Exhibit CC

Möller & Müller, *Effects of Anaerobic Digestion on Digestate Nutrient Availability and Crop Growth: A Review*, 12 Eng. Life Sci. 242 (2012)

Kurt Möller
Torsten Müller

Institute of Crop Science,
Fertilisation & Soil Matter
Dynamics, Universität
Hohenheim, Stuttgart, Germany

Review

Effects of anaerobic digestion on digestate nutrient availability and crop growth: A review

Anaerobic digestion (AD) for biogas production leads to several changes in the composition of the resulting digestates compared to the original feedstock (ammonia content, pH, carbon to nitrogen ratio, etc.), which are relevant for the plant availability of macro- and micronutrients after field application. Increased NH_4^+-N content in digested slurries compared to undigested slurries does not guarantee improved uptake efficiency of slurry nitrogen and increased savings in fertilizer nitrogen. AD of crop residues and cover crops leads to an increase in the total amounts of mobile organic manures within the farming system, resulting in a higher nitrogen use efficiency and an increased scope for target-oriented nitrogen application in time and space, when needed by the crop, as an alternative to the site-bound soil incorporation as green manures. AD of dairy manure appears to reduce the fraction of immediate plant available phosphorus and micronutrients. This does, however, not affect short-term crop availability under field conditions. More studies are needed to improve current knowledge on sulfur losses during AD and fertilizer value of digestates.

Keywords: Digestate treatment / Micronutrients / Nitrogen / Phosphorus / Sulfur

Received: September 15, 2011; *revised:* January 6, 2012; *accepted:* January 27, 2012

DOI: 10.1002/elsc.201100085

1 Introduction

Manures from stables, crop residues, wastes from food industry, municipal wastes, and dedicated energy crops are the main feedstocks for anaerobic digestion (AD) in biogas plants (Fig. 1). During AD about 20–95% of the feedstock organic matter (OM) is degraded, depending on feedstock composition. The residual product of AD, called digestate (= biogas effluents = biogas residues, or biogas slurry, when animal manures are digested), is usually used as fertilizer. For Germany, it was estimated that in the year 2011, approximately 20% of the animal wastes and the biomass harvested from an area of approximately 1.1 million ha are used as feedstock in biogas plants [1]. No data were found about the annual total amounts of available digestates in Germany. Own calculations indicate that the German biogas plants currently produce a total amount of approximately 65.5 million cubic meters of digestates, containing a total amount of 390,153 Mg nitrogen (N), 74,075 Mg phosphorus (P), and 331,472 Mg potassium (K) (Table 1). Digestates are either directly spread as manures, or treated (solid–liquid separation, drying, dilution, filtration, etc.) before field application (Fig. 1).

This paper addresses the effects of AD on digestate composition and their fertilizing effects, as well as the available digestate treatment procedures. It will give an overview of the state of the art and further research needs. Not included is potassium, as it does not become part of structural components in the plant. Therefore, most of the K^+ in plants remains dissolved in the cell sap and is therefore also found in dissolved form in manures and digestates.

2 Effects of anaerobic digestion on manure composition

Early studies about the effect of AD on manure characteristics compared the composition of digestates and solid farmyard manures. They found similar differences as commonly described when comparing liquid slurry with solid farmyard manure [2–7]. Recently, characterizations have been made mainly for liquid undigested and digested animal slurries as well as for digestates derived from dedicated energy crops; available data indicate a wide range of nutrient contents (Table 2).

Digestates have higher ammonium (NH_4^+):total nitrogen (N) ratios, decreased OM contents, decreased total and organic carbon (C) contents, reduced biological oxygen (O_2) demands (factor 5–13), elevated pH values, smaller carbon to nitrogen ratios (C:N ratios), and reduced viscosities than undigested animal manures [8–17]. The digestate NH_4^+-N content is directly

---

Correspondence: Dr. Kurt Möller (kurt.moeller@alumni.tum.de), Institute of Crop Science, Universität Hohenheim, Fruhwirthstr. 20, 70593 Stuttgart, Germany.

Abbreviations: AD, anaerobic digestion; **DM**, dry matter; **FM**, fresh matter; **OM**, organic matter

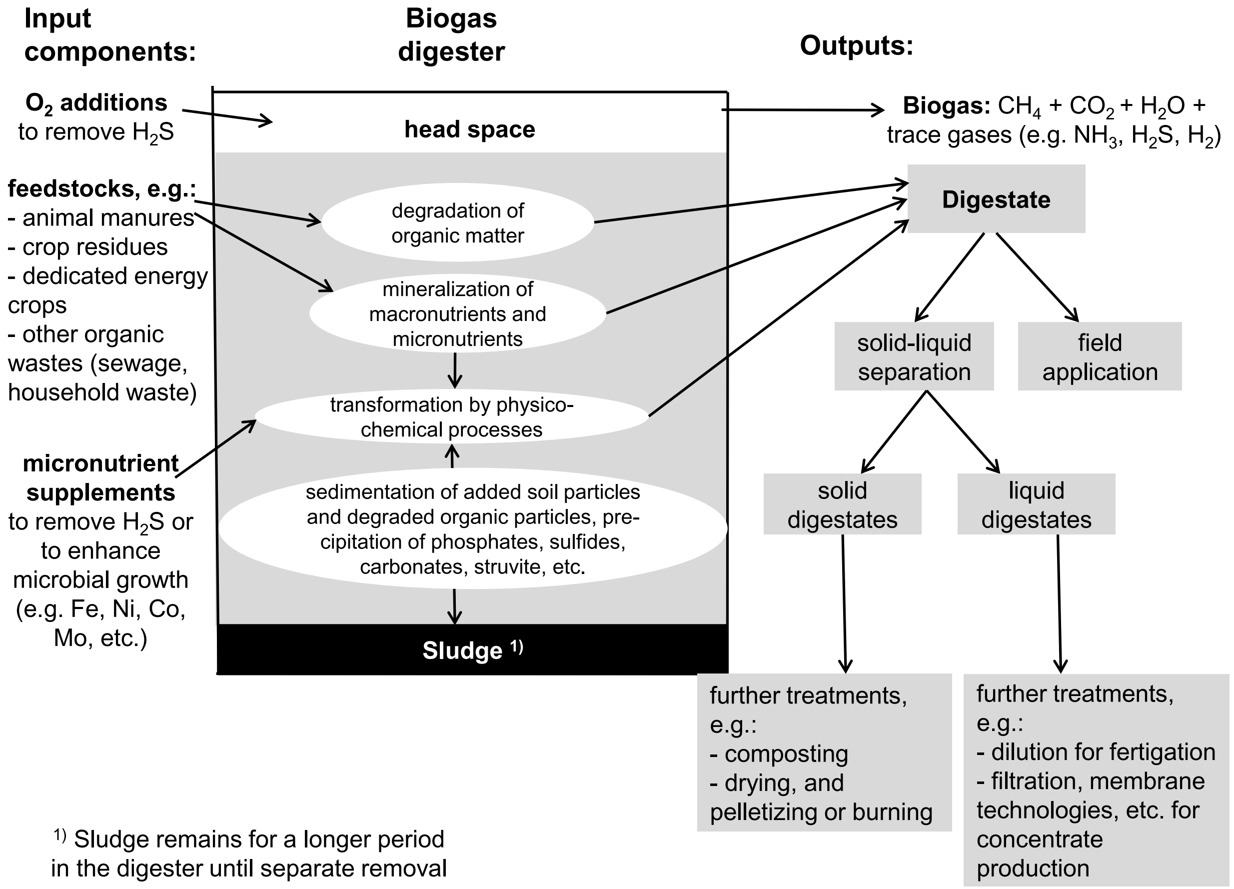

Figure 1. Overview of the matter flows and processes during anaerobic digestion and possible treatments of the resulting digestates.

related to the original feedstock total N content [18]. Digestates from feedstocks with a high degradability (e.g. cereal grains, poultry and pig manures with a diet high in concentrates) are characterized by high NH_4^+-N:total N ratios and narrow C:N ratios [8, 10, 14, 19, 20]. Cattle manures or fibrous feedstocks low in N (e.g. silage maize) lead to a low NH_4^+-N:total N ratio [8, 14, 21].

The digestate pH value is mainly controlled by the species $NH_4^+ \leftrightarrow NH_3$, $CO_2 \leftrightarrow HCO_3^- \leftrightarrow CO_3^{2-}$, and $CH_3COOH \leftrightarrow CH_3\ COO^-$ [22, 23]. A pH increase is usually due to formation of ammonium carbonate ($(NH_4)_2CO_3$) [18, 24] and the removal of CO_2 [25] as a result of the transformation of CO_3^{2-} and $2H^+$ to CO_2 and H_2O (Figs. 2 and 3). Furthermore, the fatty acid contents of feedstocks were reduced by AD (factor 2.5–13) [16, 26]. Digestate pH is also affected by the concentration of basic cations (e.g. Ca^{2+}, K^+); they increase digestate pH because the electric charge balance of the solution has to be neutral, thus, decreasing the concentration of H^+ [23]. Simultaneously, precipitation of carbonates (e.g. calcite $CaCO_3$) reduces manure pH [23]. Mineralization and reduction of multivalent ions in feedstocks (e.g. SO_4^{-2}, $Fe^{III}(OH)_3$) increase pH, as well as the addition of Fe^{III}-ions to remove hydrogen sulfide (H_2S). Precipitation of Fe^{2+}-phosphates releases protons decreasing the pH [23]. Also, the reaction between Mg^{2+}-, NH_4^+- and PO_4^{3-}-ions (to form struvite) causes the release of H^+ ions in solution (Fig. 2) [27].

Analyses of particle size distributions in raw and digested slurries showed a general shift in distribution toward larger sizes. Larger particles (i.e. $>10\ \mu m$) are more resistant to degradation [28].

It has been stated that digestates contain bioactive substances, such as phytohormones (e.g. gibberellins, indoleacetic acid), nucleic acids, monosaccharides, free amino acids, vitamins and fulvic acid, etc., with the potential to promote plant growth and to increase the tolerance to biotic and abiotic stress [29, 30]. Digestates have higher contents of indoleacetic acid than the original plant feedstock [31]. This increase could only be explained by a microbial synthesis during the digestion process.

Contradictory results have been found concerning phytotoxicity of digestates. Some authors reported that digestate application has no phytotoxic effects [32, 33], others have found phytotoxic reactions [34–36]. Phytotoxicity is related to NH_4^+-N [36, 37] and organic acid concentrations [34, 36, 37]. No data were found on the duration of possible phytotoxic effects of digestates. It is expected that the possible negative effect of any kind of digestate phytotoxicity will decrease within a short period of time after field application.

Table 1. Assessment of the annual total amounts of digestates currently produced by biogas plants in Germany, and the related amounts of nutrients

Feedstocks		Total nutrient amounts (Mg)[a]			Amounts[c] (1000 m^3)
		N	P	K	
Dedicated energy crops	Assumed area (ha)[d]				Digestate FM[b]
Silage maize	629 063	131 474	24 219	128 014	26 295
Cereals	163 090	16 146	3 425	4 893	245
Whole plant silage (cereal)	58 247	8 155	1 456	5 679	1 092
Other (potatoes, sugar beets, etc.)	58 247	7 405	1 631	11 727	1 797
Grassland	191 354	59 320	9 185	52 431	4 736
Sum	**1 100 000**	**222 499**	**39 916**	**202 744**	**34 165**
Animal excrements	Assumed amounts (1000 Mg FM)				
Cattle slurry	18 641	80 158	12 303	77 361	18 641
Pig slurry	4 924	22 651	4 530	9 011	4 826
Mixed slurries	5 116	22 766	4 042	15 297	5 065
Solid farmyard manures	1 727	12 259	3 246	9 894	1 606
Poultry manures	1 533	26 820	10 038	17 165	1 165
Sum		**164 654**	**34 159**	**128 728**	**31 302**
Total		387 153	74 075	331 472	65 467

[a] Calculations based on nutrient contents and mean yields provided by [136].
[b] FM = Fresh matter.
[c] Calculations based on assumed feedstock availability and "volume reduction factors" provided by Heidenreich (cited by [21]).
[d] Data based on the assumption that feedstocks are produced on an area of 1,1 Mio ha, including 5% of the total German grassland area; arable land feedstock composition: 69% silage maize, 18% cereal grains, 6.5% whole plant silage, and 6.5% others [1].

Table 2. Digestate characteristics

	Absolute values	Change[a]	References
DM (%)	1.5–13.2	−1.5 to −5.5	[21, 137–141]
Organic DM (% DM)	63.8–75.0	−5 to −15	[12, 137, 141]
Total N (% DM)	3.1–14.0%	[b]	[8, 12, 14, 137, 141]
Total N (kg Mg^{-1} FM)	1.20–9.10	≈ 0	[8, 10, 14, 138, 139,142]
Total NH_4^+ (kg Mg^{-1} FM)	1.5–6.8	?	[139]
NH_4^+ share on total N (%)	44–81%	+10 to +33	[8, 12, 14, 16, 140]
Total C content (% DM)	36.0–45.0	–2 to –3	[12]
C:N ratio	3.0–8.5	–3 to –5	[12, 14, 142]
Total P content (% DM)	0.6–1.7	[b]	[10, 21, 137, 141]
Total P (kg Mg^{-1} FM)	0.4–2.6	≈ 0	[21, 138, 139, 142]
Water soluble P (% of total P)	25–45	–20 to –47	[65, 143]
Total K (% DM)	1.9–4.3	[b]	[10, 21, 137, 141]
Total K (kg Mg^{-1} FM)	1.2–11.5	≈ 0	[21, 138, 139]
Total Mg (kg Mg^{-1} FM)	0.3–0.7	≈ 0	[137, 141, 142]
Total Ca (kg Mg^{-1} FM)	1.0–2.3	≈ 0	[10, 141, 142]
Total S (kg Mg^{-1} FM)	0.2–0.4	?	[142]
pH	7.3–9.0	+0.5 to +2 units	[8, 10, 12, 14, 18, 26, 112, 142, 144]

[a] In comparison to undigested liquid animal manures, absolute values.
[b] Increases with degree of DM degradation.
DM = Dry matter.
FM = Fresh matter.
? = No data found/no data available.

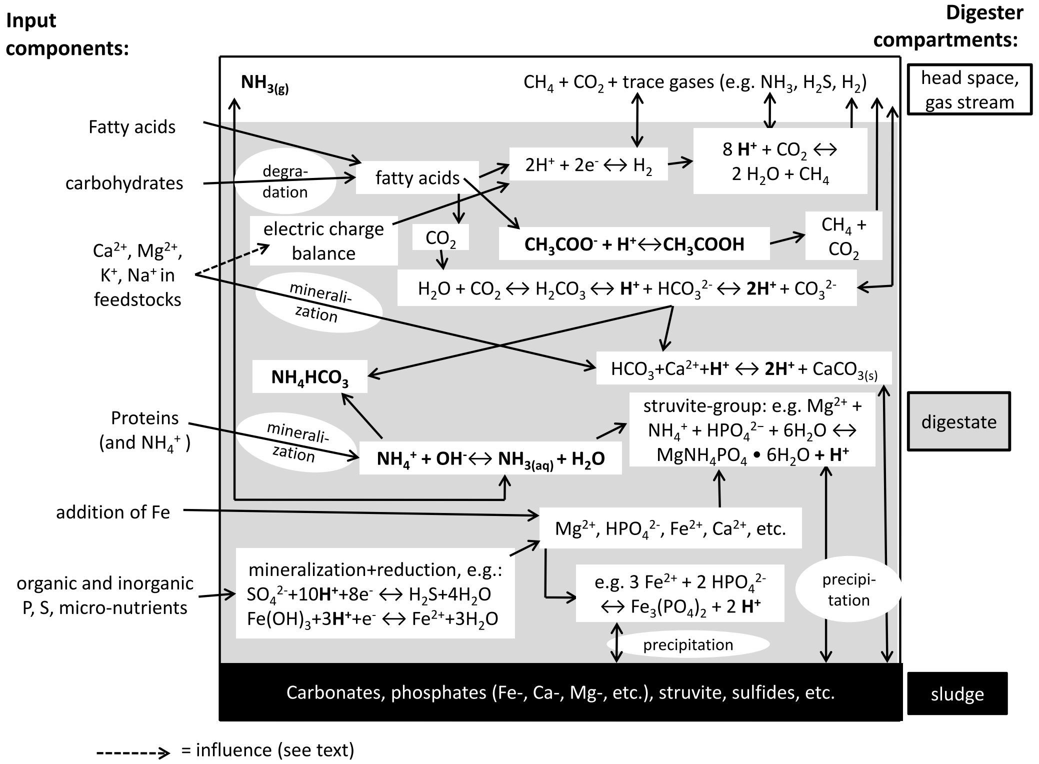

Figure 2. Factors affecting pH-value of digestates.

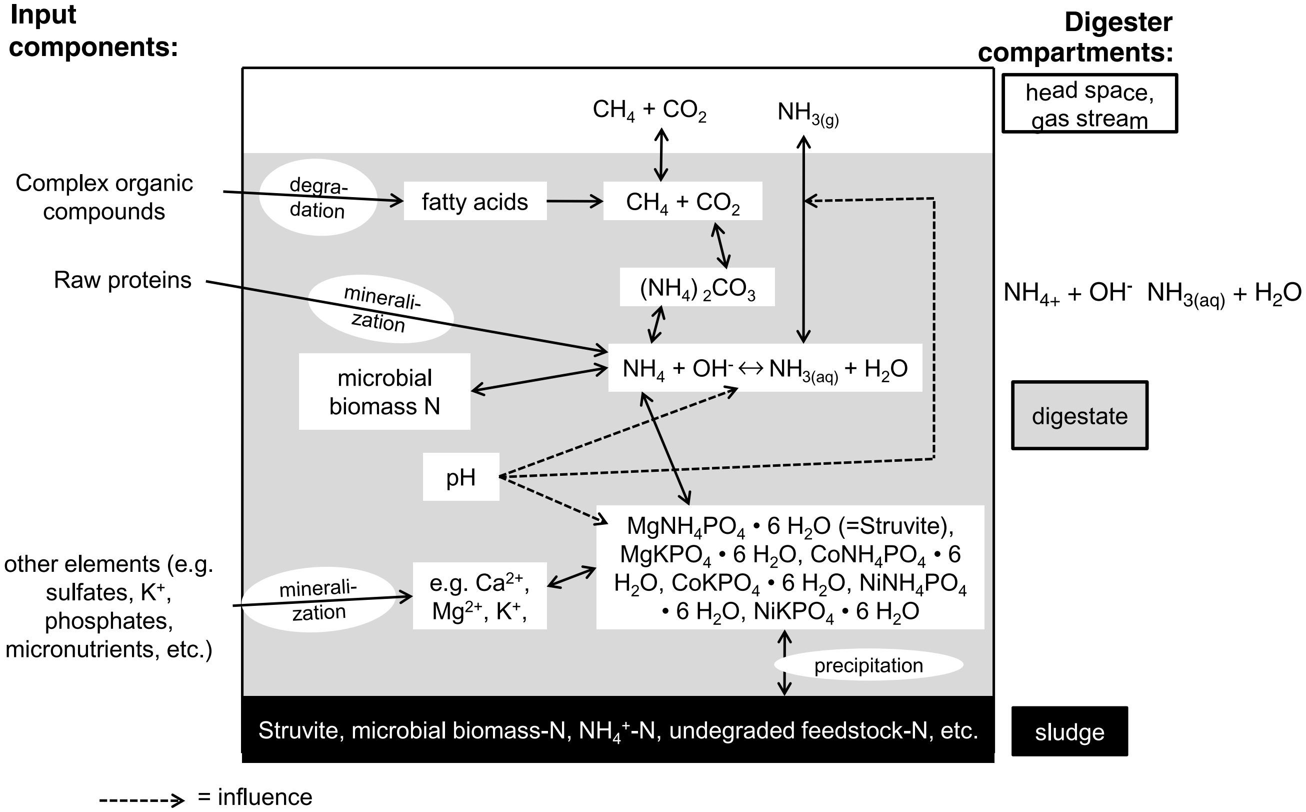

Figure 3. Nitrogen turnover in biogas digesters.

3 Effects of anaerobic digestion on nutrient availability after digestate application

3.1 Nitrogen

Complex organic N compounds are mineralized to NH_4^+-N in the digester. A part of the NH_4^+-N is used by the digester microorganism for growth. Further processes are formation of struvite and ammonium carbonate, traces are volatilized in the biogas stream ($<1\%$) (Fig. 3). The essential major element N is found in the plant in both inorganic and organic forms. A range of processes is triggered by field application of digestates. Priming effects [38], as well as an inorganic N immobilization [39–41], have been detected. A significant, negative correlation between net N-mineralization and mineralized-C has been reported [41]. Remaining organic compounds induce soil biological activity, partially immobilizing inorganic N [39,41]. However, the fundamental environmental changes (anoxic conditions in the digestate stores, oxic or semioxic conditions in the soil) may also induce decomposition of compounds, which need oxic conditions for decomposition, as present in the soil after field application [42]. The biochemical O_2 demand, the dissolved organic C, and the corresponding organic C:total N ratio of dissolved substances can be considered the most reliable indicators in describing digestate biodegradability [41].

For the year of application of organic manures, it is generally assumed that the fraction of plant available N is closely associated to the manures' NH_4^+-N contents [14,43–45]. Comparisons of digestate applications with mineral N fertilizers based on equivalent amounts of total N have been shown lower fertilizer N-values than the mineral N fertilizers [46]. However, if the application was only based on equivalent amounts of the NH_4^+-N fraction in the digestate, comparable apparent NH_4^+-N recoveries of digestates and mineral fertilizers were reported [14,20,47]. Simultaneously, with digestate field application soil organic nitrogen (N_{org})-accumulation takes place, enhancing soil N_{org}-mineralization even after a single digestate application [14]. The net N_{org}-mineralization within a six-month experimental period was 12% [47]. Though, it might be difficult to transfer these results to other kinds of digestates, as the C:N ratio of digestates varies widely in range, and the total carbon to organic N ratio (C_{org}:N_{org} ratio) is a crucial factor for the short-term N availability [12, 14]. Even organic manures with a similar C:N ratio may mineralize different amounts of N, due to differences in their chemical composition [48].

Comparisons between digested and undigested slurry in pot experiments, with equivalent amounts of applied NH_4^+-N, indicate a higher apparent N recovery for digested than for undigested slurry [20]. Field experiments with the application of equivalent amounts of total N indicate that the uptake of N from liquid digested animal slurry equaled that of undigested slurry after surface application, despite the higher NH_4^+-N content of the digestate [12,49]. A significant effect of AD on crop yields and N uptake could only be found in experiments where the manures are incorporated into the soil shortly after field application [12], indicating that substantial parts of N might have been volatilized as NH_3 [11, 50]. This is supported by pot experiments based on application of equivalent amounts of total N, where the N uptake from digestates from animal slurry exceeded that from undigested slurry by about 10% to 25% [8,16,51,52].

3.2 Phosphorus

As a constituent of adenylates, nucleic acids and phospholipids, phosphorus is an important plant macronutrient. The natural supply of P in most soils is small and the availability of P in the soil solution is usually very low. It is often stated that degradation processes during AD will improve phosphorus (P) plant availability [53–55]. However, most available results from field experiments indicated no effects of AD on manure P availability [56–58]. AD has potentially the opposite influence on crop P availability, as often stated. Manure pH strongly influences the solubility of P and micronutrients. Raising the pH moves the chemical equilibrium toward the formation of phosphate ($HPO_4^{2-} \rightarrow PO_4^{3-}$) and subsequent precipitation as calcium (Ca)- or magnesium (Mg)-phosphate (e.g. $Ca_3(PO_4)_2$) [23,59–61] (Fig. 4). Simultaneously, the binding form of other elements such as iron (Fe) may also be influenced by AD, affecting P turnover and precipitation processes during AD [62–64]. The fraction of dissolved P, mineralized during AD, associates with suspended solids [65]. The water-extractable P-fraction and ratios of extractable nutrient:total-nutrient for Ca and Mg decreased substantially during AD (Table 2) [65]. Mineralization of N, P, and Mg combined with a substantial increase of the manure pH can enhance the formation and crystallization of struvite [23,27,66]. This process can be used to remove N and P from manures to reduce the P and N loadings [64,66]. Many ionic species (e.g. Ca^{2+}, K^+, CO_2^{-3}) can influence struvite formation by reacting with its component ions [27]. Therefore, digestates contain only trace amounts of Ca^{2+}, Mg^{2+}, and inorganic P in solution [22,23].

Concerning the effects of AD on P losses, while passing through the biogas plant, small amounts of P ($<10\%$) are lost [65,67,68]. Few papers indicate much higher P losses up to 25% [69] or even 36% [28]. The probable causes are partial retention in the digesters due to the precipitation processes [28,65,67,69], (Fig. 4). No studies about the effects of AD on P losses via leaching and runoff after field application were found. The loss of P in surface runoff occurs as sediment-bound and in dissolved forms [70].

3.3 Sulfur

Sulfur (S) is a major essential nutrient, and S deficiency becomes problematic in a growing number of regions [71]. Redox level is an important factor when determining S reactions in a system [73]. Therefore, degradation of OM forms sulfate, which, in the absence of O_2, reacts with protons to H_2S and other molecules [72–74] increasing the digester pH and leading to a strong decrease of sulfate concentration and increase of sulfide and C-bonded S concentrations, metal-sulfide precipitation, and sulfur volatilization (Fig. 5). The formation of H_2S, methanethiol (CH_3-SH), dimethyl-sulfide ($(CH_3)_2S$), and dimethyl disulfide (CH_3SSCH_3) in slurry is redox dependent, while carbonyl sulfide (COS) and carbon disulfide (CS_2) are relatively constant and in low amounts at all redox levels. Most of the S emanating from

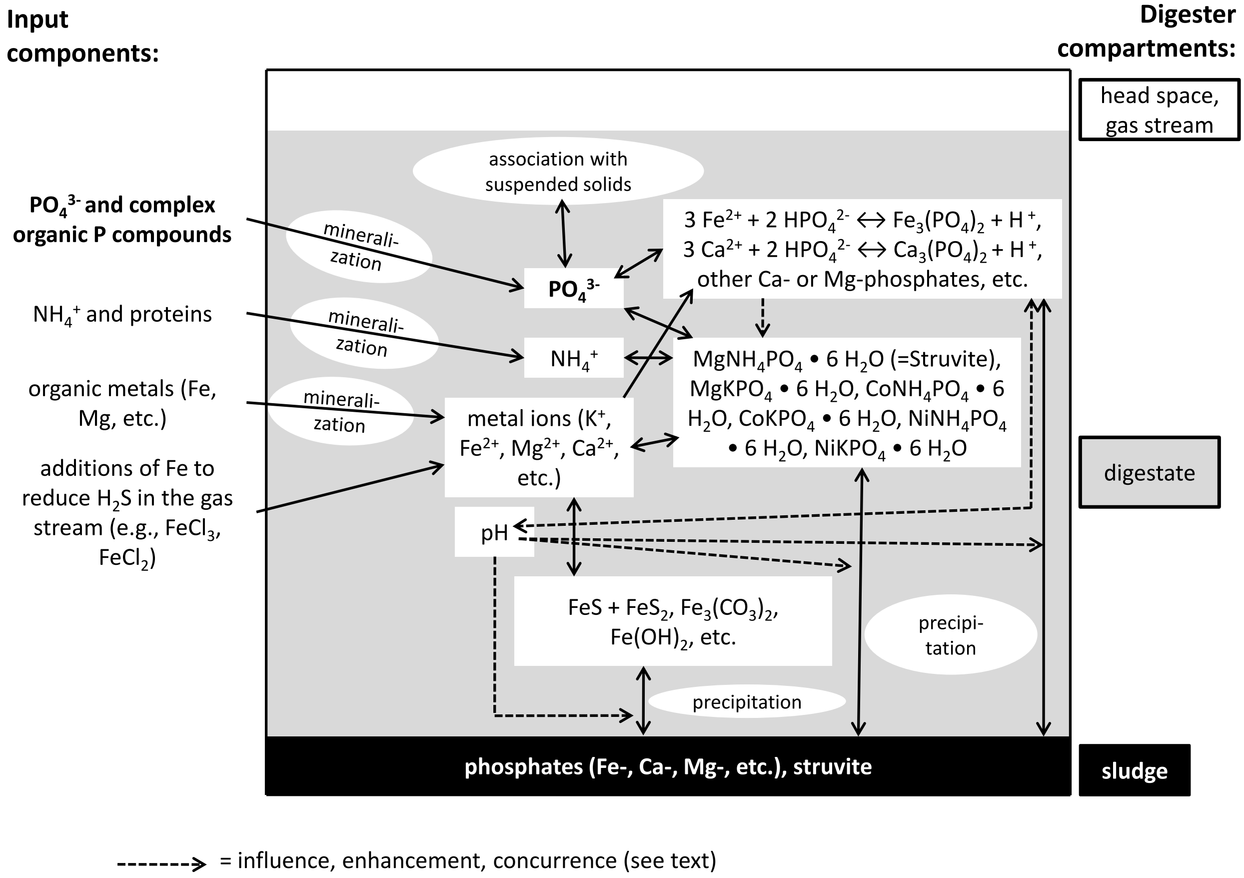

Figure 4. Phosphorus turnover in biogas digesters.

the slurry is produced under anaerobic conditions between 0 and -200 mV [74]. H_2S contents are proportional to feedstock S contents [72, 73]. Protein-rich feedstocks may increase H_2S content in biogas [72, 75], as S is introduced mainly as a constituent of amino acids.

No data were found addressing the digestate plant S availability. Sulfate ($SO_4{}^{2-}$) is the plant available sulfur form [71, 76]. Sulfide is expected to be readily oxidized to sulfate under oxic conditions [75]. Lloyd [77] found an effectiveness of S as plant nutrient in cattle slurry of 55% compared with S in gypsum. However, there are also reports of very low plant availabilities of slurry S [75]. Possible causes are S-volatilization (e.g. H_2S, CS_2, COS, CH_3SSCH_3, etc.), soil S-immobilization as metallic sulfides (e.g. FeS_2, FeS), or sorption to soil constituents [75,78]. In most cases, more than 50% of S is potentially volatile sulfide or C-bonded S [75]. Although no data were found about S volatilization after field application of digestates, a high volatilization risk during manure storage and after manure spreading can be expected due to the high proportion of potentially volatile S compounds in digestates.

There are only few data available regarding S losses in biogas plants. Some reports indicate that a part of the S is retained or lost during AD [28,69]. Less than 50% of S leaves the biodigester via digestates [69]. A part of the introduced S may potentially leave the digester with the gaseous products (Fig. 5) [79]. The lower the pH and temperature, the higher the H_2S concentration in solution. Several methods are used to partially remove H_2S from the biogas stream. A common technique is to convert the S^{2-} in H_2S to S^0 after biooxidation [72]. Iron-salts also remove H_2S from the gaseous products.

More research is needed to assess the S turnover processes in the digester depending on the inputs into the biogas plant. For example, there is no research available on the influence of different technologies for H_2S removal from the biogas stream on S losses and S speciation in digestates. Research addressing the influence of S- and Fe-loads via feedstocks (or via addition of supplements) on nutrient speciation and precipitation in the sludge is also needed. Current knowledge about the S fertilizer value of digestates is very scarce.

3.4 Ca, Mg, and micronutrients

Many studies dealt with the effect of AD on micronutrient distribution and bioavailability in sewage sludge, but rarely any with digestates. Because of the complexity of the processes in the matrix, micronutrients may be involved in many physico–chemical processes including:

(i) precipitation as sulfide (except Cr), carbonate, phosphates, and hydroxides,
(ii) sorption to the solid fraction, either biomass or inert suspended matter, and

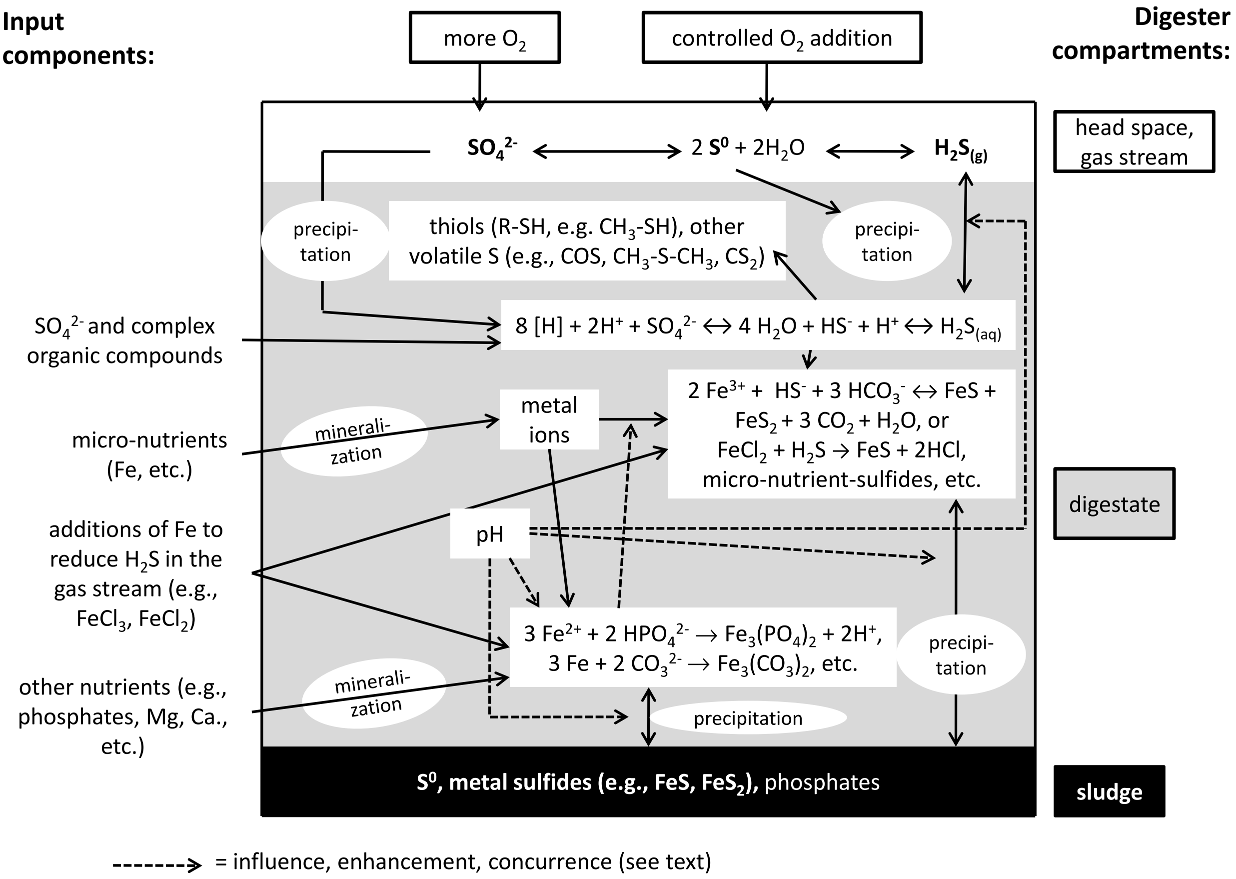

Figure 5. Sulfur turnover in biogas digesters.

(iii) formation of complexes in solution with intermediates and product compounds produced during AD [62, 80, 81].

There are only few studies available addressing aspects of Ca, Mg, and micronutrient turnover in digester. For example, on average, 8.7% of Ca, 21.0% of Mn, 18.4% of Zn, and 41.5% of Cu was retained in bioreactors [69]. However, the authors did not find a statistically significant K, Fe, Mg, and sodium retention in the digesters. Significant losses have also been observed for Ca, Mg, and manganese with 44%, 32.5%, and 32% of the respective elements, respectively [28]. They partially crystallize out as phosphates and carbonates.

The total metal concentration, the conditions during digestion such as pH and redox potential, and the kinetics of reduction, precipitation, complexation, and adsorption are expected to play a key role influencing the chemical speciation of micronutrients in liquid manures [62, 80, 82]. The increasing pH decreases solubility of metals in the matrix [59, 83]. The precipitation of metals by sulfide (S^{2-}), carbonate (CO_3^{2-}), and phosphate (PO_4^{3-}), and their deposition in the bioreactor sludge plays an important role in the nutrient turnover of macro- and micronutrients [28, 62, 84, 85]. There is also probably a strong interaction of added Fe and the micronutrients in the matrix: micronutrients may react with the Fe-sulfide releasing Fe^{2+} [81, 86] (Fig. 5). The resulting Fe^{2+} may form precipitates as hydroxides ($Fe(OH)_2$) or carbonates ($FeCO_3$) [80]. Consequently, bioreactors have a considerable ability to sequester Fe^{2+}-ions in the sludge [87]. Simultaneously, nonalkali metals (e.g. Ca^{2+}, Mg^{2+}) form soluble ion pairs with a number of anions: HCO_3^-, CO_3^{2-}, OH^-, SO_4^{2-}, S^{2-}, Se^{2-} [62]. A possible advantage of the precipitation processes is that the heavy metal loads in digestates can be reduced.

Complexation reactions play an important role in bioreactors making a particular metal either more or less bioavailable [62]. The level of soluble metals in the presence of CO_3^{2-} and S^{2-} may be increased by a factor of up to 10^4 by complexation [83], avoiding precipitation as carbonates or sulfides. Several authors describe a shift of micronutrients away from mobile forms toward more stable and less reactive and bioavailable forms during AD [84, 88–90]. However, in a growth chamber experiment, it has been found that AD does not reduce the plant bioavailability of micronutrients [90]. The relevant processes driving the underlying effects are not well understood. Furthermore, no data were found concerning the effects of a long-term digestate field application on the heavy metal accumulation in the soil and their bioavailability to plants.

No data are available on the nutrient and micronutrient loads of the sludge of biogas reactors. It is probable that the nutrient loads are very high in the reactor sludge, demanding an accurate management of the sludge after removal from the bioreactor, in order to avoid high application of nutrients or pollutants on a small area.

4 Effects of feedstocks on the digestates' fertilizer values

To address the effects of different feedstocks on the digestates' quality and on crop growth after digestate application, three approaches should be discussed separately:

(i) The digestion of animal manures alone, AD is commonly an additional intermediate step in the whole nutrient cycle. The effects on the overall inner farm nutrient flows are limited [91].

(ii) The digestion of green manure crops and crop residues in combination with animal manures does not alter the total amounts of available organic manures, however it modifies the manure flows within the farming system, influencing their allocation in time and space [91].

(iii) The digestion of dedicated energy crops alone or in combination with animal manures leads to additional amounts of organic manures [91, 92].

Concerning (i), contradictory effects on crop yields have been found between undigested and digested cattle slurry after surface application under field conditions: some authors report no effects on crop yield [10, 12, 56], others report a positive effect of AD on crop yields [93]. On grassland, it seems that AD of slurry positively affects yields, but only in some years [12, 94, 95]. In pot experiments, however, a significant positive effect of AD of slurries on the manuring effect and crop yields have been congruently found [8, 16, 39, 51, 52, 96]. The contradictions of the results obtained with pot experiments versus field conditions with surface amended digestates were likely based on methodological reasons. In pot experiments, digestates were usually mixed immediately with soil, reducing N losses [12]. Probable causes of the reported inhomogeneous results depending on manured crop and application technique are:

(a) Higher ammonia losses after spreading digested slurry, because manure AD increases NH_4^+ concentration as well as pH value and both factors promote gaseous N losses [10, 12, 50, 97].

(b) Vegetation periods in pot experiments are often short and soil volume is often limited, reducing the fertilization effects to immediately available nutrients, for nitrogen mainly NH_4^+, promoting digestates with a higher share of NH_4^+ on total N. In field experiments with a longer vegetation period and a larger rooting area N_{org} of undigested manures may, however, have enough time to become partially mineralized and available to crops [12, 52, 98].

Regarding AD of green manure crops and crop residues (ii) increased soil N availability, crop yield and N use efficiency in comparison to direct soil incorporation of feedstocks have been found [12, 91, 99, 100]. Short-term availability of plant N is increased when digestates are returned to soil, compared with direct soil incorporation as green manure or crop residues after harvest. Another factor that must be considered when green manure and crop residues are used for AD is the spatial nutrient translocations within the farming system. A yield increase of between 15% and 28% have been found for organic cropping systems, where fertilization is based on AD of crop residues and green manure crops and reallocation via digestates [99, 100]. Instead of a site-bound manure incorporated directly by soil tillage, AD, thus, enables the farmer to remove the plant biomass, including their nutrients for digestion, leading to a "mobile" manure. The "degree of freedom" of fertilization organic manures is increased, as they can be applied to crops with higher N demand at an optimal application time. In conventional cropping systems, such mass and nutrient reallocations within the cropping system will result in an equivalent reduction of mineral fertilizer requirements. In organic cropping systems, the reallocation opens for a more target-oriented application of fertilizers, thus, reducing potential losses by an improved synchronization of crop nutrient demand and nutrient availability.

AD of dedicated energy crops (iii, e.g. silage maize) generally results in additional amounts of available organic manures within the farming system, as animal stocking is often only slightly influenced by the implementation of biogas plants [92]. Very often, additional feedstocks are purchased from surrounding farms. In principle, these factors lead to similar consequences and risks as reported for increased animal stocks, e.g. higher nutrient surpluses, increased manure application in autumn in order to clear the stores, lower N use efficiency, etc. [91, 92]. Thus, challenges in manure handling and allocation are increasing so that high nutrient use efficiencies and low emissions can be obtained.

5 Digestates as fertilizers for vegetable crops

Few publications address the use of digestates as fertilizers for vegetables demonstrating that digestates are an effective nutrient source [29, 101, 102]. Digestates may be most beneficial in organic vegetable cultivation, where quick release fertilizers are lacking [101, 102]. Incubation studies carried out under different soil temperatures (8 and 16°C) demonstrate that the short-term N-release of digestate N is similar (e.g. blood meal, vinasse, etc.) or even higher (e.g. castor cake, poultry solid manure, feather meal, meat and bone meal, etc.) than the N-release of many commercial organic fertilizers often used as manures in organic vegetable crops, especially under low soil temperatures [102]. This indicates the high suitability of digestates as a fertilizer even in the cool season (e.g. early spring), especially for high N demanding vegetables with a short growing period.

Under soilless conditions, digestates from animal slurries are an effective nutrient source in vegetable production. Undiluted digestates with high electrical conductivity are not suitable [29]. The key problems obstructing their application in soilless culture are the variability of components and the imbalance in the elemental composition [103]. Appropriate dilutions are 1:4 to 1:8 (digestate:water) [29].

Also hydroponic production of lettuce using digestates or the liquid fraction after a solid–liquid separation in adequate dilution was comparable to a commercial hydroponic fertilizer regime [104, 105]. In tomatoes, a conversion of NH_4^+-N to nitrate and a supplementation with Mg were required before digestate application in hydroponic culture [105, 106]. This was necessary because of the high sensitivity of tomatoes to high NH_4^+-N levels, and the low content and availability of Mg in digestates [105], due to struvite formation and precipitation during AD. Other studies have reported that supplementation by addition of P and micronutrients (particularly Fe) increases the shoot biomass of lettuce [103]. Such a supplementation balances the relative P deficiency compared to N and improves Fe availability [103].

Most investigations have shown that the vegetable nitrate content decreased significantly, when applying digestates as an alternative to mineral fertilizers under soilless [29] and sand culture [107], as well as in pot experiments [108]. The reduction in nitrate content has been related to differences in N composition. In contrast to nutrient solutions supplying nitrate, biogas digestates supply NH_4^+-N and as organic components mainly amino- and amide-N [29, 107]. In one study, no effects were found under field conditions [101]. It seems that described effects are most relevant when vegetables are fertilized with nutrients solution.

Results on the effect of application of digestates derived from animal wastes on vitamin C content of vegetables are inconsistent [103, 108]. The use of concentrated digestates (fertilizer obtained after solid–liquid separation, filtration, etc., see Fig. 1) from animal manures had significant effects on tomato fruits, including decreases in water content, and increases in electrical conductivity, contents of total N, total P, amino acids, proteins, soluble sugars, β-carotene, tannins, and vitamin C [30].

6 Agronomical relevant effects of digestate treatment

Manure treatment technologies include physical (e.g. solid–liquid separation), chemical (e.g. flocculation, precipitation), and biological (e.g. composting) approaches. Commonly, the first step of each digestate treatment procedure is the physical solid–liquid separation (Fig. 1), e.g. with a screw-press separator. Mostly, the resulting solid manure high in dry matter (DM) and the liquid manure low in DM is directly applied as fertilizer [1]. Further treatments, for example drying of solid digestates or water removal from the liquids by membrane technologies to produce concentrates are not widespread.

6.1 Solid–liquid separation

Separation of digestates creates two products, a liquid and a fibrous material, both need to be stored and handled separately (Fig. 1). Separation is performed in approximately 7% of the German biogas plants [1] and facilitates controlling the nutrient content of manure fractions and the NH_3 losses from the liquid fractions [109]. The solid phase often comprises approximately 20–25% of the total digestate fresh matter derived from dedicated energy crops (with a high silage maize and grass share) and has DM contents similar to solid farmyard manure (Table 3). The higher the DM content of the inflow to the separator, the lower the proportion of the liquid phase [110, 111]. The composition of separated solid digestates can vary greatly (Table 3). The relatively high mineral N content of solids indicates a high potential for N losses during manure handling and application [112–115], in particular ammonia volatilization, leaching and gaseous loses by denitrification after nitrification of the NH_4^+ to NO_3^- during (partially) aerobic storage and handling [21 and references therein]. Most of the total P is allocated to the solid phase. The liquid phase is characterized by low DM and P contents and high N and K contents [14, 21]. Therefore, N and K of digestates are partitioned according to the proportion of solid and liquid phases [12, 21, 105, 111]. A total of 45–80% of the N in the liquid phase is present as NH_4^+-N.

No data were found about the influence of a single feedstock on the separation index (ratio of solid to liquid fractions) and on the nutrient content of both components. Furthermore, no data are available addressing the N-turnover processes (e.g. N-immobilization and -(re)mineralization) after application of separated liquid or solid digestates, and how these processes are influenced by the digestate composition, as previously done for example for separated animal slurries [116]. Field application of digested and separated liquids resulted in similar yields and N uptake in comparison to plots treated with commercially available N fertilizers [14, 105, 117, 118]. Available data indicate that a considerable share of N_{org} fractions, in separated liquid digestates, is rapidly mineralized in soil [14]. Application of the solids results in significant lower yields compared to the liquids and to reference plots with mineral fertilizer [14, 105, 117]. Incubation experiments indicated a net N immobilization after application of separated solid digestates [14, 119]. Other studies indicate that considerable N losses during storage reduced the plant available N [114].

In summary, the solid phase may be characterized as an organic fertilizer comparable with solid animal manure, but, with highly available N and P contents having a high potential for gaseous N losses, best suited to application on arable land in order to increase soil humus reproduction and to substitute P losses via harvested P-rich biomass such as grains. Separated liquid digestates are characterizes as N–K fertilizers comparable to mineral N–K fertilizers or animal urine. A digestate solid–liquid separation, with a target-oriented separate application of the liquid and solid phase, is, therefore, a technique for further improvement of the nutrient use efficiency after field application due to the following effects:

(i) Production of a liquid fraction, which is easy to handle and therefore allows the implementation of more sophisticated field application techniques, such as liquid manure injection with a reduced risk of blockages of tubes [59].
(ii) Implementation of application strategies that increase the agronomic value of manure by matching the crop nutrient requirements more closely, both in amount and in time [21, 69].
(iii) Production of liquids with distinctly reduced levels of P and heavy metals [59, 120].
(iv) Improved plant uptake of digestate-derived N in the liquid phase due to a high NH_4^+:total N share, lower organic carbon contents and therefore lower N immobilization after

Table 3. Digestate characteristics after solid–liquid separation

	Liquid fraction of digestates	Solid fraction of digestates	References
DM (%)	4.5–6.6	19.3–24.7	[21, 111, 139, 140, 111]
Organic DM (% DM)		40–86	[145]
Total N (% DM)	7.7–9.2	2.2–3.0	[21, 140]
Total N (kg Mg^{-1} FM)	4.0–5.1	4.6–6.5	[21, 111, 139, 140]
Total NH_4^+ (kg Mg^{-1} FM)	1.8–3.0	2.6–2.7	[21, 139, 140]
NH_4^+ share on total N (%)	40–80	26.0–49.4	[12, 14, 21, 105, 139, 140]
Total C (% DM)	48.0	39.6–40.0	[12, 111, 145]
C:N ratio	3.7–4.8	11.2–19.3	[12, 21]
Total P (% DM)	0.4–0.7	1.9	[12, 21]
Total P (kg Mg^{-1} FM)	0.7–1.0	2.0–2.5	[21, 111, 139]
Total K (% DM)	3.9	3.6	[12, 21]
Total K (kg Mg^{-1} FM)	3.5–5.2	3.4–4.8	[12, 21, 111, 139]
Total Mg (% DM)	?	0.2–0.4	[12]
pH	7.9	8.5	[140]

DM = Dry matter; FM = Fresh matter.
? = No data found/no data available.

field spreading, faster soil infiltration, and higher short-term N-manuring effects resulting in a better control of the applied N [121, 122].

(v) Reduction of the required storage volume for liquid phase [21].

(vi) Creation of separated solid manure rich in OM and nutrients (mainly P) with higher maximum economically feasible transport distances of the manure [21].

(vii) Lower requirement for stirring of the liquid prior to spreading.

6.2 Drying or composting of separated solid digestates

To improve the economically feasible transport distance, it was proposed to dry the digestates [123]. This is done in approximately 1% of the German agricultural biogas plants [1]. Drying of digestates is related to significant N losses as NH_3 [123, 124]. Long-term aerobic incubation experiments with thermally dried pig slurry demonstrated that such manures enhanced N availability only to a limited extent compared to an unmanured control [125]. Dried digestates can be pelletized before field spreading: no data were found on the agronomical implications of pelletizing manures or digestates (nutrient composition, nutrient availability, effects of used field spreading technology, e.g. broadcast application versus application near crop rows).

Another often discussed option for the treatment of solid digestates is composting [34, 35, 126, 127]. However, also composting is related to strong losses of N [113–115, 128]. Beside direct NH_3 losses, this is due to denitrification (N_2O and N_2), following nitrification of the NH_4^+ component to NO_3^- during aerobic turnover. From application of fresh and composted solid animal manures, it is known that the effect on N availability and on soil humus reproduction of fresh manures directly applied to the soil is comparable to composts derived from the same amounts of fresh manures [129, 130]. Therefore, composting reduces the fertilizer value of digestates in terms of direct nutrient availability and probably also the effect on long-term preservation of soil fertility, and is related to strong emissions of greenhouse gases (N_2O among others). Consequently, from a plant nutrition point of view, composting is not an appropriate management option for solid digestates. After a solid–liquid separation of digestates, the solid manures should be—whenever possible—applied to the fields as soon as possible, as the main emissions take place in the first weeks of storage [131, 132], especially during the warmer season due to the temperature dependency of the emission rates [131]. If storage is unavoidable, anaerobic conditions should be maintained.

6.3 Effects of other digestate treatment procedures

Currently, further digestate treatment procedures are in a developing stage, as burning solid digestates, or water removal from liquid digestates by using more sophisticated technologies, e.g. membrane technologies (Fig. 1). Regarding burning, it is well known that most of the N and S compounds volatilize above 200 and 375°C, respectively [133], resulting in a loss of the fertilizer value of the remaining wastes. No data were found concerning the use of solid digestates as a feedstock for biochar production and the related agronomical implications. Similarly, only few published data were found regarding the effects of the use of membrane technologies to produce concentrates from digestates on nutrient composition and the agronomical implications of their use as fertilizer [e.g. 23, 30].

7 Feedstock scheduling in biogas plants

Digestates are produced throughout the year and must therefore be stored until field application. The efficiency of N applied via organic manures is much higher when field application takes place in spring and not in autumn [134, 135]. Calculations of the nutrient outputs from digesters indicated that only approximately 50% of the N outputs are available for spring application, whereas approximately 20–25% and 25–30% are available for application in summer and autumn, respectively [21]. To achieve high N use efficiencies and to minimize N emissions, a high share of total N for late winter until early summer applications would be desirable using digestates with narrow C:N ratios. To meet this demand, three approaches can be identified to optimize the management of the biogas digester from a plant nutritional point of view:

(i) Utilization of feedstocks high in N contents during late autumn and winter (for digestate application in spring) and utilization of feedstocks low in N contents in summer (for digestate application in autumn) [21].
(ii) Utilization of feedstocks with a high biodegradability in late autumn and winter (for digestate application in spring), leading to a narrower digestate C:N ratio.
(iii) Use of feedstocks with high water content especially in spring. Higher digestate water contents decrease the risk of N losses via NH_3 volatilization during summer.
(iv) Introduction of feedstocks with high DM content in autumn and winter (for digestate application in spring). Digester capacity is limited by the OM inputs. Therefore, feedstocks high in OM content and low in water content reduce the needs of reactor and in particular storage volume. The latter opens for more seasonal flexibility in storage and target-oriented application.

Table 4. Effects of anaerobic digestion on digestate composition and main agronomic effects depending on the kind of feedstock

	Digestates from		
	Liquid animal manures	Crop residues and green manures	Dedicated energy crops
Total amounts of organic manures within the farming system	0	0	+++
Manure handling and allocation	+	+++	+++
NH_4^+/total N ratio	+	+++	+++
Manure pH	++	++	++
Biological O_2 demand	- -	- - -a)	- - -a)
N availability	0	++	++
N immobilization	-	- - -a)	- - -a)
N use efficiency	0 +	+++	–
P availability	0	0	0
S availability	?	?	?
Heavy metal solubility/availability	0 -	0 -	0 -
Crop growth	0	++	+++

- - - = Very strong reduction; - - = Strong reduction; - = Small reduction; 0 = No effects or contradictory effects; + = Small increase; ++ = Strong increase; +++ = Very strong increase.
a) Assumed, as no data are available.
? = Unclear effects, no data found.

8 Conclusions

Digestates have potential benefits regarding N availability and crop yields in comparison to untreated animal manures, as shown by pot experiments. However, under field conditions, the available data on agronomic assessments of digestates from animal slurries differ in their results with small or inconsistent benefits compared to undigested slurries (Table 4). Increased slurry NH_4^+-N share in digested slurries does not guarantee improved utilization efficiencies of slurry N. Significant positive effects can only be expected if the digestates are applied directly with incorporation into the soil immediately after field spreading. Handled like this, digestates provide plant available N corresponding to their NH_4^+-N content plus a small part of the N_{org} fractions (10–20%). The contradiction of the results from pot and field experiments emphasizes the need of field experiments to get a reliable assessment of the most important factors driving the agronomic effects of digestate application.

There are no systematic studies available on the influence of single feedstocks on nutrient contents and nutrient speciation in digestates, also including the C_{org} and organic N (N_{org}) components. For a better understanding of the driving factors governing N turnover in the soil, an accurate characterization of digestates' nutrient and OM composition, combined with experiments to assess the N-mineralization and N-immobilization processes after field spreading, would be essential for a better characterization of the driving factors governing N turnover in the soil. Research addressing the influence of the single feedstocks and the design of the fermentation process on composition of digestates is also needed. Furthermore, a better knowledge on the influence of single feedstocks on digestate composition is an important key for optimization of the feedstock management throughout the year, in order to obtain a higher share of the circulating N for spring amendments.

AD of crop residues and cover crops leads to an increase in the total amounts of mobile organic manures within the farming system, resulting in higher N use efficiency and an increased scope for target-oriented N application. AD of dedicated energy crops often leads to an increase of the total amounts of organic fertilizers within the farming system, with all potential risks. AD of dairy manure does not affect short-term crop P availability under field conditions. AD potentially increases plant S availability, but simultaneously also the risk of S volatilization. However, current knowledge about the S fertilizer value of digestates is very scarce.

The authors would like to thank the reviewers for their careful reading and very helpful and constructive comments.

The authors have declared no conflict of interest.

9 References

[1] Witt, J., Rensberg, N., Hennig, Ch., Naumann, K. et al., Monitoring zur Wirkung des Erneuerbare-Energien-Gesetz (EEG) auf die Entwicklung der Stromerzeugung aus Biomasse – März 2011. Available at: http://www.dbfz.de/web/fileadmin/user_upload/Userupload_Neu/Stromerzeugung_aus_Biomasse_Zwischenbericht_Maerz_2011.pdf, accessed November 14, 2011.

[2] Scheffer, F., Welte, E., Kemmler, G., Über Veränderungen in der stofflichen Zusammensetzung des Stallmistes bei der biologischen Gaserzeugung. *Landwirtsch. Forsch.* 1953, *4*, 61–68.

[3] Joppich, W., Das neue Wirtschaftsdüngemittel Bihuschlamm. *Deut. Landwirt.-Gesell. Mitt.* 1956, *72*, 559–560.

[4] Sauerlandt, W., Groetzner, E., Eigenschaften und Wirkungen der bei der biologischen Gasgewinnung aus Stallmist anfallenden organischen Dünger. Münchn. Beiträge zur Abwasser-, Fischerei- und Flußbiologie1956, *3*, München.

[5] Tietjen, C., Bilanzuntersuchungen bei Stallmistaufbereitung in Biogasanlagen. *Zeitschrift für Pflanzenernährung, Düngung, Bodenkunde* 1957, *77*, 198–212.

[6] Wick, H., Die Stoffbilanz bei Stalldünger nach Lagerung und nach Faulgärung mit Vegetationsversuchen über die Düngewirkung der gewonnen Rotteprodukte. PhD thesis, University of Hohenheim, Germany 1960.

[7] van Brakel, J., Biogas before 1970: a review. *Trop. Sci.* 1980, *22*, 105–148.

[8] Asmus, F., Linke, B., Dunkel, H., Eigenschaften und Düngerwirkung von ausgefaulter Gülle aus der Biogasgewinnung. *Arch. Acker- Pflanzenbau Bodenkd. Berl.* 1988, *32*, 527–532.

[9] Zethner, G., Pfundtner, E., Humer, J., *Qualität von Abfällen aus Biogasanlagen*, Available at: http://www.umweltbundesamt.at/fileadmin/site/publikationen/M160.pdf. Monographien des Umweltbundesamtes, Vol. 160, Wien 2002, pp. 50.

[10] Pötsch, E. M., Nutrient content of fermentation residues from agricultural biogas systems and their utilization on permanent grassland. Final report, 2005, pp. 32.

[11] Chantigny, M. H., Angers, D. A., Rochette, P., Belanger, G. et al., Gaseous nitrogen emissions and forage nitrogen uptake on soils fertilized with raw and treated swine manure. *J. Environ. Qual.* 2007, *36*, 1864–1872.

[12] Möller, K., Stinner, W., Deuker, A., Leithold, G., Effects of different manuring systems with and without biogas digestion on nitrogen cycle and crop yield in mixed organic dairy farming systems. *Nutr. Cycl. Agroecosys.* 2008, *82*, 209–232.

[13] Tambone, F., Scaglia, B., D'Imporzano, G., Schievano, A. et al., Assessing amendment and fertilizing properties of digestates from anaerobic digestion through a comparative study with digested sludge and compost. *Chemosphere* 2010, *81*, 577–583.

[14] Fouda, S., Nitrogen availability of biogas residues. PhD thesis, Technische Universität München, 2011.

[15] Massé, D. I., Talbot, G., Gilbert, Y., On farm biogas production: a method to reduce GHG emissions and develop more sustainable livestock operations. *Anim. Feed Sci. Technol.* 2011, *166–167*, 436–445.

[16] Koriath, H., Herrmann, V., Vollmer, G. R., Franz, J., Nährstoffdynamik während der anaeroben Fermentation von Gülle und Wirkung auf den Ertrag und Inhaltsstoffe von Mais im Gefäßversuch. *Arch. Acker- u. Pflanzenbau u. Bodenkd.* 1985, *29*, 741–747.

[17] Singh, K., Lee, K., Worley, J. Risse, L. M. et al., Anaerobic digestion of poultry litter: a review. *Appl. Engineering in Agriculture* 2010, *26*, 677–688.

[18] Webb, A. R., Hawkes, F. R., Laboratory scale anaerobic digestion of poultry litter: Gas yield-loading rate relationship. *Agric. Waste* 1985, *13*, 31–49.

[19] Emmerling, Ch., Barton, J., Anaerobic co-digestion of topinambour (*Helianthus tuberosus* L.) and properties of the remaining biogas manure. *Arch. Agron. Soil Sci.* 2007, *53*, 683–690.

[20] de Boer, H. C., Co-digestion of animal slurry can increase short-term nitrogen recovery by crops. *J. Environ. Qual.* 2008, *37*, 1968–1973.

[21] Möller, K., Schulz, R., Müller, T., Substrate inputs, nutrient flows and nitrogen loss of two centralized biogas plants in southern Germany. *Nutr. Cycl. Agroecosys.* 2010, *87*, 307–325.

[22] Sommer, S. G., Husted, S., The chemical buffer system in raw and digested animal slurry. *J. Agric. Sci. Camb.* 1995, *124*, 45–53.

[23] Hjorth, M., Christensen, K. V., Christensen, M. L., Sommer, S. G., Solid–liquid separation of animal slurry in theory and practice. A review. *Agron. Sustain. Dev.* 2010, *30*, 153–180.

[24] Georgacakis, D., Sievers, D. M., Iannotti, E. L., Buffer stability in manure digesters. *Agric. Wastes* 1982, *4*, 427–441.

[25] Sommer, S. G., Husted, S., A simple model of pH in slurry. *J. Agric. Sci. Camb.* 1995, *124*, 447–453.

[26] Pain, B. F., Misselbrook, T. H., Clarkson, C. R., Rees, Y. J., Odour and ammonia emissions following the spreading of anaerobically-digested pig slurry on grassland. *Agric. Wastes* 1990, *34*, 259–267.

[27] Le Corre, K. S., Valsami-Jones, E., Hobbs, P., Parsons, S. A., Phosphorus recovery from wastewater by struvite crystallization: a review. *Crit. Rev. Env. Sci. Technol.* 2009, *39*, 433–477.

[28] Marcato, C. E., Pinelli, E., Pouech, P., Winterton, P., Guiresse, M., Particle size and metal distributions in anaerobically digested pig slurry. *Biores. Technol.* 2008, *99*, 2340–2348.

[29] Liu, W., Yang, Q., Du, L., Soilless cultivation for high-quality vegetables with biogas manure in China: feasibility and benefit analysis. *Renew. Agr. Food Syst.* 2009, *24*, 300–307.

[30] Yu, F., Luo, X., Song, C., Zhang, M., Shan, S., Concentrated biogas slurry enhanced soil fertility and tomato quality. *Acta Agric. Scand. Sect. B Soil Plant Sci.* 2010, *60*, 262–268.

[31] Sensel, K., Wragge, V., Pflanzenbauliche Verwertung von Gärrückständen aus Biogasanlagen unter besonderer Berücksichtigung des Inputsubstrats Energiepflanzen. 2008. Available at: http://www.nachwachsenderohstoffe.de/, accessed March 9, 2009.

[32] Sánchez, M., Gomez, X., Barriocanal, G., Cuetos, M. J. et al., Assessment of the stability of livestock farm wastes treated by anaerobic digestion. *Int. Biodeterior. Biodegradation* 2008, *62*, 421–426.

[33] Gell, K., van Groenigen, J. W., Cayuela, M. L., Residues of bioenergy production chains as soil amendments: immediate and temporal phytotoxicity. *J. Hazard. Mater.* 2011, *186*, 2017–2025.

[34] Abdullahi, Y. A., Akunna, J. C., White, N. A., Hallett, P. D. et al., Investigating the effects of anaerobic and aerobic post-treatment on quality and stability of organic fraction of municipal solid waste as soil amendment. *Bioresour. Technol.* 2008, *99*, 8631–8636.

[35] Poggi-Varaldo, H. M., Trejo-Espino, J., Fernandez-Villagomez, G., Esparza-Garcia, F., Caffarel-Mendez, S., Rinderknecht-Seijas, N., Quality of anaerobic compost from paper mill and municipal solid wastes for soil amendment. *Water Sci. Technol.* 1999, *40*, 179–186.

[36] Salminen, E., Rintala, J., Anaerobic digestion of organic solid poultry slaughterhouse waste—a review. *Biores. Technol.* 2002, *83*, 13–26.

[37] Drennan, M. F., DiStefano, T. D., Characterization of the curing process from high-solids anaerobic digestion. *Bioresour. Technol.* 2010, *101*, 537–544.

[38] Bernal, P. M., Kirchmann, H., Carbon and nitrogen mineralization and ammonia volatilization from fresh, aerobically and anaerobically treated pig manure during incubation with soil. *Biol. Fertil. Soils* 1992, *13*, 135–141.

[39] Kirchmann, H., Lundvall, A., Relationship between N immobilization and volatile fatty acids in soil after application of pig and cattle slurry. *Biol. Fertil. Soils* 1993, *15*, 161–164.

[40] Friedel, J. K., Bezler, A., Fischer, W. R., Stickstoffmineralisierung von verflüssigtem, anaerob fermentiertem Rindermist im Boden. *Agribiol. Res.* 1996, *49*, 1–9.

[41] Alburquerque, J. A., de la Fuente, C., Bernal, M. P., Chemical properties of anaerobic digestates affecting C and N dynamics in amended soils. *Agric. Ecosys. Environm.* 2011. doi:10.1016/j.agee.2011.03.007

[42] Parnaudeau, V., Nicolardot, B., Pagès, J., Relevance of organic matter fractions as predictors of wastewater sludge mineralization in soil. *J. Environm. Qual.* 2004, *33*, 1885–1894.

[43] Chambers, B. J., Smith, K. A., Soil mineral nitrogen arising from organic manure applications. *Asp. Appl. Biol.* 1992, *30*, 135–143.

[44] van Kessel, J. S., Reeves, J. B., Meisinger, J. J., Nitrogen and carbon mineralization of potential manure components. *J. Environ. Qual.* 2000, *29*, 1669–1677.

[45] Gutser, R., Ebertseder, T., Weber, A., Schraml, M. et al., Short-term and residual availability of nitrogen after long-term application of organic fertilizers on arable land. *J. Plant Nutr. Soil Sci.* 2005, *168*, 439–446.

[46] Quakernack, R., Pacholski, A., Techow, A., Herrmann, A. et al., Ammonia volatilization and yield response of energy crops after fertilization with biogas residues in a coastal marsh of Northern Germany. *Agric. Ecosyst. Environ.* 2011, doi:10.1016/j.agee.2011.05.030.

[47] Gunnarsson, A., Bengtsson, F., Caspersen, S., Use efficiency of nitrogen from biodigested plant material by ryegrass. *J. Plant Nutr. Soil Sci.* 2010, *173*, 113–119.

[48] Diacono, M., Montemurro, F., Long-term effects of organic amendments on soil fertility. A review. *Agron. Sustain. Dev.* 2010, *30*, 401–422.

[49] Loria, E. R., Sawyer, J. E., Barker, D. W., Lundvall, J. P. et al., Use of anaerobically digested swine manure as a nitrogen source in corn production. *Agron. J.* 2007, *99*, 1119–1129.

[50] Möller, K., Stinner, W., Effects of different manuring systems with and without biogas digestion on soil mineral nitrogen content and on gaseous nitrogen losses (ammonia, nitrous oxides). *Eur. J. Agron.* 2009, *30*, 1–16.

[51] Gutser, R., Nitschke, A., Klasink, A., Umweltschonende Verwertung von Reststoffen verschiedener Gülleaufbereitungsverfahren. In: *KTBL-Arbeitspapier 242*, 1997: Umweltverträgliche Gülleaufbereitung und –Verwertung, pp. 97–108.

[52] Morris, D. R., Lathwell, D. J., Anaerobically digested dairy manure as fertilizer for maize in acid and alkaline soils. *Commun. Soil Sci. Plant Anal.* 2004, *35*, 1757–1771.

[53] Messner, H., Düngewirkung anaerob fermentierter und unbehandelter Gülle. *Diss. TU München* 1988, pp. 166.

[54] Roschke, M., Verwertung der Gärrückstände, in: Ministerium für Landwirtschaft, Umweltschutz und Raumordnung Landes Brandenburg (Ed.), Leitfaden Biogas, Potsdam, Germany. 2003, pp. 29–33. Available at http://www.mluv.brandenburg.de

[55] Massé, D. I., Talbot, G., Gilbert, Y., On farm biogas production: a method to reduce GHG emissions and develop more sustainable livestock operations. *Anim. Feed Sci. Technol.* 2011, *166–167*, 436–445.

[56] Loria, E. R., Sawyer, J. E., Extractable soil phosphorus and inorganic nitrogen following application of raw and anaerobically digested swine manure. *Agron. J.* 2005, *97*, 879–885.

[57] Möller, K., Stinner, W., Effects of organic wastes digestion for biogas production on mineral nutrient availability of biogas effluents. *Nutr. Cycl. Agroecosys.* 2010, *87*, 395–413.

[58] Bachmann, S., Wentzel, S., Eichler-Löbermann, B., Co-digested dairy slurry as a phosphorus and nitrogen source 1 for *Zea mays* L. and *Amaranthus cruentus* L. *J. Plant Nutr. Soil Sci.* 2011, *174*, 908–915.

[59] Burton, C. H., The potential contribution of separation technologies to the management of livestock manure. *Livestock Science* 2007, *112*, 208–216.

[60] Christensen, M. L., Hjorth, M., Keiding, K., Characterization of pig slurry with reference to flocculation and separation. *Water Res.* 2009, *43*, 773–783.

[61] Nelson, N. O., Mikkelsen, R. L., Hesterberg, D. L., Struvite precipitation in anaerobic swine lagoon liquid: effect of pH and Mg:P ratio and determination of rate constant. *Biores. Technol.* 2003, *89*, 229–236.

[62] Callander, I. J., Barford, J. P., Precipitation, chelation, and the availability of metals as nutrients in anaerobic digestion. *I. Methodology. Biotechnol. Bioeng.* 1983, *25*, 1947–1957.

[63] Henze, M., Harremoes, P., Jansen, J. L. C., Arvin, E., *Wastewater Treatment: Biological and Chemical Processes*, 2nd ed. Springer, Berlin 1996.

[64] Moody, L. B., Burns, R. T., Stalder, K. J., Effect of anaerobic digestion on manure characteristics for phosphorus precipitation from swine waste. *App. Eng. Agric.* 2009, *25*, 97–102.

[65] Field, J. A., Caldwell, J. S., Jeyanayagam, S., Reneau, R. B. et al., Fertilizer recovery from anaerobic digesters. *Trans. ASAE* 1984, *27*, 1871–1876.

[66] Suzuki, K., Tanaka, Y., Osada, T., Waki, M., Removal of phosphate, magnesium and calcium from swine wastewater through crystallization enhanced by aeration. *Water Res.* 2002, *36*, 2991–2998.

[67] Schievano, A., D'Imporzano, G., Salati, S., Adani, F., On-field study of anaerobic digestion full-scale plants (Part I): an on-field methodology to determine mass, carbon and nutrients balance. *Biores. Technol.* 2011, *102*, 7737–7744.

[68] Neuner, K.-H., Raba, C., Ahrens, W., Mineralstoff-Gehalte in Gärresten von Biogas-Anlagen, in: Elsäßer, M., Diepolder, M., Huguenin-Eile, O., Pötsch, E., Nußbaum, H.,

Messner, J. (Eds.), Proc. of the conference, Gülle 11 – Gülle und Gärrestdüngung auf Grünland" in Kloster Reute, 2011, pp. 75–77.

[69] Massé, D. I., Croteau, F. Masse, L. The fate of crop nutrients during digestion of swine manure in psychrophilic anaerobic sequencing batch reactors. *Biores. Technol.* 2007, *98*, 2819–2823.

[70] Haygarth, P. M., Sharpley, A. N., Terminology for phosphorus transfer. *J. Environ. Qual.* 2000, *29*, 10–15.

[71] Scherer, H. W., Sulphur in crop production—invited paper. *Eur. J. Agron.* 2001, *14*, 81–111.

[72] Straka, F., Jenicek, P., Zabranska, J., Dohanyos, M. et al., Anaerobic fermentation of biomass and wastes with respect to sulfur and nitrogen contents in treated materials. Proceedings Sardinia 2007, 11th International Waste Management and Landfill Symposium S. Margherita di Pula, Cagliari, Italy 2007.

[73] Abatzoglou, N., Boivin, S., A review of biogas purification processes. *Biofuels, Bioprod. Bioref.* 2009, *3*, 42–71.

[74] Beard, W. E., Guenzi, W. D., Volatile sulfur compounds from a redox-controlled-cattle-manure slurry. *J. Environ. Qual.* 1983, *12*, 113–116.

[75] Eriksen, J., Mortensen, J. V., Kjellerup, V. K., Kristiansen, O., Forms and plant-availability of sulfur in cattle and pig slurry. *Z. Pflanzenernähr. Bodenk.* 1995, *158*, 113–116.

[76] Brown, K. A., Sulphur in the environment: a review. *Environ. Pollut.* 1982, *3*, 47–80.

[77] Lloyd, A., Effectiveness of cattle slurry as a sulphur source for grass cut for silage. *Grass Forage Sci.* 1994, *49*, 203–208.

[78] Banwart, W. L., Bremner, J. M., Identification of sulfur gases evolved from animal manures. *Jour. Environm. Qual.* 1975, *4*, 363–366.

[79] Callander, I. J., Barford, J. P., Precipitation, chelation, and the availability of metals as nutrients in anaerobic digestion. *I. Methodology. Biotechnol. Bioeng.* 1983, *25*, 1947–1957.

[80] Callander, I. J., Barford, J. P., Precipitation, chelation, and the availability of metals as nutrients in anaerobic digestion. II. Applications. *Biotechnol. Bioeng.* 1983, *25*, 1959–1972.

[81] Chen, Y., Cheng, J. J., Creamer, K. S., Inhibition of anaerobic digestion process: a review. *Biores. Technol.* 2008, *99*, 4044–4064.

[82] Jin, H., Chang, Z., Distribution of heavy metal contents and chemical fractions in anaerobically digested manure slurry. *Appl. Biochem. Biotechnol.* 2011, *164*, 268–282.

[83] Callander, I. J., Barford, J. P., Precipitation, chelation, and the availability of metals as nutrients in anaerobic digestion. II. Applications. *Biotechnol. Bioeng.* 1983, *25*, 1959–1972.

[84] Bloomfield, C., McGrath, S. P., A comparison of the extractabilities of Zn, Cu, Ni and Cr from sewage sludges prepared by treating raw sewage with the metal salts before and after anaerobic digestion. *Environ. Pollut.* 1982, *3*, 193–198.

[85] Ahring, B. K., Westermann, P., Toxicity of heavy metals to thermophilic anaerobic digestion. *Eur. J. Appl. Microbiol. Biotechnol.* 1983, *17*, 365–370.

[86] Jansen, S., Steffen, F., Threels, W. F., van Leeuwen, H. P., Speciation of Co(II) and Ni(II) in anaerobic bioreactors measured by competitive ligand exchange-adsorptive stripping voltammetry. *Environ. Sci. Technol.* 2005, *39*, 9493–9499.

[87] Jackson-Moss, C. A., Duncan, J. R., The effect of iron on anaerobic digestion. *Biotechnol. Lett.* 1990, *12*, 149–154.

[88] Lake, D. L., Kirk, P. W. W., Lester, J. N., The effects of anaerobic digestion on heavy metal distribution in sewage sludge. *Water Pollut. Control* 1985, *84*, 549–558.

[89] Lavado, R. S., Rodriguez, M. B., Taboada, M. A., Treatment with biosolids affects soil availability and plant uptake of potentially toxic elements. *Agric. Ecosyst. Environ.* 2005, *109*, 360–364.

[90] Marcato, C. E., Pinelli, E., Cecchi, M., Winterton, P. et al., Bioavailability of Cu and Zn in raw and anaerobically digested pig slurry. *Ecotoxicol. Environm. Safety* 2009, *72*, 1538–1544.

[91] Möller, K., Effects of biogas digestion on soil organic matter and nitrogen inputs, flows and budgets in organic cropping systems. *Nutr. Cycl. Agroecosys.* 2009, *84*, 179–202.

[92] Möller, K., Schulz, R., Müller, T. Effects of setup of centralized biogas plants on crop acreage and balances of nutrients and soil humus. *Nutr. Cycl. Agroecosys.* 2011, *89*, 303–312.

[93] Odlare, M., Organic residues: a resource for arable soils. PhD thesis, Swedish University of Agricultural Sciences, Uppsala, Sweden, 2005.

[94] Rubæk, G. H., Henriksen, K., Petersen, J., Rasmussen, B. et al., Effects of application technique and anaerobic digestion on gaseous loss from animal slurry applied to ryegrass (*Lolium perenne*). *J. Agric. Sci. Camb.* 1996, *126*, 481–492.

[95] Elsässer, R. M., Kunz, H. G., Briemle, G., Unterschiedliche technische Behandlung von Gülle und deren Auswirkungen auf intensiv genutztes Grünland. *J. Agron. Crop Sci.* 1995, *174*, 253–264.

[96] Dahlberg, S. P., Lindley, J. A., Giles, J. F., Effect of anaerobic digestion on nutrient availability from dairy manure. *Trans. ASAE* 1988, *31*, 1211–1216.

[97] Gericke, D., Bornemann, L., Kage, H., Pacholski, A., Modelling ammonia losses after field application of biogas slurry in energy crop rotations. *Water Air Soil Pollut.* 2012, *223*, 29–47.

[98] Svensson, K., Odlare, M., Pell, M., The fertilizing effect of compost and biogas residues from source separated household waste. *J. Agric. Sci. Camb.* 2004, *142*, 461–467.

[99] Stinner, W., Möller, K., Leithold, G., Effects of biogas digestion of clover/grass-leys, cover crops and crop residues on nitrogen cycle and crop yield in organic stockless farming systems. *Europ. J. Agron.* 2008, *29*, 125–134.

[100] Gunnarsson, A., Lindén, B., Gertsson, U., Biodigestion of plant material can improve nitrogen use efficiency in a red beet crop sequence. *Hort. Sci.* 2011, *46*, 765–775.

[101] Furukawa, Y., Hasegawa, H., Response of spinach and komatsuna to biogas effluent made from source-separated kitchen garbage. *J. Environ. Qual.* 2006, *35*, 1939–1947.

[102] Kelderer, M., Stimpfl, E., Thalheimer, M., Stickstoffmineralisierung von organischen Bodenverbesserern und Handelsdüngern bei unterschiedlichen Temperaturen (8 °C/16 °C) – Übersicht über die Düngemittel. Versuchsbericht des Land- und Forstwirtschaftlichen Versuchszentrums Laimburg, 2008.

[103] Liu, W., Yang, Q., Du, L., Cheng, R., Zhou, W., Nutrient supplementation increased growth and nitrate concentration of lettuce cultivated hydroponically with biogas slurry. *Acta Agric. Scand. Sect. B Soil Plant Sci.* 2011, *61*, 391–394.

[104] Liedl, B. E., Cummins, M., Williams, M. L., Chatfield, J. M., Hydroponic lettuce production using liquid effluent from poultry waste bioremediation as a nutrient source, in: Cantliffe, D. J., Stoffella, P. J., Shaw, N. (Eds.), *Proceedings VII IS on Prot. Cult. Mild Winter Climates, ISHS Acta Hort.* 2004, *659*, 721–728.

[105] Liedl, B. E., Bombardiere, J., Chatfield, J. M., Fertilizer potential of liquid and solid effluent from thermophilic anaerobic digestion of poultry waste. *Water Sci. Technol.* 2006, *53*, 69–79.

[106] Liedl, B. E., Cummins, M., Williams, M. L., Chatfield, J. M., Liquid Effluent from poultry waste bioremediation as a potential nutrient source for hydroponic tomato production, in: Cantliffe, D. J., Stoffella, P. J., Shaw, N. (Eds.), *Proc. VII IS on Prot. Cult. Mild Winter Climates, ISHS Acta Hort.* 2004, *659*, 647–652.

[107] Liu, W., Du, L., Yang, Q., Biogas slurry added amino acids decreased nitrate concentrations of lettuce in sand culture. *Acta Agric. Scand. Sect. B Soil Plant Sci.* 2009, *59*, 260–264.

[108] Lošák, T., Zatloukalová, A., Szostková, M., Hlušek, J. et al., Comparison of the effectiveness of digestate and mineral fertilizers on yields and quality of kohlrabi (*Brassica oleracea* L.). *Acta Universitatis Agriculturae et Silviculturae Mendelianea Brunensis* 2011, *59*, 117–121.

[109] Hjorth, M., Nielsen, A. M., Nyord, T., Hansen, M. N. et al., Nutrient value, odour emission and energy production of manure as influenced by anaerobic digestion and separation. *Agron. Sustain. Dev.* 2009, *29*, 329–338.

[110] Møller, H. B., Sommer, S. G., Ahring, B. K., Separation efficiency and particle size distribution in relation to manure type ansd storage conditions. *Bioresour. Technol.* 2002, *85*, 189–196.

[111] Bauer, A., Mayr, H., Hopfner-Sixt, K., Amon, T., Detailed monitoring of two biogas plants and mechanical solid–liquid separation of fermentation residues. *J. Biotechnol.* 2009, *142*, 56–63.

[112] Chantigny, M. H., MacDonald, J. D., Beaupré, C., Rochette, Ph. et al., Ammonia volatilization following surface application of raw and treated liquid swine manure. *Nutr. Cycl. Agroecosyst.* 2009, *85*, 275–286.

[113] Thorman, R. E., Chadwick, D. R., Harrison, R., Boyles, L. O. et al., The effect on N_2O emissions of storage conditions and rapid incorporation of pig and cattle farmyard manure into tillage land. *Biosyst. Eng.* 2007, *97*, 501–511.

[114] Petersen, J., Sørensen, P., Loss of nitrogen and carbon during storage of the fibrous fraction of separated pig slurry and influence on nitrogen availability. *J. Agric. Sci. Camb.* 2008, *146*, 403–413.

[115] Hansen, M. N., Henriksen, K., Sommer, S. G., Observations of production and emission of greenhouse gases and ammonia during storage of solids separated from pig slurry: effects of covering. *Atmos. Environ.* 2006, *40*, 4172–4181.

[116] Peters, K., Jensen, L. S., Biochemical characteristics of solid fractions from animal slurry separation and their effects on C and N mineralization in soil. *Biol. Fertil. Soils* 2011, *47*, 447–455.

[117] Chantigny, M. H., Angers, D. A., Bélanger, G., Rochette, Ph. et al., Yield and nutrient export of grain corn fertilized with raw and treated liquid swine manure. *Agron. J.* 2008, *100*, 1303–1309.

[118] Manfredini, A., Nergri, M., Cavalli, D., Bechini, L. et al., Carbon and nitrogen mineralization of raw and separated, digested animal manures. *Proceedings of the 14. Ramiran International Conference: Treatment and Use of organic residues in agriculture: Challenges and opportunities towards sustainable management*, Lisboa, Portugal, 2010.

[119] Laboski, C. A. M., Earhart, S. M., Baxter, C. A., Evaluation of nitrogen availability from raw and treated dairy manures. 19th World Congress of Soil Science, Soil solutions for a Changing World, Brisbane, Australia, 2010.

[120] Møller, H. B., Lund, I., Sommer, S. G., Solid-liquid separation of livestock slurry: efficiency and cost. *Bioresour. Technol.* 2000, *74*, 223–229.

[121] Dosch, P., Gutser, R., Reducing N losses (NH_3, N_2O, N_2) and immobilization from slurry through optimized application techniques. *Fertil. Res.* 1996, *43*, 165–171.

[122] Dahlin, S., Kirchmann, H., Kätterer, Th., Gunnarsson, S., Bergström, L., Possibilities for improving nitrogen use from organic materials in agricultural cropping systems. *Ambio* 2005, *34*, 288–295.

[123] Maurer, C., Müller, J., Drying characteristics and nitrogen loss of biogas digestate during the drying process, in: *Proceedings of the 27th World congress of the International Commission of Agricultural and Biosystems Engineering*, Québec, Canada, 2010, pp. 1–8.

[124] Isikhuemhen, O. S, Mikiashvili, N. A., Kelkar, V., Application of solid waste from anaerobic digestion of poultry litter in *Agrocybe aegerita* cultivation: mushroom production, lignocellulolytic enzymes activity and substrate utilization. *Biodegradation* 2009, *20*, 351–361.

[125] Ramírez, M., Pujolà, M., Quemada, M., Jarauta-Bragulat, E. et al., Soil nitrogen availability after addition of thermally dried pig slurry. *Soil Sci. Soc. Am. J.* 2011, *75*, 940–948.

[126] Meissl, K., Smidt, E., High quality composts by means of cocomposting of residues from anaerobic digestion. *Compost Sci. Util.* 2007, *15*, 78–83.

[127] Teglia, C., Tremier, A., Martel, J.-L., Characterization of solid digestates: part 2, assessment of the quality and suitability for composting of six digested products. *Waste Biomass Valor.* 2011, *2*, 113–126.

[128] Rotz, C. A., Management to reduce nitrogen losses in animal production. *J. Anim. Sci.* 2004, *82*, 119–137.

[129] Rauhe, K., Hesse, M., Über die Wirkung verschieden gelagerten Stalldüngers auf leichten und schweren Böden. *Zeitschrift für Acker- und Pflanzenbau* 1960, *110*, 135–152.

[130] Rauhe, K., Effects of organic manuring and cropping on soil humus and fertility, in: Welte, E., Szabolccs, I. (Eds.), *Proceedings of the 4th International CIEC Symposium Agricultural Waste Management and Environmental Protection*, Braunschweig, Germany 1987, pp 55–76.

[131] Dinuccio, E., Berg, W., Balsari, P., Gaseous emissions from the storage of untreated slurries and the fractions obtained after mechanical separation. *Atmos. Environ.* 2008, *42*, 2448–2459.

[132] Chadwick, D. R., Emissions of ammonia, nitrous oxide and methane from cattle manure heaps: effect of compaction and covering. *Atmos. Environ.* 2005, *39*, 787–799.

[133] Kookana, R. S., Sarmah, A. K., Van Zwieten, L., Krull, E. et al., Biochar application to soil: agronomic and environmental benefits and unintended consequences. *Adv. Agron.* 2011, *112*, 103–143.

[134] Chambers, B. J., Smith, K. A., Pain, B. F., Strategies to encourage better use of nitrogen in animal manures. *Soil Use Manag.* 2000, *16*, 157–161.

[135] Matsunaka, T., Sawamoto, T., Ishimura, H., Takakura, K. et al., Efficient use of digested cattle slurry from biogas plant with respect to nitrogen recycling in grassland. *Intern. Congr. Ser.* 2006, *1293*, 242–252.

[136] Wendland, M., Diepolder, M., Capriel, P., Leitfaden für die Düngung von Acker- und Grünland. Bayerische Landesanstalt für Landwirtschaft (LfL) (ed.). LfL-Information. Available at: http://www.lfl.bayern.de/publikationen/daten/informationen/p_24402.pdf, accessed February 24, 2009.

[137] Roschke, M., Plöchl, M., Eigenschaften und Zusammensetzung der Gärreste, in: Linke, B. et al. (Eds.), *Biogas in der Landwirtschaft - Leitfaden für Landwirte und Investoren im Land Brandenburg*, Freising-Weihenstephan, Germany, 2006, pp. 36–39.

[138] Pfundtner, E., Swoboda, M., Qualität von Biogasgülle und Gärrückständen – Aktuelle Situation in Niederösterreich, in: ALVA (Ed.), *Proceedings ALVA – Jahrestagung* 2005, Linz Mai 23.–25, 2005, 190-194. ISSN 1606-612X.

[139] Institut für Agrarökologie, Ökologischen Landbau und Bodenschutz (ed): Einsatz von Gärresten aus der Biogasproduktion als Düngemittel. LfL-Information, 2008.

[140] Martin, J. H., A Comparison of Dairy Cattle Manure Management with and without Anaerobic Digestion and Biogas Utilization. Report for the AgSTAR Program, U.S. Environmental Protection Agency, 2004, pp. 58. Available at: http://www.ncgreenpower.org/documents/nydairy2003.pdf, accessed February 2, 2007.

[141] Voća, N., Krička, T., Ćosić, T., Rupić, V. et al., Digested residue as a fertilizer after mesophilic process of anaerobic digestion. *Plant Soil Environ.* 2005, *51*, 262–266.

[142] Kluge, R., Wagner, W., Mokry, M., Dederer, M. et al., 2008. Final report oft he project "Inhaltsstoffe von Gärprodukten und Möglichkeiten zu ihrer geordneten landwirtschaftlichen Verwertung". Available at: http://www.landwirtschaft-mlr.baden-wuerttemberg.de/servlet/PB/show/1235603_l1/ltz_Projektbericht.

[143] Güngör, K., Karthikeyan, K. G., Phosphorus forms and extractability in dairy manure: a case study for Wisconsin on-farm anaerobic digesters. *Biores. Technol.* 2008, *99*, 425–436.

[144] Kirchmann, H., Witter, E., Composition of fresh, aerobic and anaerobic farm animal dungs. *Biores. Technol.* 1992, *40*, 137–142.

[145] Teglia, C., Tremier, A., Martel, J.-L., Characterization of solid digestates: part 1, review of existing indicators to assess solid digestates agricultural use. *Waste Biomass Valor.* 2011, *2*, 43–58.