the other hand, it also shows significantly higher intensity of mineralization than soil nitrification, which results in low nitrate conversion rate and fixed rate. The ample organic matter in biogas slurry and low content of nitrate in ATW assist in complete absorption. The nitrate content in the bottom of soil gets to the maximum and keeps constant. That's because the potential of soil in the oxide layer is high, leading to stronger nitrification and NH_4^+ can be converted to NO_3^- and migrate to the anoxic layer.

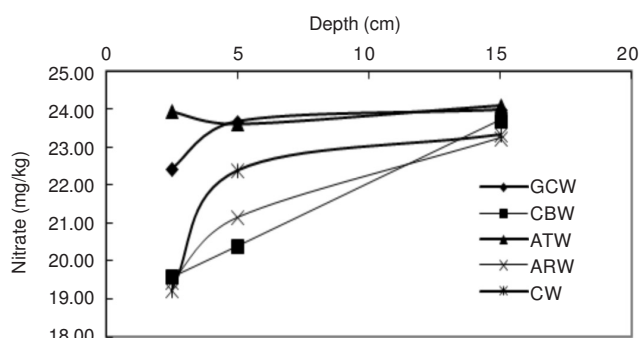


Fig. 2. Changes of soil nitrate nitrogen by different quality wastewater irrigation

Available phosphorus: In the absence of any interference, the migration and conversion of phosphorus in soil is extremely unnoticeable. When there is input of some phosphorus, the migration of phosphorus became apparent in soil. When soluble phosphate in wastewater enters into the soil, some of it is converted to Ca^{2+}P and absorbed by plants. Part of them slowly produced effective phosphorus such as Al-P and Fe-P. In the 0-5 cm soil depth, the effective phosphorus content of GCW, CBW, CW and AE are less than 100 mg/kg (Fig. 3). In the 5-10 cm soil layer, the contents in GCW, CBW, ATW, CW and AE increases, especially CBW and CW (10 and 11 %, respectively). Effective phosphorus content increased in the middle layer of soil and pH is close to neutral which can reduce phosphorus fixation and improve its effect. In the middle layer the redox potential decreased. The reduction of ferric ion to the ferrous iron and a higher solubility of the low-phosphate iron also increase the phosphorus availability. In the 10-20 cm depth of soil, the phosphorous in tests GCW, CBW, ATW

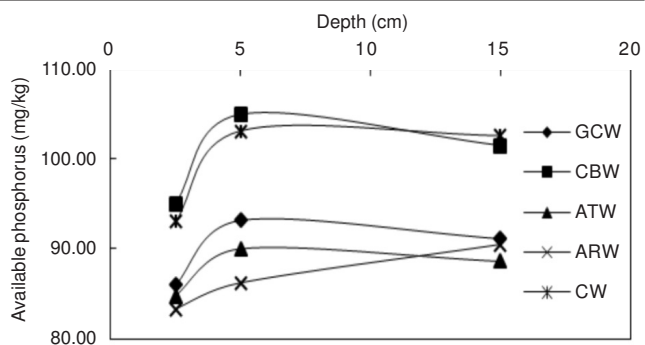


Fig. 3. Changes of available phosphorus in soil by different wastewater irrigation

and CW tended to decrease. Most of the effective phosphorus in plant roots can be absorbed, but its performance no longer improved. The effective phosphorus contribution rate of test ATW is very low, showing phosphorus adsorption is not obvious. This is due to the competition of attaching potential between ammonium nitrogen and soluble phosphate at the higher soil level. Test ATW contain higher organic matter content which makes the organic acid ions and phosphate compete the attaching points, reducing the absorption of phosphorus.

Phosphorus absorption coefficient: According to the relevant specifications, the phosphorus absorption coefficient that is less than 500 belongs to the weak absorptive capacity of the soil. As Fig. 4 shows, in the test groups GCW, CBW, ATW, CW and AE the phosphorus absorption coefficients are all less than 500. It is positively correlated to the effective phosphorus content in the Fig. 4. After one month, the phosphorus absorption coefficient of CW reached to the peak of 570. The CW irrigation makes phosphorus over-resolved and improves the capacity of absorption of phosphorus in the mid-term. But with the pH value decreasing later, it reduced the phosphorus fixation ability, as seen by the decreasing trend of the later part of the curve. After one month of irrigating GCW and CBW, which contain more organics, their phosphorus adsorption coefficients dropped by 56 and 94 %, respectively. Because of the competition between the organic acid ions and phosphate to solid surface points, the phosphorus absorption in the soil reduced. The increasing of adsorption points after absorption of the crop made the phosphorus absorption coefficient slightly increase in later period. The phosphorus absorption coefficient of AE is decreasing due to the low aerobic effluent organic matter as well as the low phosphate content.

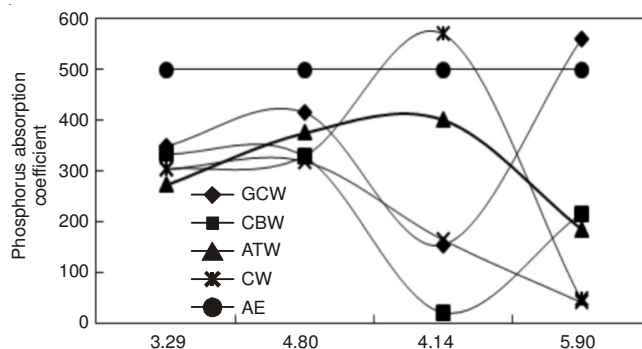


Fig. 4. Changes of phosphorus absorption coefficient in soil by different wastewater irrigation

Soil carrying capacity of ammonium and nitrate

nitrogen: By continuous daily irrigation, the maximum carrying value of ammonium, nitrate and available phosphorus, phosphorus absorption coefficient in mixed soil layer can be obtained. As is shown in Fig. 5, after biogas slurry irrigation soil ammonium nitrogen carrying value goes up to the peak value of 1355 mg/kg on the 21st day. After 2 days, the nadir value will appear at 389 mg/kg. The reason of the decline is that organic nitrogen mineralization has to be catalyzed by microbial enzyme and the excessive input of organic matter and organic nitrogen will directly affect the activity of the enzyme. At the beginning of irrigation, the C/N ratio of biogas slurry is much less than 15:1. Once mineralization starts, the nitrogen it produces will exceed the amount of microbial assimilation. If the C/N ratio of accumulation is more than 30:1, the mineralization is unable to supply nitrogen, causing the nitrogen deficiency of plants. The nitrate in the soil is 24.65 mg/kg after four days of irrigation before approaching the peak value and the later declined slightly without much fluctuation, reaching the mean value of 24.19 mg/kg. Nitrate is prone to nitrification and denitrification. It is in dynamic equilibrium, in which the conversion is active. Because of negative charge of the NO_3^- , it is easy to be removed by leaching and movement. The type of soil determines the basic content of nitrate and fertilizer and nitrogen supplied are the primary factors effecting nitrate content¹⁷. The experiment proved the purple soil carrying capacity of nitrate is very limited.

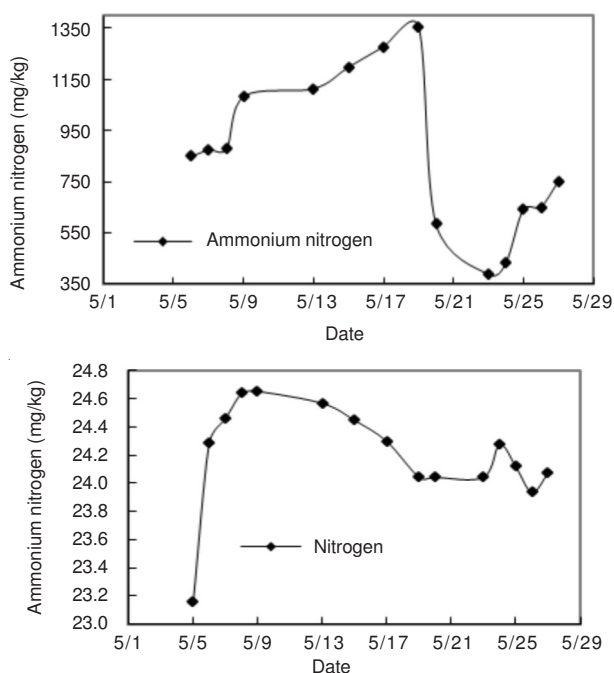


Fig. 5. Biogas slurry irrigation carrying value of soil ammonium and nitrate nitrogen

Soil carrying capacity of available phosphorus and phosphorus absorption coefficient:

In the initial stage of biogas slurry irrigation, the available phosphorus in the soil goes up slowly and get to the peak value of 163.66 mg/kg on the 25th day (Fig. 6). After the downward curve, it is nearly constant relative to the previous value. This proves that the content of phosphorus in soil is relatively stable. As long as

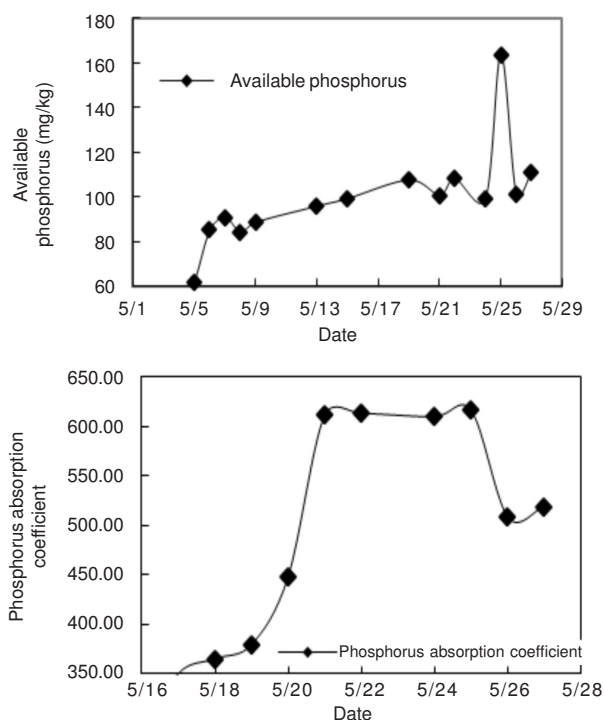


Fig. 6. Biogas slurry irrigation carrying value of phosphorus in the soil

the pH and organic matter content in soil stays stable, the content of phosphorus will remain unchanged. Soil phosphorus absorption coefficient is above 500 from day 21 to day 25, exhibiting the high phosphorus absorption capacity, though it declines a little after this. After a few days of irrigation, the pH will reduce, deteriorating the ability of phosphorus fixation which is the downward part of the curve. Because the competition to the specific adsorption points between the organic acid ions and phosphate solid, the absorption of soil phosphorus was reduced. The available phosphorus in the soil is indicator of the nutrient level of the soil. The level of phosphorus content reflected storage and supply capacity of phosphorus in the soil to some extent¹⁸. The southwest of China belongs to the humid area and the available phosphorus content in the purple soil decreases significantly with the increased average annual precipitation and average annual temperature. In the Fe-Al and Al-rich soil, the presence of a large number of Fe and Al oxides has strong adsorption capacity^{19,20}. Greatly reduces the content of available phosphorus, phosphorus fixation and precipitation. Therefore, physical property of the purple soil reduces the available phosphorus and phosphorus absorption coefficient.

Physical properties of soil by biogas slurry irrigation through scanning electron microscopy (SEM):

Soil texture is the proportions of the grain content and the composition of the soil. The soil solid phase material rarely exhibits as single particles but as clusters of different shapes. Mineral soil particles are the main component of the soil solid structure. Comparing the different soil and normal soil samples after long-term biogas slurry irrigation, the soil structure after biogas slurry irrigation seems to have changed. SEM photographs of different scales reflect the spatial distribution of soil particle and clusters in different soil layers. The following Fig. 7 are 400 times larger than the field of view with low magnification

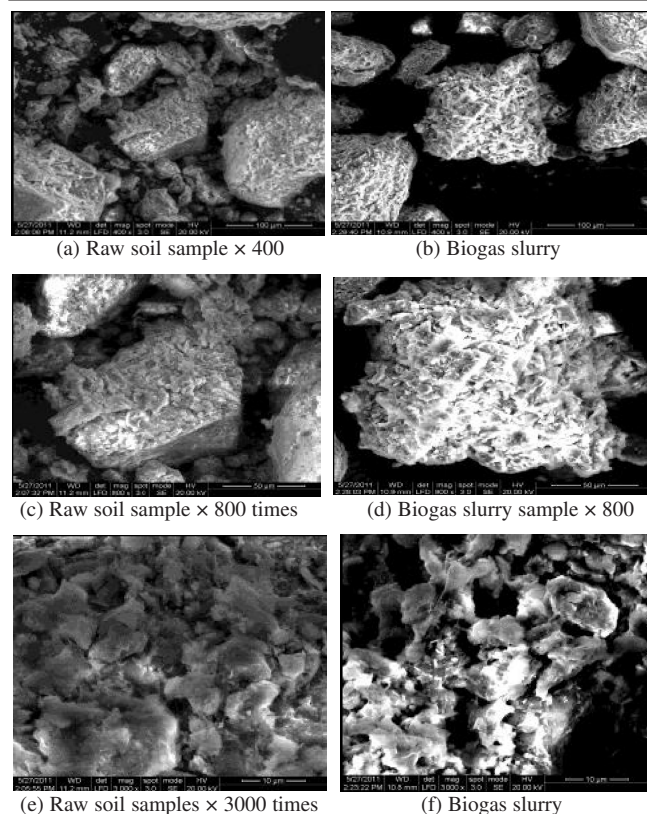


Fig. 7. Comparison soil by biogas slurry irrigation with the original irrigation using SEM

and a working distance of 11.2 mm. The scan photos show the soil structure is relatively loose with more small particles. After the ATW irrigation the soil clusters increased. By scanning at magnification of 800 times and 3000 times, with a working distance of 10.9 mm, one can see that biogas slurry irrigated soil porosity increased. It has also improved the capacity of water and fertilizer retention. At the same time it increased the amount of microorganism attached to the clusters and improved the stability of soil. The increase of effective microorganisms can promote mineralization and nitrogen fixation and help the conversion of nitrogen and phosphorus cycle.

Conclusion

Precipitation is abundant in southwest mountain towns. Exploitation of nutrient resources in biogas slurry is a type of efficient irrigation. Not only is it necessary to be able to take full advantage of dung resources, but also to avoid undermining the growth of plants and environment.

In this experiment, the wastewater of different quality from the large scale livestock and poultry farms is used for irrigation and results show that the ammonium nitrogen content can reach the maximum value of 860 mg/kg in the surface soil. It is slightly higher in the middle layer soil than the surface soil. In the bottom layer of soil, except for the test clear water, the ammonium nitrogen content of the other tests has decreased. The nitrate content of the surface soil by biogas slurry irrigation is 23.95 mg/kg. Similarly, nitrate content in the middle layer increased slightly which meets the needs of the growth of plant. In the surface soil, the effective phosphorus content of the four trials, except the test group, are less than 100 mg/kg. In the middle layer of soil the phosphorus content goes down,

among which CBW and CW irrigation group have the maximum increase of 10 and 11 %, respectively. In the bottom soil the phosphorus content of all the tests except AE decreased, signifying complete absorption of phosphorus.

The phosphorus absorption coefficient of irrigation water of different quality changes over time. After one month irrigation of CW the peak value of 570 was obtained, but it still lies in the low level category. After one month of irrigation of GCW and CBW which containing more organic the phosphorus absorption coefficients dropped 56 and 94 %, respectively. Overall phosphorus absorption capacity of water of various qualities is weak in most cases, except the individual case where it becomes weaker.

In the test of soil carrying capacity, soil carrying value of ammonium is 1355 mg/kg at the maximum, nitrate is 24.65 mg/kg, effective phosphorus is 163.66mg/kg and phosphorus absorption coefficient between the 21st day and 25th day is above 500. After a long-term irrigation of biogas slurry, the soil porosity will increase and the presence of microorganism around the clusters will increase. Besides, the minerals become more diverse and stability of soil improves.

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