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Review

Closing the Global Energy and Nutrient Cycles through Application of Biogas Residue to Agricultural Land – Potential Benefits and Drawbacks

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Abstract: Anaerobic digestion is an optimal way to treat organic waste matter, resulting in biogas and residue. Utilization of the residue as a crop fertilizer should enhance crop yield and soil fertility, promoting closure of the global energy and nutrient cycles. Consequently, the requirement for production of inorganic fertilizers will decrease, in turn saving significant amounts of energy, reducing greenhouse gas emissions to the atmosphere, and indirectly leading to global economic benefits. However, application of this residue to agricultural land requires careful monitoring to detect amendments in soil quality at the early stages.

Keywords: Biogas residue; fertilization; agriculture.

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1. Biogas residue

Anaerobic digestion of organic waste has significant potential to reduce global warming and climate change [1] as it promotes enhanced cycling of nutrient resources through nutrient-rich end products [2,3] (hereafter referred to as biogas residue) and presents an alternative to the energy-demanding generation of mineral fertilizers [4-6]. Anaerobic waste treatment leads to the generation of renewable energy in the form of biogas (carbon dioxide and methane) [7] and indirect decrease in methane emissions from landfill areas [8] through alternative recycling of residual products that were formerly landfilled or incinerated [9]. Moreover, application of biogas as an alternative fuel may moderate the use of fossil fuels and mitigate release of greenhouse gases [1]. However, to guarantee

the maximum recovery value of organic wastes, the residual product, i.e. biogas residue, should have a meaningful purpose, and optimal benefits derived from its production. The application of residue as a fertilization agent that is recycled back to arable land ensures that crops receive the majority of the essential nutrients required for growth [2,10-12], i.e., soil fertility is conserved [13], and the soil structure and humus balance is improved [14,15], thus promoting closure of the natural nutrient and energy cycles. In contrast, application of inorganic fertilizers to crop fields is supplementary to the nutrient cycle, resulting in the need for increased production of fertilizers requiring significant energy input [4-6], along with continued escalation in the amount of residual waste treatment products [16] with no way of benefiting from its nutrient-rich nature. Thus, the use of biogas residue as an alternative should not only close the global nutrient cycle, but also indirectly reduce greenhouse gas emissions to the atmosphere through decreased need for inorganic fertilizers and new landfill sites.

In 2006, about 18% of organic waste from Swedish households was treated in biogas or compost plants, struggling towards the national goal of treating 35% of organic waste using biological approaches by 2010 [17]. The entire quantity of biogas residue produced in Sweden in 2006 (273,000 tons) was used within agriculture [17]. The use of biogas residue as a crop fertilizer within agriculture is a relatively new concept [14], and different types of waste are routinely employed as input substrate for digesters [18-22]. Common sources of feedstock include source-separated household or commercial food waste, slaughterhouse waste, as well as agricultural waste and slurry. Depending on the country and location of the biogas plant, sewage sludge may be applied as input substrate [23]. However, in view of its restricted use within agriculture in several European countries [24], sewage sludge will not be discussed and included in the term “biogas residue” within this article, unless stated otherwise.

Biogas residue is the final remnant of the original waste placed into digesters that cannot be utilized by microbes involved in the anaerobic degradation process [7]. The residue additionally contains the mineralized remains of dead bacterial mass derived from within the digesters [7]. To ensure that biogas residue is an acceptable crop fertilizer, the waste needs to be of high quality with proven value as an efficient plant nutrient source and/or soil conditioner [16]. The quality of biogas residue is assessed based on three criteria, specifically, chemical, biological and physical features [15], and is significantly dependent on the origin of the organic waste used as feedstock. Based on the source and possible pre-treatments applied, the resulting residue may contain persistent organic matter, such as dioxin-like compounds [25,26], polychlorinated bromines (PCB) and pesticides [27], polyaromatic hydrocarbons (PAH) [28], chlorinated paraffins [29], phenolic compounds [28,30,31] and phthalates [28,32,33]. The potential risks of introducing these contaminants to agricultural land in terms of soil perturbation need to be considered prior to application of biogas residue. For instance, the concentration of the contaminant, its chemical reactivity, volatility, water solubility and absorption capacity are crucial determinants [34,35], as well as the degradation capacity of soil and potential long-term effects on soil processes [36-38]. The biological quality of biogas residue is additionally related to the presence of pathogenic microorganisms and seeds [39-42], which may facilitate new transmission routes of pathogens between humans, animals and the environment. Finally, biogas residue may contain various types of physical impurities, such as glass, plastic, metal and/or stones [43]. In addition to significant effects on the suitability of biogas residue as a crop fertilizer, physical and chemical properties of

untreated feedstock affect the rate of bioconversion, and hence its potential as a biogas generation substrate.

Anaerobic zymogenous microorganisms that are inoculated in biogas plants degrade the organic fractions of feedstock to CH_4, CO_2 and digested residue. Essential nutrients (N, P, K, Mg), including trace elements required by plants, are conserved in the residue [44-51]. However, nutrients are present in inorganic plant-available forms at a markedly higher extent in digested residue, compared to untreated waste [47,48,50,52-54], due to the large input of organic nutrients that are mineralized during the digestion process [7]. For instance, digested residue contains 25% more accessible ammonium (NH_4^+-N) than untreated liquid manure [55]. Consistent with these findings, several trials show that biogas residue enhances crop yield [10,11]. Additionally, biogas residue inhibits plant diseases and induction of microbial resistance [56], and has a direct effect on soil-borne diseases [57] and indirect effect on stimulation of biological activity [58].

Overall, the application of biogas residue as fertilizers within agriculture has not been as extensively evaluated as other types of organic waste, emphasizing the urgent need for further studies within this field to obtain products with positive implications for the global environment. This article focuses on the known effects of biogas residue as a crop fertilizer and soil conditioner. Additionally, a brief discussion about the modern molecular methods suitable for monitoring the land application of biogas residue is included along with a section dealing with the future challenges in the use of biogas.

2. Effects of biogas residue on soil microbiology and quality

Organic matter is an essential component of soil that not only provides nutrients for crops. but also improves soil aggregation, facilitating the maintenance of structure, drainage and aeration [59], which are necessary for good crop yields. Consequently, addition of organic matter makes the soil less erodible and easier to plough, and enhances nutrient retention. Moreover, soil acquires increased resistance to crusting and compaction, enabling better growth of crop roots, and stimulates microbial activity [44,45], indirectly leading to improved crop yield. For instance, application of organic waste enhances the soil N and P content [60], improves soil structure and water holding capacity [61], suppresses crop disease [57], and diminishes the need for chemical weed control [62]. Furthermore, microbial biomass [63,64] and various soil enzymatic activities, including those of urease, alkaline phosphatase and β-glucosidase [65,66], are increased, implying that a broad range of soil functions benefit from biogas residue amendment.

As the soil microbial biomass is a living metabolizing unit, it responds more quickly to changes in the surrounding environment, compared to organic matter as an entity. Changes in soil microbial parameters may therefore reflect perturbations in soil quality induced by biogas residue long before these modifications are envisaged in chemical properties, such as the C, N and P content [14]. Consequently, evaluation of the structure, function and/or activity of the microbial community, either as a whole or in terms of specific phylogenetic/functional groups, presents the best “live view” of the events occurring in soil, providing rapid and reliable information on soil quality.

Nyberg *et al.* [67] investigated whether organic household waste biologically treated in different ways (anaerobic digestion, composting, swine manure and cow manure) affects the ammonia-oxidizing activities and compositions of indigenous bacterial communities in soil. The group showed that the

ammonia-oxidizing bacterial community composition was not affected by organic matter. However, while no community shift was detected, application of swine manure and residue produced by thermophilic anaerobic digestion suppressed the rate of potential ammonia oxidation in the soil after 12 weeks of incubation. The authors speculate that compounds inhibitory to ammonia-oxidizing activity are present in these residues. Based on previous data obtained from organic fraction extracts of residue, it was concluded that the inhibitory compounds are organic in nature, possibly constituting organic pollutants detected in other batches of the same anaerobic residue [25,31,32].

Soil microorganisms are generally stimulated as a result of fertilization with biogas residue, as evident from the addition of inorganic nutrients and organic matter [68]. Similar results were obtained by Odlare *et al*. [58] who performed a 4-year field trial in Sweden focusing on the effects of organic waste (composted household waste, biogas residue from household waste, anaerobically digested sewage sludge, pig manure, cow manure and mineral fertilizer) on soil chemical and microbiological parameters. The researchers observed that biogas residue enhanced microbial biomass (measured as substrate-induced respiration) and the proportion of metabolically active microorganisms, compared to the untreated control. Furthermore, in contrast to the short-term study discussed above [67], biogas residue increased the rate of potential ammonia oxidation, nitrogen mineralization capacity and the specific growth rate constant of denitrifiers [58]. However, this increase was not statistically significant, compared to that of the control amended with mineral fertilizer. Due to the chemoautotrophic nature of nitrifying bacteria, higher benefits of ammonium-rich biogas residue for soil nitrifiers were expected in relation to the actual effects, as their prime source of energy is ammonia. Mineral nitrogen-phosphorus-sulphur (N-P-S) fertilizer mainly utilizes nitrate as its source of nitrogen, and would thus be a suitable control for the ammonium oxidation rate in soil amended with biogas residue [58]. Generally, no negative effects of organic waste products were observed on the soil microbial parameters analyzed. Furthermore, biogas residue contained higher concentrations of mineral nitrogen and easily degradable carbon, leading to greater efficiency in promoting soil biological activity. The authors concluded that changes in the microbial properties of the soil adjust more rapidly than chemical properties to amendment by organic waste, further confirming the suitability of microbial processes as sensitive indicators of short-term alterations in the soil environment [58].

In contrast to the results of Odlare *et al.* [58], Ernst and co-workers [69] reported reduced amounts of readily available nutrients and increased levels of barely decomposable organic matter in the digested residue. The recalcitrant nature of the residue led to reduced microbial activity in the soil and decreased biomass of earthworms, compared to conventional cattle slurry. Moreover, negative effects of earthworms on soil nitrification, microbial biomass and basal respiration by the digested residue were observed [69]. As fertilizers were applied at the same amount of NH_4-N, treatment with the digested residue resulted in lower total C input (since the proportion of NH_4-N is higher than that in untreated slurry), which possibly explains the reduced stimulation of microorganisms by earthworms upon application of biogas residue [69]. The authors further discuss the qualitative differences in organic C among the treatments, which may additionally contribute to the variations in microbial activity observed with biogas residue and conventional cattle slurry [69].

The significant variations in the qualitative composition of C among biogas residues and its decisive role in supporting microbial consortia further emphasize the need for an aerobic post-

treatment stage (i.e., curing/maturation, particularly if the original feedstock contains woody/plant material) where recalcitrant organic compounds, such as lignin, are further degraded by aerobic microorganisms, such as fungi [70].

3. Effects of biogas residue on plant growth

Upon anaerobic degradation, the energy in organic waste is predominantly transformed into methane, whereas nitrogen is mainly conserved in the resultant residue as ammonium [7]. The anaerobic digestion procedure leads to a decreased C/N ratio from 17.0 in raw swine manure to 10.5 in biogas residue, which may be explained by loss of carbon as CH_4 and CO_2 during this process [71]. This finding is consistent with other studies reporting a lower C/N ratio in biogas residue after anaerobic digestion [48,49]. When considering the organic fractions only, the C/N_{org} ratio is increased following anaerobic digestion due to a decrease in the organic N concentration [50]. However, N may be immobilized in organic materials with high C/N ratios (above 18) upon application to soil [50], which should be taken into account when calculating the crop requirement of biogas residue (i.e., N). A lower level of carbon remaining in the residue is available for microbial degradation, compared to that in untreated waste and/or manure and/or slurry, and digested residues contain less total C as a result of conversion to CH_4 during the degradation process [1,47,50,53,69]. Moreover, the amount of lignin is higher in anaerobically digested residues than conventional slurry [72], similar to that in residues produced during thermophilic composting [73].

The low C/N ratio in biogas residue, compared to untreated manure, leads to decreased N immobilization, and consequently, reduced N mineralization and bioavailability at the time of application [53,74-76]. Conversely, Loria and Sawyer [77] reported that raw and digested swine manure generated similar net inorganic N and mineralization, although the chemical oxygen demand (COD) was significantly decreased after digestion. Rubaek *et al* . [78] showed that N uptake by ryegrass was higher with biogas residue than raw manure in the first cut. However, the opposite phenomenon was observed in the second cut [78]. Moreover, the amount of N lost by denitrification was higher in plots treated with raw, compared to digested slurry [78]. Other studies show that plots fertilized with biogas residue and raw manure provide similar crop yields [74,79]. In general, biogas residue presents an efficient nitrogen source for plants with the potential to improve crop yield and soil properties [80-83]. However, it is important to remember that N is the most common limiting factor for crop growth in organic farming systems [84-87] owing to failure in synchronizing crop N demand and supply to the soil by mineralization of organic fertilizers [88].

The issue of how effectively biogas residue can substitute common artificially produced mineral fertilizers in terms of crop yield is of significant interest. A recent report by Montemurro *et al.* [89] focused on determining the potential of biogas residue in crop yield. During a two-year field experiment, no significant differences were observed in the cumulative plant dry weight of alfalfa subjected to different fertilizer treatments (anaerobic digestates and mineral fertilizers), whereas for cocksfoot crops, mean yield was higher in plots treated with biogas residue in relation to control plots. At the end of the trial, no heavy metals were detected in either plants or soil, and plant nutrient content was not affected by fertilizer application. The authors concluded that biogas residue could be effectively utilized in the short term to provide nutrients to crops [89]. In another study, Kocar [90]

compared the fertilizer value of anaerobically digested cattle slurry with those of commercial organic and chemical fertilizers. Higher yields of safflower were obtained with biogas residue than commercial organic and chemical fertilizers. The authors propose that the input of chemical fertilizers should decrease with the use of anaerobically digested residues, whereas soil texture is improved [90]. Chantigny and colleagues [91] reported similar fertilizer values of raw and anaerobically treated liquid swine manure to that of mineral fertilizer upon immediate incorporation into soil [91], supporting the significant potential of biogas residue as a valuable substitute and/or complement to mineral fertilizers. Moreover, the risk of postharvest NO_3 accumulation with swine manure was no higher than that with mineral fertilizer [91].

Båth and Rämert [2] reported a higher content of mineral nitrogen in soil amended with biogas residue derived from domestic household waste, compared to that fertilized with compost during the initial 70 days after planting. The group further demonstrated improved yield of leeks following fertilization with biogas residue in relation to compost amendment [2], which may be explained by the higher amount of N in forms immediately available to plants (i.e. inorganic N, predominantly ammonium). A study by Rivard *et al*. [10] showed that dried and composted biogas residue produced from municipal solid waste induced an increase in crop weight (i.e., corn) and plant yield in direct proportion to the residue application rate. Moreover, Garg and co-workers [92] reported that fertilization of soil with biogas slurry generated from cattle dung improved the yield of wheat over non-modified controls. Grain yield increased with the application of biogas residue, which was attributed to the lower bulk density of soil, increased hydraulic conductivity, and greater moisture retention. Consequently, the improved status of nutrients through amendment of the physical properties of soil contributed to the higher yield of wheat [92]. An investigation by Marchain [93] further disclosed that biogas residue induced a 6-20% higher yield in vegetable production, clearly signifying that a broad range of plants potentially benefit from this mode of fertilization, including vegetables and cereals. However, since biogas residue contains a significant proportion of mineralized N, crops that display a short and intensive period of N uptake should preferably be fertilized using this method [16,48] to minimize N leakage. Furukawa and Hasegawa [94] reported that biogas residue produced from source-separated household waste was comparable to NPK fertilizers in terms of early N uptake, fresh yield, and N uptake at harvest of spinach and komatsuna. Since biogas residue is rich in NH_4^+-N and K but low in P [95], and soil-exchangeable K is high [94], its fertilizer value may be mainly attributed to the N effect [94]. Consistently, Tiwari *et al.* [11] showed that significant amounts of mineral N could be substituted with biogas slurries in cropping of wheat, and Svensson and colleagues [16] reported that biogas residue derived from source-separated household waste contained equivalent quantities of mineral N to that supplied by organic fertilizers of agricultural crops, and enhanced both crop yield and grain quality of oats and spring barley (i.e., the N content of grain). Additionally, biogas residue was equally as good as or better than cow manure, pig slurry and mineral fertilizer in terms of fertilization of agricultural crops [58]. Odlare *et al.* [58] concluded that biogas residue may contain higher amounts of mineral N and easily degradable C [14] (for instance, compared to compost), and should hence be more efficient in supplying available N to crops than other types of organic waste [58]. In contrast, El-Shakweer *et al.* [96] reported similar crop yields using soil amended with air-dried biogas residue and unmodified soil, and other studies report that anaerobic digestion results in relative enrichment of heavily degradable compounds [1,47,50,69]. Nevertheless, biogas

residue is evidently an efficient N source for the fertilization of agricultural crops [16]. Notably, soil fertilized with biogas residue requires phosphorus (i.e. superphosphate) supplementation to avoid P deficits [16], emphasizing the need to analyze and monitor the quality of biogas residue before indiscriminate application to agricultural land as a fertilizer.

4. Post-treatment of biogas residue

Biogas residue resulting from anaerobic digestion of organic waste has significant potential as a crop fertilizer and soil conditioner. However, the residue may not be a suitable soil improver in its basic form, owing to possible phytotoxicity [97-99], viscosity and odor [100], difficult handling, and expensive soil application approaches [101]. Therefore, further treatment is essential to enhance its applicability as a crop fertilizer before use as an acceptable saleable product [102], such as composting (i.e., aerobic degradation) and/or air-drying.

Biogas residue displays high water content (95-98%), raising the issue of whether it should be dewatered and dried before application within agriculture. These procedures may eliminate the need for spraying, resulting in reduction of application costs and improved targeting of nutrient deficiency spots [15]. On the other hand, upon drying, up to 90% of NH_4^+ may be lost as ammonia (NH_3) [10], which would dramatically reduce the benefits of biogas residue as a crop fertilizer. In case of distribution to the crop field without prior drying, the residue can be spread through conventional irrigation techniques, which presents an advantage over dried residue, since application is possible throughout the crop cycle [15]. However, the application time needs to be taken into account to match nutrient availability with the needs of crops and avoid leakage of mineralized N into soil and subsequently, groundwater [48]. Loss of N within agriculture occurs through nitrate leaching, microbial denitrification and NH_3 volatilization, results in decreased supply of N to crops, and simultaneously constitutes a threat to sustainable management [88]. NH_3 volatilization may lead to eutrophication of aquatic and terrestrial ecosystems, which are limited in N, and contribute to increased acidification of sensitive ecosystems [88,103]. Additionally, the spreading equipment used should ensure minimization of NH_3 emissions occurring due to the potentially high NH_3 content and high pH of the residue. However, cattle slurries with a lower content of dry matter are reported to infiltrate the soil more easily than slurries with a higher content of dry matter [104-106], which may have implications for the soil infiltration potential of liquid biogas residue. Moreover, the dry matter content of manure significantly affects NH_3 emission [107]. Specifically, higher emission is observed at elevated dry matter levels (i.e., from cattle than pig slurry) [108]. Misselbrook *et al.* [105] suggested that the physical nature of dry matter content (fibrous vs. colloidal) is an important factor influencing the soil infiltration potential of slurries. As rapid infiltration into soil reduces NH_3 emissions, it is important that farmers replace techniques such as simple land spreading and band spreading with shallow injection to minimize NH_3 loss to optimize benefits of the digested residue [48]. In conjunction with suitable application techniques, anaerobic digestion of organic material represents a potential key procedure for producing organic waste fertilizers via reduction of solid concentrations and particle sizes [48,51,109,110].

The decreased carbon content in biogas residue, compared to untreated waste (such as manure or slurry), may lead to reduced formation of the potent greenhouse gas, nitrous oxide [111], and resulting

emissions [88,112]. Due to the potential presence of a more recalcitrant form of C in digested residue (easily degradable C compounds are decomposed in the digestion process) compared to untreated waste [1,47,50,69], the rate of microbial degradation in soil, and hence, oxygen consumption may be reduced [49,113-117]. This results in less anoxic microsites, and possibly, decreased rates of denitrification, indicating significant potential to reduce N_2O and N_2 loss [88].

To further reduce the risk of N leakage, biogas residue can be further processed and stabilized in compost. This results in a fertilizer product of higher quality, as mineralized N is fixed onto humus-like fractions. Additionally, composting of the digested residue induces the degradation of resistant organic elements, such as lignin [70], which are usually not completely degraded by anaerobic microorganisms. The aerobic microbes present in compost transform phytotoxic NH_3 into nitrates, resulting in an end-product with improved fertility that is more suitable as a soil conditioner. Composting additionally contributes to odor reduction, making the residue more acceptable as a soil improver.

A report by Abdullahi *et al*. [102] showed that the phytotoxicity of fresh waste and anaerobic digests decreased along with the degradation of easily biodegradable organics of waste during the composting process. Moreover, seed germination (*Raphanus sativus* L.) increased with dilution of the mature (composted) residue and extension of the incubation time. Accordingly, the authors recommend lower application rates of composted residue in combination with longer lag periods between the spreading of composted residue and planting, which would potentially reduce the amount of biodegradable organic material in the residue, and consequently, phytotoxicity [102].

Regardless of the preferred approach of fertilizer application, post-treatments available for biologically treated organic waste (biogas residue), such as composting, should be an increasing focus of research interest as the amount of waste accumulates and future surveys continue to prove the suitability of biogas residue as a crop fertilizer for agricultural land. However, it is important to consider that the quality of the resulting residue depends on the quality of original input waste, highlighting the importance of proper source separation systems. Accordingly, interference of toxic chemicals and non-degradable inclusion in the process should be minimized, ultimately leading to improved quality of the product residue.

5. Monitoring the application of biogas residue to arable land

For the safe application of biogas residual fertilizer, it is crucial to monitor the resulting changes in the surrounding soil environment, which usually includes large amounts of nutrients (mineralized and organic) and organic C. Several methods currently available for the evaluation of treatment effects on soil quality mainly focus on chemical properties, including the C, N and P content, that slowly adjust to the altered conditions [58]. However, there is an imminent risk of overlooking the short-term effects of residue application when relying on solely these analyses. Therefore, to distinguish short-term changes (including the resulting long-term effects) in soil quality, it is essential to analyze the structure, function and/or activity of microbial communities present in the soil [37,118-121], which present a more rapid response to environmental changes [58]. An accurate picture of the early changes in soil quality can be obtained by evaluating microbial properties, preferably in combination with

chemical characteristics, since perturbations affecting the function of soil are reflected at an early stage.

A number of methods are currently available for monitoring changes in structure and function among microbial communities, including metabolic activity [122]. However, studies on soil microflora should greatly benefit from the application of new molecular tools [121,123] in combination with traditional methods, which should provide a representative picture of the community structure, including species not adapted to monoculturing and functional groups. It is important to consider that the dominant genotypes are primarily identified with general PCR-based molecular techniques, and in cases where the aim is to explore the total diversity of complex samples, such as soil, other approaches [124-126] are additionally necessary.

To date, relatively few studies have focused on molecular methods to monitor changes in soil quality induced as a result of biogas residue application [67]. Molecular tools facilitating the characterization of complex microbial communities should be further exploited in relation to land application of biogas residue.

6. Conclusions and future challenges

Overall, the potential of biogas residue as a crop fertilizer and soil conditioner appears predominantly positive. However, application of the residue to cropland requires rigorous monitoring to detect early perturbations in soil quality, which may result in reduced crop yield. Conflicting results are reported on the effects of biogas residue on soil chemical and/or microbiological properties, including increased [44,45,58,63,64] and decreased [69] microbial activity and biomass. However, the majority of published investigations confirm its significant value in improving crop yield [2,10,11,16,58,92,93] and grain quality [16]. Biogas residue, which commonly contains large amounts of mineralized N and low concentrations of heavy metals, presents a promising alternative to mineral fertilizers that require substantial energy input at production. However, careful analysis of organic pollutants, reported to exist at high concentrations in organic household waste, is essential.

In Sweden, biogas is commonly upgraded to vehicle fuel, since this is the most profitable method of gas production [127]. However, improved regulations and recommendations are warranted, both from an environmental perspective and in terms of turning costs related to fertilizer production into a profitable income. Ideally, farmers, the food industry, as well as scientific expertise should be involved in such communications, which would promote confidence and trust among the involved partners. Irrespective of its perceived importance by specific groups (for instance, scientists), biogas residue will not be used and recycled unless farmers accept the product. To convince doubtful farmers and the general public, the value of biogas residue as crop fertilizer and soil conditioner needs to be further confirmed, emphasizing the urgent need for more extensive studies in this field. This type of research will have wide-ranging implications in global energy and nutrient cycling, as well as world economics, including the finances of individual farmers.

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