Establishment and Application Demonstration of Standards for Agricultural Biogas Slurry Returning to Field in Citrus Orchard

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Abstract. In this paper, we take citrus orchard as target, evaluate the safety of agricultural biogas slurry by comparing the properties of unfermented manure and biogas slurry from 27 farms in Chongqing. The results indicate that the amount of harmful heavy metal element in biogas slurry completely meets the requirements in China agricultural standards “Biogas Fertilizer” (NY/T 2596) and “Organic Fertilizer” (NY 525), indicating the biogas slurry is safe to use as fertilizer. These results provide data support in formulating a stricter standard about the limitations of harmful heavy metal containment ratio in biogas slurry. Biogas slurry can replace chemical fertilizer partly, and can be popularized as a good new type of liquid fertilizer. A certain amount of biogas slurry irrigation can basically meet the supply of nitrogen and phosphorus nutrition, and zero use of chemical fertilizer (nitrogen and phosphorus) come true. However, the content of biogas slurry varies greatly, the measurement of fertilizer efficiency is complex, and it cannot meet the balanced supply of all mineral nutrients, which will lead to the imbalance of nutrient abundance and deficiency. The nutritional diagnosis should be used to monitor the nutritional level of trees, guide the control of abundance and deficiency, enhance the efficiency of citrus orchards to absorb the effective elements of biogas slurry, and improve the yield and quality of citrus. Through monitoring the runoff quality of the orchard returned with biogas slurry, it is found that the runoff quality of the orchard is inferior V. Total phosphorus and granular phosphorus are the main contaminating sources of the outflow runoff in orchard. This indicates that the problems of nitrogen and phosphorus pollution need to be prevented and controlled in the process of returning the biogas slurry to the orchard. It is necessary to establish the landscape system of fruit grass in the orchard and the interception system of flood interception ditches, sediment pockets and buffer ponds in order to sand, retention and reduction of particulate phosphorus. Based on this, a
bunch of agricultural biogas slurry returning technology model suitable for modern ecological citrus orchard planting was summarized. The technical standards for biogas slurry harmlessly returning to citrus orchard and technical specification for formula fertilization of citrus nutrition diagnosis, were formed. It has been applied on a large scale in Chongqing three gorges reservoir area and national modern eco-agricultural demonstration base, and has achieved remarkable socio-economic and ecological environmental benefits. The results of this study provide data and technical support for the formulation of two new national standards of "Agricultural Biogas Slurry" and "Technical Specification for Harmless Treatment of Agricultural Biogas Slurry".

1. Introduction
The agricultural biogas slurry is a kind of residue of liquid state fermentation made from agricultural organic wastes such as the manure of livestock and poultry as well as the crop straws through adequate anaerobic fermentation in biogas fermentation after harmless and stabilizing treatment. It is used for farmland production in the way of organic liquid fertilizer, water manure and irrigation water [1]. The anaerobic fermentation of organic matters involves a lot of microorganism species. In addition, the metabolite of anaerobic fermentation is very complex, and so are the components of the produced biogas slurry, which includes not only abundant macronutrient elements such as nitrogen, phosphorus and potassium as well as micronutrient elements such as copper and zinc, but also 17 kinds of amino acids and active enzymes [2, 3]. These nutrient elements mainly exist in the form of quick-acting available nutrient. Therefore, the biogas slurry is a polybasic available compound fertilizer that can be quickly absorbed and used by crops [4, 5]. However, for the replacement of chemical fertilizer, it is necessary to take a large amount of biogas slurry to reach the fertilizer efficiency equivalent to that of chemical fertilizer, and it is inconvenient to apply [6, 7], as the high-water content and low available composition.

As an evergreen fruit tree in tropical and subtropical zones as well as the most popular fruit in the world, citrus is the main fruit plant in South China and the main crop in Chongqing [8, 9]. It likes the warm and humid climate, and is mainly distributed between 16°N and 37°N. The upper and middle reaches of the Yangtze River is the most suitable region for citrus in China and the advantageous area planned by the state. By 2018, Chongqing has 230,000 ha (about 3.45 million mu) of citrus with a total production of 3.2 million tons [10], which are mainly distributed in 18 districts and counties of Three Gorges Reservoir Area including Zhongxian, Kaizhou, Changshou, Yunyang, Fengjie and Wanzhou. The citrus orchards in this area were selected for the empirical study and effect test of biogas slurry returning to field, which is typical for the test [11].

The integrated irrigation system of water and fertilizer for biogas slurry can be set on a mobile platform. It consists of six parts [12, 13]: harmless treatment tank of biogas slurry, liquid storage tank, irrigation head, explosion-proof and blockage-proof pipe network, hand-irrigated system and field salt-proof systems. The pneumatic pump group is connected to the top of the biogas tank, the top of the clear water tank and the top of the mixing tank through several pneumatic pipelines. The bottom of the biogas tank is connected to the top of the mixing tank through the biogas pipeline. The bottom of the clean water storage tank is connected to the top of the mixing tank through the clear water pipeline. The bottom of the mixing tank is provided with a liquid outlet. The liquid outlet is provided with two branch pipelines with an electronic cut-off valve, a set of pipe is connected to the sprayer, and a branch pipeline is connected with the infusion coil pipe. The system satisfies the requirements of equipping, simplifying and standardizing the biogas slurry.

In this research, in combination with the soil property and the trend of acid conversion of citrus plantation area in Chongqing [14], the contents of nutrients and heavy metals in fermented manure and biogas slurry were compared to determine the safety and quality of biogas slurry. A certain amount of biogas slurry irrigation was carried out in the demonstration orchard to explore the substitution of biogas slurry for chemical fertilizer. To monitor the runoff water quality of biogas slurry returning to
orchards, the pollution problems that need to be prevented and controlled in the process of biogas slurry returning to fields. Based on this, a bunch of agricultural biogas slurry returning to field techniques suitable for citrus cultivation is summarized, forming the technical regulation standard for the agricultural biogas slurry returning to field technique of citrus orchard, which is applied into the demonstration of normalized returning to field of citrus orchard.

2. Materials and Methods

2.1. Test base
The test base is located at the Zhaojiawan Base in Shuanglong Town, Chongqing and lies in the Changshou Lake Region of Longxi River, the tributary of Three Gorges Reservoir Area. It has a covered area of 180 ha, and the most of the species planted is W. Murcott late-maturing hybrid citrus with a planting density of 600 strains/ha. The biogas slurry comes from the 5,000 live pigs on hand cultured by the base. The manure discharged by the pig farm is treated by solid-liquid separation, and the argol produces the organic fertilizer through high-temperature aerobic composting fermentation. The separated manure is fermented in biogas fermentation, and the biogas slurry is returned to the field in the way of whole irrigation by fertilizer and water integrated irrigation equipment. For difficulties in biogas slurry pipeline returning to the fields such as gas explosion and blockage of ammonium magnesium phosphate (urine scale) generated by crystallization, the base has designed and been equipped with the pond for harmless treatment of agricultural biogas slurry, automatic exhaust and pressure regulating device for pipeline as well as the technology and collection device of solid self-flushing. For quick change and difficult measurement of the effective constituent in biogas slurry, the base has been equipped with the diagnostic techniques for the nutrient of citrus, carried out formula fertilization and supported the biogas slurry to replace chemical fertilizer and irrigation water [4 & 5].

2.2. Method of sampling
The unfermented manure and fermented biogas slurries from 27 bases employing biogas slurry returning to field in Chongqing were sampled as 100 ml for each time.

2.3. Methods of determination and evaluation of nutrient elements and heavy metal elements
The nutrient elements in the unfermented manure and fermented biogas slurry determined are nitrogen, phosphorus, potassium, mercury, arsenic, lead, copper, zinc, chromium and cadmium. Nitrogen and phosphorus were determined based on the agricultural industry standards in China Water-soluble Fertilizers - Determination of Total Nitrogen, Phosphorus and Potassium Content (NY/T 1977) [15]; potassium were determined based on the agricultural industry standards in China Fertilizers - Determination of Potassium Content (NY/T 2540) [16]; mercury, arsenic, lead, chromium and cadmium were determined based on the national standards in China per Ecological Index of Arsenic, Cadmium, Lead, Chromium and Mercury for Fertilizers (GB/T 23349) [17]; and copper and zinc were determined based on the agricultural industry standards in China Water-soluble Fertilizers - Determination of Copper, Iron, Manganese, Zinc, Boron and Molybdenum Content (NY/T 2540) [18].

2.4. Detection of leaves
The collected leaf samples were put into a clean, poriferous and double-layered plastic bag, and labels were placed in both inner and outer bags. The bag was sealed and delivered to the pretreatment laboratory of leaves within 10 h. The cleaning, enzyme elimination and drying procedures were completed within 24 h. Specific procedures were as follows: washed with tap water and 0.1% neutral detergent, twice with fresh water, twice with purified water and once with distilled water; placed in the oven at 105°C for enzyme elimination for 30 min., dried at the constant temperature of 70-80°C for 10-12 h; smashed, sealed and placed in the dryer for later detection; and delivered together to the Citrus Research Institute, Chinese Academy of Agricultural Sciences for detection.
2.5. Effect monitoring
The determination of orchard yields as well as the water quality testing on biogas slurry, precipitation and exit runoff were conducted. The determinations of orchard yields were carried out by third-party experts and technical staff of the company onsite. For the water quality testing, as the orchard locates at shallow hill, citrus was planted on both the top and the bottom of the slope, and most of the runoff was generated by precipitation, the nitrogen and phosphorus contents in its exit runoff were monitored to evaluate the effect of cutting down and digestion of agricultural biogas slurry. The biogas slurry was sampled on a sunny day from the storage pool of biogas slurry. For the sampling of rainwater and surface runoff, since continuous rain occurred and no irrigation took place in practical production, the sampling was carried out during the dry seasons in spring, summer and autumn. The samples of runoff and rainwater in the first rainfall period were collected after irrigating with biogas slurry and delivered for detection. For the specific sampling of rainwater and exit runoff of orchard, a desilting pool of 5 m³ was built at the end of the flood intercepting and drainage trench to collect the runoff water gathered in the pool. A rain shelter of colored steel was put up over the pool to prevent rainwater from falling directly into the pool and to collect the rainwater as rainwater harvesting machine. Collected samples were placed into cleaned mineral water bottles, which were fastened down and kept at low temperature, without any air gap and delivered the Chongqing Soil Fertilizer Detection Center for detection in time.

3. Results and Analysis

3.1. Comparison of nutrient elements and heavy metal elements in the unfermented manure and biogas slurry

Table 1. Contents of Nutrient Elements and Heavy Metal Elements in Unfermented Manure and Biogas Slurry

| S/N | pH | N (mg/kg) | P (mg/kg) | K (mg/kg) | Hg (mg/kg) | As (mg/kg) | Pb (mg/kg) | Cu (mg/kg) | Zn (mg/kg) | Cr (mg/kg) | Cd (mg/kg) |
|-----|----|----------|---------|----------|-----------|-----------|-----------|----------|---------|---------|---------|
|     | Standard value | 5-8 |       | 5 | 10 | 50 | 50 | 10 | 10 | 10 | 10 |
| 1.  | 7.3 | 689 | 125 | 295 | 0.8×10⁻³ | 0.6 | 16.0×10⁻³ | 10.0 | 2.9 | 40.9×10⁻³ | 1.8×10⁻³ |
| 2.  | 7.4 | 443 | 73 | 190 | 0.8×10⁻³ | 0.0 | 9.4×10⁻³ | 4.7 | 4.0 | 11.5×10⁻³ | 0.3×10⁻³ |
| 3.  | 6.5 | 273 | 114 | 185 | 0.0 | 0.2 | 10.4×10⁻³ | 5.6 | 15.5 | 40.3×10⁻³ | 0.9×10⁻³ |
| 4.  | 7.6 | 526 | 55 | 421 | 0.7×10⁻³ | 0.0 | 4.3×10⁻³ | 0.7 | 1.5 | 16.5×10⁻³ | 0.3×10⁻³ |
| 5.  | 7.4 | 449 | 90 | 205 | 0.9×10⁻³ | 0.0 | 10.7×10⁻³ | 2.0 | 10.5 | 9.2×10⁻³ | 1.6×10⁻³ |
| 6.  | 6.7 | 613 | 151 | 388 | 0.1×10⁻³ | 0.1 | 9.2×10⁻³ | 2.1 | 1.8 | 32.1×10⁻³ | 1.4×10⁻³ |
| 7.  | 7.5 | 1037 | 147 | 741 | 2.3×10⁻³ | 1.0 | 4.5×10⁻³ | 13.5 | 12.3 | 6.8×10⁻³ | 0.1×10⁻³ |
| 8.  | 6.9 | 487 | 132 | 446 | 0.2×10⁻³ | 0.1 | 4.5×10⁻³ | 0.6 | 1.2 | 12.0×10⁻³ | 0.2×10⁻³ |
| 9.  | 7 | 1156 | 211 | 491 | 4.7×10⁻³ | 1.9 | 15.7×10⁻³ | 14.4 | 11.5 | 92.3×10⁻³ | 2.9×10⁻³ |
| 10. | 7.3 | 777 | 84 | 427 | 0.9×10⁻³ | 0.6 | 5.8×10⁻³ | 7.3 | 10.2 | 14.5×10⁻³ | 0.3×10⁻³ |
| 11. | 6.5 | 1557 | 365 | 831 | 0.2×10⁻³ | 0.7 | 12.5×10⁻³ | 29.7 | 40.0 | 19.0×10⁻³ | 0.1×10⁻³ |
| 12. | 7.5 | 1119 | 66 | 559 | 0.0 | 0.1 | 33.1×10⁻³ | 1.2 | 7.9 | 10.6×10⁻³ | 0.1×10⁻³ |
| 13. | 7.5 | 931 | 158 | 407 | 0.0 | 0.1 | 12.4×10⁻³ | 0.1 | 0.8 | 8.0×10⁻³ | 0.3×10⁻³ |
| 14. | 7.1 | 282 | 58 | 115 | 0.5×10⁻³ | 0.1 | 3.9×10⁻³ | 0.6 | 7.6 | 4.1×10⁻³ | 0.1×10⁻³ |
| 15. | 7.7 | 156 | 22 | 72 | 0.6×10⁻³ | 0.0 | 2.1×10⁻³ | 0.0 | 0.5 | 3.5×10⁻³ | 0.1×10⁻³ |
| 16. | 6.8 | 557 | 189 | 353 | 2.2×10⁻³ | 0.2 | 16.6×10⁻³ | 6.1 | 8.0 | 11.2×10⁻³ | 0.8×10⁻³ |
| 17. | 6.7 | 500 | 131 | 206 | 5.2×10⁻³ | 0.2 | 6.1×10⁻³ | 6.0 | 2.8 | 14.4×10⁻³ | 0.7×10⁻³ |
| 18. | 6.6 | 1156 | 147 | 741 | 5.4×10⁻³ | 0.3 | 33.8×10⁻³ | 5.4 | 7.3 | 21.8×10⁻³ | 1.3×10⁻³ |
| 19. | 7.1 | 219 | 60 | 155 | 1.9×10⁻³ | 0.4 | 5.7×10⁻³ | 0.5 | 1.2 | 3.4×10⁻³ | 0.2×10⁻³ |
| 20. | 7.3 | 286 | 56 | 224 | 0.7×10⁻³ | 0.3 | 11.7×10⁻³ | 2.7 | 2.8 | 5.9×10⁻³ | 0.2×10⁻³ |
| 21. | 7.2 | 872 | 97 | 1043 | 0.4×10⁻³ | 0.1 | 19.9×10⁻³ | 0.6 | 2.3 | 19.9×10⁻³ | 2.2×10⁻³ |
| 22. | 7.5 | 708 | 93 | 457 | 0.2×10⁻³ | 1.3 | 5.6×10⁻³ | 1.5 | 1.7 | 9.3×10⁻³ | 0.3×10⁻³ |
| 23. | 7.3 | 409 | 116 | 314 | 0.0 | 0.3 | 8.2×10⁻³ | 3.3 | 10.4 | 6.5×10⁻³ | 0.3×10⁻³ |
| 24. | 6.6 | 2458 | 549 | 1460 | 0.9×10⁻³ | 0.1 | 30.8×10⁻³ | 1.3 | 5.8 | 66.1×10⁻³ | 4.3×10⁻³ |
| 25. | 7.1 | 930 | 104 | 612 | 0.2×10⁻³ | 0.1 | 3.8×10⁻³ | 2.4 | 9.4 | 7.5×10⁻³ | 0.7×10⁻³ |
| 26. | 7.4 | 392 | 54 | 607 | 0.2×10⁻³ | 0.1 | 16.3×10⁻³ | 0.2 | 0.6 | 6.8×10⁻³ | 0.7×10⁻³ |
| 27. | 8.4 | 2751 | 222 | 662 | 1.4×10⁻³ | 0.1 | 10.5×10⁻³ | 0.0 | 0.2 | 13.1×10⁻³ | 0.3×10⁻³ |
| Average value | 7.2 | 805 | 132 | 471 | 1.2×10⁻³ | 0.3 | 11.6×10⁻³ | 4.5 | 6.7 | 18.8 | 0.8×10⁻³ |
Note: Source of standard value: Technical indexes of Anaerobic digested fertilizer (NY/T 2596-2014), and so do Table 2.

Summarize the contents of nutrient elements and heavy metal elements in the unfermented manure and fermented biogas slurry collected from 27 bases and list in Tables 1 and 2. By comparing the data in the two tables and the corresponding indexes in Anaerobic digested fertilizer (NY/T 2596-2014) [19], it can be discovered that none of the contents of five harmful heavy metals (As, Cr, Cd, Pb and Hg) exceeds the standard limit. As a kind of fluid fertilizer, however, the biogas slurry has high water content and relatively low content of total nutrition, and thus fails to meet the limiting value of fertilizer efficiency in the existing agricultural industrial standard Anaerobic digested fertilizer. To promote the agricultural biogas slurry returning to field, it is necessary to collect and sort the indexes of biogas slurry extensively, study and establish the standard parameters for safe returning to field of low-concentration biogas slurry of fertilizer (waste) with biogas slurry of all kinds, and to meet the requirements of resource utilization and zero emission.

The data from Tables 1 and 2 are shown in Figure 1. It can be inferred that compared with the unfermented manure, the total nutrient content of biogas slurry has slightly reduced, while the content of harmful heavy metals also reduced, especially mercury and lead reduced sharply. This means that, during the fermentation, some heavy metal elements are absorbed by bacteria, and are collected and disposed as waste with precipitates. The safety of biogas slurry has therefore significantly improved.

Compared with industrial standard Anaerobic digested fertilizer (NY/T 2596-2014), there are five harmful heavy metals that meet the limits specified in Anaerobic digested fertilizer (NY/T 2596-2014) in the inspected biogas slurry, which means that the biogas slurry is safe and can be extended as a kind of new fluid fertilizer and agricultural irrigation water.

### Table 2. Contents of Nutrient Elements and Heavy Metal Elements in Biogas Slurry

| S/N | pH | N (mg/kg) | P (mg/kg) | K (mg/kg) | Hg (mg/kg) | As (mg/kg) | Pb (mg/kg) | Cu (mg/kg) | Zn (mg/kg) | Cr (mg/kg) | Cd (mg/kg) |
|-----|----|-----------|-----------|-----------|------------|------------|------------|------------|------------|------------|------------|
|     |    | Standard value | 5-8 | 5 | 10 | 50 | - | - | 50 | 10 |
| 1.  | 7.3 | 500 | 52 | 191 | 0.0 | 0.1 | 2.6×10⁻³ | 0.0 | 0.1 | 19.0×10⁻³ | 0.3×10⁻³ |
| 2.  | 6.9 | 305 | 68 | 67 | 0.0 | 0.0 | 7.0×10⁻³ | 0.7 | 1.0 | 16.9×10⁻³ | 1.0×10⁻³ |
| 3.  | 7.4 | 588 | 83 | 297 | 0.0 | 0.1 | 4.2×10⁻³ | 0.2 | 0.3 | 20.9×10⁻³ | 1.0×10⁻³ |
| 4.  | 7.3 | 467 | 86 | 304 | 0.0 | 0.0 | 1.4×10⁻³ | 0.1 | 0.2 | 19.0×10⁻³ | 0.3×10⁻³ |
| 5.  | 5.8 | 1345 | 33 | 630 | 0.0 | 1.6×10⁻³ | 0.5 | 2.0 | 30.5×10⁻³ | 3.1×10⁻³ |
| 6.  | 7.7 | 703 | 107 | 553 | 0.2×10⁻³ | 3.6×10⁻³ | 0.7 | 1.2 | 35.7×10⁻³ | 2.2×10⁻³ |
| 7.  | 7.3 | 535 | 78 | 311 | 0.1×10⁻³ | 1.9×10⁻³ | 0.1 | 0.1 | 10.2×10⁻³ | 0.3×10⁻³ |
| 8.  | 7.0 | 117 | 46 | 99 | 0.2×10⁻³ | 3.4×10⁻³ | 0.0 | 0.0 | 12.0×10⁻³ | 1.0×10⁻³ |
| 9.  | 7.5 | 772 | 54 | 468 | 0.2×10⁻³ | 1.3×10⁻³ | 0.2 | 0.1 | 10.2×10⁻³ | 0.5×10⁻³ |
| 10. | 7.5 | 769 | 62 | 458 | 0.0 | 2.2×10⁻³ | 0.2 | 0.2 | 9.9×10⁻³ | 0.5×10⁻³ |
| 11. | 7.2 | 2122 | 166 | 987 | 0.0 | 6.8×10⁻³ | 2.7 | 5.6 | 25.0×10⁻³ | 1.2×10⁻³ |
| 12. | 7.4 | 922 | 88 | 482 | 0.2×10⁻³ | 4.1×10⁻³ | 0.4 | 1.3 | 14.0×10⁻³ | 0.8×10⁻³ |
| 13. | 7.6 | 1405 | 125 | 647 | 0.0 | 7.7×10⁻³ | 2.7 | 8.7 | 47.4×10⁻³ | 2.2×10⁻³ |
| 14. | 7.5 | 513 | 81 | 226 | 0.2×10⁻³ | 1.5×10⁻³ | 0.0 | 0.0 | 7.1×10⁻³ | 1.0×10⁻³ |
| 15. | 7.4 | 390 | 76 | 139 | 0.1×10⁻³ | 1.9×10⁻³ | 0.0 | 0.1 | 12.1×10⁻³ | 0.3×10⁻³ |
| 16. | 7.1 | 432 | 121 | 250 | 0.6×10⁻³ | 3.7×10⁻³ | 0.0 | 0.0 | 8.5×10⁻³ | 0.9×10⁻³ |
| 17. | 7.4 | 547 | 85 | 280 | 0.3×10⁻³ | 4.1×10⁻³ | 0.1 | 0.2 | 7.9×10⁻³ | 0.6×10⁻³ |
| 18. | 7.4 | 891 | 78 | 593 | 0.7×10⁻³ | 5.8×10⁻³ | 0.2 | 0.3 | 5.8×10⁻³ | 0.5×10⁻³ |
| 19. | 7.3 | 441 | 74 | 246 | 0.8×10⁻³ | 3.0×10⁻³ | 0.0 | 0.2 | 12.1×10⁻³ | 0.3×10⁻³ |
| 20. | 7.5 | 244 | 43 | 178 | 0.4×10⁻³ | 3.4×10⁻³ | 0.1 | 0.2 | 8.4×10⁻³ | 0.2×10⁻³ |
| 21. | 7.6 | 750 | 44 | 1048 | 0.1×10⁻³ | 2.2×10⁻³ | 0.0 | 0.1 | 8.0×10⁻³ | 0.3×10⁻³ |
| 22. | 7.1 | 632 | 121 | 307 | 0.2×10⁻³ | 1.2×10⁻³ | 0.2 | 0.2 | 7.8×10⁻³ | 0.2×10⁻³ |
| 23. | 7.2 | 730 | 185 | 348 | 1.0×10⁻³ | 7.0×10⁻³ | 1.8 | 0.0 | 18.6×10⁻³ | 1.1×10⁻³ |
| 24. | 7.8 | 71 | 41 | 72 | 0.3×10⁻³ | 4.7×10⁻³ | 0.0 | 0.0 | 5.2×10⁻³ | 0.4×10⁻³ |
| 25. | 7.6 | 2133 | 72 | 117 | 0.0 | 4.2×10⁻³ | 2.4 | 4.1 | 17.1×10⁻³ | 1.8×10⁻³ |
| 26. | 7.6 | 576 | 36 | 910 | 0.6×10⁻³ | 4.9×10⁻³ | 0.1 | 0.1 | 9.7×10⁻³ | 1.1×10⁻³ |
| 27. | 7.7 | 2154 | 82 | 598 | 0.0 | 8.5×10⁻³ | 0.0 | 0.2 | 11.0×10⁻³ | 1.4×10⁻³ |
| Average value | 7.3 | 780 | 81 | 400 | 0.2×10⁻³ | 3.8×10⁻³ | 0.5 | 1.0 | 14.9×10⁻³ | 0.9×10⁻³ |
3.2. Application of biogas slurry in citrus orchard

Changes of biogas slurry dosage, nitrogen, phosphorus, and potassium and zinc contents in leaves, and fruit yield with time in citrus orchards in five years were listed in table 3. According to the detection results in table 3, the ecological system of orchard can effectively absorb the nitrogen and phosphorus nutrition in biogas slurry. After application of biogas slurry for five consecutive years, the application amount has increased by 40.0% from 90 t/ha to 150 t/ha, and the biogas slurry has completely replaced the nitrogenous fertilizer. Under the zero utilization of nitrogenous fertilizer, the yield of orchard has increased by 145.5% from 16.5 t/ha to 40.5 t/ha. For the nutrient diagnosis monitoring on citrus, from 2014, two kinds of fertilizers lacking mineral elements - potassium sulfate and zinc sulfate were added to supplement potassium and zinc and balance the nutrient of tree body. And from 2015, the per unit yield of orchard has been increased by the increase of biogas slurry application amount, which proves that the yield increase of orchard can increase the absorption and removal efficiency of nitrogen and phosphorus (see Table 3). Between 2013 and 2014, the nitrogen nutrition of citrus tree has reduced from 27.4 mg/L-28.3 mg/L (normal and high level) to 23.0 mg/L-26.8 mg/L (normal and low) between 2015 and 2017 respectively. And for the low phosphorus nutrition of citrus tree and leaves between 2016 and 2017, each tree was supplemented with 0.5 kg of 12% calcium superphosphate for recouping phosphorus between 2017 and 2018, with a total amount of 36 kg/ha (scalar quantity). The removal amounts of nitrogen and phosphorus are calculated by the nitrogen (N, 0.6%) and phosphorus (P$_{2}$O$_{5}$, 0.015%) contents in fruits, in total 303.7 kg/ha, including 243.0 kg/ha of nitrogen and 60.7 kg/ha of phosphorus, which are larger than the input of chemical fertilizer. Biogas slurry can thus be an ideal replacement of chemical fertilizer (nitrogen and phosphorus).

Table 3. Changes of biogas slurry dosage, nitrogen, phosphorus, potassium and zinc contents in leaves, and fruit yield with time in citrus orchards in five years

| Year | Amount of biogas slurry (t/ha) | Yield of citrus (t/ha) | Nitrogen content in leaves (g/kg) | Phosphorus content in leaves (g/kg) | Potassium content in leaves (g/kg) | Zinc content in leaves (g/kg) |
|------|--------------------------------|-----------------------|----------------------------------|-------------------------------------|----------------------------------|------------------------------|
| 2013 | 90                             | 16.5                  | 27.4                             | 1.3                                 | 8.0                              | 15.5×10^{-3}                |
| 2014 | 90                             | 21.8                  | 28.3                             | 1.4                                 | 10.9                             | 16.5×10^{-3}                |
| 2015 | 150                            | 31.5                  | 23.0                             | 1.4                                 | 10.5                             | 5.9×10^{-3}                 |
| 2016 | 150                            | 37.5                  | 24.6                             | 1.0                                 | 9.6                              | 12.0×10^{-3}                |
| 2017 | 150                            | 40.5                  | 26.8                             | 1.5                                 | 9.4                              | 14.8×10^{-3}                |
| Appropriate Standard Values | 150                           | -                     | 25.0-28.0                        | 1.2-1.6                             | 10.0-15.0                       | 25.0×10^{-3}, 100.0×10^{-3} |

Note: The appropriate standard value is derived from Technical Rules for Formula Fertilization of Citrus Nutrition Diagnosis (DB50/T 487-2012) [21]

3.3. Effect of reduction of biogas slurry pollution in citrus orchard

The limit value of national environmental quality standard for surface water and monitoring result of runoff water quality in orchard of Nongzheng Company were listed in table 4 and 5, respectively. According to the standard limit values of Table 4 and the analysis on test results of Table 5, the
The average pH value of the biogas slurry is 7.83, which is alkaline. The total nitrogen is 18.98 mg/L. The ammonium nitrogen (NH$_4^+$-N) included in the monitoring of limit value of water quality pollution is 3.54 mg/L, which is of the water quality of inferior Class V. The total phosphorus is 18.52 mg/L, which is of the water quality of inferior Class V, including 3.59 mg/L dissolvable phosphorus, which accounts for 19.38% of total phosphorus, indicating that particulate phosphorus is the main source of phosphorus pollution in biogas slurry. The water quality of biogas slurry is of general inferior Class V and the main sources of pollution are ammonium nitrogen and total phosphorus, which will infiltrate the farmland and water bodies in large quantities, causing double environmental pollution of nitrogen and phosphorus.

The average pH value of rainfall in the citrus orchard is 6.54, which is slightly acidic. The total nitrogen is 2.41 mg/L, including 0.17 mg/L ammonium nitrogen (NH$_4^+$-N), belonging to Class I, and 1.96 mg/L nitrate nitrogen (NO$_3^-$-N), and accounting for 81.33%. The total phosphorus is 0.64 mg/L, which belongs to inferior Class V, including 0.23 mg/L dissolvable phosphorus, accounting for 35.94%, and the water quality of rainfall is of general inferior Class V. The main source of pollution is total phosphorus or particulate phosphorus, which will infiltrate the farmland in a large amount, causing phosphorus enrichment in the plant leaves and damage to the green algae of the tree.

The pH value of soil in the citrus orchard is 5.06, which is acidic. The contents of total nitrogen (890 mg/kg) and the total phosphorus (260 mg/kg) are higher.

The average pH value of the exit runoff in the citrus orchard is 6.79, which is basically neutral and is improved. The total nitrogen is 4.82 mg/L, with a decrease of 74.60% over biogas slurry. The ammonia nitrogen (NH$_4^+$-N) is 0.31 mg/L, which is classified as Class II water quality with a decrease of 91.24%, and the purification effect for nitrogen pollution is obvious. The total phosphorus is 4.63 mg/L, which belongs to Class V with a decrease of 75.0% over biogas slurry. The dissolvable phosphorus is 0.86 mg/L, accounting for 18.57%, decreasing 76.04% over biogas slurry and being lower than the reduction efficiency of ammonium nitrogen, which may be related to the low phosphorus demand of citrus trees (1.2 ~ 1.6 mg/L, less than 1/3 of the nitrogen demand). The runoff water quality in citrus orchard is of inferior Class V, and the main sources of exit runoff pollution are total phosphorus and particulate phosphorus in the citrus orchard. The above-mentioned information provides technical requirement basis for the establishment of the forest-fruit-grass landscape system and flood intercepting trench, sediment deposition pool, buffering pond interception system, conservation of water and soil, prevention and controlling of sediment, as well as the retention and reduction of particulate phosphorus.

### Table 4. Limit Value of National Environmental Quality Standard for Surface Water

| Items                      | Limit Value for Surface Water in National Standard |
|----------------------------|---------------------------------------------------|
|                            | I | II | III | IV | V |
| pH                         |   | 6-9|     |    |   |
| Ammonia nitrogen (NH$_4^+$-N) mg/L ≤ | 0.15 | 0.5 | 1.0 | 1.5 | 2.0 |
| Total phosphorus (calculated with P) mg/L ≤ | 0.02 | 0.1 | 0.2 | 0.3 | 0.4 |

Note: According to the national standard *Environmental Quality Standards for Surface Water* (GB 3838) [22], the calculation of nitrogen is based on ammonium nitrogen (NH$_4^+$-N) and phosphorus is based on total phosphorus (TP).
Table 5. Monitoring Result of Runoff Water Quality in Orchard of Nongzheng Company

| Items                  | Testing Samples | pH Value | Total Nitrogen (TN) | Ammonium Nitrogen NH₄⁺-N | Nitrate Nitrogen NO₃⁻-N | Total Phosphorus (TP) | Dissolvable Phosphorus (DP) |
|------------------------|-----------------|----------|---------------------|--------------------------|------------------------|-----------------------|-----------------------------|
| Biogas slurry (mg/L)   | Biogas slurry irrigation 1 | 8.42     | 19.37               | 3.58                     | 7.39                   | 18.76                 | 3.55                        |
|                        | Biogas slurry irrigation 2 | 7.24     | 18.58               | 3.50                     | 7.98                   | 18.28                 | 3.63                        |
|                        | Average quality   | 7.83     | 18.98               | 3.54                     | 7.69                   | 18.52                 | 3.59                        |
|                        | Water quality V    | coincidence | V                 | V                        | -                      | V                     | -                           |
| Rainwater deposition (mg/L) | Rainfall 1     | 6.30     | 2.51                | 0.17                     | 2.18                   | 0.77                  | 0.25                        |
|                        | Rainfall 2       | 6.56     | 2.41                | 0.17                     | 1.90                   | 0.58                  | 0.22                        |
|                        | Rainfall 3       | 6.77     | 2.29                | 0.18                     | 1.80                   | 0.56                  | 0.22                        |
|                        | Average water quality | 6.54    | 2.41                | 0.17                     | 1.96                   | 0.64                  | 0.23                        |
|                        | Water quality V   | coincidence | -                 | I                        | -                      | V                     | -                           |
| Orchard soil (mg/kg)   | Exit runoff 1    | 5.06     | 890                 | -                        | -                      | 260                   | 4.21                        |
|                        | Exit runoff 2    | 6.48     | 4.90                | 0.27                     | 4.48                   | 6.98                  | 0.85                        |
|                        | Exit runoff 3    | 6.93     | 4.72                | 0.32                     | 4.28                   | 3.77                  | 0.87                        |
|                        | Average water quality | 6.79    | 4.82                | 0.31                     | 4.14                   | 4.63                  | 0.86                        |
|                        | Water quality V  | coincidence | -                 | II                       | -                      | V                     | V                           |

3.4. Establishment of technical standards for agricultural biogas slurry returning to field in citrus orchard

Through summary of five years’ researches on the application test for biogas slurry returning to field in citrus orchard, it is found that through a certain amount of biogas slurry irrigation, nutrition diagnosis and monitoring, and guidance of controlling abundance and supplying loss to balance fertilization, the main demand for nutrient elements (e.g., nitrogen and phosphorus) in the orchard can be satisfied. The high quality and high yield of the citrus orchard (which applies the recycling technology of biogas slurry and manure of livestock) and the efficient utilization of biogas slurry can be supported and the zero utilization of chemical fertilizer (e.g., nitrogen and phosphorus) can be basically realized.

The project of returning biogas slurry pipeline to the field should be selected at a base with the scale of farming more than 1000 pigs per year and the area of cultivation and absorption base more than 10 ha. The system is composed of six parts, harmless treatment pond of biogas slurry, storage pond, irrigation head part, explosion-proof and blockage-proof pipeline system, hand-watering system and field salt-proof measures. When the biogas slurry enters the explosion-proof and blockage-proof pipe network system, secondary fermentation gas-producing tube burst may be occurred, and the system will automatically adjust the pressure of the pipeline to prevent tube burst. With the anaerobic bacteria entering the biogas slurry can grow to form colonies, bird droppings, etc. The sediment collection device will automatically collect solid wastes, keep the flow of biogas slurry smoothly, and return fertilizer and water into the field through the terminal manual irrigation system. Combining with the technical measures of insufficient irrigation, two adjacent holes of 30×30×30 cm were excavated in the inner third of the drip line of fruit trees, which were filled with water more than 50 L with grass covering to reduce the evaporation loss. Based on the strong water-absorbing function of roots, the water requirement of fruit trees such as citrus trees for more than 5-7 days can be guaranteed. For the orchards with shallow groundwater table, rising water or poor drainage, drainage ditches should be increased, and the depth of drainage ditches should be more than 80 cm, to facilitate rainwater to wash out salt and prevent waterlogging.

4. Conclusion

Through the monitoring of nutrient and heavy metal contents in fermented manure and biogas slurry, it is confirmed that the total nutrient content and harmful heavy metal elements in biogas slurry have decreased, but the quality and safety have been improved. Biogas slurry can replace chemical fertilizer
to some extent, and can be popularized as a good new type of liquid fertilizer. A certain amount of biogas slurry irrigation can basically meet the supply of nitrogen and phosphorus nutrition, and zero use of chemical fertilizer (nitrogen and phosphorus) come true. However, the content of biogas slurry varies greatly, the measurement of fertilizer efficiency is complex, and it cannot meet the balanced supply of all mineral nutrients, which will lead to the imbalance of nutrient abundance and deficiency. The nutritional diagnosis should be used to monitor the nutritional level of trees, guide the control of abundance and deficiency, enhance the efficiency of citrus orchards to absorb the effective elements of biogas slurry, and improve the yield and quality of citrus. Through monitoring the runoff quality of the orchard returned with biogas slurry, it is found that the runoff quality of the orchard is inferior V. Total phosphorus and granular phosphorus are the main contributing sources of the outflow runoff pollution of the orchard. This indicates that the problems of nitrogen and phosphorus pollution need to be prevented and controlled in the process of returning the biogas slurry to the orchard. It is necessary to establish the landscape system of fruit grass in the orchard and the interception system of flood interception ditches, sediment pockets and buffer ponds in order to sand, retention and reduction of particulate phosphorus. Based on this, a bunch of agricultural biogas slurry returning technology model suitable for modern ecological citrus orchard planting was summarized. And technical standards such as harmless returning of agricultural biogas slurry to the field in citrus orchard and monitoring of application effect based on technical specifications of nutrition diagnosis formula fertilization of citrus were formed. The standard was applied to the demonstration of returning to the field in citrus orchard, and good effect was achieved. The application demonstration also provides data and technical support for the two national standards of "Agricultural Biogas Slurry" and "Technical Specification for Harmless Treatment of Agricultural Biogas Slurry". It also provides technical support for the large-scale utilization of agricultural biogas liquor in citrus orchards and the replacement of chemical fertilizers.

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