Influence of biogas-digestate processing on composition, N partitioning, and N_2O emissions after soil application

Dissertation

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“To him that will, ways are not wanting”

– George Herbert

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Abbreviations used in this work are defined at their first mention in text.

Standard abbreviations according to the International System of Units (SI) as well as chemical elements are used and are not listed below. Chemical elements are abbreviated using the respective chemical symbol.

ADF	Acid detergent fiber
ADL	Acid detergent lignin
aNDF	Neutral detergent fiber (measured by adding of α-amylase)
ASS	Ammonium sulfate solution
BGP	Biogas plant
CC	Concentrate after vacuum evaporation
CHP plant	Combined heat and power plant
C_{hws}	Hot water extractable carbon
C_{org}	Organic carbon
C_t	Total carbon
DM	Dry matter
DOC	Dissolved organic carbon
DON	Dissolved organic nitrogen
DS	Dry solid
FM	Fresh matter
GC	Gas chromatograph
GHG	Greenhouse gas
M	Moles per liter (mol L^{-1})
N_{hws}	Hot water extractable nitrogen
N_{min}	Mineral nitrogen
N_t	Total nitrogen
P	Pellet
PE-LD	Low-density polyethylen
PVC	Polyvinylchlorid
RD	Raw digestate
SL	Separated liquid
SS	Separated solid
temp.	Temperature

TN	Total nitrogen
VOC	Volatile organic compounds
WFPS	Water-filled pore space

Summary

The ever-growing need for agricultural products represents a global issue, particularly with a view to the limited availability of cultivable land. According to the latest estimates, the arable land per capita decreases and, in 2050, is expected to account for about 60% less than in the 1960s.

In order to meet the demand, agriculture has evolved into industrial-like structures. This development often goes along with nutrient surpluses (e.g., excess of nitrogen and phosphorus) and increased emissions, caused by mismanagement and inappropriate agricultural practices (e.g., over-fertilization). Biogas plants offer a possibility to valorize organic residues and wastes, but potentially aggravate this problem since additional organic residues (referred to as digestates) with considerable nutrient contents are generated as by-products.

A simple approach to adjust nutrient levels in the affected regions is the transfer of manures and digestates. However, to make this feasible, a reduction of water content (and consequently of total mass/volume) of digestates is required. Up to now, various techniques for digestate downstream processing are available. Previous research mainly addressed single processing stages or differences between feedstock mixtures. Only limited information was found about the influence of a completed downstream processing on total mass reduction and nitrogen concentration in digestate. Studies about the (gaseous) N losses that occur after the application of the respective intermediate and final products to soils were equally scarce.

Therefore, the aims of the current doctoral thesis were to determine (i) the mass reduction achieved by the gradual removal of water within competing processing chains, (ii) the nitrogen partitioning after every single processing step and its recovery in the end products, and (iii) the amount of greenhouse gases (especially N_2O) released after the application of intermediate and end products to soils in comparison to untreated, raw digestate.

For that purpose, two commercial, full-scale biogas plants were examined, which completely processed either the solid or the liquid fraction after mechanical screw-press separation of raw digestate. The separated solid fraction was subsequently dried and pelletized, while the liquid fraction was treated by vacuum evaporation with partial NH_3 scrubbing. As final products, digestate pellets and N-enriched ammonium sulfate solution were generated. Calculation of a mass flow balance served as the basis for determining (total) mass reduction, the partitioning of fresh mass and nitrogen during digestate processing, and the recovery of initial N in the products. Additionally, the environmental impact of utilizing digestate as an organic fertilizer was studied by measuring the N_2O release after application to soil under field and laboratory conditions. A further in-depth analysis was performed to observe the main factors influencing the production and release of climate-relevant N_2O from digestate pellets.

It was found that the mass reduction caused by water removal during subsequent processing accounted for 6% (solid chain) and 31% (liquid chain) of the total mass of raw digestate. Liquid processing required 40% less thermal energy per ton of water evaporated than solid processing. At the end of the downstream processing, the recovery of initial nitrogen in pellets was 33% lower than in ammonium sulfate solution. Regarding the environmental impact of digestate application to soil, mechanical solid-liquid separation showed the potential to reduce N_2O emissions. Contrary to expectations, pelletizing of dry solid boosted the emissions, which was linked to the properties and composition of the pellet. Here, indigenous microbial activity triggered N_2O production and release from denitrification immediately after wetting.

Overall, the present work has shown that the subsequent processing of separated solid or liquid digestate generates different products with individual benefits and challenges. Solid digestates are characterized by a high share of recalcitrant organic compounds and therefore can serve, e.g., as soil improver. After processing to pellets, they can be easily transported, stored, and commercialized. However, it is questionable whether the pelletizing process is advisable, since pellets emitted a considerable amount of GHGs during utilization. Liquid processing produces ammonium sulfate solution, which can be utilized as a valuable inorganic fertilizer rich in plant-available N.

Besides the discussed advantages, a final decision for or against digestate processing always depends on individual factors, such as local situation and financial means. Smart decision-making must include fertilizer properties, technological performance, and economic feasibility.

With a view to future research, additional aspects were identified, such as returning to a laboratory-scale biogas plant for more accurate digestate sampling and analysis, consideration of digestate storage and transport, and economic evaluation of the entire digestate value chain including the assessment of digestate fertilizer value (expressed as e.g., N use efficiency or N fertilizer replacement value).

Zusammenfassung

Der ständig wachsende Bedarf an landwirtschaftlichen Erzeugnissen stellt ein globales Problem dar, welches durch die begrenzte Verfügbarkeit von Anbauflächen noch weiter verschärft wird. Jüngsten Schätzungen zufolge nimmt die Ackerfläche pro Kopf ab und wird im Jahr 2050 voraussichtlich etwa 60 % weniger betragen als im Jahr 1960.

Um die steigende Nachfrage zu bedienen, haben sich in der Landwirtschaft industrieähnliche Strukturen ausgebildet. Diese Entwicklung geht jedoch häufig mit Nährstoffüberschüssen (z. B. Stickstoff- und Phosphorüberschüsse) und erhöhten Emissionen einher, die durch Missmanagement und unsachgemäße landwirtschaftliche Praktiken (z. B. Überdüngung) verursacht werden. Biogasanlagen bieten eine Möglichkeit, organische Rückstände und Abfälle zu verwerten, können das Problem jedoch weiter verschärfen, da zusätzliche organische Rückstände (sogenannte Gärreste) mit erheblichen Nährstoffgehalten anfallen.

Ein einfacher Ansatz, um die Nährstofffracht in betroffenen Regionen zu regulieren, ist die Verbringung von Gülle und Gärresten. Hierfür muss jedoch zunächst eine Verringerung des Wassergehalts (bzw. der Gesamtmasse/des Gesamtvolumens) der Gärreste erfolgen, welche mittels verschiedener Verfahren und Technologien realisiert werden kann. Die zugehörige Forschung befasste sich bislang hauptsächlich mit einzelnen Verfahrensschritten oder mit den Auswirkungen unterschiedlicher Ausgangsstoffe/Gemische. Über den exakten Einfluss einer abgeschlossenen Nachbehandlung auf die Gesamtmassenreduktion und die Stickstoffkonzentration im Gärrest sind kaum Informationen verfügbar. Gleichermaßen konnten nur wenige Studien gefunden werden, welche sich mit den (gasförmigen) N-Verlusten nach der Ausbringung der jeweiligen Zwischen- und Endprodukte beschäftigen.

Die Ziele der vorliegenden Dissertation waren daher die Untersuchung

(i) der Massenreduktion, die durch den Wasserentzug innerhalb verschiedener Aufbereitungsketten erzielt werden konnte,

(ii) der Stickstoffverteilung nach den einzelnen Aufbereitungsschritten und der N-Rückgewinnung in den Endprodukten, sowie

(iii) der freigesetzten Treibhausgase (insbesondere N_2O) nach der Ausbringung von Zwischen- und Endprodukten auf Böden (im Vergleich zu unbehandelten Rohgärresten).

Zu diesem Zweck wurden zwei kommerzielle Biogasanlagen im laufenden Betrieb untersucht. In beiden Anlagen wurde nach einer ersten, mechanischen Schneckenpressenseparation des Rohgärrestes entweder die feste oder die flüssige Fraktion vollständig aufbereitet. Die abgetrennte Feststofffraktion wurde anschließend getrocknet und pelletiert, wohingegen die Flüssigfraktion mittels Vakuumverdampfung mit partieller NH_3-Wäsche behandelt wurde. Als Endprodukte fielen dabei Gärrestpellets und N-angereicherte Ammoniumsulfat-Lösung an. Die Bilanzierung der Massenflüsse diente als Grundlage für die Ermittlung der (Gesamt-)Massenreduktion, der Verteilung von Frischmasse und Stickstoff während der Gärrestaufbereitung, sowie der Rückgewinnung des ursprünglichen Stickstoffs in den Produkten. Darüber hinaus wurden die Umweltauswirkungen einer Düngung mit Gärresten mit Hilfe von N_2O-Messungen unter Feld- und Laborbedingungen untersucht. Im Anschluss daran wurde eine weitergehende Analyse der Gärrestpellets durchgeführt, um die Hauptfaktoren zu bestimmen, welche die verstärkte Produktion und Freisetzung von N_2O beeinflussen.

Im Rahmen dieser Arbeit konnte festgestellt werden, dass die Massenreduktion (durch Wasserentzug) bei der Aufbereitung des separierten Feststoffes 6 % der Gesamtmasse des Rohgärrests betrug, wohingegen die flüssige Fraktion 31 % erzielte. Dabei benötigte die Flüssigaufbereitung etwa 40 % weniger thermische Energie (pro Tonne verdampftes Wasser) als die Feststoffaufbereitung. Am Ende des Verfahrens war die Rückgewinnung des ursprünglichen Stickstoffs in Pellets um 33 % geringer als in Ammoniumsulfat-Lösung. Was die Umweltauswirkungen der Gärrestausbringung betrifft, so konnten durch die mechanische fest-flüssig-Trennung N_2O-Emissionen verringert werden. Entgegen den Erwartungen erhöhte die Pelletierung der festen Fraktion diese Emissionen. Es wurde nachgewiesen, dass die autochthone mikrobielle Zusammensetzung der Pellets die N_2O-Produktion und Freisetzung aus der Denitrifikation unmittelbar nach der Befeuchtung auslöst.

Insgesamt konnte in der vorliegenden Dissertation gezeigt werden, dass die Weiterverarbeitung von separierten festen oder flüssigen Gärresten vielfältige Produkte mit spezifischen Vor- und Nachteilen erzeugt. Feste Gärreste zeichnen sich durch einen hohen Anteil an stabilen organischen Verbindungen aus und können daher z.B. als Bodenverbesserer dienen. Nach der Verarbeitung zu Pellets lassen sie sich leicht transportieren, lagern und vermarkten. Allerdings bleibt fraglich, ob eine Pelletierung generell sinnvoll ist, da bei der Anwendung der Pellets erhebliche Mengen an Treibhausgasen freigesetzt werden können. Durch die Aufbereitung der flüssigen Fraktion entsteht eine Ammoniumsulfat-Lösung, die als wertvoller anorganischer Dünger, mit einem hohen Gehalt an pflanzenverfügbarem Stickstoff, genutzt werden kann.

Neben den genannten Vorteilen hängt die endgültige Entscheidung für oder gegen die Aufbereitung von Gärresten stets von individuellen Faktoren ab, wie den örtlichen Gegebenheiten und den finanziellen Möglichkeiten. Ebenfalls müssen weitere Aspekte, wie Düngereigenschaften, technische Performance und Wirtschaftlichkeit einbezogen werden.

Überdies konnten im Hinblick auf die Durchführung künftiger Forschungsvorhaben weitere wichtige Aspekte identifiziert werden. So wird beispielsweise empfohlen Folgearbeiten mit einer Forschungs-Biogasanlage durchzuführen, um eine bessere Gärrestbeprobung und -analyse zu ermöglichen. Des Weiteren sollten Gärrestlagerung und -transport miteinbezogen werden, sowie eine wirtschaftliche Bewertung der gesamten Gärrest-Wertschöpfungskette (einschließlich der Bewertung des Gärrestdüngerwerts, z. B. in Form der N-Nutzungseffizienz).

1 Introduction

1.1 General aspects

The demand for agricultural products increases rapidly [1] as a result of the growing population, changes in consumer behavior (e.g., meat consumption [2–4]), and alternative usages (e.g., bioenergy). The required cropland is an area of conflict since it is simultaneously utilized for the production of food, feed, energy crops, and materials. At the same time, the arable land per capita decreases and, in 2050, is expected to account for 58% less than in 1961 [5]. In order to meet the global demand, agriculture has developed into industrial-like structures, characterized by intensified livestock farming, high levels of mechanization, extensive utilization of synthetic fertilizers and plant protection agents, and long-distance transportation.

This development comes at a high cost for the environment and is further exacerbated by mismanagement and inappropriate agricultural practices. Soil degradation caused by human activities, for example, currently affects about 6 billion ha [6] and is expected to expand to 90% of the total global soils in 2050 [5,7]. Inappropriate fertilization (e.g., over-fertilization) is also associated with nutrient losses in the form of leaching to the groundwater, runoff to the surface water, or gaseous emissions into the atmosphere.

In 2019, a total of 189 million tons of inorganic NPK fertilizer was used in worldwide agriculture, which was about 40% higher than in 2000 [1]. Considering the grain production, it was estimated that about 60% of the annually applied N and 48% of P were utilized in excess and can be lost to the environment (based on the years 1997-2003) [8,9]. About 66% of the worldwide excess N and P were present in China, USA, and India, and were primarily linked to the production of wheat, maize, and rice [8].

A significant amount of N is volatilized in the form of gaseous N_2O. Besides CO_2 and CH_4, N_2O is one of the strongest contributors to global warming, which also catalyzes ozone depletion [10,11]. In 2019, 22% of the global anthropogenic greenhouse gas (GHG) emissions were caused by the agricultural sector. Land use change and enteric fermentation accounted for 74% of the agricultural emissions, while managed soils and pasture, manure management, and application of synthetic fertilizers added up to 17% [12]. Regarding solely anthropogenic N_2O emissions, nitrogen fertilizers make up the largest share [10,11,13]. In Germany, roughly 70% of the total agricultural N_2O emissions come from agricultural soils (including direct and indirect emissions from livestock farming, manure management, nitrate leaching, and N volatilization) [11].

Aside from GHG emissions, regional nutrient surpluses are another critical challenge. Generally located in rural areas and closely linked to intensive livestock farming, this excess is caused by the necessity for additional purchase and transportation of fodder, and the reallocation of nutrients into residual manures. In Germany, a significant surplus of nutrients can be found in Lower Saxony and Bavaria [14,15], which are the regions characterized by the highest grain production (31% of the total area planted with grain) [16], livestock density (48% of total pig fattening, cattle, and dairy cow) [17], and number of biogas plants (45% of total) [18].

In order to mitigate the negative impacts of the agricultural sector, fundamental objectives are regularly decided at a European level and implemented in national legislation. For example, to protect soil and water bodies, limit values for fertilizer contaminants (Regulation EU No 2019/1009 [19]) and water pollutants (91/676/EEC [20], 2000/60/EC [21], and 2006/118/EC [22]) were enacted. Based on these regulations, the latest draft of the German fertilizer ordinance further restricts the application periods and amounts of fertilizers and organic amendments, such as effluents from biogas production (referred to as digestates) [23]. In addition, operators of biogas plants must provide facilities, which can store digestates between 6-9 months [23].

A practical approach to tackle many of the previously described issues, which gained increasing popularity in the recent years, is circular agriculture. Circular agriculture is designed to utilize minimal amounts of external inputs, close nutrient cycles, regenerate soils, and minimize the impact on the environment [24]. In this way, land-use, resource requirements, wastes, and ecological footprint of agriculture can be reduced (e.g., up to 80% less use of synthetic fertilizers in food systems) [24].

An evident option for waste and biomass valorization in (circular) agriculture is anaerobic digestion of organic substrates (e.g., biowaste, animal manure, or harvested biomass) to biogas [25,26]. Here, residual carbon is partly recovered in the form of CH_4 and CO_2, which reduces direct emissions and provides green energy [24,27]. Additionally, biogas production helps to generate added value and employment in rural areas. Worldwide, biogas plants are mostly located in the USA, China, and Europe. Germany leads the field with an installed electric power of about 6,000 MW_{el} (2021) [18,28].

In an effort to close the corresponding nutrient loop, the digested effluent must be brought back to the field. Its value and utilization can substantially be improved by subsequent processing [29,30]. Water removal via digestate processing, for example, facilitates storage and transportation [29–33], which helps to re-distribute nutrients cost-effectively in a broader area. Also, by separating and concentrating main plant nutrients in the product(s), fertilization in line with specific soil requirements is simplified. With appropriate downstream processing, marketable organic fertilizers can be produced, which serve as an additional source of income and have the potential to substitute commercial synthetic fertilizers [34–36].

During the last decades, various methods and technologies for treatment of organic residues were developed. In the following chapter, main reasons for initial anaerobic digestion of raw manure are briefly presented. Afterward, the focus is placed on techniques for subsequent processing of digestates, which is the main research object of this thesis.

1.2 Comparison between raw manure/slurry and biogas digestate

In general, manure and slurry can be directly utilized as organic amendments or further processed via different techniques. With regard to subsequent treatment options, upstream anaerobic digestion is a common practice, which changes multiple properties of these organic residues and facilitates downstream processing. Key differences between raw and digested substrates, which affect, i.a., usability, handling, and environmental impact are shortly addressed in the next paragraph.

Untreated manures and slurries are characterized by a high amount of recalcitrant organic compounds [37] and, in particular, a high share of organic N [38], which negatively influences the short-term fertilizing effect when applied to soil [39]. The comparison between raw substrates and anaerobically digested residues has shown that the digestion process increases the relative amount of small, soluble particles [37] and the NH_4-N:total N ratio [40,41]. This enables better N availability and plant uptake of the digestate in the year of application compared to untreated slurry [42]. Digestates also have the potential to reduce gaseous N losses after fertilization due to lower dry matter (DM) content and higher infiltration rate [43,44]. As described by Möller [45], this effect can be observed for N_2O release after digestate application to soil and to some extent for NH_3 volatilization. However, many factors, such as soil type, soil water content, or digestate characteristics (organic matter degradability and pH value) influence the gaseous losses [43–48]. Besides that, the digestion of manure and slurry lowers odor emissions during storage [42] and reduces the volume of the original feedstock (up to 30% of total fresh matter (FM) [49]) due to degradation of a significant part of initial DM.

As substantial losses of N, C, and organic matter (due to gaseous emissions) were observed during storage of raw manure/slurry/digestate [42,50] and separated solid digestates [51], subsequent processing seems advisable. For example, a simple mechanical digestate separation decreased the NH_3 volatilization during storage and after soil application of the liquid fraction due to its lower DM content and pH value compared to unseparated raw digestate [42]. Consecutive processing can offer additional benefits. Compressing, for instance, significantly reduces the total volume and improves storability [30], field spreading [52,53], and transportability [31] of organic residues. Compressed (pelleted) digestate is also characterized by sufficient fertilizing properties (e.g., high P and K availability) and its application enhances soil microbial biomass and activity [30].

In the following, a brief literature overview of the currently most used digestate processing techniques is given.

1.3 Processing techniques for treatment of biogas digestates

1.3.1 Solid-liquid separation

The most common technique applied for volume reduction of animal residues and digestates is the physical separation of solid particles from the liquid. The generated solid and liquid phases are characterized by different properties, individual handling and benefits [54]. Depending on the applied technology and its separation efficiency, the two phases split at a ratio of 10–30% of total FM (solid) to 70–90% liquid [49,55–57]. Established techniques are settling (or sedimentation), mechanical separation performed with screen separator, belt or screw press separator, or centrifugation.

In the case of **sedimentation**, the gravitational force is used for solid-liquid separation [58]. Here, the slurry or manure is split into an ‘underflow’ and an ‘overflow’; i.e., after introducing it into a tank, the solids settle at its bottom, where they can be removed [50,58,59]. This, for example, can be implemented by using a thickener – a container with a conical bottom (see Fig. 1-1a) [50]. The settling and separation efficiency of this technique depend on the particle size distribution (and therefore viscosity) of introduced substrate and settling time. Concerning the nutrients removal, increasing settling time positively influences the P settling and does not affect the removal of N and K [37,50].

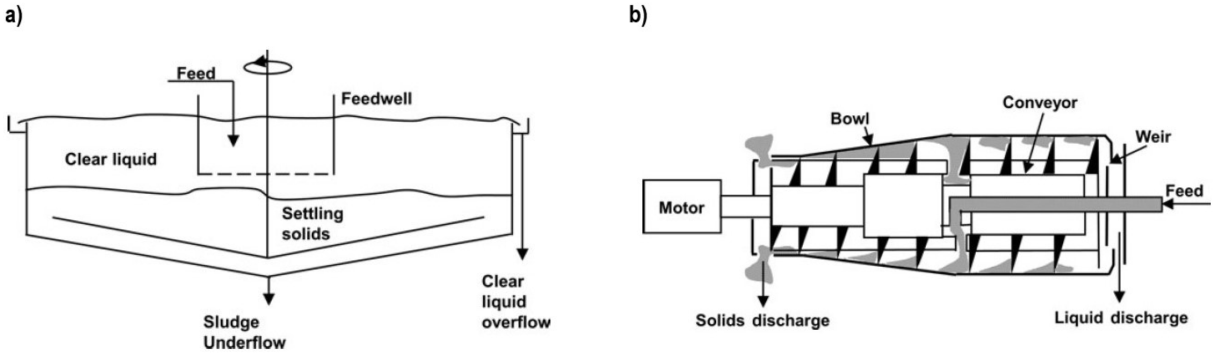

Figure 1-1 Exemplary schematic depiction of techniques for physical solid-liquid separation: thickener **(a)** and decanter centrifuge **(b)**. Both pictures derived from Haan et al., 2020 [58], creator unknown.

Settling time can be reduced by applying a centrifugal force within the separation vessel [50]. This allows the additional separating of finer particle sizes, which are usually stable in the gravity field [58]. The most common technical device used for separating animal manures or digestates is the **decanter centrifuge** (e.g., horizontal decanter, Fig. 1-1b). The substrate is introduced through an axial tube into the interior of the centrifuge. The centrifugal force generated by the continuous turning of the cylinder separates the feed into a solid and a liquid phase. The solids settle on the inner wall, which has a conical shape, and are then transported to the smaller end by a helical screw conveyor. At the same time, the liquid phase, which remains in the middle of the cylinder, moves to the larger end. Cylinder and conveyor operate at different speeds [50,58]. In general, the separation efficiency of a centrifuge depends on various factors, such as type of centrifuge, composition of the introduced substrate, feed rate, retention time, G-force, dewatering volume, etc. [50,56,58,60]. A decanter centrifuge can effectively retain P and DM in the solid phase. This effect is reported to be higher after preceding anaerobic digestion than without pre-treatment [50,60,61].

Solid-liquid separation can also be performed with various screen or press separators. Especially after treating with either a belt or screw press separator, the solid fraction is characterized by lower water content than after separation with a decanter centrifuge

[62]. This is achieved due to the additional pressure applied during the separation process. In the case of the **screw press separator** (Fig. 1-2), the digestate is conveyed by the screw along a drum screen. Particles characterized by a size smaller than the slit width of the screen pass the screen and thus the liquid fraction is generated. At the same time, the held-back solids are compressed and led out of the separator by the rotating screw [62]. During the compressing, additional water is removed from the solid filter cake [56]. This is additionally enhanced due to the pressure induced by the flaps at the solid output [54].

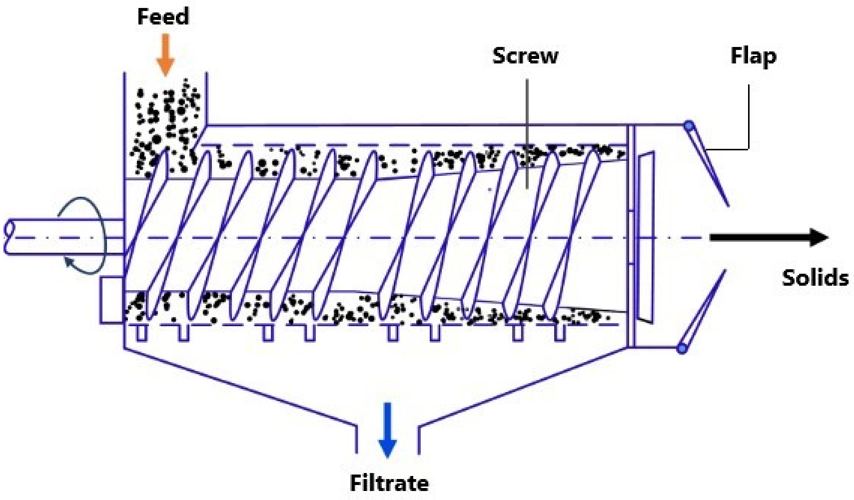

Figure 1-2 Schematic depiction of a screw press separator. Picture derived from Fechter [62] and was adjusted with the kind permission of the creator.

The separation efficiency of a screw press primarily depends on DM content of inserted substrate, particle size distribution and slit width of the screen [55–57]. Furthermore, relative rotational speed of the screw and consequently retention time, or the compression pressure of the flaps can also affect the separation process [63].

Retention time and compression pressure are also important factors influencing the efficiency of a **belt separator**. Here, a gravity dewatering of the feed (at the beginning) is combined with a subsequent pressure filtration by compacting the substrate between two filter belts, which pass over various pressure rolls [62]. Depending on the mash size and rotation speed of the filter belts as well as the induced pressure during filtration, the belt separator is suitable for generating a DM-rich solid fraction (up to 40% DM content) and a particle-free filtrate, respectively [50,62].

To better retain nutrients like N and P, and DM in the solid fraction during separation, **chemical treatments** can be additionally applied prior to physical separation. Common methods are coagulation, flocculation as well as struvite crystallization (mainly used to improve the removal of P and NH_4-N from slurry or digestate) [50,62]. Here, the aggregation of colloidal particles and, therefore, their improved separation are realized by adding of (i) multivalent cations in the form of metallic salts (e.g., Fe^{3+} in $FeCl_3$), and, subsequently, of (ii) flocculants, i.e. cationic polymers such as polyacrylamide [50,62].

In order to achieve a more accurate separation of solids from liquids and a better partitioning of contained nutrients, further treating of both generated fractions (i.e., separated solid or separated liquid) is necessary.

1.3.2 Post-treating of separated liquid fraction

A simple post-treatment, which is applied to centrate or filtrate (i.e., the liquid fraction resulting from separation with decanter centrifuge or screw press), is the separation by a **vibrating screen**. Depending on its mesh width (usually in the range of 150–250 µm), the vibrating screen can retain further fine solid particles, which are still in the liquid fraction at the end of the physical separation [62].

If more efficient particle removal is targeted, the filtration of the separated liquid fraction using various **membrane techniques** can additionally be applied. This filtration especially aims at generating a clean effluent with the characteristics of portable water, and a residual, nutrient-rich stream [62]. Membrane techniques primarily differ in particle size that should be retained, membrane structure (i.e., symmetrical or asymmetrical membrane type [64]), module design, and driving force [64]. In this thesis, only ‘pressure-driven’ membrane techniques are considered, namely the most common ones used in the industry: microfiltration, ultrafiltration, nanofiltration, and reverse osmosis. The functional principle of those separation techniques consists of a membrane, which splits the feed into a retentate stream and a permeate stream. The permeate passes through the membrane and is rich in particles, which are smaller than the pores of the membrane. The retentate, in turn, is the concentrated liquid residue, which leaves the membrane module without passing [64] and can be further treated or fed back into the fermenter.

During **microfiltration**, particles in the size range of 0.1–10 µm, such as microorganisms, colloids, etc., are separated from the liquid stream [50,64–66]. The process occurs as a ‘cross-flow’ filtration (i.e., the feed stream flows across the membrane surface) at a transmembrane pressure between 100 kPa and 200 kPa, usually [50,67]. The membrane module consists, in most cases, of porous tubes, as shown in Fig. 1-3. Microfiltration can effectively retain 75% of suspended solids and >80% of P [65].

Higher retention of macromolecules and colloids can be achieved using **ultrafiltration** – a pressure-driven cross-flow filtration performed with membrane filters, which are characterized by smaller pore sizes than for microfiltration. Here, water and microparticles, such as solvents and ions, can pass through the membrane (pore size in the 1–100 nm range) [64–66]. In the case of ultrafiltration and microfiltration, the feed must be pre-treated, for example by a solid-liquid separation performed with decanter centrifuge, in order to reduce the particle load and decrease the viscosity. This lowers the risk for clogging of the filter and consequent fouling [50,62].

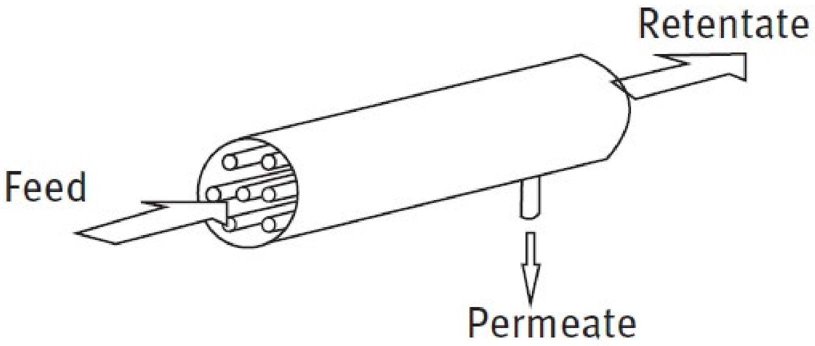

Figure 1-3 Schematic depiction of a tubular membrane module utilized for micro- and ultrafiltration. Picture derived from Haan et al. [64], creator unknown.

For the removal of low molecular weight solutes (e.g., synthetic dye, dissolved salts, etc., larger than 200 Da [65,66]), which are still present in the permeate generated by ultrafiltration, the application of **nanofiltration** and/or **reverse osmosis** is common. In both cases, nonporous membranes are used for the separation. Nanofiltration is a pressure-driven ‘submicron filtration process’ [64], while, for reverse osmosis, the water flux is related to the difference between the pressure applied to the feed and the osmotic pressure. A water flux occurs through the membrane when the applied pressure is higher than the osmotic pressure [66]. Common membrane modules for nanofiltration and reverse osmosis are, i.a., spiral-wound module and hollow fiber module [64,66]. In general, reverse osmosis achieves the rejection of up to 99% of dissolved salts [65,66]. Regarding the rejection of NH_3, both techniques have a drawback. According to Masse et al. [65], simple, one-stage reverse osmosis can retain less than 40% of NH_3 contained in the feed. For substantial NH_3 rejection, at least two successive running reverse osmosis modules are recommended [67]. Here, the addition of, e.g. sulfuric acid, to the permeate resulting from the first module should be implemented as an intermediate treatment to trap and scrub the residual NH_3 due to the generation of ammonium sulfate [62,67].

Further processing of separated liquid digestate does not only target the effective removal of residual solid particles but also aims at a volume reduction of the initial raw digestate. In this context, the removal of water from the liquid by **evaporation** is also a suitable approach and a common practice. In that case, the liquid fraction is inserted into a heated, stainless steel vacuum vessel. The evaporation process utilizes the heat generated by a combined heat and power (CHP) plant. The temperature needed for boiling the liquid phase is reduced below 100 °C by applying low pressure (80–400 hPa) [62,67]. As a result of these conditions, a vapor phase is formed, which consists of water and volatiles such as CO_2, NH_3, and other gases [62]. Next, the vapor phase is removed from the vacuum vessel and the contained NH_3 is stripped before condensing [50,62]. To scrub NH_3 from the vapor-gas mixture, a washing column is used, which can operate with various scrubbing media (e.g., sulfuric acid) [62,68,69]. According to Ukwuani et al. [70], the optimum conditions for high NH_3 recovery by vacuum evaporation are 65 °C and about 250 hPa. Furthermore, the water content of separated liquid fraction can be reduced by up to 70%, when a one-stage vacuum evaporator is utilized [62]. For two- or three-stage evaporation units, which include many evaporators in series, this effect is significantly higher [50,62,67].

1.3.3 Post-treating of separated solid fraction

Volume reduction due to water removal can be also achieved by **thermal drying** of the untreated or treated digestate and manure, e.g., after mechanical separation performed with screw press or decanter centrifuge. Here, the water is removed by convection via a drying agent (in this case hot air), which is supplied to the material surface or passes through its body [71].

If a reduction of initial water content without applying pre- or post-treatments is targeted, the drying unit can be installed as an intermediate step between the post-fermenter and the final storage tank [62]. In this case, about 50% reduction of the total initial volume of digestate can be attained [62].

In the case of drying as post-treatment applied to the separated solid fraction, various technologies are currently available. Examples are feed-and-turn dryer, belt dryer, greenhouse dryer, etc. The first two technologies usually use the CHP-waste-heat, while the last primarily operates with solar energy. In the case of a belt dryer (Fig. 1-4a), the material is fed into the drying chamber, where it is placed on a circulating belt. A hot-air stream flows across the material's surface, passes through its body, and removes the water [71]. The operation of a greenhouse dryer is explained here using the example of a dryer produced by Thermo-Systems (Germany) and has already been shown in the studies of Maurer et al. [29,72] and Bux et al. [73]. In brief, the solid material is evenly spread out on the floor of the greenhouse and continuously mixed by a small robot, the 'electric mole' (Fig. 1-4b). The fresh air enters the greenhouse through ventilation flaps and is distributed by various fans. The saturated air stream leaves the greenhouse through the exhaust air fan. For drying of the material, solar energy and such provided by the CHP-waste-heat are utilized [72,73]. Solar drying can achieve a total volume reduction of up to 97% [73]. At the same time, high NH_3 losses occur during the process [72]. However, to counteract this drawback, a subsequent NH_3 scrubbing from the exhaust air can be performed as described previously for vacuum evaporation.

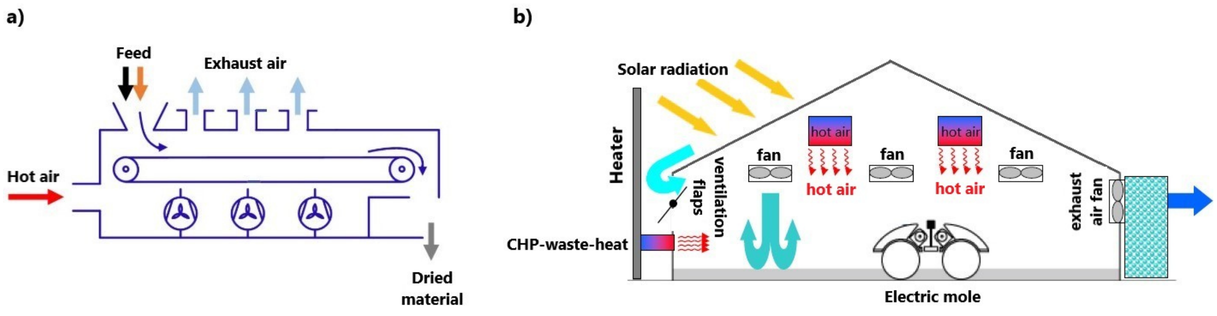

Figure 1-4 Exemplary schematic depiction of techniques for thermal drying: belt dryer **(a)** and solar greenhouse dryer **(b)**. Pictures derived from Fechter [62] (a) and Karle [74] (b), and were adjusted with the kind permission of the creators.

For further volume reduction and simultaneous concentrating of contained nutrients, the **pelletizing** of dried digestate or manure is an option. Here, two different types of technologies are available: (i) diskpelleter (see Fig. 1-5), suited for molding of solid substrate with a moisture content <25%, and (ii) extruder, which shows best performance at 40% water content of the substrate [52]. In both cases, the substrate is forced into the channels of a die, where it is compressed [52,63]. This is realized by the grinder rollers of the diskpelleter, or the conveyor screw of the extruder [52,63]. As a result of the applied pressure and the friction occurring between solid and channel wall, the temperature of the substrate significantly increases during the compression process [75] and, consequently, water evaporates [52], while the lignin structure on the pellet surface stabilizes. In general, pelletizing has the potential to reduce the initial volume of the substrate by 10–50% [52]. In addition, such pellets are characterized by a high P availability [30].

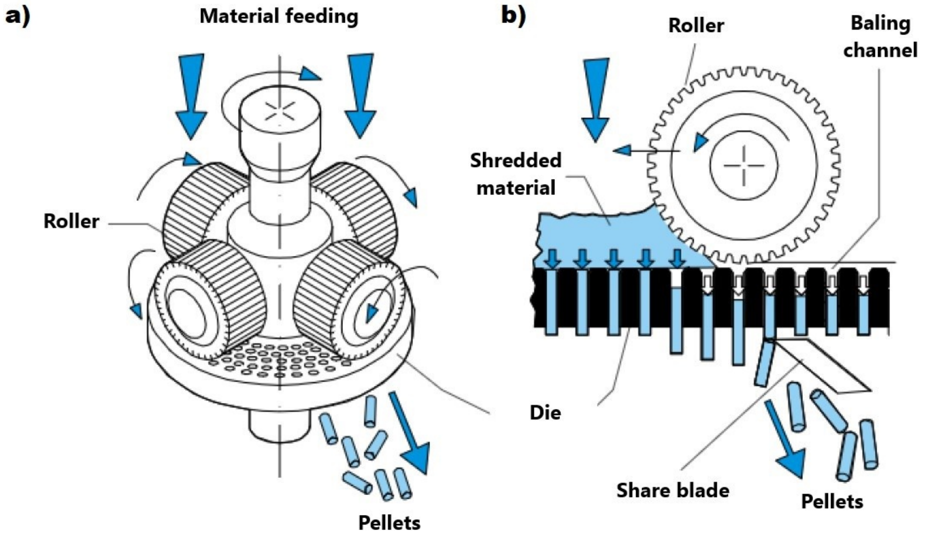

Figure 1-5 Schematic depiction of a diskpelleter, **a:** overview, **b:** cross-section. Pictures derived from Kaltschmitt et al. [76], creator unknown.

1.3.4 NH_3 Stripping

Another technique for efficient separating and concentrating of nutrients is direct N removal from digestate by NH_3 stripping. This technique is applied, for example, at the Benas farm located in Ottersberg, Germany. In brief, it consists of three consecutively operating units: stripping column, scrubbing column, and filter press. The raw digestate is fed to the stripping column, where it is heated up to 80-90°C [62,69]. At a continuously increasing pressure (0.1–0.8 bar), the production of CO_2 and NH_3 is promoted. Next, the stripped gas stream is cooled down and transferred into the scrubbing column, where the contained NH_3 is trapped by an adsorption agent (dehydrate calcium sulfate in the case of the Benas biogas plant). The resulting suspension, which consists of ammonium sulfate and liming substrate (calcium carbonate), is finally introduced to a filter press to separate both components [62,69]. The N-depleted digestate generated from the stripping column is fed back to the fermenter, which leads to a reduction of the total N content of the raw digestate [69]. Overall, the total N content of the product (i.e., ammonium sulfate) can be increased by a factor of 6 in comparison to the raw material [69].

1.4 Knowledge gaps and study goals

The above-mentioned techniques were studied to a certain extent in earlier works, which mainly addressed: (i) improving the efficiency by optimizing technologies and operation parameters, (ii) suitability of different feedstocks or substrate mixture for anaerobic digestion, (iii) economic feasibility and profitability of the applied technique(s), and (iv) practical value of produced digestates for the agricultural sector and the environment. It was previously demonstrated that the separation efficiency depends, among other things, on utilized technique and feedstock composition [50,55–57,61]. Decanter centrifuges, for example, are characterized by a high efficiency but require non-fibrous input material, such as pig slurry or sludge [55]. Concerning the techno-economical assessment, Bolzonella et al. [33] stated the following trend in increasing order of capital and operational costs for subsequent digestate processing: NH_3 stripping < drying < membrane techniques. Fertilization with raw or processed digestates positively influences soil aggregate stability, microbial population, and enzyme activity [77–80]. However, proper application is of major importance in order to protect the environment. This requires fundamental knowledge about nutrient availability in such organic substrates.

1.4.1 Research hypotheses

Although various factors influencing digestate properties have been extensively studied (e.g., [41,57,81–83]), only few data were found on changes in N concentration and water content during downstream processing. Additionally, most of the previous works examined pilot facilities [32,61,84,85] or biogas plants including only a partial digestate processing [29,30,32,57]. Therefore, the main goal of the current thesis was to create a more comprehensive picture of ‘the fate of N as a result of digestate processing’. For this purpose, two commercial, full-scale biogas plants were selected and the digestates generated during the different steps of the entire processing chain were evaluated. Each biogas plant represents a practical example for processing the separated solid or liquid fraction, including the precursor ‘raw digestate’.

In general, subsequent processing reduces the water content and the total mass of the substrate [33,56,73,86]. The first processing step, mechanical solid-liquid separation, generally shifts most of the initial water and N (especially NH_4-N) to the liquid fraction [41,57,87]. In both evaluated biogas plants, the separation was performed by a screw press. The applied techniques, which led to a reduction in water content and consequently a concentration of nutrients, were solar greenhouse drying (solid fraction) and vacuum evaporation with partial NH_3 scrubbing (liquid fraction). It was previously shown that 50% of the total initial digestate mass can be removed from separated liquid by specific NH_3 stripping processing cascades or via ultrafiltration and reverse osmosis [32,86]. For drying with/without subsequent pelletizing of solids, lower removal rates were reported [52,62]. Expecting a similar tendency for the studied liquid and solid processing chains, the first research hypothesis was formulated as follows:

(i) liquid processing reduces the water content more effectively than solid processing.

As already mentioned, treating both separated fractions also changes the nutrient concentration in the subsequent products. When focusing on N, Awiszus et al. [84] noted a considerable loss of about 50% of total N during digestate drying with a two-belt conveyor dryer. Nonetheless, concentration of N in the final product can be achieved. This was, for example, shown for ammonium sulfate produced via ultrafiltration and subsequent reverse osmosis (up to 18-fold) [32] or in the case of NH_3 stripping from raw digestate with gypsum as scrubbing media (~6-fold) [69]. As total N partitioning is strongly affected by the initial mechanical separation in favor of the liquid chain and, especially in solid processing, considerable losses may occur, it was assumed that the N recovery follows this trend up to the evaluated final products (pellet and ammonium sulfate solution (ASS)). Consequently, the second hypothesis was defined as:

(ii) liquid processing results in a higher N recovery than solid processing.

Hypotheses (i) and (ii) were addressed in chapter 3 of the current work. It primarily describes the effect of subsequent processing on FM and N partitioning in the digestate products derived from continuous, full-scale biogas production.

In order to expand the picture of the ‘fate of N’, losses during storage, transport, and utilization must also be taken into consideration. They are particularly relevant with a view to product properties/value and environmental protection. Since most of the commonly applied techniques for digestate processing are performed in closed devices, such as screw presses, decanters, vacuum vessels, or membrane modules, N losses have so far only been measured during thermal drying. As mentioned before, between 7 and 50% of total N volatilizes as NH_3 during drying, depending on technology and process conditions [72,84]. Regarding storage and transport, gaseous N losses (N_2O, NH_3, and N_2) were primarily reported for the solid fraction and are mainly linked to the quality of storage and transport facilities [45,51]. Digestate utilization is also associated with N losses into the atmosphere that occur during and after application to soils [46,88,89], or losses to the groundwater bodies (e.g., via NO_3^- leaching) [90,91]. Early studies mainly took into account the evaluation of N losses from individual organic substrates (untreated and digested animal residues) or assessed the effect of mechanical separation with and without preliminary digestion. As shown by Holly et al. [89,92], fertilization with the separated liquid fraction induced lower GHG emissions from soil than with untreated substrate. Similar findings were reported by Askri et al. [93], who also highlighted the potential of the solid-liquid separation to reduce the N_2O release after digestate application to soils. The authors assumed that the separation of organic matter (especially organic C) and mineral N into solid and liquid fractions was the main reason for the lower N_2O release compared to raw digestate, as it decreases the N_2O production from denitrification [93]. Based on this assumption, a similar trend was expected in terms of the complete downstream processing of raw digestate, since further processing aims at better separation of C-containing particles from the N-enriched liquid. Consequently, hypothesis three was formulated as follows:

(iii) raw digestate releases more N_2O than the respective intermediate or end products after application to soil.

Another factor that controls N_2O release is the mineral N content of organic fertilizers. It was previously assumed that a higher NH_4-N concentration in fertilizers increases the N_2O emission rate after application to soil [92,94]. In this context, Fanguero et al. [95] noted that the addition of organic substrate to soil (in this case slurry), which contains a high amount of NH_4-N and available C, not only stimulates rapid initial nitrification, but also denitrification activity. Furthermore, the authors demonstrated that the finest organic particles of a fertilizer contain the highest amount of readily degradable C and are characterized by the highest N availability [96]. As described in various studies, most of DM, total C, and organic C is shifted to the solid fraction, while NH_4-N and small particles mainly remain in the liquid [49,55,57,60]. Therefore, assuming that the simultaneous application of sufficient amounts of easily degradable C and NH_4-N in the liquid digestate directly influences the N_2O emission rate from soils, the following hypothesis was made:

(iv) solids release less N_2O than liquids after application to soil.

Chapter 4 deals with the 'effects of digestate processing on soil-borne N_2O emissions' and shows data collected in field and lab experiments. It presents a comparison between untreated and processed digestates in terms of their potential to reduce N_2O emissions after soil application. Furthermore, the relation between processing method, resulting digestate composition, and N_2O release after digestate application was investigated.

It was generally expected that a higher degree of processing leads to lower N_2O release due to a continuously decreasing amount of easily available C, which serves as an electron donator for denitrifiers [97]. However, in the current work, an opposite trend was observed after the application of pelleted digestate to soil. The significant increase in emissions cannot be explained by the main drivers for N_2O production in soil (e.g., moisture and mineral N content). So far, only a few studies reported similar results and assumed different reasons, such as simultaneous occurrence of nitrification and denitrification [98], or denitrification activity inside the pellets [99]. In order to investigate the mechanisms responsible for the unexpected N_2O release from pellets, the last research hypothesis was stated:

(v) N_2O release from pellets is caused by the activity of autochthonous microflora already present in the pellet body.

It was also assessed whether pellet size and moisture additionally influence the N_2O emissions. The experimental results of these aspects are presented in chapter 5.

1.5 Data repository

Raw data sets used for the preparation of chapters 4 and 5 are available online at https://osf.io/6gvc5/?view_only=0b277d9adfad403c9ad66ad192353859.

Here, metadata are provided, which accurately describe the experimental set-up. Besides that, additional raw data of the research project "GÄRWERT – GÄRprodukte ökologisch optimiert und WERTorientiert aufbereiten und vermarkten" (grant numbers 22402312 and 22402113) are summarized, which are not presented in the current thesis.

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2 Collection and composition of digestates

Raw and processed digestates evaluated in the current work were obtained from two biogas plants located in South Germany. Biogas plant 1 (BGP1, geographic position 49°14'29.1"N 9°38'28.9"E) digested a mixture of cattle and poultry manures, pig slurry, energy crops, pomace, and grape marc. In addition to cattle manure and pig slurry, the feedstocks used in the second biogas plant (BGP2, located at 48°50'35.7"N 10°50'24.2"E) were silage maize, cereal and grass silage, and cereal grist. Detailed information about the share of the different feedstock materials is given in chapter 4.3.1.

Digestates were collected in 2015 and 2016. The digestate sampling of each biogas plant occurred once a year on the same day. Consequently, time-related fluctuations in share and composition of feedstock materials could not be taken into consideration. Since the actual N concentration of digestates was of major importance for the preparation of the experiments presented in this work, collection and chemical analysis of digestates took place immediately before starting with the practical work. In order to prevent progressing conversion of organic matter and thus minimize gaseous N losses before utilization, collected digestates were kept in closed containers in a dry and cool storehouse. For homogenization and to prevent the forming of settling and floating layers, the liquid digestates were stirred with a hand agitator (Collomix GmbH, Germany) directly before utilization.

The analysis of evaluated digestates included the determination of pH, contents of DM, total carbon (C_t), and macronutrients, as well as the share of the recalcitrant fractions lignin, cellulose, and hemicellulose. Description of the analytical methods applied for measuring pH, DM, C, N, and fiber fractions, and respective analysis results are shown in chapter 4.3.1. The contents of the primary and secondary macronutrients phosphorus (P), potassium (K), sulfur (S), magnesium (Mg), and calcium (Ca) were determined after aqua regia digestion, using inductively coupled plasma optical emission spectroscopy (ICP-OES VISTA Pro, Varian).

Tables 2-1 and 2-2 summarize the share of the main nutrients contained in the tested digestates. Nitrate was detected only in dry solid and pellets in both sampling years. The NO_3–N content of the other digestates fell below the detection limits (<0.001% of total FM).

Table 2-1 Concentrations of primary macronutrients (g kg^{-1} DM) (nitrogen (N), phosphorus (P) and potassium (K)) present in the tested biogas digestates.

Digestate	**N**		**P**		**K**	
	g kg^{-1} DM					
	2015	2016	2015	2016	2015	2016
Raw digestate (RD1)	64.1	47.6	10.6	5.7	45.1	40.0
Sep. liquid (SL1) [1]	86.5	78.4	14.8	8.0	66.3	69.9
Sep. solid (SS1) [1]	25.2	18.6	5.4	3.8	11.2	15.6
Dry solid (DS1) [2]	25.6	21.4	9.8	4.7	36.5	26.2
Pellet (P1) [3]	35.1	34.9	10.3	5.6	35.1	36.5
Raw digestate (RD2)	96.1	68.6	10.3	8.0	92.1	60.8
Sep. liquid (SL2) [1]	103.4	106.4	10.6	4.7	98.1	97.8
Sep. solid (SS2) [1]	28.1	32.1	9.5	6.3	17.9	25.8
Concentrate (CC2)	48.8	38.7	13.7	6.7	94.7	84.9
ASS2 [4]	185.8	202.9	<0.01	0.03	<0.03	0.9

Number behind treatment abbreviations (e.g., RD1, SL2): number of respective biogas plant; [1] Sep. liquid/solid: separated liquid/solid fraction; [2] 1.3 g NO_3–N kg^{-1} DM (2015) and 1.6 g NO_3–N kg^{-1} DM (2016); [3] 3.6 g NO_3–N kg^{-1} DM (2015) and 2.7 g NO_3–N kg^{-1} DM (2016); [4] ASS2: ammonium sulfate solution.

Table 2-2 Concentrations (g kg^{-1} DM) of sulfur (S), magnesium (Mg) and calcium (Ca) present in the tested biogas digestates.

Digestate [1]	**S**		**Mg**		**Ca**	
	g kg^{-1} DM					
	2015	2016	2015	2016	2015	2016
RD1	4.0	3.95	5.4	5.6	16.8	18.3
SL1	4.9	4.7	7.3	8.3	23.3	23.1
SS1	2.7	4.7	3.3	3.8	7.8	10.2
DS1	4.4	3.4	5.4	4.8	16.4	14.0
P1	4.2	4.1	5.8	5.6	17.5	15.5
RD2	5.5	4.1	4.4	7.9	21.7	16.0
SL2	5.6	5.4	4.4	5.2	25.7	21.5
SS2	2.8	3.4	6.4	6.2	8.6	8.4
CC2	5.3	5.7	6.7	6.7	27.1	21.7
ASS2 [2]	247.3	230.0	<0.01	0.1	<0.03	0.3

[1] number behind treatment abbreviations: number of respective biogas plant; [2] ASS2: ammonium sulfate solution.

3 N partitioning during digestate processing[*]

This chapter displays the processing-related changes in FM, N_t, and NH_4–N in detail, which are represented as mass flows of the respective compound based on a fixed, predefined total amount of input material.

3.1 Abstract

The high water content and low nutrient concentration of digestate complicate its storage, transportation, and utilization. Subsequent digestate processing can effectively remove water and influence nutrient partitioning among digestate fractions and final products.

The current study was carried out to evaluate the performance of two typical digestate processing chains, solid and liquid ones, respectively, and to give practical recommendations for optimization. Two fully operating biogas plants with advanced heat utilization were considered as data sources. The digestate mass flow balance of dry matter (DM), water, total N (TN), and ammonium-N mass flows was performed and the efficiency of the examined processing units was calculated.

It was found that solid-liquid separation of raw digestate shifted 73–87% of TN and 60–93% of NH_4–N to the liquid phase. Subsequent drying of separated solid fraction removed about 6% of the initial water and required 84% less thermal energy per kg N recovered than the processing of separated liquid. The final product, pellets, contained 14% of initial TN, but only 2% of initial NH_4–N as a result of microbial conversion of inorganic N during drying.

Vacuum evaporation of separated liquid fraction removed 34% of the initial water and left a DM-rich concentrate. At the same time, an ammonium sulfate solution (ASS) containing 21% of initial TN and 34% of initial NH_4–N was produced.

Both evaluated processing chains showed specific advantages and challenges. Solid products were characterized by a high share of recalcitrant organic compounds and

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could serve as a soil improver. Liquid processing concentrated plant-available N in ASS, which could be used as valuable inorganic fertilizer.

Keywords: N mass flow; solid-liquid separation; solar drying; vacuum evaporation

3.2 Introduction

The excess of nitrogen (N) and phosphorus (P) represents a global issue. Those nutrients are particularly concentrated in regions with intensified livestock and crop production. Biogas plants, which utilize animal manures, energy crops, or different kinds of organic waste [1,2], aggravate this problem due to the generation of additional organic effluents, referred to as digestates [3,4].

During biogas production, anaerobic digestion converts organic carbon into methane, used for transportation or energy generation [5], and transforms most of the organic N into mobile, mineral NH_4^+ [6]. The residual digestate still contains significant amounts of organic compounds and plant-available nutrients (especially N and P) and can be used both as soil amendment and mineral fertilizer.

However, inappropriate and excessive utilization cause soil acidification, surface water eutrophication, and groundwater pollution [7–9]. As for animal manures, legal regulations also restrict the timeframe and application amount, leading to the side issue of assuring a sufficient and prolonged storage capacity [10,11]. As a consequence, nutrients accumulate locally, unless they are frequently removed from the source areas.

Since untreated manures and digestates are characterized by high water content [12] and low nutrient concentration, transportation over large distances proves to be unfeasible. Moreover, the nutrient availability of digestates varies with their chemical and physical characteristics, which are influenced by feedstock, treatment methods, and process parameters [13,14].

In order to improve not only the digestion process [15] but also the composition and properties of the digested effluent [16,17], pre- and post-treatments are applied. Processing techniques, such as solid-liquid separation or membrane filtration, are commonly used to reduce water content and concentrate nutrients in the digestate [18,19]. A combination of ultrafiltration with reverse osmosis, for example, results in a reduction of total initial volume by 49% and a concentrating of N up to 31% in the form of ammonium sulfate [20]. Drying the digestate can remove about 90% of the initial moisture [16,21], but a significant amount of mineral N is lost in the exhaust air in the form of ammonia (NH_3) [21,22]. Gaseous N losses were also reported during storage [23] and after application of digestates to soils and vary depending on substrate composition and aggregate state [24,25].

Several technologies for NH_3 recovery from gaseous streams are available on the market, which mainly utilize three different scrubbing media: nitric acid solution, sulfuric acid solution, and calcium sulfate dihydrate (gypsum) [21,26,27]. While during application of the first two, salts are formed, the latter produces a lime-based fertilizer mixture [26]. To the authors' knowledge, the most common medium is sulfuric acid solution due to its low price and easy availability. Nitric acid is rather expensive and produces explosive ammonium nitrate, which also requires official permission/registration. Gypsum, on the other hand, might be cheap and available, but the technology is patented and the final product must either be treated by a filter press or used as some form of mixed fertilizer [26].

Digestate treatment methods also influence the partitioning of the primary plant nutrients N and P. In the case of the common solid-liquid separation, for example, P mainly accumulates in the solid phase [21,28], while N is greatly shifted into the liquid [21,29]. Since processed digestates are suitable organic amendments with a good fertilizing value [30,31], the options for pre- and post-treatment of digestate should be considered not only from a technical point of view but also with regard to the generation of marketable organic fertilizers, such as pellets or ammonium sulfate, and their characteristics. Up to now, most of the previous research focused on improving the process parameters or selecting the superior technique. The current work shows the partitioning of the most essential plant nutrient, N, and gives recommendations for digestate processing from a practical point of view. For that purpose, a balancing of TN and NH_4–N mass flows was performed for two different commercial, full-scale biogas plants. This framework allowed us to evaluate valuable data from practical operation. Both selected plants were characterized by downstream processing cascades, which enable an almost complete heat utilization during digestate upgrading. The following treatment steps were considered in the evaluation: solid-liquid separation of raw digestate, drying and pelletizing of separated solid fraction, and vacuum evaporation of the separated liquid fraction with partial NH_3 stripping to produce ammonium sulfate. The focus was placed on (i) the effect of processing on fresh matter (FM) and nitrogen partitioning, (ii) the determination of total mass reduction, and (iii) the recovery of initial N in the final products.

3.3 Materials and methods

3.3.1 Digestates

Digestate characteristics were derived from a previous work [25]. Sampling of the digestate was carried out once a year on the same day and in two biogas plants [25]. Consequently, time-related variations resulting from different properties and composition of feedstocks, hydraulic retention time, fluctuation in temperature, etc. were not accounted for in our analysis. Since digestate samples from different years were tested in the aforementioned work [25] and their composition varied considerably, two raw digestates (i.e., one per biogas plant) characterized by similar DM and TN contents were chosen (see Table 3-1) and served as a reference for this research.

In general, both biogas plants have been supplied by energy crops in addition to animal manure and slurry. Detailed information on the fresh weight of the different feedstocks used in both biogas plants can be found in Petrova et al. [25]. Relevant chemical characteristics of digestates and data used for the calculations performed in this study are summarized in Table 3-1.

Table 3-1 Dry matter (DM, g kg^{-1} FM), total nitrogen (TN, g kg^{-1} DM), ammonium nitrogen (NH_4–N, g kg^{-1} DM) contents, and pH values of the initial raw digestates and the subsequent fractions and products obtained by the two processing chains at the two respective full-scale biogas plants. Data derived from Petrova et al. [25,32].

Biogas plant	**Product**	**DM**	**TN**	**NH_4–N**	**pH**
		g kg^{-1} FM [2]	g kg^{-1} DM	g kg^{-1} DM	
1	Raw digestate	79	64.1	30.2	8.1
	Separated liquid fraction	56	86.5	43.1	8.0
	Separated solid fraction	311	25.2	6.4	8.2
	Dry solid fraction	902	25.6	1.7	8.2
	Digestate pellets	889	35.1	4.3	7.7
2	Raw digestate	77	68.6	41.8	7.7
	Separated liquid fraction	47	106.4	60.8	7.9
	Separated solid fraction	174	32.1	14.4	8.9
	Digestate concentrate	136	38.7	6.5	8.9
	ASS [1]	278	202.9	193.7	2.4

[1] ASS: ammonium sulfate solution after vacuum evaporation.
[2] FM: fresh matter.

3.3.2 Digestate processing techniques

Raw digestate was separated into solid and liquid fractions in both the biogas plants. The first biogas plant (BGP1) further processed the solid fraction only, while in the second (BGP2), both the separated fractions were treated subsequently. However, only the liquid processing chain in BGP2 was considered here. Fig. 3-1 shows the respective processing chains and their corresponding products.

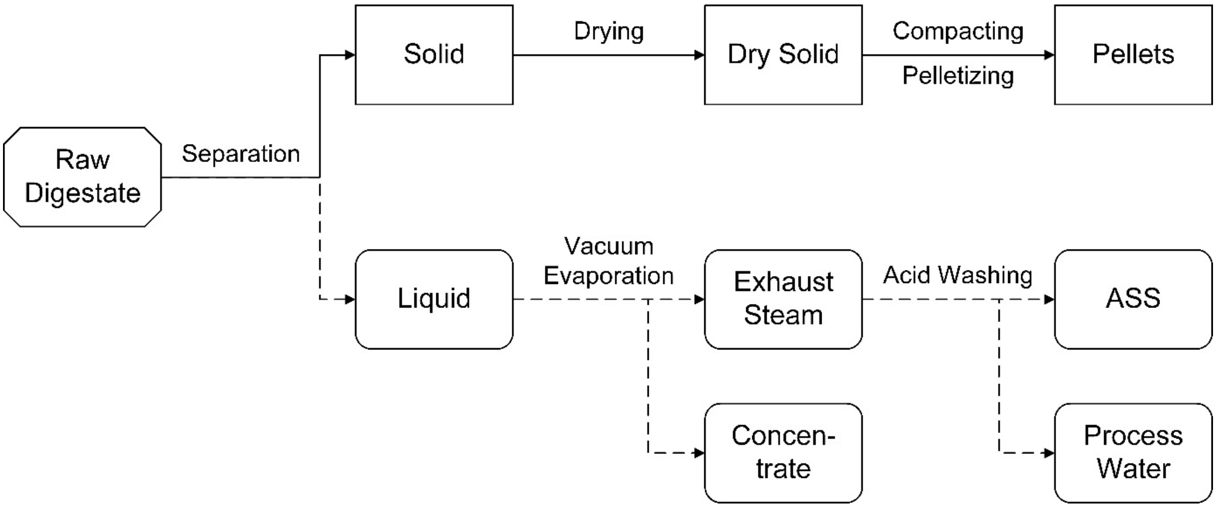

Figure 3-1 Digestate processing chains and their intermediate and end products; **solid lines**: solid processing in BGP1, **dashed lines**: liquid processing in BGP2; ASS: ammonium sulfate solution.

3.3.2.1 Mechanical separation of raw digestate

A screw press separated the liquid from the solid fractions in both processing chains. The raw digestate was inserted into a drum screen with a slit width of 0.5 mm. While the liquid and particles smaller than 0.5 mm passed the screen, the held-back solid was compressed and exited by a rotating screw.

3.3.2.2 Drying of separated solid

After solid-liquid separation, the separated solid fraction of BGP1 was dried to about 90% DM content. The process took place in a solar greenhouse dryer having a total size of 40 m in length, 12.8 m in width, and 4 m in height. Here, the substrate was turned and mixed by an electric mole. For further details on the technical characteristics of this process, the reader is referred to Maurer et al. [16,22].

3.3.2.3 Pelletizing the dried separated solid fraction

Prior to pelletizing, the dried solid fraction is usually conditioned, i.e., its DM content is adjusted to exactly 86% by rewetting, since the moisture content at the end of the drying process can vary depending on time and temperature. In the pelletizer of BGP1, pan grinder rollers forced the dried solid through a die with channels of 6 mm in diameter. During the compression, the substrate heated up, which led to partial evaporation of the remaining water and a change in the physical state of several components [32]. After exiting the baling channels, the compacted solid was cut into pellets with a diameter of 6 mm and an average length of 14 mm by a shear blade and cooled to ambient temperature [25,32].

3.3.2.4 Vacuum evaporation with partial NH_3 stripping from the separated liquid fraction

After the separation of the raw digestate, the liquid phase of BGP2 was concentrated in a two-step vacuum evaporator, described in a previous paper [25]. In brief, the evaporation of water and volatiles, such as NH_3 and other gasses, occurred in a stainless steel vessel at around 65 °C and 250 hPa. Afterward, NH_3 was removed from the exhaust steam in a washing column using sulfuric acid to produce an ASS. The remaining concentrate was pumped into a storage tank as soon as it reached a DM content of 15%. The vacuum evaporation utilized the heat from a combined heat and power (CHP) plant.

3.3.3 Mass balance

To gain an overview of changes in N concentrations due to the processing techniques presented in this study, a mass balance procedure was applied to the data derived from the chemical constituents of digestates (Table 3-1). As mentioned previously, raw digestates with similar DM and TN contents were used as data input for the following calculations. In the case of implausible variations in digestate composition, calculations were performed with the respective pre-product.

Total mass flows were quantified to determine TN and NH_4–N flows, i.e., the fresh matter of digestates in tons per year ($t\ a^{-1}$) that enters and leaves every processing step. To determine the FM mass flows of each processing step, the input FM mass flow of the first processing step must be known. Assuming no FM is lost, all FM mass flows that enter must also exit. The same is true for the DM mass flows, which are calculated by multiplying the FM mass flow with the DM content. Solving those linear equations completes the mass balance for the whole processing step, which is shown in the following. Afterward, NH_4–N and TN mass flows are derived by multiplying the corresponding FM mass flow with their NH_4–N or TN contents. Mismatches within the mass balance, i.e. mathematical differences between inflows and outflows, resulted from the variability of raw data and were described as mass balance delta (Δ). Fig. 3-2 exemplarily shows the balance of the flows through the screw press separator.

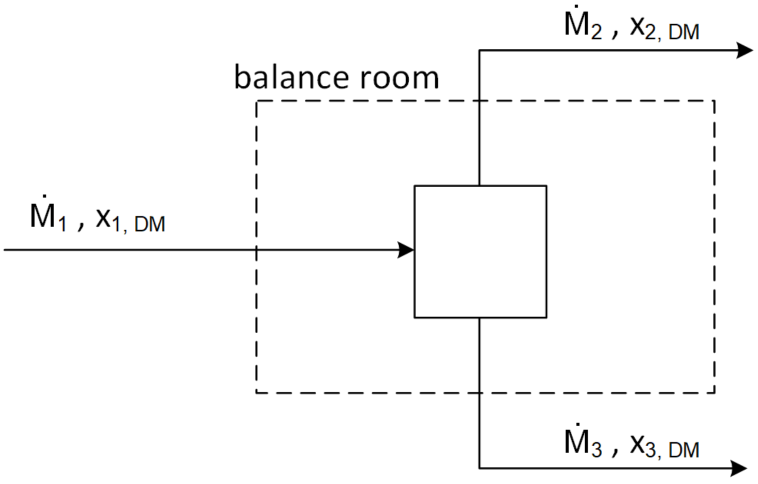

Figure 3-2 Mass flow balance through a screw press separator; $\dot{M}_1$: input mass flow, $\dot{M}_2$ and $\dot{M}_3$: output mass flows; $x_{1,DM}$, $x_{2,DM}$ and $x_{3,DM}$: dry matter contents of the respective substance flows.

Assuming mass conservation applies across the separator, the following equation represents the total mass balance

$$\dot{M}_1 = \dot{M}_2 + \dot{M}_3 \tag{1}$$

where $\dot{M}_1$ is the mass flow in t a^{-1} of raw digestate (as received) entering the separator, and $\dot{M}_2$ and $\dot{M}_3$ the mass flows in t a^{-1} of separated solid and liquid fractions, respectively. For both biogas plants, a total mass flow of raw digestate ($\dot{M}_1$) of about 10,000 t a^{-1} was used as a calculation basis. To set up the DM mass balance

$$\dot{M}_{1,DM} = \dot{M}_{2,DM} + \dot{M}_{3,DM} \tag{2}$$

DM mass flows in t a^{-1} of input ($\dot{M}_{1,DM}$) and outputs ($\dot{M}_{2,DM}$ and $\dot{M}_{3,DM}$) were applied correspondingly. Here, each flow is determined by the following equation:

$$\dot{M}_{i,DM} = \dot{M}_i x_{i,DM} \tag{3}$$

The DM mass flow in t a^{-1} results from the respective total mass flow ($\dot{M}_i$, in t a^{-1}), where i is the index of the respective mass flow shown in Fig. 3-2, multiplied by its corresponding DM content of $x_{i,DM}$. If equation (3) is universalized as follows

$$\dot{M}_{i,j} = \dot{M}_i x_{i,j} \tag{4}$$

it is also valid for calculating TN and NH_4–N flows, respectively (in kg a^{-1}). In these cases, $x_{i,j}$ is the concentration of the j-th nutrient (TN or NH_4–N) in the i-th mass flow.

The mass flows of the outputs, e.g., separated solid and liquid exiting the screw press separator, are determined with the following two equations:

$$\dot{M}_2 = \dot{M}_1 * \left(\frac{x_{1,DM} - x_{2,DM}}{x_{2,DM} - x_{3,DM}}\right) \tag{5}$$

and

$$\dot{M}_3 = \dot{M}_1 - \dot{M}_2 \tag{6}$$

Besides the mass flows, energy inputs are also presented. They were determined from the manufacturers' specific heat and electricity demand, as well as the plant operator's balance. Considering drying operations, first, the change in DM content was used to calculate the evaporated water. Then the specific demand for heat and electricity was used to work out the total energy flows per year. Since the available solar energy considered in BGP1 is dependent on the location rather than the manufacturer, the incident solar radiation was determined using solar intensity data reported by Recknagel et al. [33] and applied to the installation site. Furthermore, the calculation of the solar energy included the dimensions and orientation of the solar dryer.

All determined flows shown in the current work were plotted with the software E!-Sankey.

3.3.4 Separation index

To compare the results of this study with already published literature and to evaluate how efficient the single tested processing techniques are, a separation index was calculated according to Hjorth et al. [19] and described by the following equation:

$$E_t(x) = \frac{m_{x,output}}{m_{x,input}} \qquad (7)$$

The separation index E_t expresses the transfer of a specific compound x (DM, TN, or NH_4–N) into the resulting product as a proportion of its total input. In the case of the separation technique, $m_{x,output}$ is the mass of the considered compound presented in the separated solid or liquid fraction after passing the separator, and $m_{x,input}$ that of the same compound in the raw digestate. In addition, equation (7) was used to determine the subsequent removal of the respective compound due to further digestate processing and thus to assess how efficient the downstream processing techniques are. Here, $m_{x,output}$ is the mass of the compound in the product, for example the TN or NH_4–N content in the concentrate after the vacuum evaporation run on the separated liquid fraction.

3.3.5 Statistical analysis

To quantify the effect of DM and water contents on the distribution and transport of TN and NH_4–N during the different digestate processing steps, two linear regression models were run using the statistical package SigmaStat integrated in the software SigmaPlot (v 11.0).

Deviations between in- and outflows of ≤5% were not discussed in the following.

3.4 Results

3.4.1 Total mass and energy flows within the processing chains

Raw digestate of both biogas plants contained about 92% water and 8% DM (Table 3-1). The mechanical separation split the total mass flow of approximately 10,000 t a^{-1} (Fig. 3-3) as follows: 91% (liquid) to 9% (solid) in BGP1 and 77% to 23% in BGP2. At least 79% of the initial amount of water from raw digestate was shifted to the liquid after separation, while the partition of DM fraction varied depending on the biogas plant. In BGP1 most of the initial DM was moved to the separated liquid (502 vs. 274 t a^{-1}), and in BGP2 a share of 53% (solid) to 47% (liquid) was found (396 vs. 347 t a^{-1}). Since the separation of raw digestate was conducted similarly in both biogas plants, the electric energy (W in MWh) demands of the screw press separators were assumed to be similar, approx. 5.4 MWh a^{-1} each.

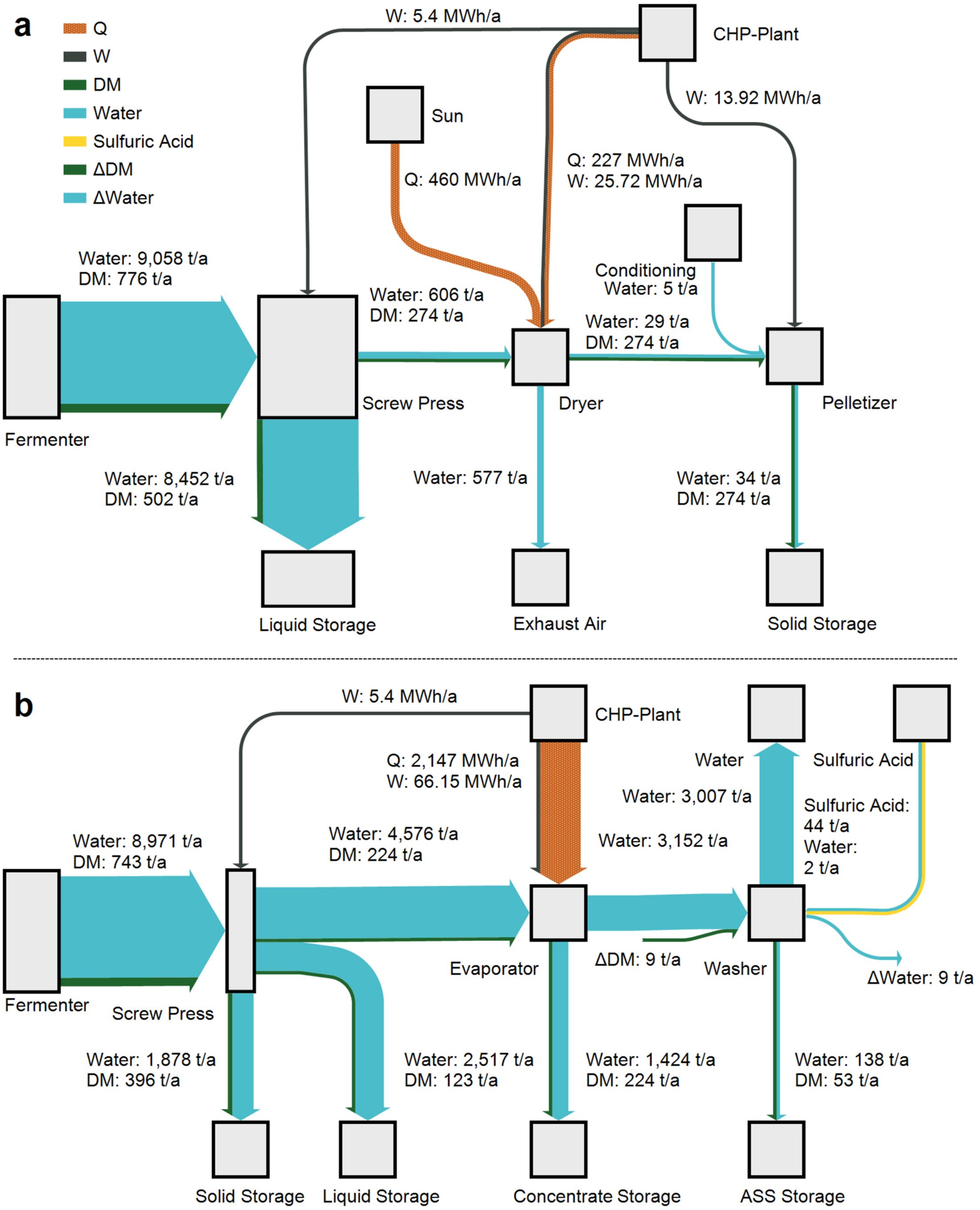

Figure 3-3 Total mass and energy inflows of examined processing chains, **a**: solid processing of BGP1, **b**: liquid processing of BGP2; Q: thermal energy demand (MWh a^{-1}); W: electric energy demand (MWh a^{-1}); DM: dry matter; ASS: ammonium sulfate solution; Δ: mass balance delta.

During the next processing step (i.e., drying of the separated solid fraction in BGP1) the incoming mass flow was reduced by about 66%. A water removal of 95% was achieved during drying. This is equivalent to a reduction of the total mass of only 6% compared to the initial mass of the raw digestate. During drying, about 67% of thermal energy (Q, 460 vs. 227 MWh_{th} a^{-1}, Fig. 3-3a) was provided by solar energy. The electric energy required for this processing step accounted for about 57% of the total electric energy demand in BGP1. The DM mass flow of 274 t a^{-1} remained unchanged during the solid fraction processing (Fig. 3-3a).

As the dry solid was conditioned prior to pelletizing, a small increase in total mass flow of about 2% was observed. Pelletizing consumed 31% of the electric energy required for the whole processing chain and accounted for 13.9 MWh_{el} a^{-1} (Fig. 3-3a).

Regarding the liquid fraction after separation (BGP2, Fig. 3-3b), only 65% of the total liquid mass flow was consecutively treated in a one-stage vacuum evaporator with a nominal capacity of 4800 t a^{-1} FM. The remaining 35% was directly moved into a separate liquid storage and was not relevant for the following results. The subsequent processing by vacuum evaporation split the incoming mass flow of 4800 t a^{-1} FM liquid into 34% concentrate and 66% vapor which was treated in the downstream scrubber. The DM fraction of the separated liquid (224 t a^{-1} DM, Fig. 3-3b) completely remained in concentrate. Furthermore, 31% of the water contained in separated liquid was shifted to concentrate, while 3% and 66% were found in ASS and process water, respectively. During the DM measurement of ASS, ammonium sulfate precipitates, which is shown as dry matter in the ASS stream (53 t a^{-1}, Fig. 3-3b). As this precipitation only occurs during analysis but not in the regular washing process, the DM value was not considered for further interpretation of the results. In general, the subsequent treatment of separated liquid led to a total mass reduction of 31% due to water removal from the washing column. During vacuum evaporation, the electric energy demand was about 92% of the total electric energy demand required for the whole liquid processing chain. It accounted for 66.2 MWh a^{-1}, while the thermal energy demand was 2147 MWh a^{-1}. In the last processing step (i.e., the washing of NH_3 from the exhaust steam in BGP2) the total energy demand of the washing column was negligible and is thus not shown in the graph.

3.4.2 Total N flows within the processing chains

After separation, most of the initial TN derived from raw digestate remained in the liquid fraction regardless of the biogas plant (about 87% in BGP1 and 74% in BGP2). The TN mass flows towards the separated solids accounted for 6890 kg TN a^{-1} (BGP1, Fig. 3-4a) and 12,711 kg TN a^{-1} (BGP2, Fig. 3-4b), which equals roughly 16% and 34% of the respective liquids.

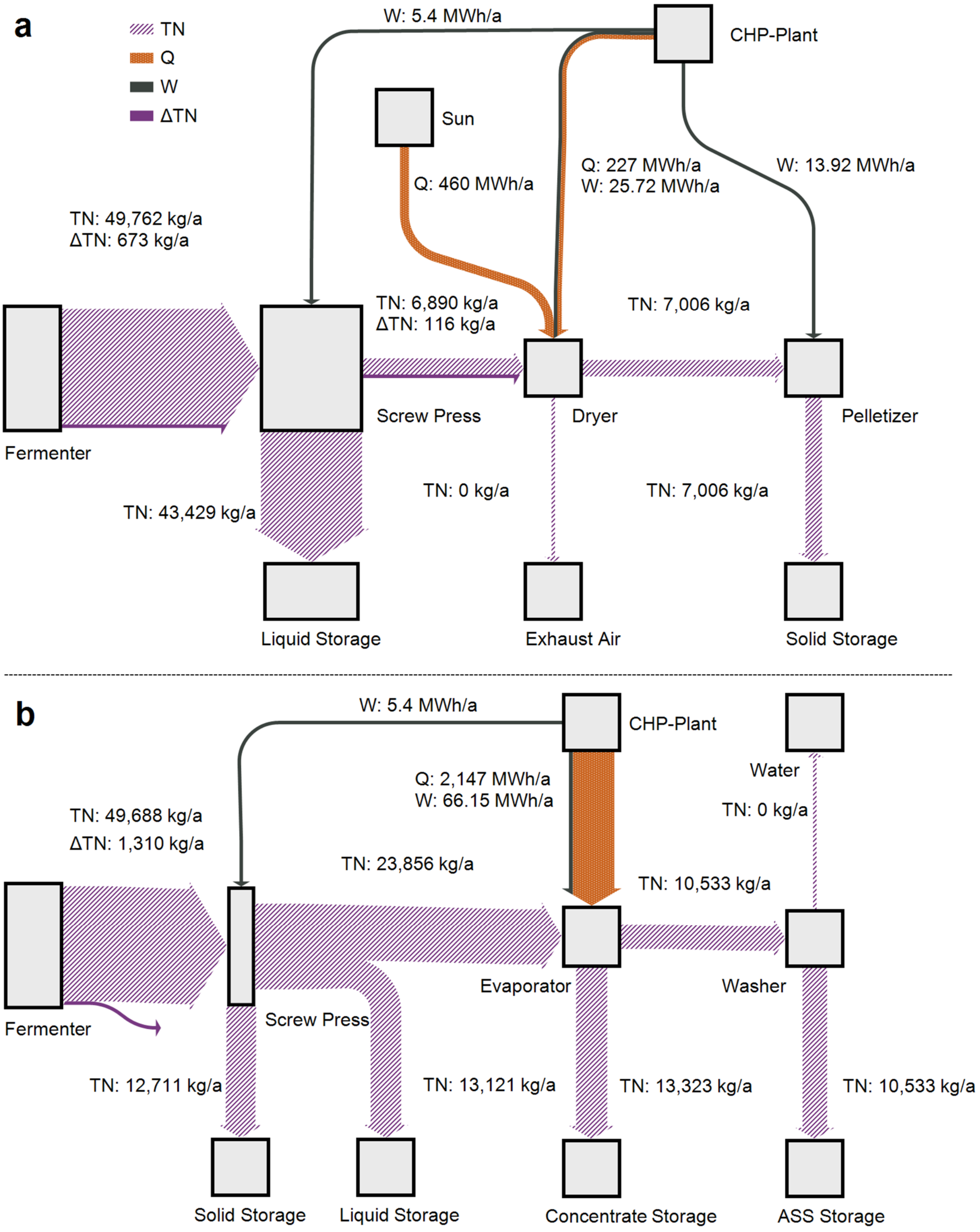

Figure 3-4 Total nitrogen (TN) mass flows of examined processing chains, **a**: solid processing of BGP1, **b**: liquid processing of BGP2; Q: thermal energy demand (MWh a^{-1}); W: electric energy demand (MWh a^{-1}); ASS: ammonium sulfate solution; Δ: mass balance delta.

When the separated solid fraction was dried and pelletized, the TN mass flows remained almost constant with virtually no losses in the exhaust air (Fig. 3-4a).

Further treating of separated liquid in BGP2 split the incoming TN mass flow of 23,856 kg TN a^{-1} (Fig. 3-4b) into 44% ASS and 56% concentrate.

Within BGP1, a positive significant correlation between TN mass flows and DM mass flows was observed ($r^2 = 0.88$, $p = 0.02$), while for BGP2 this effect was not statistically significant ($r^2 = 0.69$, n.s.).

3.4.3 NH_4–N flows within the processing chains

Total NH_4–N flow in BGP2 was reduced by about 20% during solid-liquid separation. In accordance with TN, most of the NH_4–N was also moved to the liquid fraction after the separation of raw digestate in both biogas plants. The NH_4–N mass flow towards the separated solid accounted for 1742 kg NH_4–N a^{-1} (BGP1, Fig. 3-5a) and 6458 kg NH_4–N a^{-1} (BGP2, Fig. 3-5b). These values equal about 8% and 35% of the respective liquids.

Drying with pelletizing of separated solid decreased the NH_4–N mass flow by around 74% (461 kg NH_4–N a^{-1} in dried solid, Fig. 3-5a).

Regarding BGP2, vacuum evaporation transferred about 88% of NH_4–N from separated liquid to ASS (10,533 kg NH_4–N a^{-1}) and 12% to concentrate (1467 kg NH_4–N a^{-1}) (Fig. 3-5b).

A positive correlation between NH_4–N mass flow and water mass flow was observed in both biogas plants (BGP1: $r^2 = 0.99$, $p < 0.001$; BGP2: $r^2 = 0.95$, $p = 0.02$). In BGP2, the last processing step (NH_3 scrubbing) was not considered for this analysis.

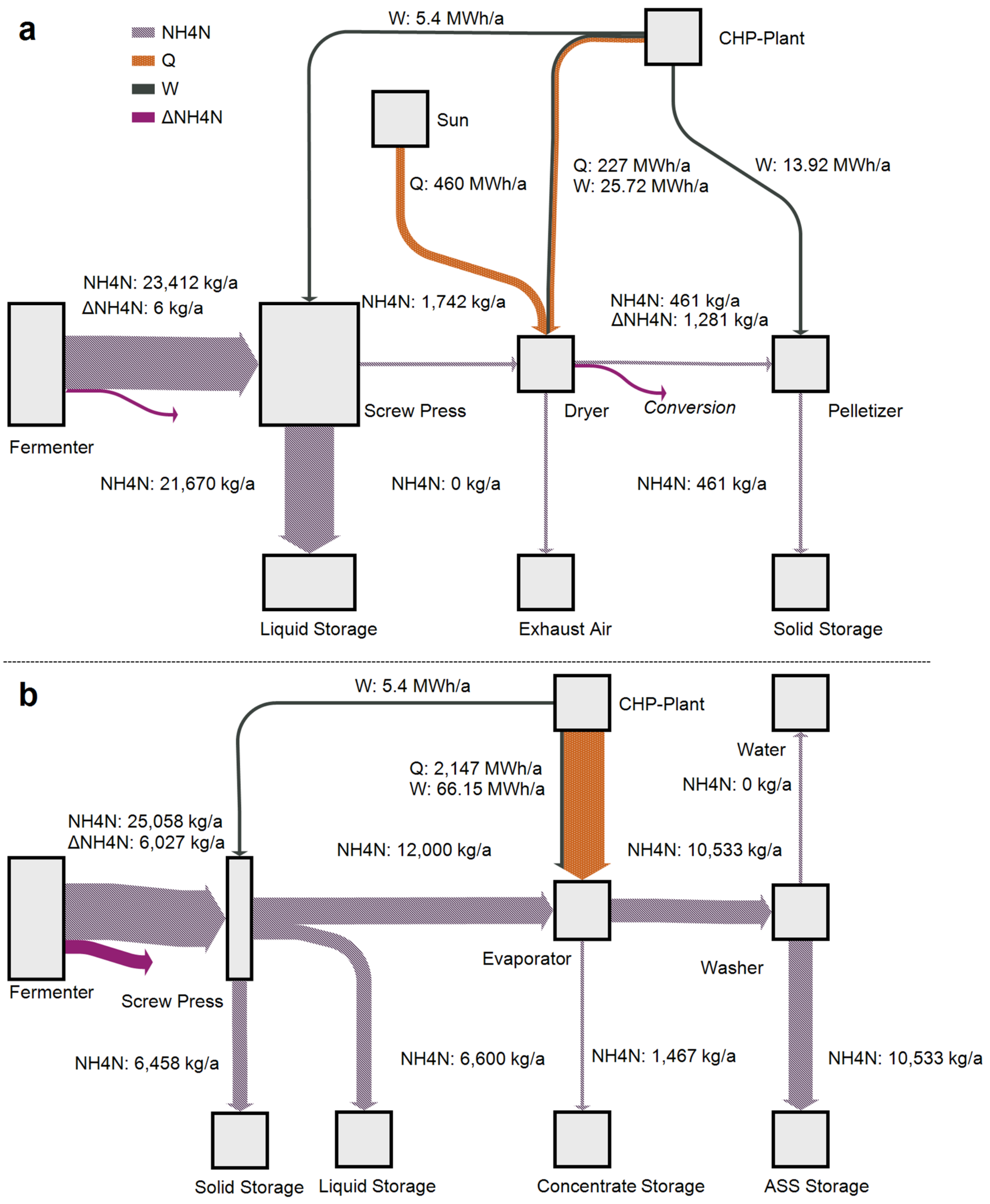

Figure 3-5 Ammonium nitrogen (NH_4–N) mass flows of examined processing chains, **a**: solid processing of BGP1, **b**: liquid processing of BGP2; Q: thermal energy demand (MWh a^{-1}); W: electric energy demand (MWh a^{-1}); ASS: ammonium sulfate solution; Δ: mass balance delta.

3.4.4 Separation index of tested processing techniques

The partitioning of DM, TN, and NH_4–N after solid-liquid separation of raw digestate, as well as the ongoing removal of these compounds due to subsequent processing operations, are shown in Table 3-2. The separation index of the screw press varied depending on the biogas plant. The recovery of DM, TN, and NH_4–N in separated solid was higher in BGP2 than in BGP1 and accounted for 53%, 25%, and 21% of the initial amount, respectively (Table 3-2).

Table 3-2 Separation index (E_t) of each tested processing step calculated for dry matter (DM), total nitrogen (TN), and ammonium nitrogen (NH_4–N); values are accurate to two significant figures.

Biogas plant	**Processing technique**	**Product**	**Separation index (%)** [3]		
			DM	TN	NH_4–N
1	Screw press separator	Sep. liquid [1]	65	87	93
		Sep. solid [1]	35	14	7
	Solar greenhouse dryer	Dry solid	35	14	2
	Pelletizer	Pellet	35	14	2
2	Screw press separator	Sep. liquid [1]	47	72.5	60
		Sep. solid [1]	53	25	21
	Vacuum evaporator	Concentrate	30	26	5
	NH_3 washing column	ASS [2]	7 [4]	21	34

[1] Sep. Liquid/solid: separated liquid/solid.

[2] ASS: ammonium sulfate solution after vacuum evaporation of separated liquid and NH_3 washing from the exhaust steam.

[3] Separation index: removal of a compound (e.g., DM, TN, or NH_4–N) into the product relative to its initial amount presented in raw digestate.

[4] Value means sulfate detected as DM during the chemical analysis.

Processing of separated solid in BGP1 did not significantly change the DM and TN amount in the respective products. 35% of the initial DM and 14% of the initial TN of raw digestate were found in dry solid and pellets (Table 3-2). Only 2% of initial NH_4–N was recovered in dry solid and pellets in contrast to about 7% in separated solid.

Similar to the solid processing, the entire DM of separated liquid remained in the concentrate after vacuum evaporation and was equivalent to 30% of the initial DM amount. In this product, 26% of initial TN and 5% of initial NH_4–N derived from raw digestate were found (Table 3-2). The recovery of NH_4–N was significantly higher in ASS than in concentrate.

3.5 Discussion

In general, the partitioning of DM, water, TN, and NH_4–N among the digestate products depended on the treating method and biogas process parameters.

3.5.1 Effects of digestate processing on total mass flows

Despite the same slit width of the drum screen, a higher performance of the screw press was noted in BGP2 compared to BGP1. Total mass flows showed a solid-to-liquid ratio of 9:91 in BGP1 and 23:77 in BGP2 (Fig. 3-3), which was in the range of previous literature [18,26]. In general, such differences can be explained by: (i) variation in feedstocks, composition, and/or particle size distribution in digestate [18,20,34], (ii) hydraulic retention time during anaerobic digestion or (iii) technical settings of the separator, such as relative rotational speed of the screw and compression pressure induced by the flaps at the solid output [35]. It is assumed that the digestate of BGP2 was mostly characterized by large particles, whereas in BGP1, a significant amount of floating undigested fiber was transferred to the liquid. The electric energy required for the evaluated solid-liquid separation was about 2 times higher than reported by Bauer et al. [28], which could be explained by the enhanced throughput of their screw press (about a factor of 10 higher).

Regarding subsequent processing of the solid phase, the total mass reduction at the end of the drying unit equaled that measured by Bux et al. [36] for a solar dryer. They noted a similar amount of thermal energy but consumed about 45% less electric energy. This difference is likely attributed to the additional fans needed to regulate the airflow across the heat exchanger of the CHP plant's cooling system and to send it into the greenhouse in our case.

The partition of total mass flow after vacuum evaporation of separated liquid was similar to previously reported values for comparable vacuum evaporation systems [37,38] and inferior to that achieved by ultrafiltration with reverse osmosis [20,21]. However, as also shown by Bolzonella et al. [21] and Fechter [39], the tested vacuum evaporation only requires about half of the electric energy as ultrafiltration with reverse osmosis.

3.5.2 N fate depending on the digestate processing method

3.5.2.1 Mechanical separation of raw digestate

In accordance with previous literature, the separation of raw digestate resulted in shifting the main part of TN and NH_4–N to the liquid phase [18,28,34]. In BGP1, the initial DM was also mainly recovered in separated liquid (Table 3-2), as previously reported [26,34,39]. Therefore, the high recovery of TN in separated liquid can partly be explained by N compounds, such as amino acids and proteins, which were likely organically bound in small particles (<0.5 mm) and thus transported through the drum screen. In BGP2, the enhanced share of NH_4–N derived from raw digestate (Table 3-1) was likely responsible for the high TN and NH_4–N recovery in separated liquid, which was also confirmed by the positive correlation between NH_4–N and water mass flows. It might be a result of a different degree of degradability of the initial substrate. However, the mass balance showed a reduction of total NH_4–N flow after initial separation of about 20%, while changes in TN were negligible. In general, a decrease in total NH_4–N content can be a result of its conversion into NO_3^- or gaseous NH_3, triggered by suitable conditions such as temperature and pH. Since the mechanical separation occurs in a closed, unheated environment with a short retention time, NH_3 volatilization is only possible after exiting the separator (e.g., during uncovered storage of the separated solid fraction). However, the TN mass flows, on the other hand, do not reflect considerable gaseous N losses. It is consequently assumed that the raw digestate sample contained remnants of an earlier batch, caught in the dead zone between the main pipe and the sampling valve. The sample was probably characterized by a proceeded anaerobic conversion of organic N into NH_4^+, which led to an overestimation of the NH_4–N content in the raw digestate. The comparison of the liquid fraction and the raw digestate samples supports this assumption. Since NH_4^+ is dissolved in the water, it tends to stay in the liquid fraction, while non-dissolved N, such as organic N, tends to be transferred to the solid fraction. Therefore, the NH_4–N to TN ratio should stay the same or increase from raw digestate to the liquid fraction. However, in our case, it was 0.6 in raw digestate and 0.5 in the liquid fraction.

Concerning the solid after separation, the separation indexes of TN (14% BGP1 and 25% BGP2) were up to 3 times higher than the literature values reported for similar or bigger screen sizes of screw press separators [29,40]. In this context, Møller et al. [41] found an increase in the amount of solid fraction produced and TN transferred to separated solid with increasing dry matter content of raw material. Furthermore, Møller et al. [41,42] and Tambone et al. [34] showed that a variation in the nature and composition of feedstock may also lead to different separation efficiencies. It is assumed that the enhanced DM contents of the evaluated raw digestates were mainly responsible for the higher separation indexes observed. Another factor is the initial NH_4–N to TN ratio. Pantelopoulos and Aronsson [40], for example, treated digestate with a ~12% higher NH_4–N:TN, which resulted in better NH_4–N transport to separated liquid and a lower separation index of the solid. A high NH_4–N:TN is also an indicator for better microbial digestion, resulting in smaller particles passing the screen more easily. Consequently, most of the recovered N in our separated solids was probably organic N in the form of more complex organic compounds. In BGP2, the enhanced moisture content likely carried additional NH_4–N to the separated solid.

Overall, it can be concluded that the splitting of water and DM during solid-liquid separation generates products that (i) can be used as an organic amendment with a relatively high amount of plant available nutrients like NH_4–N and a good infiltration rate (separated liquid) or (ii) can be considered as a pre-stage for significant volume reduction and improved transportability due to water removal (separated solid). However, separated liquid cannot be defined as a standardized organic fertilizer, since its TN content is lower than the predefined value according to the latest draft of the Regulation EU No 2019/1009 [43]. It can be applied on cropland or pasture as an organic supplement in combination with other fertilizers. Anyway, the low energy consumption of solid-liquid separation compared to the subsequent processing steps tested in this work makes this technique an attractive option for treating raw digestate.

3.5.2.2 Subsequent processing of separated solid

The measured decrease in NH_4–N mass flow after drying (Fig. 3-5a) is in line with already published results [44–46]. Since the solid after separation, as well as after drying, has a slightly alkaline pH (Table 3-1), one possible explanation for this finding can be gaseous N losses, such as NH_3 volatilization during storage and drying. NH_4^+ losses due to NH_3 volatilization can also be triggered by drying temperature, or intensive mixing of the substrate [22,44,47]. However, TN flows did not change in the respective product. At the same time, the tested dry solid was characterized by a significant amount of NO_3^-, which was not present in the precursors (data not shown) and indicates a microbial conversion of mineral N (NH_4^+ into NO_3^-) during the drying process. Such a conversion was likely promoted by the prolonged retention times (~three months) in the greenhouse and is assumed to be the main reason for the significant decrease in NH_4–N concentration and respective mass flow after solar drying.

According to the chemical analysis of evaluated digestates (Table 3-1), pelletizing of dry solid increased TN and NH_4–N contents (at a comparable level of DM) and would consequently increase TN and NH_4–N mass flows. Such an increase is implausible since mechanical compressing of the solid would rather decrease the TN flow due to gaseous N losses. Consequently, it was assumed that the evaluated pellets belong to an earlier batch, which was characterized by a higher TN content. However, changes in NH_4–N mass flow and, therefore, higher concentration in pellets (Table 3-1) might have arisen and can be attributed to processing-related changes in pelleted biomass as previously reported [17,32].

The energy-intensive processing of separated solid only led to negligible water removal from raw digestate but can be an advisable treatment option, when considering pelletizing. Overall, about 15% of TN derived from raw digestate can be recovered in pellets, which are easily storable and worthwhile for transport and further utilization.

3.5.2.3 Subsequent processing of separated liquid

Although the tested vacuum conditions were reported to be the most suitable for effective NH_3 removal from separated liquid digestate [48], the total amount of condensate gained for subsequent production of ASS was up to 14% less in comparison to vacuum evaporation at a lower pressure level [37] or in combination with previous NH_3 stripping and successive reverse osmosis [38]. Also, the water reduction was up to 23% lower than previously reported by Tampio et al. [38]. In addition to the differences in treatment conditions and utilized processing techniques, a possible reason for the discrepancies is the higher DM content of raw digestate or rather of separated liquid evaluated in the current study.

The complete shifting of DM to the concentrate was in line with the literature [26,38]. As the TN mass flow was also about 26% higher than the mass flow towards ASS, it was assumed that a concentrating of organic N took place in concentrate during the vacuum-induced NH_3 stripping. However, in comparison to the literature, the amount of TN and NH_4–N recovered in concentrate was at least 20% (TN) and 33% (NH_4–N) lower [20,26]. This can be explained by technologies and production parameters of previously mentioned works: in the case of Brienza et al. [26], a relatively mild stripping method was applied, which leads to lower total nitrogen removal from the initial substrate and requires significantly less energy, while Ledda et al. [20] combined ultrafiltration with reverse osmosis to strip NH_3 from a two-stage separated liquid.

With a view to the tested vacuum evaporation, NH_4^+ was almost completely transferred to ASS. The recovery of TN and NH_4–N showed comparable results as reverse osmosis and ultrafiltration [20,21].

It can be concluded that, although only a third of the water amount from the separated liquid was removed, vacuum evaporation at 65 °C and 250 hPa with subsequent NH_3 scrubbing can effectively separate the soluble part of N from the organic matter fraction. However, high energy consumption compared to previously reported techniques, such as direct NH_3 stripping [26], and thereby resulting costs are further essential factors that should be considered during decision-making.

3.5.3 Study implications

A closer look at the two processing chains evaluated in the current study shows that each of these paths aims at generating different products with distinctive benefits. The solid phase after separation represents an organic soil improver with a high share of recalcitrant compounds including organic N, is marketable and easy to transport and store after processing up to pellets. The liquid processing chain targets the concentrating of inorganic and soluble NH_4–N and generates a fertilizer readily absorbed by crops. However, the technology required for the production of ASS is relatively costly [26].

The decision-making to subsequently process solid or liquid after separation is complex and primarily depends on the local situation, individual requirements, and financial means. Presuming that (i) the manure or digestate, which should be processed, is produced in a region characterized by surplus nutrients such as N, but (ii) the soil, where it can be applied, is poor in humus, it would be beneficial to locally utilize the solid phase and advisable to further process the liquid. On the other hand, if a suitable storage facility is available on site and the liquid phase can be utilized as organic fertilizer according to legal regulations, the processing of the solid phase could be recommended.

From an environmental point of view, the energy requirements of each processing chain also represent an important factor. In our case, the solid processing chain demanded 6.4 kWh_{el} and 32 kWh_{th} kg^{-1} N recovered in pellets, while the production of ASS required 6.8 kWh_{el} and 203 kWh_{th} kg^{-1} N recovered. However, at the same time, the TN recovery in pellets was about 33% lower than in ASS.

In order to optimize energy demand and working flow in the presented processes, several modifications are suggested. In the liquid processing chain, a one-stage vacuum evaporator was utilized. Nowadays, three- or four-stage vacuum evaporator units are common practice, which are characterized by higher heat recovery and therefore operate more efficiently. Further improvement in liquid processing could be achieved by producing solid ammonium sulfate, as reported in the literature [37,48]. Solid ammonium sulfate with an estimated DM content of 80–90% would require a lower storage volume and facilitate transportation and application.

Regarding the solid processing, optimization of energy demand, as well as shorter drying times and reduced gaseous N losses could be achieved by: (i) using a contact dryer for improved heat transfer, or (ii) implementing a two-stage drying process with an initial, shorter solar greenhouse drying, followed by a feed-and-turn dryer, which uses CHP-waste-heat more efficiently. Due to the increased process control, conditioning of the dried solid (prior to pelletizing) can be omitted.

A further option is the implementation of intelligent navigation for the electric mole. If the mole can systematically mix and turn the substrate while continuously transporting it from one end of the greenhouse to the other (over the course of three months), the screw press could be installed inside the greenhouse. In this way, drying would work autonomously and continuously instead of batch wise.

3.6 Conclusions

The current study has shown that the partitioning of DM, water, TN, and NH_4–N varied with substrate composition, processing technique, and operation parameters of the biogas plant. The main part of TN and NH_4–N was generally moved to the liquid phase, while the recalcitrant compounds remained in the solid.

Mechanical separation via screw press proved to be a useful option for an initial splitting of solids from liquids with a relatively low specific energy consumption. During this processing step, a substantial part of the total DM remained in the liquid.

Subsequent drying of the separated solid significantly reduced the NH_4–N mass flow due to microbial conversion into NO_3^-, whereas vacuum evaporation of the liquid partitioned the entire DM to concentrate and most of the NH_4–N to ASS.

It can be concluded that drying with pelletizing of the solid fraction removed less moisture from raw digestate than vacuum evaporation with partial NH_3 stripping from separated liquid. Also, the TN recovery in pellets was only two-thirds of the value obtained in ASS. On the flipside, vacuum evaporation required six times more thermal energy per kg N recovered than solar drying and subsequent pelletizing.

In order to make a recommendation, local situation, individual requirements, and financial means must be taken into account. Both processes generate different products with individual benefits. The solid phase after separation can be applied as an organic soil improver, whereas the liquid chain produces an NH_4-rich fertilizer, which is promptly absorbed by crops.

3.7 References

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4 N_2O emissions after digestate application[†]

In order to track subsequent changes in N_t recovered in the products and to evaluate the environmental impacts related to their utilization as organic fertilizers, the N_2O release from soil after the application of raw and processed digestates was investigated under field and laboratory conditions.

4.1 Abstract

Manures can be treated by solid–liquid separation and more sophisticated, subsequent approaches. These processes generate fertilizers, which may differ in composition and N_2O release potential. The aim of the study was to investigate the influence of processing-related changes in digestate composition on soil-derived N_2O emissions after application to soil.

For that purpose, N_2O emissions within the first 7 weeks after fertilization with two raw and eight processed digestates (derived from solid–liquid separation, drying and pelletizing of separated solid, and vacuum evaporation of separated liquid) were measured in the field in 2015 and 2016. Additionally, an incubation experiment was run for 51 days to further investigate the effect of subsequent solid and liquid processing on soil-derived N_2O release.

The results showed that, only in 2016, the separation of digestate into solid and liquid fractions led to a decrease in N_2O emissions in the following order: raw digestate > separated liquid > separated solid. N removal during subsequent processing of separated solid and liquid did not significantly influence the N_2O emissions after fertilization. In contrast, the concentrated application of the final products led to contradictory results. Within the solid processing chain, utilization of pellets considerably increased the N_2O emissions by factors of 2.7 (field, 2015), 3.5 (field, 2016), and 7.3 (incubation) compared to separated solid. Fertilization with N-rich ammonium sulfate solution led to the lowest emissions within the liquid processing chain.

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It can be concluded that the input of less recalcitrant organic C into the soil plays a greater role in N_2O release after fertilization than the input of ammoniacal N. Digestate processing did not generally reduce emissions but apparently has the potential to mitigate N_2O emissions substantially if managed properly.

Keywords: nitrous oxide; treated digestates; techniques; denitrification; separation; pelletization

4.2 Introduction

Regional nutrient surpluses caused by a concentration of livestock farming represent a relevant issue worldwide. In Germany, for example, the northwest is the most affected region due to its high livestock density of about 3.5–4.1 livestock units per ha [1,2]. Biogas plants, often based on the digestion of animal manure and dedicated energy crops such as silage maize, further increase the amount of organic manures in such regions [3,4]. Moreover, the timeframe and total amount of organic fertilizer application are limited by legal regulations, such as the German fertilizer ordinance [5,6]. In addition to nitrate leaching, acidification, and eutrophication, the management of organic fertilizers is directly linked to significant gaseous N losses in the form of N_2O [7–10]. Therefore, strategies are needed to either reduce livestock density or to export nutrients out of the affected regions. Due to their high water content, the transportation of liquid manures over large distances is not feasible.

An approach to facilitate the export of excess nutrients is to reduce the water content by digestate processing. This results in a marketable organic fertilizer which is worth being transported. A common processing technique is solid–liquid separation. This generates a dry-matter-rich solid fraction with a high proportion of the initial phosphorus and a liquid fraction with a high share of nitrogen and potassium [11,12]. In addition to water reduction and improved transportability, processing of digestates might have the potential to reduce climate-relevant N_2O emissions via partial separation of N and organic matter [13–15]. When considering solid and liquid after separation, varying experimental results were reported. Whether the solid or liquid leads to higher emissions after soil application is highly dependent on the digestate feedstock and pretreatment procedure [13,16–20].

Previous studies (e.g., [13,16–24]) mainly focused on the effect of feedstocks in combination with management practices. However, no evaluation of the single steps within an entire processing chain could be found. Therefore, the main objective of the present work was to identify which processing techniques and respective products have the potential to reduce N_2O emissions after soil application in comparison to the untreated digestates. Furthermore, the following aspects were addressed: (i) How does the treatment influence the composition of intermediate and final products? (ii) What is the impact of composition and treatment of digestates on N_2O emissions after application to soil?

For that purpose, solid (raw digestate–separation–drying–pelletizing) and liquid processing chains (raw digestate–separation–vacuum evaporation with partial ammonia stripping) from two fully operating biogas plants were selected, and the composition and emissions after soil application of the respective intermediates and final products were measured. It was generally expected that process-related N removal and the resulting decrease in N content of digestates (solids and liquids) would contribute to lower N_2O production from fertilized soils.

4.3 Materials and methods

4.3.1 Digestate collection and composition

The digestates were collected at two biogas plants, which processed liquid and solid fractions after separation, respectively. The feedstocks of the first biogas plant were cattle manure and pig slurry, dedicated energy crops such as silage maize and sunflower (400 g kg^{-1} total fresh matter, FM), pomace and grape marc (200 g kg^{-1} FM), and poultry manure (50 g kg^{-1} FM). In the second plant, pig slurry and cattle manure were digested with silage maize (approximately 220 g kg^{-1} FM), grass silage (70 g kg^{-1} FM), and cereal silage and grist (180 g kg^{-1} FM).

In both biogas plants, raw digestate (RD1 and RD2, respectively) was separated into a solid (SS1 and SS2) and a liquid (SL1 and SL2) fraction using a screw press separator (pore size 0.5 mm). After the separation, plant 1 subsequently treated the solid. Biogas plant 2 further processed the solid and liquid, but only the liquid products were considered in this study.

In plant 1, the separated solid (SS1) was dewatered to about 80% dry matter (DM) content (dry solid, DS1) in a solar greenhouse drier and subsequently pelletized (without addition of binding agents). The final pellets (P1) had a diameter of 6 mm and an average length of 14 mm.

In plant 2, water was removed from the separated liquid (SL2) in a two-step vacuum evaporator. The evaporation took place at 65 °C and 250 hPa. The low pressure induced an evaporation of water, ammonia (NH_3) and other gasses. Next, NH_3 was removed from the exhaust steam in a sulfuric-acid-containing washing column to produce ammonium sulfate (ammonium sulfate solution, ASS2). In a second vacuum vessel, the remaining liquid digestate was further dewatered, and a concentrate (CC2) was produced.

The chemical and physical characteristics of raw and treated digestates were analysed according to VDLUFA [25] and van Soest and Wine [26], and the characteristics are shown in Tables 4-1 and 4-2. In addition, the calculated fractions of soluble materials, hemicellulose, and cellulose can be found in Table S1.

Table 4-1 Chemical characteristics of the applied raw and processed digestates.

Biogas plant	Product	Year	DM [4]	C_t [6]	C_{org} [7]	N_t [8]	NH_4–N [9]	NH_4–N:N_t	C:N	pH
			(g kg^{-1} FM[5])	(g kg^{-1} DM)						
1	Raw digestate (RD1)	2015	79	348	345	64.1	30.2	0.47	5.4	8.1
	Sep. liquid (SL1) [1]		56	358	354	86.5	43.1	0.50	4.1	8.0
	Sep. solid (SS1) [1]		311	431	429	25.2	6.4	0.25	17.1	8.2
	Dry solid (DS1)		902	416	413	25.6	1.7	0.07	16.2	8.2
	Pellet (P1)		889	402	398	35.1	4.3	0.12	11.5	7.7
	Raw digestate (RD1)	2016	108	435	432	47.6	18.2	0.38	9.1	7.3
	Sep. liquid (SL1) [1]		65	398	394	78.4	36.0	0.46	5.1	7.8
	Sep. solid (SS1) [1]		299	456	454	18.6	3.9	0.21	24.6	8.6
	Dry solid (DS1)		546	461	459	21.4	1.0	0.05	21.5	7.8
	Pellet (P1)		851	447	445	34.9	2.4	0.07	12.8	7.9
2	Raw digestate (RD2)	2015	54	381	376	96.1	62.2	0.65	4.0	7.8
	Sep. liquid (SL2) [1]		50	368	362	103.4	68.6	0.66	3.6	7.8
	Sep. solid (SS2) [1]		225	398	396	28.1	15.0	0.53	14.1	8.3
	Concentrate (CC2) [2]		85	375	373	48.8	19.7	0.40	7.7	9.0
	ASS2 [3]		322	< 2	< 2	185.8	181.9	0.98	0.01	1.3
	Raw digestate (RD2)	2016	77	406	403	68.6	41.8	0.61	5.9	7.7
	Sep. liquid (SL2) [1]		47	393	388	106.4	60.8	0.57	3.7	7.9
	Sep. solid (SS2) [1]		174	434	432	32.1	14.4	0.45	13.5	8.9
	Concentrate (CC2) [2]		136	399	395	38.7	6.5	0.17	10.3	8.9
	ASS2 [3]		278	1	1	202.9	193.7	0.95	0.007	2.4

[1] Sep. liquid/solid: separated liquid/solid; [2] CC2: concentrate after vacuum evaporation; [3] ASS2: ammonium sulfate solution after vacuum evaporation; [4] DM: dry matter; [5] FM: fresh matter; [6] C_t: total carbon; [7] C_{org}: organic carbon; [8] N_t: total nitrogen; [9] NH_4–N: ammonium N.

Table 4-2 Detergent fiber analysis of raw and treated digestates used in this study, according to van Soest and Wine [26].

Biogas plant	Product	aNDF [4] (g kg^{-1} DM)		ADF [5] (g kg^{-1} DM)		ADL [6] (g kg^{-1} DM)	
		2015	2016	2015	2016	2015	2016
1	Raw digestate (RD1)	411	477	377	438	170	223
	Sep. liquid (SL1) [1]	205	379	204	382	109	244
	Sep. solid (SS1) [1]	683	785	518	649	216	426
	Dry solid (DS1)	533	653	493	607	227	393
	Pellet (P1)	517	583	463	520	225	316
2	Raw digestate (RD2)	96	455	228	411	134	187
	Sep. liquid (SL2) [1]	21	189	254	298	174	193
	Sep. solid (SS2) [1]	727	693	563	524	207	179
	Concentrate (CC2) [2]	89	169	260	259	112	141
	ASS2 [3]	< 10 [7,8]	< 10 [7,8]	< 5 [7,8]	< 5 [7,8]	< 5 [7,8]	< 5 [7,8]

[1] Sep. liquid/solid: separated liquid/solid; [2] CC2: concentrate after vacuum evaporation; [3] ASS2: ammonium sulfate solution after vacuum evaporation; [4] aNDF: neutral detergent fiber; [5] ADF: acid detergent fiber; [6] ADL: acid detergent lignin; [7] measured values fall below the detection limits; [8] the value is presented as g kg^{-1} FM.

Dry matter content was measured by drying at 105 °C until constant weight. The pH of solid digestates was measured in 10^{-2} M $CaCl_2$ solution, while, in the case of the liquids, the original substance was used. The total C content was determined by elemental analysis (vario MAX CN, Elementar Analysensysteme, Hanau, Germany). Total nitrogen (N_t) and NH_4^+–N contents were measured using the Kjeldahl method and by steam distillation with titration, respectively.

4.3.2 Experimental site

A field trial was carried out in spring 2015 and 2016 at the experimental station “Heidfeldhof” (48°42’40”N, 9°11’45”E; 389 m a.s.l.). The mean annual air temperature was 10.2 °C and the total annual precipitation 628 mm (mean for the period 2007–2016). During the measuring period, the air temperature averaged 15.0 °C (2015) and 11.4 °C (2016). Total precipitation was 110 mm in year 1 (27 April–12 June 2015) and 122 mm in year 2 (11 April–30 May 2016).

The experimental fields were located close to each other (approximately 50 m distance), with almost similar soil characteristics (Table 4-3). Soil type was a Haplic Luvisol from periglacial loess.

Table 4-3 Main soil characteristics in the A_p-horizon (0–0.3 m depth) of the experimental fields in 2015 and 2016 before fertilization.

Year	Sand	Silt	Clay	Bulk density	pH	C_{org}	N_t	N_{min} [1]
	(%)	(%)	(%)	(Mg m^{-3})	($CaCl_2$)	(%)	(%)	(kg ha^{-1})
2015	2	68	30	1.29	6.5	1.8	0.16	19.9
2016	9	69	22	1.24	7.0	1.1	0.14	7.3

[1] Initial N_{min} (NH_4^+ and NO_3^-) at the beginning of each experiment.

4.3.3 Field experiment

The field trial was set up on fallow land (between crop rotations) in order to avoid changes in N turnover resulting from plant growth and N uptake. It represented a randomized complete block design with four replicates. We tested two raw and eight processed digestates and an unfertilized control. A total of 44 microplots with a size of 2.25 m^2 each were established and used for the statistical analyses. The fertilizers were applied once at the beginning of the experiment at a rate of 170 kg N_t ha^{-1} (the maximum amount of applied N in the form of organic fertilizer as regulated by the German fertilizer ordinance in 2015 [27]; total amounts are presented in Table S2). N_2O emissions after digestate application were measured using the closed chamber method [28]. Each fertilizer was incorporated in a small furrow within the base ring (0.3 m inner diameter) of the chamber. After closing the chamber, four gas samples were taken from the chamber's atmosphere periodically (15 min intervals) and transferred into 20 mL pre-evacuated glass vials with a syringe.

During the gas measurements, the air temperature inside the chamber was determined. Samples were collected three times a week within the first 2 months after fertilization between 9:00 a.m. and 12:00 p.m., since this time period covers the mean daily soil temperature. Thus, biases during extrapolation of flux rates to daily fluxes due to diurnal soil temperature variations were minimized [29].

After each gas sampling, soil moisture (TDR sensor, FP/mts, Easy Test, Institute of Agrophysics, Polish Academy of Science, Poland), soil temperature (10 cm depth), and air temperature were determined. To verify the volumetric measurement of soil moisture, the gravimetric soil water content was additionally analyzed by collecting 10 random soil samples of the top soil and drying them at 105 °C until constant weight. At the beginning of the experiments (27 April 2015 and 11 April 2016, respectively), stainless-steel cylinders (100 mL) were used to measure the bulk density of the A_h horizon. As a function of the bulk density, the current water-filled pore space (WFPS) was calculated as described by Ruser et al. [30]. The mineral nitrogen (N_{min}) content of the topsoil was determined colorimetrically after extraction of a soil aliquot with 0.5 M K_2SO_4 solution (Continuous Flow Analyzer, AA3 HR; SEAL Analytical, Inc., Norderstedt, Germany). The main physical and chemical characteristics of the soil, such as soil texture and C_{org} and N content, are shown in Table 4-3.

4.3.4 Incubation experiment

For the incubation experiment, the following digestates were compared: solid after separation (SS1), dried (DS1) and pelleted digestates (P1), raw digestate (RD2), liquid after separation (SL2), concentrate (CC2), and untreated control (control). The setup was a completely randomized design with four replicates. For comparison with the field investigation, soil was taken from an area next to the 2016 field trial. It was obtained from the A_p horizon, sieved ≤4 mm, and air-dried prior to the experiment. Physical and chemical soil characteristics are shown in Table 4-3.

A mixture of digestate and soil was incubated in 2.5 L glass jars in a climate chamber at 20 °C for 51 days (in the dark). Each jar contained 700 g air-dried soil, mixed with the respective amount of organic fertilizer equivalent to a total of 170 kg N_t ha^{-1} (45.8 mg N_t per glass jar). At the beginning of the incubation, distilled water was added to adjust the soil water content to 60% water-holding capacity (equal to ~50% WFPS, [30]). This ensured the development of aerobic conditions in the soil and was in the range of the field trials, as well as that reported in previous literature [31]. It was chosen in order to simplify the comparison between the results obtained in both experiments. A 20 mL beaker glass was filled with distilled water and set into each glass jar to avoid potential water losses as a result of soil evaporation during the experiment. The glass jars were equipped with a PVC lid and closed airtight. A bulkhead tube fitting was fixed in the middle of the lids and closed with a septum according to the closed chamber method previously outlined. To ensure aerobic conditions during incubation, the jars were opened daily for aeration. Throughout the first 2 weeks, gas samples were taken once a day, whereas, during the rest of the experimental period, the sampling interval was reduced to once a week. For measuring the N_2O flux rates, four samples were collected from the jar's headspace at 15 min intervals. Before taking the first gas sample, the glass jars were opened for aeration. To avoid low pressures during sampling, 150 mL of N_2 was injected into each jar. The collected samples were kept in gas vials until the analysis was performed.

4.3.5 Trace gas analysis and flux rate calculation

The analysis of the gas samples was performed using a gas chromatograph (GC 450, Bruker Daltonik, Bremen, Germany) coupled with an autosampler (GX-281, Gilson, Limburg, Germany). Further details on the GC measurements can be found in Petrova et al. [32].

The calculation of flux rates took into account N_2O concentration of the four gas samples (ppb), air temperature (°C), covered soil area (m^2), and volume (L) of the chamber headspace. While, for the field experiment, the volume of the headspace was equivalent to the internal volume of the closed chamber, for the incubation jars, it was calculated differently. The sum of actual headspace (above soil surface), 150 mL N_2 injection, and air-filled pore space in the soil formed the total air volume. The N_2O fluxes were calculated using the R-Package "gasfluxes" [33,34].

4.3.6 Statistical analysis

The datasets were statistically analyzed using the software SAS (v 9.4). Residuals were tested for normality and homogeneity of variance. If required, data were logarithmically transformed prior to analysis to fulfil the pre-requirements. For estimating the effect of digestate treatment on cumulative N_2O emissions, a one-way ANOVA was performed for each experimental year and for both experiments separately. This model used data of 44 experimental units. Here, the digestate treatment acted as a main independent variable. Additionally, the significant differences among the treatments were calculated using a Tukey HSD test ($p \leq 0.05$). Differences were presented using a letter display [35]. If transformed data were analyzed, means were back-transformed for presentation purpose only. In this case, standard errors were back-transformed using the data methods. Furthermore, two linear regression models were run to quantify the effect of C:N or NH_4^+–N:N_t of digestates on the cumulative N_2O emissions. Biogas plant was used as a dummy variable. To test the effect of environmental variables (air and soil temperature, rainfall, and WFPS) on the N_2O fluxes, a stepwise multiple regression (forward procedure, F to enter: 4.000, F to remove: 3.900) was conducted for each combination of year and digestate.

4.4 Results

4.4.1 Field experiment

4.4.1.1 Weather conditions in 2015

Within the first measuring period, the main rainfall events were in weeks 1, 3, 5, and 7 with total amounts of precipitation ranging between 16 and 36 mm per week (Fig. 4-1a). Air temperature (2 m height) varied between 8 and 25 °C, whereas soil temperature (10 cm depth) ranged between 10 and 32 °C (Fig. 4-1a). The highest soil moisture contents were associated with rainfall events and accounted for 55% and 56% WFPS in the first and third weeks of the measurements (Fig. 4-1a).

4.4.1.2 Daily N_2O fluxes in 2015

In 2015, the N_2O flux rates ranged between 4 (DS1, 27th April) and 930 µg N_2O– N m^{-2} h^{-1} (P1, 4th May) (Fig. 4-1b,c). The highest flux was determined 1 week after fertilizer application within the first period of steady rainfall (36 mm in total, 27 April–3 May 2015)

(Fig. 4-1b). An increase in flux rates was also observed in the other treatments, including the control.

At the beginning of week 3, air temperature rose by 5 °C. The separated liquid of both biogas plants showed increasing flux rates, which averaged 537 (SL1) and 216 µg N_2O–N m^{-2} h^{-1} (SL2). A similar pattern was also found in plots treated with RD1 and SS2. At the end of week 3, the next rain event occurred, followed by a second N_2O peak in P1. Furthermore, air and soil temperature dropped and WFPS increased to 56%. Despite additional rainfall events during the following 2 weeks, N_2O fluxes remained low. During the sixth experimental week, flux rates increased again in all treatments before dropping to the baseline level in week 7.

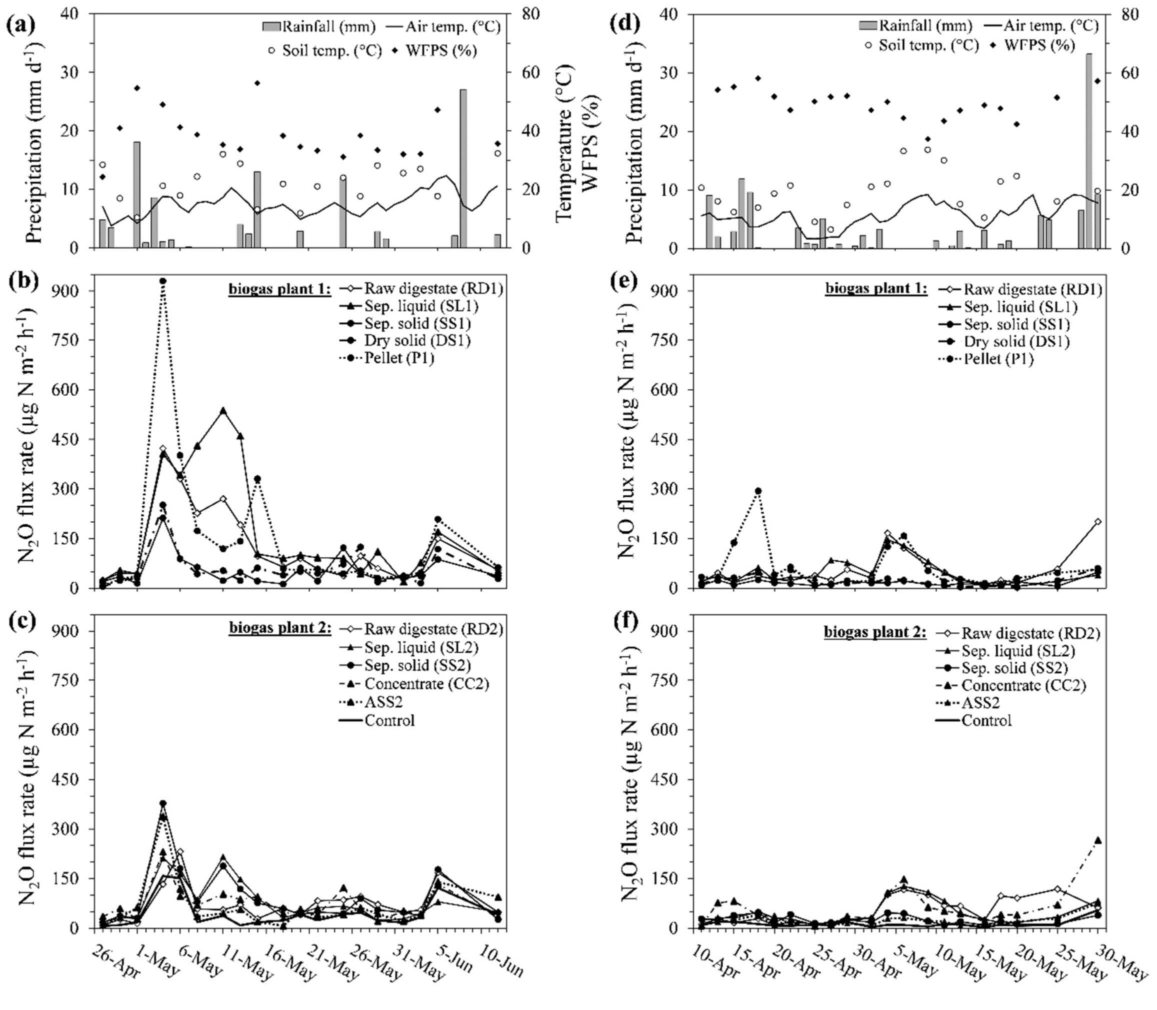

Figure 4-1 Air temperature (2 m height), soil temperature (10 cm depth), daily precipitation and mean water-filled pore space during the field trial (**a:** year 2015, **d:** year 2016); mean N_2O flux rates (n = 4) as affected by digestate from biogas plant 1 (**b:** year 2015, **e:** year 2016) and plant 2 (**c:** year 2015, **f:** year 2016); sep.: separated, concentrate: concentrate after vacuum evaporation, ASS2: ammonium sulfate solution of biogas plant 2.

The stepwise multiple regression indicated a significant effect of the environmental conditions on the mean N_2O fluxes (air temperature: $r^2 = 0.36$, $p < 0.05$ (independent variable entered in step 1) and WFPS: $r^2 = 0.66$, $p < 0.05$ (independent variable entered in step 2)). It can be noted that 27–65% of the N_2O variability was predicted by differences in air temperature among the sampling dates (Table 4-4). With the exception of RD1, SL1, P1, and SL2, N_2O fluxes were also affected by soil temperature. In these three treatments, an additional effect of the WFPS on N_2O release was found.

Table 4-4 N_2O release as affected by air temperature (x_1), water-filled pore space (x_2), soil temperature (x_3) and rainfall (x_4) during the first experimental year (2015). Coefficient of determination and function of stepwise multiple regression (Forward procedure, F to enter: 4.000, F to remove: 3.900).

N_2O release [1] (**g N_2O-N ha^{-1} d^{-1}**)	**Model R^2**	**Air temp. (°C)**		**Rainfall (mm)**	**Soil temp. (°C)**		**WFPS** [2] **(%)**		**Final equation of stepwise forward regression**
		partial R^2	p value		partial R^2	p value	partial R^2	p value	
RD1	0.55	0.29	0.002	n.s.		n.s.	0.26	0.008	$y = -250.1 + 10.6x_1 + 4.4x_2$
SL1	0.27	0.27	0.020	n.s.		n.s.		n.s.	$y = -78.7 + 12.4x_1$
SS1	0.61	0.33	<0.001	n.s.	0.28	0.004		n.s.	$y = -11.7 + 8.6x_1 + 3.7x_3$
DS1	0.68	0.31	<0.001	n.s.	0.15	<0.001	0.22	n.s.	$y = 8.3 + 11.2x_1 - 6.1x_3$
P1	0.65	0.28	0.003	n.s.		n.s.	0.37	<0.001	$y = -553.9 + 16x_1 + 10.7x_2$
RD2	0.67	0.34	<0.001	n.s.	0.33	0.001		n.s.	$y = -26.2 + 15.5x_1 - 6.9x_3$
SL2	0.60	0.36	<0.001	n.s.		n.s.	0.24	0.007	$y = -126.3 + 6.1x_1 + 2.2x_2$
SS2	0.65	0.32	<0.001	n.s.	0.33	0.001		n.s.	$y = -23.9 + 17.3x_1 - 7.8x_3$
CC2	0.68	0.32	<0.001	n.s.	0.36	<0.001		n.s.	$y = -5.5 + 12.1x_1 - 5.6x_3$
ASS2	0.64	0.37	<0.001	n.s.	0.27	0.003		n.s.	$y = -43.2 + 15.7x_1 - 6.5x_3$
Control	0.75	0.35	<0.001	n.s.	0.40	<0.001		n.s.	$y = -24.4 + 12.5x_1 - 5.9x_3$

[1] RD1/2: raw digestate; SL1/2: liquid fraction; SS1/2: solid fraction; DS1: dry solid; P1: pellet; CC2: concentrate; ASS2: ammonium sulfate solution; numbers behind treatments abbreviations: number of respective biogas plant; [2] WFPS: water-filled pore space.

4.4.1.3 Weather conditions in 2016

Compared to year 1, the second observation period was characterized by a higher precipitation (122 mm) and lower mean air temperature, which ranged between 3 and 18 °C (Fig. 4-1d). The soil temperature fluctuated between 7 and 33 °C (Fig. 4-1d). The water-filled pore space reached two main peaks in the beginning of the experiment (58% WFPS, 18 April) and on the last measurement day (57% WFPS, 30 May).

4.4.1.4 Daily N_2O fluxes in 2016

In 2016, all treatments showed lower N_2O fluxes than in 2015 (Fig. 4-1e,f). One week after fertilization, the highest flux rate (294 µg N_2O–N m^{-2} h^{-1}) was measured in P1 (Fig. 4-1e). It was observed in combination with the highest WFPS peak, which occurred after total rainfall of 36 mm and a temperature drop to 7 °C within the first experimental week.

During week 4 (2–8 May), a second significant increase in flux rates was observed in the treatments RD1, SL1, P1 and RD2, SL2, CC2 (Fig. 4-1e,f). In addition, a continuous temperature rise and a decrease in WFPS were measured (Fig. 4-1d). After the next heavy rain (at the end of week 7), N_2O fluxes in all treatments increased once again with exception of RD2.

In contrast to the results in year 1, the stepwise multiple regression indicated that weather conditions had a lower effect on the mean N_2O fluxes during 2016 (temperature: $r^2 = 0.19$, $p < 0.05$ (independent variable entered in step 1 of stepwise regression) and WFPS: $r^2 = 0.46$, $p < 0.05$ (independent variable entered in step 2)). The N_2O fluxes measured in untreated control, SS1, DS1, and ASS2 were partly predicted by daily rainfall (Table 4-5). In plots treated with SL2, air temperature showed an effect on N_2O production in the soil. Furthermore, a significant relationship between soil temperature and N_2O flux rates, as well as between WFPS and N_2O flux rates, was observed in the treatments RD1 and CC2. In the treatments SL1, P1, and SS2, weather conditions did not contribute to the variability of the flux rates.

Table 4-5 N_2O release as affected by air temperature (x_1), rainfall (x_2), water-filled pore space (x_3) and soil temperature (x_4) during the second experimental year (2016). Coefficient of determination and function of stepwise multiple regression (Forward procedure, F to enter: 4.000, F to remove: 3.900).

N_2O release [1] **(g N_2O-N ha^{-1} d^{-1})**	**Model R^2**	**Air temp. (°C)**		**Rainfall (mm)**		**Soil temp. (°C)**		**WFPS** [2] **(%)**		**Final equation of stepwise forward regression**
		partial R^2	p value	partial R^2	p value	partial R^2	p value	partial R^2	p value	
RD1	0.54		n.s.	0.40	<0.001	0.14	0.037		n.s.	$y = -22.1 + 14x_2 + 2.2x_4$
SL1			n.s.		n.s.		n.s.		n.s.	y = Intercept
SS1	0.50		n.s.	0.50	<0.001		n.s.		n.s.	$y = 7.4 + 3.1x_2$
DS1	0.31		n.s.	0.31	0.010		n.s.		n.s.	$y = 10.6 + 3.5x_2$
P1			n.s.		n.s.		n.s.		n.s.	y = Intercept
RD2	0.49	0.20	0.018	0.29	0.016		n.s.		n.s.	$y = -35.8 + 6.2x_1 + 11.1x_2$
SL2	0.36	0.36	0.005		n.s.		n.s.		n.s.	$y = -11.6 + 3.7x_1$
SS2			n.s.		n.s.		n.s.		n.s.	y = Intercept
CC2	0.77		n.s.	0.57	<0.001	0.13	0.002	0.06	0.051	$y = -215.8 + 18.6x_2 + 3.2x_3 + 4.3x_4$
ASS2	0.45		n.s.	0.45	0.001		n.s.		n.s.	$y = 10.2 + 4.8x_2$
Control	0.70		n.s.	0.70	<0.001		n.s.		n.s.	$y = 4.9 + 4x_2$

[1] RD1/2: raw digestate; SL1/2: liquid fraction; SS1/2: solid fraction; DS1: dry solid; P1: pellet; CC2: concentrate; ASS2: ammonium sulfate solution; numbers behind treatments abbreviations: number of respective biogas plant; [2] WFPS: water-filled pore space.

4.4.1.5 Cumulative N_2O emissions

The average cumulative N_2O emissions in year 1 were significantly ($p < 0.05$) higher than in year 2 (Fig. 4-2a,b). This effect was also observed in the untreated control, which emitted almost 70% less in 2016 compared to 2015.

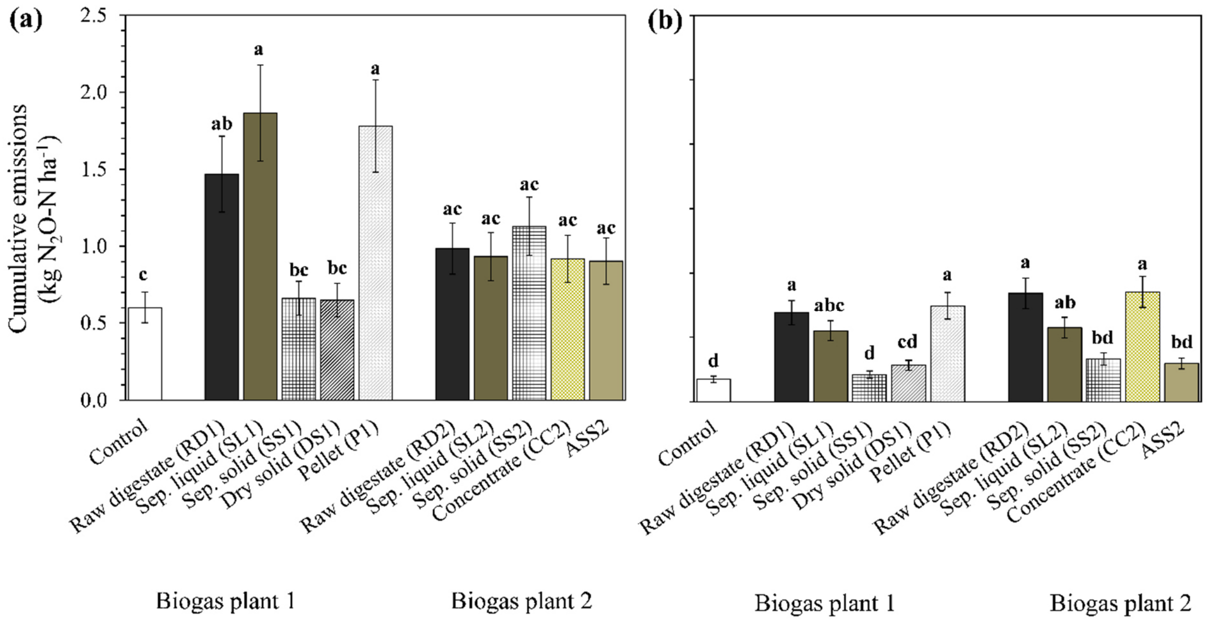

Figure 4-2 Mean cumulative N_2O emission in the field trial (n = 4 ± standard error) as affected by digestate and biogas plant in the two experimental years (**a:** 2015; **b:** 2016); concentrate: concentrate after vacuum evaporation, ASS: ammonium sulfate solution; at least one identical letter indicates non-significant differences among treatments, according to Tukey HSD test ($p \leq 0.05$).

Concerning biogas plant 1 (solid processing chain) in both experimental years, the treatments raw digestate (RD1), separated liquid (SL1), and pellet (P1) showed higher cumulative emissions than the solids SS1 and DS1. In 2015, the separation of raw digestate (RD1) led to a slight increase in N_2O emissions after application of the subsequent liquid fraction (SL1). This was not the case in the second experimental year. After utilization of the separated liquid, 0.2–0.7% of applied N_t was released as N_2O. In terms of the further processing of separated solid, increasing cumulative emissions were determined especially after pellet (P1) application. On average, they were equivalent to 0.05 (dry solid, DS1) and 0.5% of applied N_t (P1), respectively.

Within biogas plant 2 (liquid processing chain), the differences in digestate composition did not significantly influence the cumulative N_2O emissions in 2015 (Fig. 4-2a). In 2016, SL2 and SS2 resulted in lower emissions (0.2–0.09% of applied N_t) when compared to RD2 (Fig. 4-2b). Regarding the subsequent processing of SL2, the cumulative emissions increased after applying the N-depleted concentrate (0.4% of applied N_t) and decreased after ASS2 utilization (0.07% of applied N_t).

Within biogas plant 1, N_2O emissions were negatively correlated to the C:N ratio of the digestates (2015: $r^2 = 0.71$, $p < 0.05$; 2016: $r^2 = 0.64$, n.s.), while in plant 2, this effect could not be verified (data not shown). Concerning the influence of the fertiliser NH_4^+–N:N_t ratio on the N_2O emissions, no correlation was found during both observation periods.

4.4.2 Incubation experiment

4.4.2.1 Daily N_2O fluxes

During the first week of incubation, the N_2O release increased in all fertilizer treatments (Fig. 4-3). The highest N_2O flux rate (679 µg N_2O–N m^{-2} h^{-1}) was determined three days after fertilization in the pellet treatment of biogas plant 1 (P1, Fig. 4-3a). Concerning the liquids of plant 2, SL2 and CC2 showed the first significant N_2O peaks on day 4 followed by a second small increase in SL2 on day 8 (Fig. 4-3b). During the next six weeks, the flux rates remained on a low level in all treatments of both biogas plants. Additional N_2O peaks were measured in SS1 (75 µg N_2O–N m^{-2} h^{-1}, day 16), DS1 (89 µg N_2O–N m^{-2} h^{-1}, day 25) and SL2 (58 µg N_2O–N m^{-2} h^{-1}, day 44).

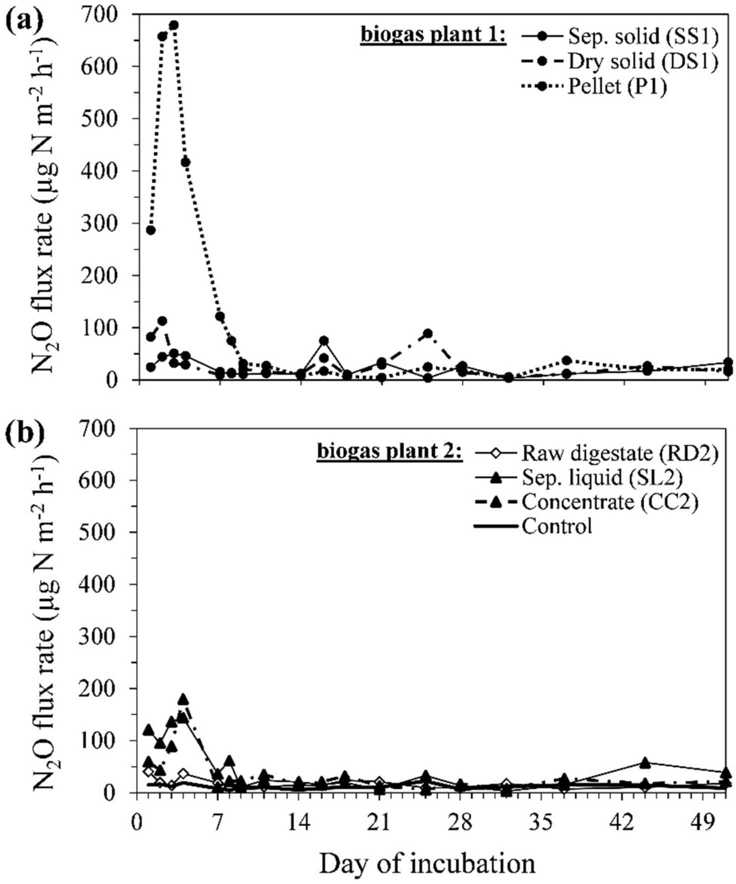

Figure 4-3 Mean N_2O flux rates (n = 4) as affected by digestate and biogas plant measured during the incubation; sep.: separated, concentrate: concentrate after vacuum evaporation.

4.4.2.2 Cumulative N_2O emissions

The subsequent processing of solid significantly affected N_2O emissions. The highest cumulative N_2O emission during the whole incubation period (1.5 kg N_2O–N ha^{-1} on average) was determined in the pellet treatment (P1) and corresponded to 0.8% of applied N_t (Fig. 4-4). Lower cumulative emissions (0.03 and 0.2% of applied N_t) were observed when separated and dry solid (SS1 and DS1) were utilized. Concerning the liquid processing (biogas plant 2), treatments showed no significant effect on the N_2O release. The application of raw digestate (RD2) caused the lowest cumulative emissions within the plant (0.18 kg N_2O–N ha^{-1} or 0.02% of applied N_t), which did not differ significantly from those of the untreated control (0.15 kg N_2O–N ha^{-1}). The post-treatments, SL2 and CC2 showed slightly higher cumulative emissions than RD2 and released 0.2% (SL2) and 0.14% of applied N_t (CC2), respectively.

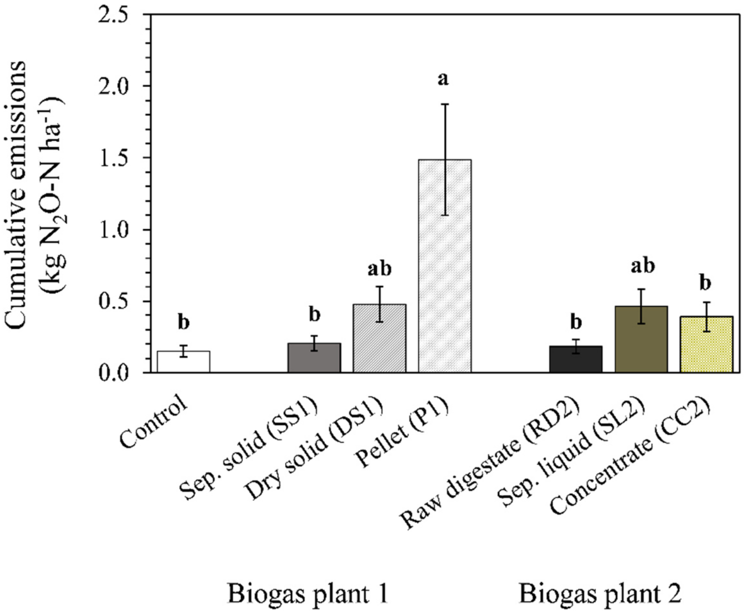

Figure 4-4 Mean cumulative N_2O emissions (n = 4 ± standard error) as affected by digestate and biogas plant measured during the incubation; sep.: separated, concentrate: concentrate after vacuum evaporation; at least one identical letter indicates non-significant differences between the treatments, according to Tukey HSD test ($p \leq 0.05$).

A strong negative correlation ($r^2 = 0.96$, $p < 0.05$) between the cumulative emissions and the C:N ratio of the digestates was found within biogas plant 1. For plant 2, the C:N ratio did not show any effect on the N_2O release. Furthermore, the N_2O emissions were not affected by the NH_4^+–N:N_t ratio of digestates (data not shown).

4.5 Discussion

4.5.1 General factors influencing the N_2O release

In the current study, the field application of raw or treated digestate caused a temporary increase in soil N_2O emissions. Although different feedstocks and processing approaches were used in both biogas plants, the resulting emissions of corresponding products did not differ significantly in most cases. It is assumed that, in our work, the environmental conditions, especially soil moisture and temperature, were of major importance and mostly overlaid digestate composition-related effects. During the first experimental year, warmer conditions with relatively high precipitation favored N_2O production and release. Increasing fluxes after fertilizer application and in connection with soil wetting (i.e., rainfall) (Fig. 4-1) have already been reported in literature [22,36–39]. In accordance with Hayakawa et al. [22] and Häfner et al. [40], the highest N_2O

peaks were observed within the first rainfall event (week 1). Hayakawa et al. [22] assumed denitrifying activity as the main driver, since they measured a simultaneous increase in CO_2 release. The simultaneous CO_2 release was also noted by Häfner et al. [40], who stated that at least part of the emitted CO_2 originates from digestate carbonate C, indicating that such a CO_2 release cannot only be assigned to the decomposition of organic matter. In the present study, the N_2O release directly after fertilization might have been a result of nitrification followed by denitrification, which was triggered by the high initial NH_4^+ content of digestate. On the other hand, the supply of easily degradable organic C and ammoniacal N with the digestates might have further promoted denitrification by (i) providing electrons as reduction equivalents [41], and (ii) stimulating O_2 consumption and consequently leading to more anoxic conditions [21,42–44].

The subsequent peaks in N_2O fluxes determined during the following weeks can be partly associated with further rainfall events, which was also described in previous studies [40,45–47]. During rather dry periods organic decomposition was reduced [48]. Subsequent rainfall induced soil moisture content which favored mineralization of residual organic molecules derived from digestates [48,49]. It provided labile N and C for denitrifying bacteria. Thus, denitrification was promoted and is assumed to be the main source for the N_2O production. Measurements of WFPS during the relevant N_2O peaks (WFPS of 55–58%, Fig. 4-1a,d) also indicate that nitrification and denitrification occurred simultaneously [50]. It can be concluded that weather conditions affected the emissions mainly immediately after digestate application and their influence decreased with time.

4.5.2 N_2O emissions affected by changes in digestate composition due to processing

4.5.2.1 Solid-liquid separation

Generally, the application of the same amount of N_t as separated solid or liquid led to similar or lower emissions than the utilization of raw digestate. This can be explained by the partial separation of two important factors: organic C (solid) which supplies electrons during nitrate reduction and ammoniacal N (liquid) which serves as substrate for combined nitrification–denitrification [13]. If the actual N partition due to the solid–liquid separation into single fractions (12% separated solid, 88% separated liquid) [51] is taken into account, the cumulative N_2O emissions from both fractions added up to 70–95% of the value of raw digestates in most cases. These results are slightly higher than those of Askri et al. [13] who reported cumulative N_2O emissions from both separated products of up to 50% of raw digestate. Hence, it can be concluded that solid–liquid separation potentially reduces the overall N_2O emissions after field application due to a partial separation of mineral N and organic C. Therefore, in untreated digestates, the interaction of these two compounds seems to boost the emissions.

Concerning the comparison between the separated products (liquid and solid) within each plant, the lower cumulative emissions after application of the solid fraction were in line with the previous literature [16,17]. The solid was characterized by a higher total C content, higher amounts of recalcitrant fractions, and a lower content of mineral N than raw digestate (Tables 4-1 and 4-2). The mentioned characteristics mainly result from processing and subsequent gaseous N losses during storage of the solid fraction [10,52]. During anaerobic digestion, a shift in particle size distribution toward larger and more recalcitrant particles takes place [53]. The solid–liquid separation of digestate removes further solids (>0.5 mm) and allocates most of the NH_4^+ to the liquid fraction (Table 4-1). The following storage of the separated solid further increases the proportion of large to small particles due to preferred biological decomposition of the smaller ones [54] and reduces the NH_4^+ content due to N immobilization and gaseous N losses (NH_3 volatilization, denitrification) [52]. As a result, the solid contains less soluble compounds, especially mineral N (Table 4-1 and Table S1). Additionally, the larger particles are more resistant to degradation and, consequently, the O_2 consumption is probably reduced [12,55] due to the lower C mineralization. Both lower substrate availability (N as NH_4^+) and higher aeration likely reduced the N_2O release from denitrification after field application. Within 7 weeks, the cumulative N_2O emissions in the solid treatment were 30–100% of the raw digestate (Fig. 4-2a,b). This indicates the potential of separated solid to reduce the emissions after application compared to the precursor, as also reported in previous studies [15,56]. However, a concluding statement about the overall greenhouse gas reduction potential should also consider N losses, which might occur during processing and storage [10], as well as methane and carbon dioxide emissions.

4.5.2.2 Subsequent processing of separated liquid

In contrast to our initial assumption, the N removal during subsequent processing of separated liquid did not clearly affect the N_2O emissions after application of the respective products.

When comparing separated liquid with its partially dewatered concentrate post-treatment, no significant effect was found (Figures 4-2 and 4-4), although separated liquid had at least a threefold higher NH_4^+ content (based on total FM) and a lower C:N ratio. Since the proportion of recalcitrant fractions, such as lignin, was lower in concentrate (Table 4-2), it can be assumed that the presence of degradable C influenced bacterial growth and activity and, thus, triggered the N_2O emissions. The addition of labile C can also induce N_2O emissions derived from soil mineral N [47,57,58], which might have enhanced this effect in the case of concentrate (Fig. 4-2b). Furthermore, a part of initial labile N applied with separated liquid was probably immobilized by soil microflora immediately after fertilization [59], which mitigated the total amount of N_2O emitted from this treatment. These results generally suggest that the supply of ammoniacal N via liquid digestates is less relevant for the emissions after field application. This effect was also shown in the case of ammonium sulfate treatment (ASS2).

The lower emissions observed in ASS2 (year 2, field experiment) might have been a result of the negligible C supply compared to the concentrate. Moreover, a short-term NH_3 volatilization probably occurred directly after soil application of ASS2 [60–64], which reduced the amount of NH_4^+ added to soil and available for N_2O production. A reduced availability of introduced mineral N and consequently low N_2O release can also be attributed to partial N immobilization during the initial experimental phase, as reported by Fangueiro et al. [65]. Although NH_3 volatilization and N immobilization were not measured in the present work, it is assumed that the absence of C in ASS2 was the main reason for the low N_2O emissions observed in the second year. During year 1, weather conditions (higher temperature and relatively high precipitation) probably overlaid this effect.

4.5.2.3 Further processing of separated solid

Concerning the solid processing chain, the significant reductions in N_2O emissions after application of the intermediate products (separated solid and dried solid, both low in ammoniacal N) compared to raw digestate underlined, once again, the importance of simultaneous substrate availability (N as NH_4^+) in the presence of degradable organic C. Even though considerable amounts of solids (and organic matter) were applied to the soil in the separated solid and dried solid treatments (Table S2), N_2O emissions were still limited by the availability of NH_4^+ and did not differ significantly from the control. Between these two solids, emissions were also not significantly different. This result was not in line with the finding of Askri et al. [13] who reported a fourfold increase in N_2O emissions after fertilization with dried solid. However, since they assumed that the mineralization of N already present in the soil was of higher importance for the N_2O production than the introduction of additional mineral N via fertilizer, the discrepancies between both studies could be explained by soil-related effects, such as soil type, characteristics, and nutrient level. Another reason for their findings could be an elevated substrate biodegradability, which would favor microbial growth and activity.

In general, by removing water from the separated solid, a dried fertilizer with similar total C content, lower NH_4^+ concentration, and higher soluble material load is produced (Table 4-1 and Table S1). In the present study, these changes led to a slightly higher but not significant N_2O release after application compared to the separated solid (Figures 4-2 and 4-4). The lower share of recalcitrant fractions in the dried solid (Tables 4-1 and 4-2) provides some indications for consecutive changes in the composition of the organic matter during the drying process [66–70]. Consequently, it can be concluded that, in the case of dried solid, the addition of easily degradable C in combination with soil-derived NO_3^- triggered the N_2O production and release. This notion is consistent with previous findings, based on experiments with ^{15}N-labeled manures [40,47,57,58]. It highlights the complexity of the presented issue and the importance of additional determination of the responsible N source. Additionally, the interaction among soil parameters, added organic matter fractions, and weather conditions should be taken into consideration.

The high N_2O emissions observed after pellet application (Figures 4-2 and 4-4) are in accordance with the results of Hayakawa et al. [22], who compared poultry manure with its pelleted post-treatment. In general, the strong increase in temperature during pelletizing affects the properties of organic compounds and creates constant inner microsites [32,71–74]. According to Petrova et al. [32], the water addition to the pellet activated the decomposition of its organic matter by indigenous microflora. Consequently, an enhanced microbial O_2 consumption favored the development of anaerobic microsites inside the pellet and, thus, stimulated denitrification. In addition, the increase in soil NO_3^- content after pellet application measured by Hayakawa et al. [22] indicated a probable nitrification at the soil–pellet interface. Since the temporal changes in soil NO_3^- content were not observed in the present study, denitrification inside the pellets was probably the main emission driver. It seems that concentrated application of organic manures, either in the form of pellets or via fertilizer injection [42,75,76], results in a strong increase in N_2O emissions from the soil. It was shown that both the composition of organic manure and the interaction between applied manures and soil strongly affect N_2O emissions.

4.6 Conclusions

The present study showed that, aside from environmental conditions, it is not possible to draw general conclusions regarding how digestate composition influences the processes driving the N_2O emissions after fertilization. For example, the N removal during further processing of separated solid and liquid does not affect the emissions after application of the respective products. More relevant for N_2O production and release are the strong interactions between digestate composition, O_2 consumption triggered by decomposition of applied C, nitrification of fertilizer mineral N, and denitrification induced by added C and soil mineral N.

When considering the different processing techniques, it can be concluded that separation of raw digestate has the potential to reduce N_2O emissions after soil application. This reduction potential is also true for the dried separated solid. Additionally, separated solid and dried solid can outperform a mineral fertilizer, such as ammonium sulfate, with respect to soil-derived N_2O emissions. However, pelletizing of the dried product stimulates water-induced denitrifying activity inside the pellet body and results in a dilemma. Much higher N_2O emissions after soil application counteract positive aspects such as excellent storability and transportability properties. Regarding the utilization of different liquid fractions (concentrate and ammonium sulfate), further field and laboratory experiments are recommended to better understand the interactions between the processes driving N_2O release after fertilization. Last but not least, future assessments of digestate posttreatments should consider covering the whole digestate value chain, including N_2O and other emissions during processing, storage, and field application.

4.7 References

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5 Origin of N_2O emissions: in-depth pellet analysis[‡]

Due to limited information about the properties of pelleted digestate, as well as the reason for the considerable N_2O release after its application to soils, the pure pellet body was studied in detail. For that purpose, pellets of BGP1, collected in 2016, were used.

5.1 Abstract

The field application of pellets from biogas residues resulted in high N_2O emissions which could not yet be parametrized through soil drivers. Therefore, the aim of this study was to determine potential N_2O production from pellets themselves. N_2O and CO_2 release from the pure pellet body (in form of intact, crushed or finely ground pellets produced from biogas digestates) were measured during the first seven days after pellet wetting under constant laboratory conditions. Three pellet water contents were examined: 47, 62 and 72% water of the total fresh pellet weight. Additional replicates of similarly wetted intact pellets were used to determine NH_4^+, NO_3^- and DOC contents on days 0, 1 and 4 of incubation. Two further treatments of wet intact pellets (62% moisture) were sterilized prior or after moistening to investigate the emissions' origin.

N_2O release was found to increase with decreasing pellet size fraction. A maximum of N_2O fluxes within all three fractions was determined at 62% moisture, whereas lowest fluxes were measured at 72% moisture. The cumulative N_2O emissions over seven days ranged between 1 µg N_2O–N g^{-1} pellet (intact pellets at 72% moisture) and 166 µg N_2O–N g^{-1} pellet (finely ground pellets at 62% moisture).

In general, our findings indicate that denitrification was the main factor for N_2O emissions, driven by indigenous microbial communities already present in the pellets. The results show that the N_2O emissions released by the pellets themselves can explain a major portion of the N_2O fluxes measured in situ.

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Keywords: nitrous oxide; pelleted biogas digestate; pellet fraction; indigenous microbial activity; denitrification

5.2 Introduction

Anaerobic digestion primarily aims at the production of biogas but also generates digestate, a valuable organic fertilizer, as a by-product. In Germany, the local field application of digested effluent often causes nutrient surpluses in the affected regions due to irregular geographical distribution of livestock and biogas plants [1–3]. As regulated by the current amendment of the fertilizer ordinance in Germany, total amount of organic fertilizer, as well as application time frames are limited. Consequently, large storage facilities are required to enable utilization of digestates in accordance with the legal regulations [4,5]. Exemplarily, German operators of biogas plants have to provide facilities, which are able to store digestates between six to nine months depending on size of the owned cropland. A possible strategy for solving these problems is the transportation of the digestate over long distances which, in turn, is costly and non-economical due to the large water to nutrient ratio [6,7].

Processing techniques for reducing the water content of digestates facilitate the handling and also generate marketable organic fertilizers. A common technique is the mechanical separation of digested effluent into a solid and a liquid fraction. Based on the total fresh matter (FM) of the original material, the separated solid and liquid split at a ratio of 22.5 to 77.5% [8,9]. However, from an economical point of view the transportation of these products is limited as well, since the water content is still relatively high [10]. Möller et al. [9] noted that the feasible transport distance strongly depends on the dry matter (DM) content of the digestate and accounts for a maximum of 8.5 km for the solid and 7.5 km for the liquid after separation. Another important aspect is the gaseous loss during storage and handling of these fractions. In the case of the solid digestate, Hansen et al. [11] measured significant gaseous N losses, especially N_2, NH_3 and N_2O, on the surface of storage heaps. Consequently, the nutrient availability in this fraction decreases [12] and the fertilizer value is reduced.

A suitable managing approach is the subsequent processing of the separated solid. Established techniques for further treating of solid digestate are drying and pelletizing. Drawbacks of both processes are high energy demands and costs [13]. Consequently, only about 1% of biogas plants in Germany implemented drying of solid digestate [8].

During a study targeting stakeholders' interests, farmers expressed the willingness to adopt pelleted organic fertilizers. However, in the same study, a substantial lack of knowledge concerning chemical properties of such kind of fertilizers and their effect on soil organic matter dynamics was revealed [14]. Pelletizing reduces the volume of the raw material through compressing and simultaneously increases bulk density and durability of the product [15–18]. As a result, handling and transportation are facilitated and the required storage volume is minimized [15]. Additionally, the substrate is homogenized and nutrients are concentrated, which ultimately leads to improved fertilizing and amending properties [14,17,19]. Pelletizing of composted organic material for fertilizing purposes, such as manures [13,17–19], crop residues [13,17,18], butchery wastes and wastepaper [20] is widely applied. By using "co-formulates" or bulking agents, such as biochar or wood chips, storage and transportation properties, as well as field spreading characteristics of pellets can be further improved [17,18].

During the pelletizing process, agglomerations are formed in the channels of the die. The high pressure and increased friction force between biomass and channel wall lead to a considerable rise in temperature (70–100 °C depending on biomass and pelletizing process) of the solid [1,7,15,21]. Due to the high temperature, a change in the physical state of several components, e.g. lignin and extractives like waxes, occurs in the solid. According to previous studies, lignin is the most recalcitrant component of lignocellulosic biomass and thus particularly difficult to decompose during anaerobic digestion [22–25]. At low compaction pressures and a temperature in the range of its glass transition temperature, lignin undergoes plastic deformation (i.e., "softening") [25,26]. For corn stover, one of the main biomass feedstocks used to produce the respective pellets, the glass transition temperature generally ranges between 50 and 113 °C [27]. The softened natural binders, such as lignin, in combination with water contained in the solid formed the outer layer of the pellet [28,29]. In addition to a stabilization effect, this layer could help to create and keep a constant inner milieu including certain microsites.

In the case of pelleted manure, Alemi et al. [19] reported a slow release of N and P after pelletizing which generally reduced leaching and improved the nutrient uptake by plants. The availability of nutrients was also influenced by pellet diameter and application method [30]. However, information about the environmental effect of pellet application is still rare. Within a measuring period of one month, Cabrera et al. [31,32] reported nitrous oxide (N_2O) emissions from soils after pellet utilization between 0.2

and 3.9% of applied N. The N_2O flux rates depended on the soil water regime and on physical characteristics of the pellets. Pampuro et al. [33] measured N_2O emissions between 0.05 and 0.12% of applied N, depending on pellet size and application method. For CH_4 and NH_3, negligible release was reported [33].

Nitrous oxide is a climate relevant trace gas with absorption bands in the IR spectrum thus reducing the atmospheric transparency to thermal radiation from the earths' surface [34]. Since pre-industrial times, the atmospheric N_2O concentration has increased by approximately 21% to 328 ppb in 2015 (0.73 ppb per year) [35]. Nitrous oxide contributes 7.4% of the total anthropogenic radiative forcing [36]. Besides that, N_2O is also involved in stratospheric ozone depletion [37,38]. More than 60% of the anthropogenic N_2O emission originates from agricultural soils [36]. It is generally accepted that biological denitrification and nitrification are the main sources for the production and release of N_2O in soils [39]. Especially the application of stable isotopes in environmental studies opened new insights in sink and sources of N_2O. This initiated an intense discussion about the contribution of other process, such as nitrifier-denitrification, to the total release of N_2O from soils [40,41].

Concerning the N_2O emissions after pellet application to soils, Hayakawa et al. [42] observed a higher N_2O release after fertilization with pellets than with the original digestate. In an own field study with pellets and other processed biogas digestates, we could confirm this result: highest N_2O emission was measured in the pellet treatment. The reason for that emission remained unclear because the main drivers for N_2O production in soil such as mineral N (N_{min}) or moisture did not correlate with the N_2O fluxes in the pellet treatment (data not shown). In contrast to our results, the positive relationship between CO_2 and N_2O fluxes as well as increasing NO_3^- content in soil measured in the study of Hayakawa et al. [42] indicated nitrification and denitrification as emission drivers. In accordance with this conclusion, Yamane [43] stated various denitrifying activities directly in the pellets as a reason for the high N_2O release.

Therefore, our main aim was to test the assumption that the autochthonous microflora in the pellets produces and releases a substantial amount of N_2O. Another major point of interest was to study the effect of pellet moisture and pellet size on N_2O emissions.

5.3 Materials and methods

5.3.1 Pellet manufacturing and composition

The pellets used in this study were obtained from a biogas plant located in South Germany. Feedstocks were pig slurry and cattle manure, energy crops like silage maize and sunflower (400 g kg^{-1} total fresh matter, FM), pomace and grape marc (200 g kg^{-1} FM) and poultry manure (50 g kg^{-1} FM). In this biogas plant, raw digestate was separated with the help of a screw press, equipped with a tubular slit screen (0.5 mm pore size). The liquid and smaller particles passed the screen, while the retentate exited by a rotating screw [1,44]. Afterwards, the separated solid was dewatered to about 80% DM content in a solar greenhouse drier, equipped with an electric mole (THERMO-SYSTEM, Industrie- & Trocknungstechnik GmbH, Germany). During the consecutive pelletizing, pan grinder rollers forced the dried substrate through a die (5–10 mm channels diameter). During the compressing, a part of the residual water is evaporated and a tough outer layer is formed. After exiting the channels, the solid is cut by a share blade to small cylinders with a diameter of 6 mm and an average length of 14 mm. Table 5-1 shows the main physical and chemical properties of the pellets.

Table 5-1 Dry matter (DM), total carbon (C_t), organic carbon (C_{org}), total nitrogen (N_t), ammonium–N (NH_4^+–N), nitrate-N (NO_3^-–N), NH_4^+–N:N_t ratio, C:N ratio, pH, neutral detergent fiber (aNDF), acid detergent fiber (ADF) and acid detergent lignin (ADL) of the pellets.

Parameter	**Value**
DM (g kg^{-1} FM)	851
C_t (g kg^{-1} DM)	447
C_{org} (g kg^{-1} DM)	445
N_t (g kg^{-1} DM)	34.9
NH_4^+–N (g kg^{-1} DM)	2.4
NO_3^-–N (g kg^{-1} DM)	2.7
NH_4^+–N:N_t	0.07
C:N	12.8
pH [1]	7.9
aNDF (%)	58.3
ADF (%)	52.0
ADL (%)	31.6

All parameters were determined according to VDLUFA [46], no replicates.
[1] 10^{-2} M $CaCl_2$ solution.

Dry matter content was measured by drying at 105 °C until constant weight. Total C (C_t) was investigated by elemental analysis (vario MAX CN, Elemental Analysensysteme, Hanau). Carbonate content was determined with a Scheibler apparatus according to DIN EN ISO 10693. Organic C was calculated as difference between total C and inorganic C. Total N (N_t) and NH_4^+–N contents of the pellets were determined according to Kjeldahl [45] and by steam distillation with titration [46], respectively. The pH value was measured with a glass electrode (Schott, Lab 850) in a 0.01 mol L^{-1} $CaCl_2$ solution at a ratio of 1:10 (w w^{-1}) [47]. Furthermore, the fiber fractions ‘amylase-treated neutral detergent fiber’ (aNDF), ‘acid detergent fiber’ (ADF) and ‘acid detergent lignin’ (ADL) were analyzed according to van Soest and Wine [48].

5.3.2 Further pellet analysis

Prior to the experimental set-up, the amount of easily degradable C and N was quantified in intact, manually crushed and finely ground pellets (the latter processed by an agate disc swing mill, Siebtechnik, Mülheim an der Ruhr, Germany). In this way, the effect of different total surface area on water absorption, mineralization and resulting C and N release was studied. The crushed pellet fraction consisted of particles in the ranges of > 5 mm, 2.5– < 5 mm, 1– < 2.5 mm and < 1 mm with a distribution of 64%, 14%, 10% and 12%, respectively. In finely ground pellets, particles sizes of > 1 mm, 0.5– < 1 mm, 0.25– < 0.5 mm, 0.1– < 0.25 mm and < 0.1 mm were distributed as follows 3%, 14%, 26%, 26% and 31%. To determine the C and N amounts of the pellet fractions, a hot water extraction was performed according to Leinweber et al. [49] with slight modifications [50]. In brief, samples of 20 g air-dried pellets were boiled in 100 ml distilled water for 1 h. After adding 5 drops of 2 mol L^{-1} $MgSO_4$ solution, the pellet-water mixture was centrifuged for 10 min at 2600 rpm under room temperature. The supernatant was collected and filtered through a syringe filter (0.45 µm pore size). Hot water extractable carbon (C_{hws}) and nitrogen (N_{hws}) contents of the extracts were analyzed with a C/N-analyzer for liquid samples (Multi N/C 2001 S, Jenoptik, Germany). This analysis was done in triplicate.

5.3.3 Experimental set-up

To assess the effect of particle size and water content of pellet on N_2O and CO_2 emissions, a laboratory incubation experiment was conducted. It was built up as a randomized block design, consisting of 14 treatments and four replicates in total. To investigate the effect of particle size on gaseous losses, the treatments included intact, crushed and finely ground pellets. Three different pellet water contents were examined: 47, 62 and 72% of the total fresh pellet weight. We chose 47 and 72% water content as lower and upper boundary because the gravimetric water contents of the pellets in the field varied in the same order of magnitude. The third moisture level (62% water content) was approximately the moisture in the period with highest N_2O fluxes in our field experiment. For each trial, 0.5 g pellet was placed in a 20 ml vial and wetted with distilled water. Prior to each gas measurement, the vials were closed with butyl stoppers and crimped. Following each gas sampling, the vials were re-opened, covered with a gas-permeable and liquid-tight PE-LD sheet and incubated at 20 °C in the dark. To compensate for vapor losses from the pellet body during incubation, the vials were weighed daily and, where necessary, the water content was re-adjusted manually.

Two control treatments with intact pellets wetted to 62% were assessed to control the efficiency of microbial inactivation. For that purpose, those pellets were autoclaved (30 min at 120 °C and 2000 hPa) and moistened (i) before (in the following text marked as “sterile 1”) or (ii) after (“sterile 2”) the sterilization procedure. Utilized gas vials and butyl stoppers were also autoclaved. All samples were incubated as stated before.

5.3.4 Trace gas measurements and flux rate calculation

The N_2O and CO_2 release from the pellets was measured on days 0, 1, 2, 4 and 7 after pellet moistening. Gas fluxes were determined by taking three gas samples in intervals of six hours after crimping the vials.

Trace gas analysis was done with a gas chromatograph (GC 450, Bruker Daltonik, Bremen, Germany), coupled to an autosampler (GX-281, Gilson, Germany). The latter was equipped with a magnetic valve connected to a N_2 line (ECD quality) regulated to a pressure of 2000 hPa using a reduction valve. The overpressure in the vials was used to transfer the sample to the sample loops of the GC. Since the pressure in the vials before the addition of overpressure was 1000 hPa, samples were diluted 1:1. Although overpressure addition works reliable, additional gas vials with trace gas standards were included in the sample schedule in order to verify the dilution factor. The GC was equipped with a 63Ni electron capture detector (ECD) for N_2O and CO_2 analysis after separation on a Haysep D 80/100 column.

The calculation of the flux rates took into account CO_2 and N_2O concentrations of three gas samples (µL L^{-1} or nL L^{-1}, respectively), dilution factor through overpressure addition, air temperature (°C), weight of the air-dried pellet (g) and volume (L) of the headspace inside the vial. The flux rates were calculated using the linear slope of the trace gas concentrations in the headspace inside the vial over time [51]. Cumulative emissions were calculated by linear interpolation and numerical integration between sampling events.

5.3.5 Further laboratory measurements

In addition to the gas measurements, dissolved organic carbon (DOC) and mineral N (NH_4^+–N and NO_3^-–N) of intact moistened pellets were determined. For that purpose, four additional replicates were used. They were prepared and incubated identically to the intact pellet treatments with the three above-mentioned water contents. These samples were extracted on days 0, 1 and 4 of incubation with 15 mL of 0.5 mol L^{-1} K_2SO_4 solution. The mixture was filtered (filter paper MN 619 eh ¼, 2–4 µm pore size, MACHEREY–NAGEL, Germany) prior to analysis. On day 7, the extraction was carried out with the actual intact pellet treatments immediately after the last gas sampling.

Mineral N concentrations in the extracts were determined with a flow injection analyzer (3 QuAAtro.AQ2.AACE, SEAL Analytical, UK). Total N and DOC were measured using a C/N-analyzer for liquid samples (Multi N/C 2001 S, Jenoptik, Germany). Dissolved organic nitrogen (DON) was than calculated by subtracting mineral N from the total N in the liquid samples.

5.3.6 Statistical analysis

Prior to the statistical analysis, the experimental data were tested for normality and homogeneity of variance. If these criteria were not given, they were transformed by a $\log_{10}$ or a square root function. The change in N_2O and CO_2 flux rates with time was evaluated using a two-way repeated measures ANOVA. Here, the pellet fraction (intact, crushed or finely ground) and adjusted water content acted as main independent variables while the measurement day described the repeated statement. The effect of the independent variables on the cumulative emissions was tested using a two-way ANOVA. A one-way ANOVA including the previous repeated statement was performed to study the temporal change in DOC, NH_4^+–N and NO_3^-–N contents of intact pellets with three different water contents. The same model was run to analyze the influence of pellet sterilization on greenhouse gas emissions during the observation period. Significant differences between the treatments for each of the performed statistical models were calculated using a Tukey HSD test ($p \leq 0.05$).

5.4 Results

5.4.1 Hot water extractable C and N as affected by pellet fraction

The results of the hot water extraction are shown in Table 5-2. It was observed that crushing pellets resulted in a significant lower amount of extractable C than finely grinding ($p = 0.006$) or even without treating ($p = 0.019$). In the crushed fraction C_{hws} accounted for 10.7% of C_t. The corresponding values for finely ground and intact pellets were 11.9% and 12.5%. There was no statistically significant difference in N_{hws} between the three pellet fractions. It ranged between 42.6% (crushed) and 47.1% (finely ground pellet) of N_t content.

Table 5-2 Mean hot water extractable C (C_{hws}) and N (N_{hws}) contents of three different pellet fractions (n = 3 ± standard error); Means followed by a common letter are not significantly different by the Tukey HSD test at the 5% level of significance.

Pellet fraction	C_{hws}	N_{hws}
	mg C g^{-1} pellet	mg N g^{-1} pellet
Intact	45.6 ± 1.0 a	13.4 ± 0.8 a
Crushed	41.5 ± 1.0 b	12.6 ± 0.2 a
Finely ground	46.8 ± 0.5 a	14.0 ± 0.2 a

5.4.2 N_2O and CO_2 flux rates

The N_2O fluxes ranged between −0.05 (intact pellets 72%, day 2) and 1.9 µg N_2O–N g^{-1} pellet h^{-1} (finely ground pellets 62%, day 4) (Fig. 5-1a–c). We found a significant interaction ($p < 0.05$) between pellet fraction (intact, crushed and finely ground pellet) and water content (47%, 62% and 72%). On day 0, the N_2O flux rate from finely ground pellets moistened to 47% was significantly lower than those wetted to 62% or 72%. During the following three days increasing flux rates were observed in all pellet fractions wetted to 47% and 62%, while in those with 72% moisture a slight decrease was measured. In contrast to the other pellet fractions, the flux rate from intact pellets wetted to 62% dropped on day 4 from 0.9 to 0.3 µg N_2O–N g^{-1} pellet h^{-1} (Fig. 5-1b). It was approximately fourfold lower than in the treatment with crushed pellets and sixfold lower than in finely ground pellets with the latter difference being statistically significant ($p < 0.001$). Between day 4 and the end of the measurements, the N_2O fluxes decreased in all treatments.

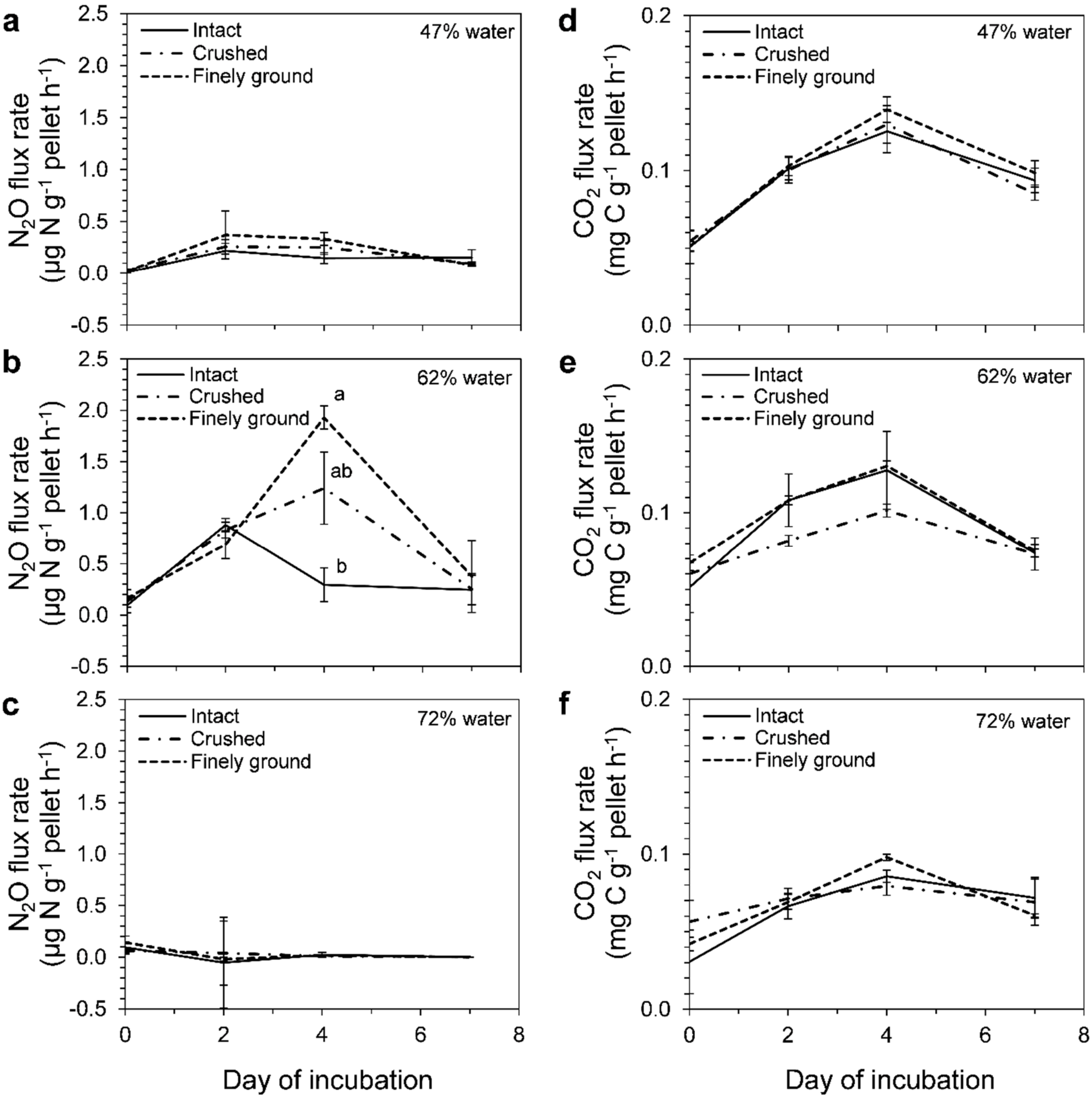

Figure 5-1 Mean N_2O and CO_2 flux rates (n = 4 ± standard error) as affected by pellet fraction (intact, crushed, finely ground) and water amount (**a, d:** 47%; **b, e:** 62%; **c, f:** 72%) during the incubation; Means followed by a common letter are not significantly different by the Tukey HSD test at the 5% level of significance. Missing letters indicate means without significance.

Concerning the CO_2 release, the flux rates increased significantly ($p \leq 0.01$) in all treatments within the first four days of incubation (Fig. 5-1d–f). The lowest CO_2 flux rate was measured on day 0 in intact pellet fraction moistened to 72% (0.03 mg CO_2–C g^{-1} pellet h^{-1}) (Fig. 5-1f). In contrast, the highest one (0.14 mg CO_2–C g^{-1} pellet h^{-1}, day 4) was determined in finely ground pellets wetted to 47% (Fig. 5-1d). Towards the end of the measurement, the CO_2 fluxes decreased in all treatments. Generally, the treatments with the highest moisture (72%) showed lower CO_2 flux rates than those with less water addition.

5.4.3 Cumulative N_2O and CO_2 emissions

The cumulative N_2O and CO_2 emissions over the experimental period of seven days are shown in Fig. 5-2. The highest cumulative N_2O emission of 166 µg N_2O–N g^{-1} pellet (corresponded to 0.6% of N_t) was measured in the treatment with finely ground pellets wetted to 62% (Fig. 5-2a). For the moisture treatments 47% and 62%, cumulative N_2O emissions increased with decreasing particle size of pellets in the order intact < crushed < finely ground. Besides that, the moisture significantly ($p < 0.001$) affected the N_2O emissions in the order 62% > 47% > 72% regardless of the pellet fraction. The N_2O emission of the treatment with the highest moisture was distinctively lower than those from the treatments with 47% and 62% moisture (by a factor of 7–21 and 31–59, respectively).

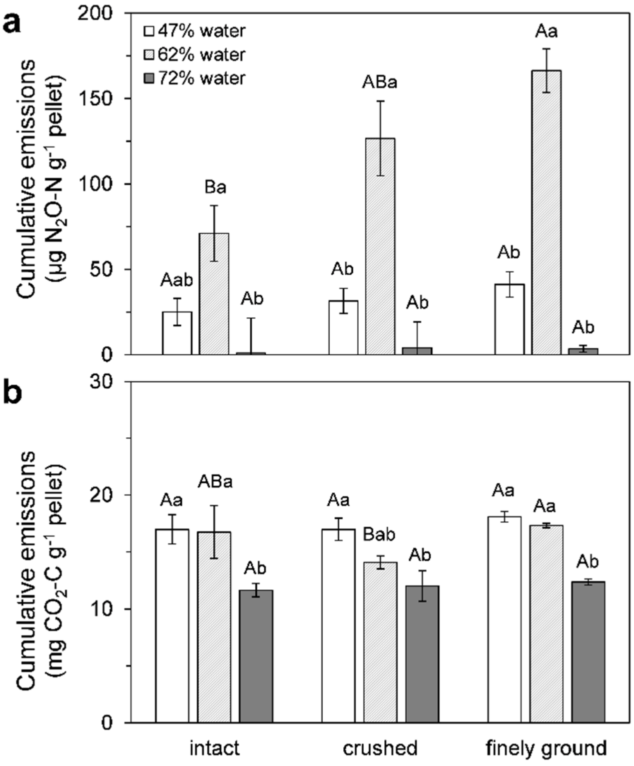

Figure 5-2 Mean cumulative N_2O and CO_2 emissions (n = 4 ± standard error) as affected by pellet fraction (intact, crushed, finely ground) and water amount during the incubation; Means followed by a common letter are not significantly different by the Tukey HSD test at the 5% level of significance. Capital letters depict differences between the pellet fractions, lowercase letters depict differences between moisture treatments.

Regardless of the pellet fraction, increasing moisture of the pellets reduced the CO_2 release (Fig. 5-2b). Here, a strong positive correlation was found ($r^2 = 0.52$, $p < 0.001$). The CO_2 emissions measured at the highest moisture (72%) were significantly lower ($p < 0.01$) than in the other treatments. Correspondingly to the cumulative N_2O emissions, the lowest CO_2 release was determined in the intact pellet treatment wetted to 72% (11.7 mg CO_2–C g^{-1} pellet). Similarly, the finely ground pellets wetted to 47% showed the highest average value (18.1 mg CO_2–C g^{-1} pellet). Within the 62% water content treatments, CO_2 emission from the crushed pellets was significantly lower ($p < 0.05$) than those from intact and finely ground.

5.4.4 Temporal DOC, DON and N_{min}-dynamics in intact pellets

On day 0 and 1 of incubation, the amount of water added to the pellets had no significant effect on DOC (Fig. 5-3a). However, a slight (but statistically not significant) decrease in DOC was observed within this time period in all moisture treatments. During the following three days, DOC concentrations in treatments with 47% and 62% moisture further declined while that in the highest moisture increased. Between day 4 and the end of the experiment, increasing DOC concentrations were observed in all treatments. The highest concentration (22.7 mg C g^{-1} pellet) was measured at 72% moisture on day 7. In this treatment, the high DOC concentrations determined on day 4 and 7 differed statistically significant from the treatments with 47% and 62% moisture ($p < 0.05$).

Nitrate concentrations measured in pellets with 62% and 72% moisture decreased steadily, except for a short-term increase on day 1 (Fig. 5-3b). Here only in the case of 62% moisture, it was statistically significant ($p = 0.035$) when compared to the NO_3^- concentration observed in the same treatment on day 0. In the treatment with the highest moisture, the NO_3^- pool was completely depleted on day 7. In contrast to the other treatments, NO_3^- concentration at 47% moisture remained rather constant.

Ammonium concentrations in the intact pellets increased in all treatments one day after incubation start (Fig. 5-3c). Here, the pellets with 72% moisture showed the highest extractable NH_4^+ concentrations over all sampling dates. On day 4 in this treatment, the highest mean value (8.5 mg NH_4^+–N g^{-1} pellet) was determined. Lowest NH_4^+ concentrations were measured in the treatment with 47% moisture where this pool was nearly depleted on day 7.

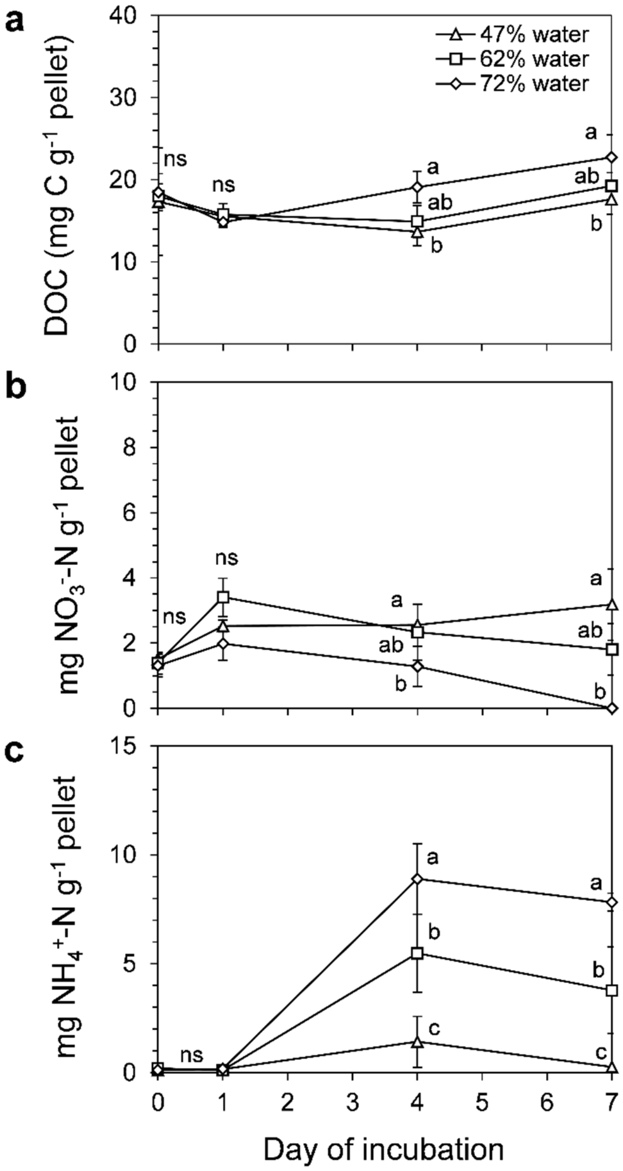

Figure 5-3 Temporal changes of mean DOC, NH_4^+–N and NO_3^-–N concentrations (n = 4 ± standard error) as affected by moisture of intact pellets; Means followed by a common letter are not significantly different by the Tukey HSD test at the 5% level of significance, ns: no statistically significant difference.

The calculated DON values (total N in extracts – mineral N in extracts) are reported in Table SS1. The highest DON content (14.9 mg N g^{-1} intact pellet) was determined immediately after pellet moistening to 72% which, afterwards, decreased continuously toward the end of observation. In contrast, pellets wetted to 47% showed almost constant DON content with a slight increase on the last measurement day. For the 62% treatment, fluctuating values (3.2 to 10.5 mg N g^{-1} intact pellet) were noticed during the whole experimental period.

5.4.5 Effect of sterilization method on N_2O and CO_2 fluxes from intact pellets

The N_2O and CO_2 flux rates in the sterilization experiment showed similar patterns as the flux rates in the main experiment. Nitrous oxide fluxes ranged between −0.005 (sterile 2, day 7) and 2.3 µg N_2O–N g^{-1} pellet (intact, day 1) (Fig. 5-4). The highest CO_2 flux rates were in the order of magnitude of those observed in intact pellets at 62% moisture during the main experiment. In contrast, N_2O flux rates after sterilization were approximately two times higher than those in the main trial.

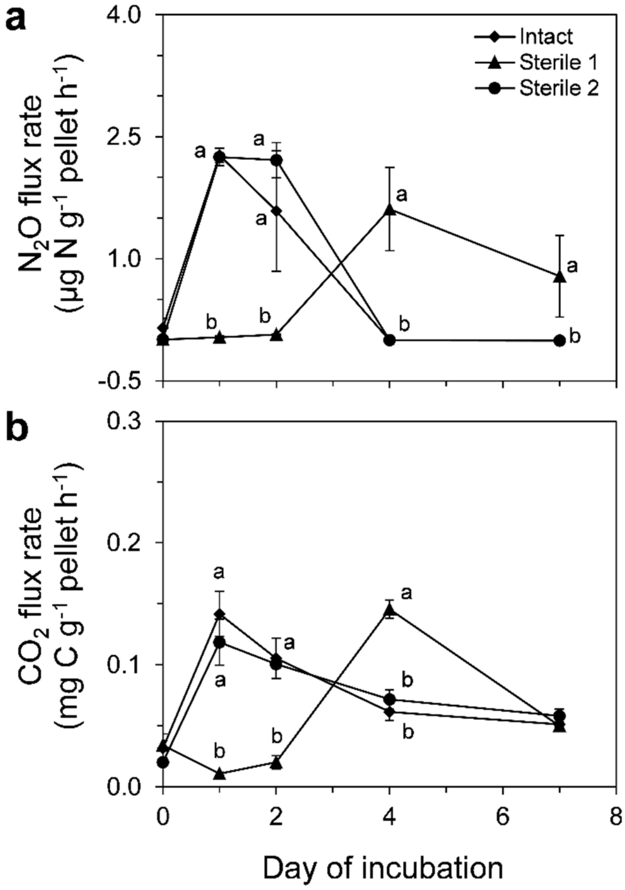

Figure 5-4 Mean N_2O and CO_2 flux rates (n = 4 ± standard error) of intact pellets as affected by sterilization method (**sterile 1:** moistening of intact pellet before sterilization or **sterile 2:** moistening of intact pellet after sterilization); Means followed by a common letter are not significantly different by the Tukey HSD test at the 5% level of significance. Missing letters depict sampling dates without statistically significant differences between the treatments.

Non-sterile pellets and those wetted after sterilization (sterile 2) showed highest N_2O and CO_2 flux rates on day 1 (Fig. 5-4). Throughout the whole experiment, neither N_2O nor CO_2 fluxes from these two treatments differed statistically significant, indicating the failure of sterilization of a dry pellet. In contrast, the sterilization performed after pellet moistening (sterile 1) significantly decreased N_2O ($p < 0.001$) and CO_2 ($p < 0.001$) release during the first two days. This indicates that the sterilization in this treatment was successful on a short-term. In this treatment, the fluxes increased with delay between day 2 and 4. Toward the end of the measurement, they remained significantly higher than those of the other treatments.

5.5 Discussion

5.5.1 General aspects

Regardless of moisture and pellet size fraction, all tested treatments released N_2O and CO_2 which indicates the ability of pellets to serve as a trace gas source in the field. Obviously, pellet indigenous microflora was provided with sufficient substrate for N_2O and CO_2 production. In this context, Flessa et al. [52] investigated the effect of grass mulch on trace gas fluxes under laboratory conditions. They showed that the treatment with mulch applied on sand induced 69% of the N_2O emissions and 72% of the CO_2 emissions when compared to its application on soil surface. Using acetylene inhibition, they could also conclude that denitrification was the main source for N_2O released during the initial phase (approximately 14 days) of their experiment. In our study, CO_2 release and its temporal dynamics clearly hints at C-heterotrophic microbial activity as main source rather than carbonate dissolution. Yamane [43] determined nitrite reductase genes (*nirK* and *nirS*) in manure compost pellets which were sampled three days and 26 days after field application. The author could show that the *nirK* and *nirS* clones in the pellets were related to the clones of several denitrifying bacteria. Concerning the plants' capability to produce N_2O, Hakata et al. [53] reported that maize, which was also a component of our pellets, has the enzymatically equipment for NO_3^- reduction and thus to denitrify. For soybean seedlings, Sun et al. [54] found eleven genera of denitrifying bacteria indicating the importance of endophyte-plant co-denitrification for N_2O emissions from plant.

5.5.2 Effect of sterilization on N_2O and CO_2 emissions

Autoclaving of intact pellets after moistening resulted in negligible emissions during the initial phase of incubation which can be explained by the high thermal conductivity of water. Hence, the effect of heat sterilization was improved and an inactivation of indigenous microorganisms and spores occurred. The retarded trace gas release indicated a delay in microbial activity and proofed our assumption that N_2O production in the pellets stems from microbial sources. Additionally, cellulose and hemicellulose in the pellets may have been degraded during sterilization [25,55–57] thus serving as an energy source for reactivated indigenous microorganisms. A consequent ongoing decomposition of organic matter and conversion of C and N pools due to reactivated indigenous microbial activity could be the reason for the subsequent rise in emissions of treatment wetted prior to autoclaving.

In contrast, the CO_2 and N_2O release from pellets moistened after sterilization can be attributed to a failed sterilization. Here, we can assume that the outer, compact layer of pellet might have hindered the heat transport into the pellet and thus protected indigenous microorganisms.

5.5.3 Effect of pellet moisture on N_2O emissions

The release of N_2O strongly depended on moisture of the pellets. Concerning the pellets wetted to 47%, the slight decrease in NH_4^+ concentrations and simultaneous increase in NO_3^- concentration between day 4 and 7 indicated a conversion of mineral N. In contrast, an inhibited nitrifying activity was assumed in the treatment with 62% moisture during the same period. There, the rise in NH_4^+ concentration and the simultaneously decreasing NO_3^- pool pointed to O_2 deficiency. As reported by Heincke and Kaupenjohann [58], O_2 diffusion in water is lower than in air by a factor of approximately 10^{-4}. Therefore, the lower O_2 diffusion at higher soil moisture and the simultaneous microbial O_2 consumption favored anaerobic conditions and hence denitrification. Increased denitrification and resulting higher N_2O losses with decreasing O_2 partial pressure were often shown for soils (i.e., [59,60]); however, there is currently no information on O_2 availability in pellets.

The lowest N_2O emission was measured in the pellets with the highest moisture which were nearly water-saturated (Figs. 5-1c and 5-4a). Based on the high CO_2 emissions observed at this moisture content, a possible explanation for the low N_2O release could be a complete denitrification. As demonstrated e.g. by Russenes et al. [61], the N_2O concentration in closed vials with soil might decrease under strong anaerobic conditions, thus resulting in negative flux rates. This was also found in our measurements, where the N_2O–N enrichment showed a negative value in at least two out of four replicates of the same treatment. The depleted NO_3^- pool on day 7 and the high NH_4^+ concentrations indicated strong anaerobic conditions which might have led to a complete N_2O reduction to N_2 [62]. Furthermore, the anaerobic conditions expected in this treatment might have induced dissimilatory nitrate reduction to ammonium which was also shown to act as a N_2O source in environments with low O_2 availability [40]. This process might have been favored by the high $C:NO_3^-$ ratio of the pellets and could also give an explanation for the negative N_2O fluxes measured in the nearly water-saturated treatment.

As already shown for soils [41,63], the moisture of the pellets can be considered as a strong driver for N_2O emissions.

5.5.4 Effect of pellet size fraction on N_2O emissions

In addition to the above mentioned effect of moisture on N_2O release, it was observed that the particle size of the pellet was the second major factor which controlled the emissions. Overall, grinding has a negative impact on pellet handling and distribution pattern and is no desirable state for actual field application. The different size fractions were chosen in order to measure the effect of total surface area on C and N release. Nevertheless, the findings reported in this work are relevant for practical uses, as they would mostly also occur if smaller pellets are applied. Regarding the highest N_2O emissions measured in finely ground pellets, two main reasons were assumed: (i) the rough surface of this pellet fraction enabled fast water spreading and penetration due to lower contact angle and greater actual surface of the solid–liquid interface [64]; (ii) the fast water spreading decreased O_2 diffusion and thus enhanced the creation of anaerobic conditions favoring N_2O release from denitrification.

Additionally, the finely grinding increased the total surface area of this fraction in comparison to intact and crushed pellets. As a consequence, microbial growth and therefore the decomposition of organic matter and conversion of N pools were promoted. Although no statistically significant differences were found, the mean CO_2 emission increased with decreasing pellet size fraction in all tested moisture classes as well. For soils, it is well known that physical crushing of aggregates results in increased organic C availability and turnover [65–67]. Navarro-García et al. [68] reported a higher mean microbial biomass determined after the first rewetting (which was equivalent to our moistening procedure of the pellets) in crushed soil aggregates compared to intact ones. Despite the higher metabolic quotient in the intact aggregates, the total CO_2 release in their work was higher in the crushed aggregate samples. Increased C turnover and consequent O_2 consumption induced O_2 limiting environment which favored denitrification and thus N_2O release. Similar results have been observed in the field after soil tillage. In this context, the studies of Staley et al. [69] and Guzman-Bustamante et al. [70] showed that a mechanical disturbance of soil (caused by tillage) can induce high N_2O fluxes.

Concerning the organic matter decomposition and more specifically the C availability after crushing, the significant lower CO_2 emissions observed in crushed pellets wetted to 62% moisture indicated the presence of additional uncertain factors. The similar trend found in the results of the hot water extraction also remains unclear. A possible explanation could be the inhomogeneity of particle size and texture of the individual pellet pieces which built up this pellet fraction. The crushed pellet fraction represented a mixture of small, medium and large pieces of the original pellet which were not distributed homogeneously. The size of the small ones was comparable with that after finely grinding. Here, the mechanical breaking down of large initial particles coming from the original solid manure might have enabled a faster decomposition of organic matter after water addition. The medium and large pieces, in turn, were still cluster formations which partly retained the original shape of the pellet and consequently consisted of various sizes of solid components. Based on that it is assumed that different pore sizes were present, which might have affected the water absorption and spreading within the larger pieces of the crushed pellet [71]. Furthermore, due to crushing, only a small part of the initial outer layer remained and the inner milieu and microsites were changed. As a consequence, lower CO_2 emissions were determined due to affected decomposition of organic matter and lower C release.

5.5.5 Study implications related to pellet application in the field

In order to assess the environmental impact of pellet application on trace gas emissions, the presented cumulative N_2O emissions were compared with those measured after pellet application in an own field experiment (data are part of a separate manuscript currently being processed). Therefore, the following assumptions were made: (i) present cumulative N_2O emissions were calculated for a pellet amount equivalent to an application of 170 kg total N ha^{-1} and (ii) N_2O fluxes measured in the field and covered the same sampling period (seven days and four field replicates) were cumulated. The N_2O emission in the field accounted for 301 g N_2O–N ha^{-1}.

The N_2O emissions scaled up from the lab measurements amounted to 144, 405 and 7 g N_2O–N ha^{-1} 7 day^{-1} after pellet wetting to 47%, 62% and 72% moisture, respectively. Although measured under constant lab conditions, these values were well in accordance with the N_2O emission determined in the field. There, the highest N_2O fluxes were also observed at around 62% pellet moisture.

Furthermore, these results are in the range reported by Pampuro et al. [30,33], who found N_2O emissions of about 30–240 g N_2O–N ha^{-1} at a fertilizer level of 200 kg N ha^{-1}. Although the period of measurements in their work was considerably longer, most emissions were also registered during the first week after application [30,33].

5.6 Conclusions

Our measurements clearly show that the indigenous microflora of the pellets has a substantial potential for N_2O production and release. The degree of N_2O release from the pellets was strongly affected by pellet moisture which, under field conditions, is controlled by the moisture of the soil after pellet application. The N_2O emissions in our lab experiment were in the same order of magnitude as the N_2O emissions in a field study. Therefore, we assume that the pellets themselves were the main contributor for the field emissions. To quantify the contribution of the pellets to the total N_2O emission in the field, relatively simple experiments, like measuring trace gas fluxes with the pellets and from the same sampling area immediately after removing the pellets, would be useful. For a closer understanding of the microbial N and C transformations in the pellets, additional in-depth studies on indigenous microbial structure as well as on changes in microbial diversity would be expedient.

In order to avoid high N_2O emission after pellet application, we suggest the utilization of pellets as big as possible because the N_2O emission increased with decreasing pellet fraction size. However, the impact of pellet size on nutrient availability should also be taken into consideration.

5.7 References

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6 General discussion

The current work has shown that the processing of digestate influences the partitioning of initial compounds (DM, water, and N) and the amount of gaseous N losses, especially after the application of the products to soils. The exact composition of intermediate and end products depends on the characteristics of raw digestate (and therefore the feedstock mixture and parameters of preliminary anaerobic digestion) and the applied processing techniques. Even though two biogas plants with similar feedstock mixture and fermentation conditions were selected, the chemical analysis indicated deviations – not only between both biogas plants but also between the years of sampling. However, these fluctuations are common in practice and do not significantly affect the aims of this study.

6.1 Changes in fresh matter composition of digestate due to processing

Within the framework of the presented thesis, it was observed that treatment of an almost equal amount of raw digestate (around 10,000 t a^{-1}) led to a significantly higher absolute water reduction in the liquid chain compared to the solid chain. Assuming that the entire separated solid or liquid fraction was processed, 6% and 52% of the total initial water were removed, respectively. The results of the evaluated one-stage vacuum evaporation were well in accordance with Fechter [1], but below the levels reported for two-stage evaporation or reverse osmosis [2,3]. However, it must be acknowledged that the amount of treatable water (and overall mass) was primarily determined by the initial mechanical separation, i.e., the liquid mass flow that can be treated was significantly higher than the solid mass flow. Nonetheless, the above-mentioned findings could be helpful to make a first decision if storage capacities are the limiting factor.

Direct comparison between both evaluated processes is further complicated by the performance of the utilized screw press. According to Guilayn et al. [4], it falls into the “high-efficiency” category in the case of the liquid treatment, while it only reaches a "low efficiency" rating in the solid chain. This directly impacts mass flows and overall operability/efficiency of downstream technologies. For example, a poorly fractionated liquid would be characterized by a higher DM content, hence the overall performance of the following evaporator and the ASS yield would be reduced, and vice versa.

The relative water reduction after initial separation (i.e., based on FM of the products "separated solid" and "separated liquid") accounts for ~63% and ~66% for the liquid and solid chain, respectively. This was achieved by almost complete evaporation of the water contained in the solid (~95%), whereas in the liquid only ~66% were removed. The observed water reduction in the solid chain was comparable to previously reported results for sewage sludge (from 97% to 7% water) in a similar drying unit during a treatment period of 2–3 months [5].

Furthermore, it was determined that a heat demand of 1190 kWh (solid drying) and 714 kWh (vacuum evaporation of liquid) was required per evaporated ton of water. Although the liquid treatment seemed to outperform solid processing, a further economic evaluation would be required, as the major energy share was provided by (free of charge) sunlight in the solid chain, whereas it required heat from the CHP plant in the liquid case (which might be sold otherwise).

Overall, **hypothesis (i)** (“liquid processing reduces the water content more effectively than solid processing”) was verified if the absolute water reduction or total energy used are taken as the decisive criteria. Concerning the relative water reduction after initial screw-press separation, both techniques performed almost similarly.

Processing of raw digestate also changes DM partitioning and content. In accordance with the findings of Bauer et al. [6], a concentrating of organic matter compounds in the solid fraction after separation was observed in both tested biogas plants. Here, an increased C_{org} content and amount of fiber fractions (lignin and cellulose) were found, while the separated liquid was characterized by a high content of soluble materials (Table S1). However, due to a large share of small particles, a significant part of the total initial solids was shifted to the liquid phase. As described by Lyons et al. [7], the exact partitioning of solids depends on feedstock composition and, especially, on particle size distribution in raw digestate. Regarding the latter, the chemical analysis indicated ongoing changes from large towards small and soluble particles due to subsequent processing. Especially in the case of vacuum evaporation, further processing enabled complete solid retention in concentrate (Table S1), which was also previously reported [3].

Concerning the concentration of macronutrients, most of N, P, K, S, and Ca was present in the soluble form or was bound in small organic particles and, consequently, shifted to the liquid fraction after mechanical separation (Tables 2-1 and 2-2). This trend was in accordance with earlier studies [1,4,6]. Particularly with regard to P, S, and Ca, Guilayn et al. [4] described this as a typical tendency for technologies characterized by low separation efficiency, such as most of the applied screw presses, sieves, rotary drum, or vibration screens. The respective end products, pellet and ASS, can be labeled as valuable, marketable multi-component fertilizers with sufficient N contents. Pellets generally represent a DM-rich, solid, organic fertilizer, which releases nutrients over a longer period. The contents of total N and S in ASS comply with the limit values predefined by the latest draft of Regulation EU No 2019/1009 for a “straight liquid inorganic macronutrient fertilizer” [8]. With about 6% N_t and 8% S, they are almost on the level of a commercial liquid ammonium sulfate fertilizer (e.g., ASL 8% N_t and 9% S, LENATEC GmbH) [9,10].

6.2 Effect of processing technique on N partitioning

The partitioning of N during subsequent processing of raw digestate depended on the utilized technique (e.g., most of N was shifted to the liquid fraction after screw-press separation; also see [6,7,11]). As shown in the work of Tambone et al. [11], the feedstock mixture additionally affected N distribution. In the case of biogas plant 1, the mixture fed into the fermenter contained a lower proportion of lignocellulosic biomass, such as maize or grass silage, than in biogas plant 2, which (i) positively influenced the degradation and release of contained nutrients, and (ii) enabled easier transport to the liquid phase during mechanical separation.

When considering the subsequent treatment, a clear splitting of organic from mineral N was observed during vacuum evaporation. Here, the organic N was completely moved to concentrate, while a NH_4-N-rich ASS was generated. In the solid processing chain, primarily organic N was present, which was contained in the larger particles transferred to the solid fraction. Besides a small amount of NH_4-N, about 50% of the total mineral N (based on FM) found in dry solid and pellets was represented by NO_3-N. Since NO_3^- had not been detected in the pre-products, it was assumed that microbial conversion of mineral N (e.g., by aerobic nitrifying bacteria) took place during drying.

Concerning the N recovery in the final products, **hypothesis (ii)** (“liquid processing results in a higher N recovery than solid processing”) was verified. Total N recovery in ASS was about 2 times higher than in pellets (33% and 14%, assuming that the respective separated fraction is completely treated). In terms of plant-available, mineral

N, a similar tendency was observed. Only about 2% of initial NH_4^+ were shifted to the pellets, whereas ~53% were found in ASS.

Consequently, with a view to N recovery and availability, liquid processing showed superior results. However, the presented findings only apply to the evaluated processing cascades and are not of general validity.

6.3 Subsequent processing of digestate – a suitable method for reducing N_2O emissions?

The current study has shown that the potential of digestate processing to reduce soil-borne N_2O emissions primarily depends on (i) organic matter composition of digestates, and (ii) prevailing weather conditions. It was further found that the simultaneous presence of easily degradable organic matter and mineral N (primarily NH_4-N) is of major importance for the production and release of N_2O after fertilization with digestates. This result is in accordance with previous literature [12–14]. In the presented work, for example, the limited amount or even the absence of one of these factors (i.e., low mineral N in dry solid of BGP1 or the absence of organic matter in ASS (BGP2)) induced only low emissions. A similar effect was observed after the evaluated mechanical (screw-press) separation.

When considering the changes in N_2O release as a result of the subsequent processing steps, it can be noted that fertilization with intermediate or end products has the potential to reduce the emissions in most cases when compared to raw digestate. A noteworthy exception is the pellet, which induced up to 21% higher N_2O emissions. Therefore, the **third hypothesis** ("raw digestate releases more N_2O than the respective intermediate or end products after application to soil") was not entirely corroborated. The application of dry solid or ASS led to an emission rate, which was at least 65% lower compared to raw digestate (based on the same amount of N_t applied). Here, it must be noted that future research should also consider losses during digestate processing (e.g., N losses during solid drying [15]). Maurer et al. [15], for example, reported a reduction of the N_t content of 7–43% during greenhouse drying. This effect was mainly caused by NH_3 volatilization and depended on digestate conditioning and drying time.

Regarding a hypothetical choice between solid and liquid processing, the results indicate a slight but not statistically significant trend. The application of liquid digestates (not including raw digestate) to soils, on average, led to higher N_2O release than the application of solids (year 1, $p = 0.79$; year 2, $p = 0.33$, both calculated by t-test). A possible reason is the high NH_4-N content of liquids. Oxidation of the NH_4-N during nitrification, thus increasing soil NO_3 level, in combination with less recalcitrant organic matter may have triggered N_2O production and release from denitrification. Anyway, a clear statement on **hypothesis (iv)**, that “solids release less N_2O than liquids after application to soil”, cannot be made and thus the hypothesis was not corroborated.

As mentioned above, the application of pellets to soils triggered N_2O release to a high degree, regardless of the experimental conditions. Similar results were reported in the earlier work of Hayakawa et al. [16], who assumed the presence of anaerobic conditions inside the pellets as the main emission driver. The subsequent in-depth study, which was performed on the pure pellet, clearly indicated the presence of further relevant factors involved in the processes of N_2O production and release. Besides water addition as initial trigger, an interaction between mineralization, nitrification, and denitrification controlled the emission rate. Furthermore, the presence of C-heterotrophic microbial activity was highlighted by the measured temporal dynamics of CO_2 release, which also verified the previous assumption of Hayakawa et al. [16]. The results underline **hypothesis (v)** “N_2O release from pellets is caused by the activity of autochthonous microflora already present in the pellet body”.

In conclusion, the N_2O emission rate can be reduced by applying (i) N organically bound in large recalcitrant fractions (separated or dry solid), or (ii) mineral N such as NH_4-N in the form of a liquid solution or digestate, which contains only a negligible amount of easily degradable C (ASS, separated liquid). Concerning the potential of the single processing techniques, separation of the raw digestate is recommended. With a view to the subsequent processing of the solid or liquid fractions, a balance between the environmental impact and individual targets must be found. For example, solar drying produces a solid, which does not significantly trigger the release of GHGs after application to soil but cannot be used as a short-term organic fertilizer due to its relatively low mineral N content.

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7 Outlook

Anaerobic digestion improves nutrient availability and allows better reuse or recycling. In the current study, pellets and ASS were produced, which are marketable fertilizers. An important aspect is their actual potential to provide a high share of N_t from raw digestate for crops. Based on the total amount of raw digestate and the applied initial nutrient separation in solid and liquid fractions, a N_t recovery of 14% (pellet) and 21% (ASS) was calculated. It must be noted that these values only refer to the respective main product and do not take into consideration the significant amounts of N shifted to by-products and storage sites. In the liquid processing chain, for example, N recovered in liquid storage or concentrate accounted for 26% in both cases. N_2O-N losses after digestate application to soil accounted for 0.5% (pellet) and 0.07% (ASS) of applied N_t. Assuming that a farmer can only realize one of the shown treatment options, the N_t amount remaining in ASS is about 1.5 times higher in comparison to pellets. At the same time, gaseous N losses are significantly lower. Consequently, if the main target is to utilize maximum N from raw digestate, the application of ASS would rather reach this goal. Nonetheless, additional factors, such as N availability and mobility, time and method of application, weather conditions, crop development stage, and nutrient demand, are also of major importance in order to avoid further N losses (e.g., to the groundwater).

In order to complete the picture of the environmental impact of digestate utilization after processing, a comprehensive determination of gaseous losses (e.g., NH_3, NO, N_2, CH_4, CO_2, VOCs, etc.) is recommended. Aside from the actual fertilization, the emission potential should also be evaluated throughout the processing chain (e.g., during drying), transport, and storage. This will allow a better understanding of emission-driving processes and will identify areas where improvements in handling should be made. With regard to the production and release of GHGs from the pure pellet, further experiments, including exact investigation of indigenous microorganisms would be beneficial. Here, it is important to gain insights into the effect of changing organic matter composition during pelletizing on the resulting microbial community. Moreover, it should be evaluated if pelletizing of organic substrates is generally linked to increased GHG emissions as this could also affect pellets for fodder and heating purposes. Based on the outcome, additional legislative actions (e.g., emission thresholds or usage restrictions) should be implemented.

The current thesis additionally pointed out some general aspects and improvement opportunities for future research in this area. The digestate sampling turned out to be a main drawback. Since all digestates were collected on the same day, the drying period of about 3 months was not adequately considered. It is also recommended to have multiple sampling events during an experimental year, in order to determine the seasonal fluctuations in feedstock mixture, fermentation process, and composition of raw digestate. Furthermore, full-scale biogas plants were evaluated, which made an accurate digestate sampling difficult due to limited access (e.g., to the solid output of the pelletizer). Here, it would be beneficial to take a step back and perform future research under controlled experimental conditions.

With a view to the fertilizer value of digestates and nutrient partitioning during processing, mass flow balances including additional macronutrients (P, K, S, etc.) should be set up. Since P is also of great importance when discussing regional nutrient surpluses, determination of the exact partitioning might reveal new approaches for better removal or recovery. As another aspect, analyzing nutrient levels in the exhaust stream of the dryer and the process waters is recommended in order to fit a perfect balance and to detect possible losses, e.g., in the form of NH_3.

To further improve the mass balance, a biogas plant could be selected that operates both processing chains simultaneously. This would eliminate feedstock-related deviations and allow for a better comparison between both chains of subsequent treating. In this context, additional techniques should be evaluated, such as the application of a decanter centrifuge instead of a screw press to achieve a more effective separation of DM towards the solid fraction [1–4]

As a final step, an extensive economic assessment is recommended. This would complete the overall picture and allow smart decision-making on the basis of fertilizer properties, technological performance, and economic feasibility.

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Annex A – Organic Matter Composition of Digestates Has a Stronger Influence on N_2O Emissions than the Supply of Ammoniacal Nitrogen

Table S1 Organic carbon composition of tested digestates. Contents of soluble materials, hemicellulose and cellulose were calculated from detergent fiber analysis.

Biogas plant	Product	Soluble materials [1]		Hemicellulose [2]		Cellulose [3]		Lignin	
		2015	2016	2015	2016	2015	2016	2015	2016
		g kg^{-1} DM							
1	Raw digestate (RD1)	589	523	34	39	207	215	170	223
	Sep. liquid (SL1) [1]	795	621	1	-3	95	138	109	244
	Sep. solid (SS1) [1]	317	215	165	136	302	223	216	426
	Dry solid (DS1)	467	347	40	46	266	214	227	393
	Pellet (P1)	483	417	54	63	238	204	225	316
2	Raw digestate (RD2)	904	545	-132	44	94	224	134	187
	Sep. liquid (SL2) [1]	979	811	-233	-109	80	105	174	193
	Sep. solid (SS2) [1]	273	307	164	169	356	345	207	179
	Concentrate (CC2) [2]	911	831	-171	-90	148	118	112	141
	ASS2 [4]	-	-	-	-	-	-	-	-

[1] Soluble materials = 100% – %aNDF; [2] Hemicellulose = %aNDF – %ADF (negative values are not plausible and could indicate matrix-related effects, e.g. a presence of insoluble tannin-fiber complexes as shown by Getachew et al., 2000, doi: 10.1021/jf990740v); [3] Cellulose = %ADF – %ADL; [4] values fall below detection limits.

Table S2 Amount of fresh matter (FM), organic carbon (C_{org}) and ammonium nitrogen (NH_4–N) equivalent to 170 kg N_t ha^{-1} applied as digestates.

Fertilizer [1]	**FM**		**C_{org}**		**N_t**		**NH_4–N**	
	2015	2016 [2]	2015	2016 [2]	2015	2016 [2]	2015	2016 [2]
	kg applied per ha							
RD1	33597	33074	913	1545	170	170	80	65
SL1	35052	33203	696	854	170	170	85	78
SS1	21711	30631	2897	4166	170	170	43	36
DS1	7359	14518	2742	3637	170	170	11	8
P1	5449	5726	1929	2166	170	170	21	12
RD2	32630	32381	664	999	170	170	110	104
SL2	32882	34205	594	619	170	170	113	97
SS2	26814	30411	2394	2286	170	170	91	76
CC2	41063	32319	1299	1735	170	170	69	29
ASS2	2843	3014	2	1	170	170	166	162

[1] RD1/2: raw digestate; SL1/2: liquid fraction; SS1/2: solid fraction; DS1: dry solid; P1: pellet; CC2: concentrate; ASS2: ammonium sulfate solution; numbers behind treatments abbreviations: number of respective biogas plant; [2] values refer to field (year 2016) and incubation experiments.

Annex B – Pellets from Biogas Digestates: A Substantial Source of N_2O Emissions

Table SS1 Mean DON (dissolved organic nitrogen) content (n = 4 ± standard error) as affected by water amount of intact pellet

Day of incubation	**DON (mg N g^{-1} intact pellet)**		
	47% water	62% water	72% water
0	9.8 ±2.8	6.5 ±1.3	14.9 ±1.7
1	7.6 ±0.5	10.5 ±1.7	6.8 ±1.2
4	7.7 ±2.5	3.2 ±2.6	1.4 ±0.4
7	10.7 ±1.6	6.3 ±3.0	2.3 ±0.6

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Publications

Fechter, M.; **Petrova, I.P.**; Kraume, M. 2023. *Balance of total mass and nitrogen fluxes through consecutive digestate processing steps: Two application cases*. Journal of Environmental Management, 326, Part B, 116791, https://doi.org/10.1016/j.jenvman.2022.116791

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Conferences

03/2017	**International Conference – Progress in Biogas IV**, Stuttgart, Germany “The influence of digestate treatment and composition on N_2O and CO_2 emissions after the application on fallow land” (oral presentation)
10/2016	**1st International Conference Bioresource Technology for Bioenergy, Bioproducts & Environmental Sustainability,** Sitges, Spain “Influence of digestate processing technique on nitrogen mass flow and concentration as an important factor for N uptake, biomass yield, and soil fertility” (poster presentation)
09/2016	**59th Conference of the Society for Plant Production Sciences (GWP e.V.),** Gießen, Germany „Einfluss der Aufbereitung von Gärresten auf ihre Zusammensetzung und die Düngewirkung bei Kulturpflanzen“ (oral presentation)
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09/2015	**127th Conference of the Association of German Agricultural Analytic and Research Institutes (VDLUFA e.V.)**, Göttingen, Germany „Einfluss der Aufbereitung von Gärresten auf Zusammensetzung, Düngewirkung und N_2O-Emissionen nach Ausbringung“ (oral presentation)

Winterbach, 10.06.2023

Place, Date	Ioana P. Petrova

Declaration in lieu of an oath on independent work

according to Sec. 18(3) sentence 5 of the University of Hohenheim's Doctoral Regulations for the Faculties of Agricultural Sciences, Natural Sciences, and Business, Economics and Social Sciences

1. The dissertation submitted on the topic

Influence of biogas-digestate processing on composition, N partitioning, and N_2O emissions after soil application

is work done independently by me.

2. I only used the sources and aids listed and did not make use of any impermissible assistance from third parties. In particular, I marked all content taken word-for-word or paraphrased from other works.

3. I did not use the assistance of a commercial doctoral placement or advising agency.

4. I am aware of the importance of the declaration in lieu of oath and the criminal consequences of false or incomplete declarations in lieu of oath.

I confirm that the declaration above is correct. I declare in lieu of oath that I have declared only the truth to the best of my knowledge and have not omitted anything.

Winterbach, 10.06.2023

Place, Date

Signature