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Improving Nitrogen Retention in Soils Treated with Pig and Cattle Slurry Through the Use of Organic Soil Amendments

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Abstract

Animal slurry has recently experienced a renaissance as organic nitrogen (N) fertilizer because, on the one hand, sustainable organic farming is receiving growing attention in order to protect the environment and, on the other hand, increasing livestock farming produces large amounts of animal manure that should be properly disposed of to avoid further environmental pollution. However, it should not be neglected that the application of animal slurries may also have negative effects, such as N losses and N contamination, especially in areas with intensive livestock production. Although there are strategies available to reduce N losses from single pathways, such as ammonia (NH_3) loss or nitrate (NO_3^-) leaching, these strategies are not widely used by farmers due to increased costs or the potential for increased N losses from other pathways. High-carbon organic soil amendments (HCAs) with large C:N ratio have shown great potential in reducing N losses and increasing the N retention capacity of the soil. The aim of this thesis was to analyze the combined effects of treating slurries with various HCAs under different conditions after application to soil.

In a laboratory experiment, the potential of three common HCAs—wheat straw, sawdust, and leonardite— to mitigate N loss was evaluated when applied to soil along with pig and cattle slurry. By analyzing N emission, we found that leonardite was most effective in reducing NH_3 and nitrous oxide (N_2O) loss. ^{15}N labeling showed that the application of leonardite was associated with the highest N retention in soil (24% average slurry N recovery), followed by wheat straw (20% average slurry N recovery). Furthermore, to investigate the effect of wheat straw or leonardite in combination with cattle slurry fertilization under field conditions, a two-year lysimeter experiment was conducted with winter wheat in the first year and winter barley in the second year using ^{15}N-labeled cattle slurry. The results showed that leonardite improved the retention of slurry N in soil, but did not reduce grain N content compared to the straw treatment, making leonardite a suitable HCA to improve N fertilizer efficiency and soil N retention after slurry application.

However, since leonardite is not a renewable resource, biochar was produced from spruce sawdust and oxidized using the Fenton reaction to introduce oxygen-rich functional groups to the biochar surface in order to find a sustainable alternative to leonardite. The results showed that oxidized biochar greatly decreased NH_3 emission from cattle slurry by increased adsorption of ammonium (NH_4^+) in cattle slurry compared to non-oxidized biochar, indicating the great potential of oxidized biochar for reducing N losses during slurry application. To test this potential, non-oxidized and oxidized biochar was investigated with three different soils amended with cattle slurry. The results showed that oxidized biochar reduced NH_3 emissions by 64-75% in all soils, while untreated biochar reduced NH_3 emissions by 61% only in sandy soil. In loamy sand, oxidized biochar increased the dissolved organic carbon (DOC) content in topsoil, which stimulated immobilization of slurry N in microbial biomass, thus improving the quality of this marginal acidic soil.

This thesis concludes that among the HCAs tested in this work, leonardite is the most suitable, when applied with animal slurries (pig and cattle slurries), to effectively bind N, mitigate N losses and improve N retention in the soil, while leonardite did not reduce N nutrition in crops under field conditions. In addition, Fenton oxidation can introduce oxygen-rich functional groups in biochar and improve its ability to adsorb NH_4^+, thus reducing NH_3 emissions from cattle slurry. And when oxidized biochar was applied with cattle slurry to three different soils, it could reduce gaseous N losses and potentially improve microbial N immobilization capacity, especially in sandy soil. In the future, research should focus on further improving the adsorption capacity of biochar to the full level of leonardite, and conducting long-term field experiments before large-scale applications, to better understand the longer-term effects of HCAs in soils.

Zusammenfassung

Tierische Gülle hat in letzter Zeit eine Renaissance als organischer Stickstoffdünger (N) erlebt. Das liegt zum einen daran, dass die nachhaltige ökologische Landwirtschaft immer mehr an Bedeutung gewinnt, um die Umwelt zu schützen, und zum anderen daran, dass in der Tierhaltung immer größere Mengen tierischer Gülle anfallen, die ordnungsgemäß entsorgt werden sollten, um weitere Umweltbelastungen zu vermeiden. Es sollte jedoch nicht vernachlässigt werden, dass die Ausbringung von Tierdung auch negative Auswirkungen haben kann, wie z. B. N-Verluste und N-Kontaminationen, insbesondere in Gebieten mit intensiver Viehhaltung. Es gibt zwar Strategien zur Verringerung (z. B. Ammoniak (NH_3)-Verluste oder Nitrat (NO_3^-)-Auswaschung), doch werden diese Strategien in der Regel von den Landwirten aufgrund der höheren Kosten oder des Potenzials für erhöhte N-Verluste auf anderen Wegen nicht angenommen. Organische Bodenhilfsstoffe mit einem hohen Kohlenstoffgehalt (HCA) und C:N-Verhältnis haben großes Potenzial zur Verringerung von N-Verlusten und zur Erhöhung des N-Rückhaltevermögens des Bodens gezeigt. Ziel dieser Arbeit war es, die kombinierten Auswirkungen der Behandlung von Gülle mit verschiedenen HCAs unter verschiedenen Bedingungen nach der Ausbringung auf den Boden zu analysieren.

In einem Laborexperiment wurde das Potenzial dreier gängiger HCAs – Weizenstroh, Sägemehl und Leonardit – zur Verringerung der Stickstoffverluste untersucht, wenn sie zusammen mit Schweine- und Rindergülle auf den Boden ausgebracht werden. Die Analyse der N-Emissionen zeigte, dass Leonardit den Verlust von NH_3 und Lachgas (N_2O) am wirksamsten reduzierte. Die ^{15}N-Markierung zeigte, dass die Ausbringung von Leonardit mit der höchsten N-Retention im Boden verbunden war (24 % durchschnittliche N-Wiederfindung aus Gülle), gefolgt von Weizenstroh (20 % durchschnittliche N-Wiederfindung aus Gülle). Um die Wirkung von Weizenstroh oder Leonardit in Kombination mit Rindergülledüngung unter Feldbedingungen zu untersuchen, wurde ein zweijähriger Lysimeterversuch mit Winterweizen im ersten Jahr und Wintergerste im zweiten Jahr mit ^{15}N-markierter Rindergülle durchgeführt. Die Ergebnisse zeigten, dass Leonardit die N-Retention der Gülle im Boden verbesserte, aber den N-Gehalt der Körner im Vergleich zur Behandlung mit Stroh nicht verringerte, was Leonardit zu einem geeigneten HCA zur Verbesserung der N-Düngeeffizienz und der N-Retention im Boden nach der Gülleausbringung macht.

Da Leonardit jedoch keine erneuerbare Ressource ist, wurde Biokohle aus Fichtensägemehl hergestellt und mit der Fenton-Reaktion oxidiert, um sauerstoffreiche funktionelle Gruppen in die Oberfläche der Biokohle einzubringen und so eine nachhaltige Alternative zu Leonardit zu schaffen. Die Ergebnisse zeigten, dass oxidierte Biokohle die NH_3-Emissionen aus Rindergülle durch erhöhte Adsorption von Ammonium (NH_4^+) in der Rindergülle im Vergleich zu nicht oxidierter Biokohle stark reduzierte, was auf das große Potenzial von oxidierter Biokohle zur Verringerung von N-Verlusten bei der Gülleausbringung hinweist. Um dieses Potenzial zu testen, wurden nicht oxidierte und oxidierte Biokohle mit drei verschiedenen mit Rindergülle angereicherten Böden untersucht. Die Ergebnisse

zeigten, dass oxidierte Biokohle die NH_3-Emissionen in allen Böden um 64-75% reduzierte, während unbehandelte Biokohle die NH_3-Emissionen nur im sandigen Boden um 61% reduzierte. In lehmigem Sand erhöhte die oxidierte Biokohle den Gehalt an gelöstem organischem Kohlenstoff (DOC) im Oberboden, was die Immobilisierung von Gülle-N in der mikrobiellen Biomasse förderte und die Qualität dieses leicht sauren Bodens verbesserte.

Diese Arbeit kommt zu dem Schluss, dass von den in dieser Arbeit getesteten HCAs Leonardit am besten geeignet ist, wenn es zusammen mit Tierdung (Schweine- und Rindergülle) ausgebracht wird, um N wirksam zu binden, N-Verluste zu verringern und die N-Retention im Boden zu verbessern, während Leonardit die N-Nahrung in Nutzpflanzen unter Feldbedingungen nicht verringert. Darüber hinaus können durch die Fenton-Oxidation sauerstoffreiche funktionelle Gruppen in die Biokohle eingebracht und ihre Fähigkeit zur Adsorption von NH_4^+ verbessert werden, wodurch die NH_3-Emissionen aus Viehdung verringert werden. Und wenn oxidierte Biokohle zusammen mit Rinderdung auf drei verschiedene Böden ausgebracht wurde, konnte sie die gasförmigen N-Verluste verringern und möglicherweise die mikrobielle N-Immobilisierungskapazität verbessern, insbesondere in sandigem Boden. Künftige Forschungsarbeiten sollten sich darauf konzentrieren, wie die Adsorptionskapazität von Biokohle weiter verbessert werden könnte, um das volle Niveau von Leonardit zu erreichen. Darüber hinaus sollten Feldversuche durchgeführt werden, um die längerfristigen Auswirkungen von HCAs in Böden bei einer großflächigen Anwendung besser verstehen zu können.

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List of abbreviations

$(NH_4)_2SO_4$	Ammonium sulfate
AFOLU	Agriculture, forestry and other land use
Al	Aluminum
ANOVA	Analysis of variance
AOA	Ammonia oxidizing archaea
AOB	Ammonia oxidizing bacteria
BET	Berunauer-Emmett-Teller
C	Carbon
C:N	Carbon-to-nitrogen ratio
Ca	Calcium
CEC	Cation exchange capacity
CFE	Chloroform-fumigation extraction
CH_4	Methane
CM	Carbonaceous material
C_{mic}	Microbial biomass carbon
CO_2	Carbon dioxide
Cu	Copper
DOC	dissolved organic carbon
EU	European Union
Fe	Iron
FTIR	Fourier transform infrared spectroscopy
GHG	Greenhouse gases
H	Hydrogen
H/C_{org}	Molar ratio of hydogen to organic carbon
H_2O_2	Hydrogen peroxide
HCA	High-carbon organic soil amendments
hl	Hectoliter
$HO\cdot$	Hydroxyl radical
K	Potassium
KCl	Potassium chloride
Mg	Magnesium
Mn	Manganese
N	Nitrogen
N_2	Elemental nitrogen
N_2O	Nitrous oxide

Na	Sodium
NaOH	Sodium hydroxide
NH_2OH	Hydroxylamine
NH_3	Ammonia
NH_4^+	Ammonium
NH_4CL	Ammonium chloride
N_{mic}	Micrbial biomass nitrogen
NO	Nitric oxide
NO_2^-	Nitrite
NO_3^-	Nitrate
O	Oxygen
O/C_{org}	Molar ration of oxygen to organic carbon
O_2	Dioxygen
OH^-	Hydroxide ions
P	Phosphorus
PM	Particulate matter
Si	Silicon
SOC	Soil organic carbon
SOM	Soil organic matter
TDN	Total dissolved nitrogen
TN	Total nitrogen
TOC	Total organic carbon
Zn	Zinc

1. Introduction

1.1 Background

Terrestrial ecosystems are major sources and sinks of the greenhouse gases (GHG) carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O). Total net anthropogenic GHG emissions increased by 54% over the period 1990-2019 (Fig.1.1) (IPCC, 2022). Agriculture, forestry and other land use (AFOLU) accounted for about 13% of global anthropogenic CO_2 emissions, 44% of CH_4 emissions and 81% of N_2O emissions during 2007-2016, collectively contributing about a quarter of total anthropogenic GHG emissions (IPCC, 2019). The main emission pathways from AFOLU activities include CO_2 emissions from deforestation, CH_4 emissions from rice and livestock manure, and N_2O emissions from nitrogen (N) fertilization (IPCC, 2019). The concentration of N_2O in the atmosphere is very small compared to CO_2 and CH_4, however, its contribution to global warming cannot be ignored, as the global warming potential of N_2O in 100 years is 265 times greater than that of CO_2 (Smith, 2017). In farmland, N_2O emissions are mainly due to over-fertilization, with about 50% of the N applied to farmland not being taken up by crops (Crews & Peoples, 2005; Zhang et al., 2017).

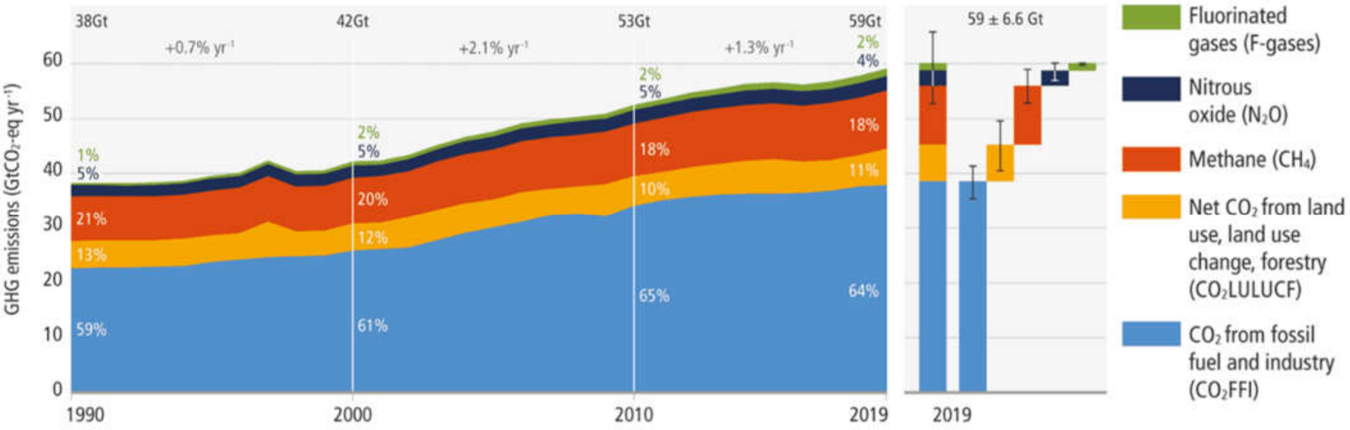

Figure 1.1 *Global net anthropogenic GHG emissions 1990–2019 (IPCC, 2022).*

In addition, ammonia (NH_3), another type of N trace gas, should not be ignored. NH_3 emitted into the atmosphere causes acid rain and forms particulate matter (e.g., PM 2.5), which in the long run threatens human health and reduces ecosystem biodiversity (Backes et al., 2016; Reichel et al., 2021). In 2012, global NH_3 emissions reached 58,671 Gg, 89% of which came from agriculture, such as farm manure (Ma et al., 2021). In the European Union (EU), about 1.4 billion metric tons of animal manure is produced per year, with France producing the most at 263 million metric tons and Germany the next largest producer at 202 million metric tons (Foged et al., 2011).

Animal manure contains high amounts of NH_4^+ and other nutrients necessary for plant growth and has been used as a traditional fertilizer for thousands of years. On the one hand, animal manure increases soil organic matter content and alleviates soil acidification that usually follows the application of mineral fertilizers (Zavattaro et al., 2017). On the other hand, it has potential negative environmental impacts, such as the aforementioned GHG and NH_3 emissions, and NH_4^+ in soil is readily transferred to mobile nitrate (NO_3^-), which can easily leach into groundwater if not taken up by plants. According to the simulation model of Lin et al. (2001), 19% of applied fertilizer is lost as NO_3^-. The leaching of NO_3^- not only reduces the fertilizer efficiency, but also leads to environmental pollution, such as eutrophication, and threatens human health, e.g., by causing methemoglobinemia and stomach cancer (Cameron et al., 2013; Padilla et al., 2018).

Animal manure as organic fertilizer is an important N source, but excessive N input to ecosystems will lead to serious environmental problems and harm human health. Therefore, it is important to understand the principles of biogeochemical cycling of fertilizer N and find potential strategies to mitigate the environmental problems of manure fertilization.

1.2 Rationale

1.2.1 N cycle

Nitrogen is essential for all life forms, is a key nutrient for plants, and provides the basis for amino acids that form proteins. N is widely present in nature in different chemical forms, such as organic N, NH_4^+, nitrite (NO_2^-), NO_3^-, N_2O, nitric oxide (NO) or elemental nitrogen (N_2). The N cycle is the conversion of N between different chemical forms through biological and physicochemical processes. The N cycle consists of four main processes: N_2 fixation, mineralization, nitrification and denitrification.

Elemental nitrogen, accounting for 78% of the Earth's atmosphere, is an important source of N (Carroll & Salt, 2004). N_2 fixation is the process by which N_2 in the Earth's atmosphere is converted to NH_3 or related nitrogenous compounds, i.e., NO_3^- and NO_2^- (Postgate, 1998). However, the triple bond between the N atoms in N_2 is very strong and has a high bond dissociation enthalpy of 945 kJ mol^{-1} (Huber & Herzberg, 1979). To break this bond, natural N_2 fixation is caused either by lightning or N_2-fixing bacteria using the N_2-fixing enzyme nitrogenase, the former accounting for at most about 10% of total annual yield of fixed N, while the main source of fixed N is biological N fixation, which accounts for about 65% of total annual yield of fixed N (Fisher & Newton, 2002). However, natural N_2 fixation cannot meet the contemporary human N demand, therefore artificial fertilizer production is now the largest source of fixed N in the Earth's ecosystem (Vitousek et al., 1997). The most common method is the Haber-Bosch process, in which N and hydrogen (H) react with each other over an iron catalyst (Fe^{3+}) at a pressure of about 200 atmospheres and 400°C to produce NH_3 (Appl, 2006).

$$N_2 + 3\ H_2 \xLeftrightarrow{Fe(\text{Ш})\ at\ 200\ atm\ and\ 400°\text{C}} 2\ NH_3 \qquad \text{(Equation 1.1)}$$

Mineralization is the conversion of organic N from plant and microbial residues or animal excreta and detritus into inorganic N compounds in a soluble and bioavailable form in the soil. This process is mainly carried out by aerobic or anaerobic bacteria and fungi (White, 2005). The depolymerization of organic N is the rate-limiting step of mineralization (Schimel & Bennett, 2004). In contrast, inorganic N, such as NH_4^+ and NO_3^-, can be taken up by organisms in the soil and converted to organic N, called N immobilization (Fig. 1.2).

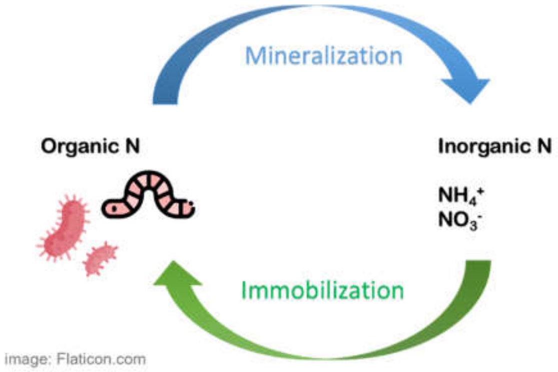

Figure 1.2 *N mineralization and immobilization in soil. This figure was modified after (Tugel, 2000) and designed using images from Flaticon.com.*

Nitrification is the conversion of reduced, less mobile NH_4^+ that is eventually oxidized to the more mobile NO_3^- (Equation 1.2 and 1.3). The first step of nitrification is the oxidation of NH_3 to NO_2^-, which is the rate-limiting step (Yao et al., 2011). It is carried out by two groups of organisms, ammonia oxidizing bacteria (AOB) and ammonia oxidizing archaea (AOA) (Hatzenpichler, 2012; Treusch et al., 2005). The second step of nitrification is NO_2^- oxidation, which is carried out by soil nitrifying bacteria, among others, to convert NO_2^- into plant-available NO_3^-. Soil clay and organic matter have negatively charged cation exchange sites that can adsorb positively charged NH_4^+, while negatively charged NO_3^- is not held by the soil and is easily leached if it is free in soil solution.

$$2\ \mathrm{N}H_4^+ + 3\ O_2 \rightarrow 2\ NO_2^- + 2\ H_2O + 4\ H^+ + energy \qquad \text{(Equation 1.2)}$$

$$2\ \mathrm{N}O_2^- + O_2 \rightarrow 2\ NO_3^- + energy \qquad \text{(Equation 1.3)}$$

Denitrification is the reduction of NO_3^- to N_2 (Robertson et al., 1988) and is an anaerobic process controlled by the availability of carbon (C) in reduced form, NO_3^- and dioxygen (O_2) (Tiedje, 1988). For example, low availability of dissolved organic carbon (DOC) will result in the accumulation of N_2O as an end product (Mary K. Firestone et al., 1980). Other studies have shown that as O_2 concentration in the soil decreases, more N_2O can be produced by denitrification (Tiedje, 1988). The sequence of denitrification is as follows:

$$\mathrm{N}O_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2 \qquad \text{(Equation 1.4)}$$

1.2.2 N fertilizers

N fertilizers play a key role in increasing crop yields to feed a growing world population. However, if the supply of N fertilizer exceeds crop demand, N is released into the atmosphere as N_2O and NH_3, leading to global warming and acid rain, or it is released through leaching of NO_3^- and dissolved organic N, leading to contamination of surface and groundwater (Backes et al., 2016; Goulding, 2004).

1.2.2.1 Limitations of mineral fertilizers

Since the 1960s, mineral fertilizers, i.e. industrially produced synthetic/chemical fertilizers, have been widely used worldwide (Tilman, 1998). They are very competitive in the market because they can directly and quickly meet the nutritional needs of plants and increase crop yields. Due to the large market, mineral fertilizers are readily available, allowing farmers to purchase mineral fertilizers with different nutrient combinations for their specific needs. In addition, mineral fertilizers are highly water soluble, so they can release nutrients quickly, which can be absorbed directly by plants.

However, if fast-release mineral fertilizers are not utilized by plants in time, this can lead to nutrient loss and reduce the efficiency of fertilizer use. While the use of controlled-release granules can alleviate this problem, this will increase costs (Chandran et al., 2021; Shaviv & Mikkelsen, 1993). In fact, the price advantage of mineral fertilizers is now being challenged. Fertilizer prices have risen to record levels due to soaring energy prices, with urea prices already exceeding the peak of the global food crisis in 2008 (Baffes & Koh, 2022). In addition, due to the high concentration of mineral fertilizers, excessive application can damage plants (Martínez-Espinoza et al., 2009). More importantly, long-term use of mineral fertilizers only can lead to nutrient imbalances in the soil, such as N surplus, reduced soil organic matter content, and heavy metal accumulation (Geisseler & Scow, 2014; Li et al., 2017; Reichel et al., 2021). Many studies have shown that excess mineral fertilizers can greatly reduce soil pH and cation exchange capacity (CEC), which may be associated with a reduction in bacterial diversity (Barak et al., 1997; Qiao et al., 2018; Sun et al., 2015). On the other hand, acidified soils deplete base ions and release toxic aluminum (Al), further reducing the buffering capacity of the soil (Bowman et al., 2008). As a result, soil fertility decreases under prolonged use of mineral fertilizers, which in turn reduces plant productivity (Qiao et al., 2018).

In recent years, with the emphasis on environmental and health issues, farmers have increasingly preferred to use organic fertilizers as an alternative to mineral fertilizers. Organic fertilizers include a variety of livestock manure and crop residues as well as other agricultural by-products. Compared to mineral fertilizers, organic fertilizers contribute to soil nutrient balance and prevent soil acidification, therefore can be used as an alternative to chemical fertilizers to mitigate environmental damage (Chalk et al., 2020).

1.2.2.2 Advantages and disadvantages of manure fertilizers

Animal manure has been used for thousands of years as an organic fertilizer to increase soil organic matter and soil microbial biomass and as an N source for plants. Compared to mineral fertilizers, animal slurry contains a large amount of organic matter and some micronutrients that both meet the needs of plants and increase microbial biomass and activity in the soil, ultimately improving soil health (Prado et al., 2022). Moreover, the large availability of animal excreta is creating opportunities for the growth of this market. In Europe alone, cattle manure can replace about 4.3 million tons of mineral fertilizer (Zavattaro et al., 2017). In some areas of Europe, such as northwestern Germany and the Netherlands, livestock production areas with high animal densities have developed, generating large amounts of animal excreta (Zerbe, 2020). Also, in developing countries, more and more people are changing their diet to meat and dairy consumption, which has stimulated the development of livestock farming.

Compared to mineral fertilizers, animal slurry contains readily available NH_4^+-N as well as organic N, which can be utilized by plants after decomposition, and this slow-release source of N can benefit plants over a longer period of time (Chalk et al., 2020; Chen, 2006). In addition to the large amounts of primary nutrients provided by mineral fertilizers, such as N, phosphorus (P) and potassium (K), animal slurries often provide secondary nutrients such as calcium (Ca), magnesium (Mg), and sulfur, as well as trace nutrients such as Fe, manganese (Mn), zinc (Zn), and copper (Cu), which are essential for plant growth (Gowariker et al., 2009; Watts et al., 2010). Manure application has been reported to improve soil fertility by affecting the physicochemical properties and microorganisms of the soil (Lazcano et al., 2013). Because animal manure contains a large amount of organic matter and decomposes slowly, long-term application of manure can significantly increase the soil organic C (SOC) content compared to mineral fertilizers (E. Liu et al., 2010; Meng et al., 2005). A 31-year field experiment showed that application of farmyard manure plus NPK fertilizer increased SOC content by 67%, while receiving NPK fertilizer alone only increased SOC content by 36% (Ebhin Masto et al., 2006).

In addition, soil organic matter plays an important role in many other soil properties. A regression analysis showed a significant negative correlation between SOC and soil bulk capacity (Khaleel et al., 1981). Because the decomposition of manure organic matter releases polysaccharides and bacterial gum, these substances can act as binding agents and promote soil aggregation, which increases soil porosity and ultimately reduces soil bulk capacity (Alam et al., 2018; Dhaliwal et al., 2019). Furthermore, high soil porosity can increase soil water retention (Zeidan, 2007), which is consistent with X. Wang et al. (2016), who found a significant increase in soil water retention capacity with increasing manure application. Soil CEC is an important factor affecting soil nutrient retention and nutrient availability, and in general it increases with increasing SOC content, so manure application should have the potential to increase soil CEC (Gao & Chang, 1996; Miller et al., 2016).

Another noteworthy effect of manure application is that it has a more pronounced effect on soil microbial communities than mineral fertilizers (Wei et al., 2017). Soil microorganisms contribute to the establishment of SOC and are an important factor in plant health, and are therefore essential for the long-term sustainability of agricultural systems (Yuan et al., 2017; Zhang et al., 2014). On the one hand, manure increases SOC and nutrients, which can stimulate microbial biomass and activity; on the other hand, manure has a buffering capacity that prevents soil pH fluctuations, which can affect microbial community structure (Wei et al., 2017; Wu et al., 2020). Long-term application of manure has a significant stimulatory effect on the amount of AOB responsible for the rate-limiting step of nitrification and therefore has an important impact on the global N cycle (Kowalchuk & Stephen, 2001; Wang et al., 2014). Application of animal manure may contribute to plant growth and productivity as it provides nutrients and improves soil properties. Manure improved wheat growth compared to an unfertilized control, and application of farmyard manure at a rate of 32 Mg dry weight ha^{-1} yr^{-1} resulted in grain yields similar to those of mineral fertilizer (120 kg N ha^{-1} yr^{-1} plus 80 kg P_2O_5 ha^{-1} yr^{-1}) (Koutroubas et al., 2016). In addition, some studies have shown that the addition of animal manure can significantly increase yields compared to mineral fertilizer alone (Geng et al., 2019; E. Liu et al., 2010).

Despite these positive effects of animal slurry in improving soil fertility and sustainable production, there are still limitations in its practical application. Usually, manure contains large amounts of liquid, which increases transportation and distribution costs. The nutrient content of manure varies widely and farmers often apply large amounts of manure to maintain plant yields, which can result in adverse effects such as N loss and environmental pollution if excess nutrients are not absorbed by plants in a timely manner (Chambers et al., 2000; Erisman et al., 2013).

1.2.3 The challenges of N loss and mitigation strategies

1.2.3.1 NH_3 volatilization

An important N loss pathway is the NH_3 volatilization from fertilizers (Fig. 1.3), and the main sources of NH_3 in the atmosphere are synthetic fertilizers and livestock manure (Sutton et al., 2013). The main form of N in animal slurry is NH_4^+, which is readily absorbed by plants but is also susceptible to NH_3

volatilization, with a median NH_3 loss of 23% for global animal slurry applications, which is higher than for synthetic N fertilizer applications (Bouwman et al., 2002; Ozlu et al., 2019). This is because the relative concentrations of NH_4^+ and NH_3 are determined by soil pH, and a NH_3 production is favored under high pH conditions. When animal slurry is applied to the soil, the hydrolysis of urea in the slurry produces NH_4^+, NH_3 and hydroxide ions (OH^-), resulting in a temporary increase in soil pH and promoting NH_3 emission (Cameron et al., 2013). Atmospheric NH_3 is deposited to the ground through wet deposition or dry deposition, leading to a contribution to fine particulate matter (i.e., PM 2.5) and is associated with the formation of acid rain, a major threat to the environment and human health (Backes et al., 2016; Cameron et al., 2013).

In order to reduce NH_3 emission during manure application, the 2020 German fertilizer ordinance stipulates that liquid manure can only be spread in strips or incorporated directly into soil on arable land from 2020 and on grassland from 2025 onwards. New on-farm management methods, such as slurry injection, have been introduced to effectively reduce odor and NH_3 losses during slurry application, but their widespread use is limited by high costs. In addition, it can have adverse effects: more NH_4^+ is left in the soil under partly anaerobic conditions, resulting in high NO_3^- leaching and N_2O emissions due to coupled nitrification-denitrification (He et al., 2014; Pan et al., 2016; Silva et al., 2022). Adding acid to manure is another effective strategy that can reduce NH_3 emissions by an average of 83% (Hou et al., 2015). However, some studies report that acidification inhibits microbial activity and organic matter biodegradation and is less attractive to farmers due to the cost of acid, infrastructure and equipment (Q. N. M. Tran et al., 2015; Wu et al., 2019). It is therefore necessary to find strategies that have less negative impact and are cost effective.

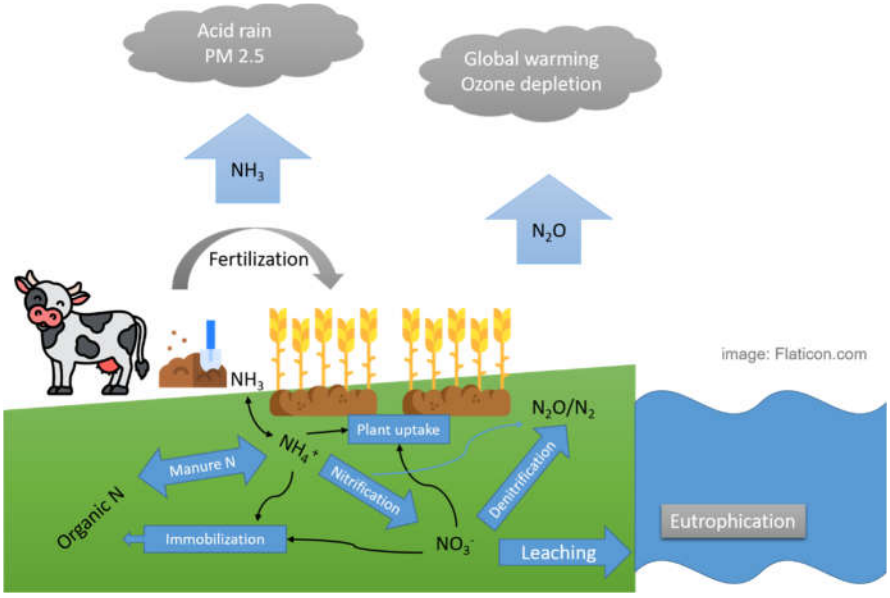

Figure 1.3 *N loss pathways after fertilization. PM2.5 refers to fine particulate matter with a diameter of 2.5 microns or smaller. This figure has been designed using images from Flaticon.com.*

1.2.3.2 NO_3^- leaching

In addition to the negative environmental and human health impacts of NH_3 emissions, NH_4^+ is a reactive N that can be converted to NO_3^- and N_2O in soil through nitrification and denitrification (Fig. 1.3), which can also lead to environmental problems such as eutrophication and global warming (Backes et al., 2016). NH_4^+ in soil can be converted to NO_3^- by nitrification, which is readily soluble in the soil solution and can therefore be leached by convection, diffusion and dispersion, while NO_3^- leaching is mainly dependent on the concentration of NO_3^- in the soil solution and the amount of drainage (Cameron et al., 2013). The leaching of NO_3^- not only reduces fertilizer efficiency, but also pollutes water bodies and leads to eutrophication (Cameron et al., 2013; Sutton et al., 2011). Excess NO_3^- in drinking water is converted to NO_2^- in the human body, which has been linked to methemoglobinemia in infants and cancer (Padilla et al., 2018). The World Health Organization and the European Union set a NO_3^- limit of 50 mg L^{-1} for drinking water, and Germany was sued by the European Court of Justice in 2018 for NO_3^- contamination of groundwater, and to this day, 27% of German arable land is located in areas where NO_3^- concentrations exceed this limit (Reichel et al., 2021).

Nitrogen fertilizer is the main N input to agricultural systems, however, it is generally accepted that N fertilizer use is inefficient, with an average of only 51% N recovery (Chien et al., 2009). In order to reduce excess N in the soil and thereby mitigate NO_3^- leaching, appropriate N fertilizer application rates matching plant requirements should be used (Jenkinson, 2001). In addition, NO_3^- leaching is associated with drainage, and fertilizer applications should be avoided at times of high leaching risk, such as in autumn when rainfall is high (Jenkinson, 2001). Nitrification inhibitors also have been reported to be an effective method of reducing NO_3^- leaching as they reduce NO_3^- production by slowing down the rate at which microorganisms convert NH_4^+ to hydroxylamine (NH_2OH), i.e. the first and rate-limiting step of nitrification (Zerulla et al., 2001). Nitrification inhibitors lead to higher NH_4^+ retention in the soil because it is less mobile compared to NO_3^-, therefore reducing NO_3^- leaching; however, this in turn may promote NH_3 emission (Qiao et al., 2015).

1.2.3.3 N_2O emission

N_2O can be formed in the soil by both nitrification and denitrification (Fig. 1.3). At low O_2 concentrations, the intermediate product of nitrification – nitroxyl – may chemically react to N_2O; NO_2^- may also be reduced to N_2O by nitrate reductase (Bremner, 1997; Cameron et al., 2013). Denitrification usually occurs under anaerobic conditions where NO_3^- can act as a terminal electron acceptor and be reduced to N_2O by various reductases (Mary K. Firestone et al., 1980; Tiedje, 1988). Although the loss of N_2O from slurry is less than 4% and has a lower impact on fertilizer efficiency than NH_3, the large global warming potential of N_2O may contribute to global warming (Chalk et al., 2020; Smith, 2017). In addition, N_2O contributes to the depletion of the ozone layer in the stratosphere (Cowling et al., 1998).

Although N_2O can be produced by nitrification, denitrification is the main pathway for N_2O production (Friedl et al., 2021; Harris et al., 2021). NO_3^- is the substrate of denitrification, so all methods of reducing the rate of nitrification will reduce the amount of NO_3^- and thus the likelihood of denitrification occurring, thus reducing N_2O production (de Klein et al., 2001; Thomson et al., 2012). In addition, reducing soil moisture and then improving soil aeration can reduce the rate of denitrification and thus reduce N_2O production (Müller & Sherlock, 2004).

1.2.3.3 Seasonal effects

Season and climate play an important role in the N loss. For example, the highest losses of NH_3 occur in the warmest months, as temperature affects the rate of NH_3 volatilization. According to a study using an inverse modelling approach, peak NH_3 emissions are more than 75% higher in summer than in the colder months of autumn and winter (Gilliland et al., 2003).

Leaching losses of NO_3^- are also highly seasonal and usually greatest in the late autumn, winter and early spring months. This is partly because NO_3^- accumulates in the soil when plants take up less N due to lower temperatures and solar radiation, or when no NO_3^- is removed from the soil solution in the absence of crops after harvest (Cameron et al., 2013; Gent, 2016). On the other hand, mineralization and nitrification rates remain high in the soil, resulting in more NO_3^- due to high soil temperatures and crop residues remaining in the field in autumn (Breimer, 1982; Frerichs et al., 2022; Viaene et al., 2017). All of these processes can lead to higher post-harvest soil NO_3^- concentrations that are prone to leaching at high intensity and frequency of autumn precipitation (Agneessens et al., 2014).

In addition, N_2O losses due to denitrification are also greatest in autumn and winter, when soil moisture content is highest. Potential denitrification rates have been reported to increase significantly when soil water content is greater than field capacity (De Klein & Van Logtestijn, 1996; Müller & Sherlock, 2004).

Strategies to reduce mineralization and nitrification in autumn, and thus the risk of NO_3^- leaching losses, include reducing the depth of tillage or postponing soil tillage from autumn to winter or even spring, as lower soil temperatures in winter and early spring can significantly reduce the rate of mineralization and nitrification rates (Rahn, 2002; Van Den Bossche et al., 2009). N fertilizer applied in autumn has been reported to have much lower use efficiency than N applied in spring due to significant NO_3^- leaching losses in autumn and winter (Jenkinson, 2001). Another strategy is to apply materials with a large carbon-to-nitrogen ratio (C:N), such as wheat straw, sawdust and lignite, to increase microbial immobilization of N and thus reduce NO_3^- leaching, as net immobilization rather than mineralization would occur (Agneessens et al., 2014; Chen et al., 2013).

1.2.3.4 Effects of soil type

Another important factor related to N loss is soil properties such as pH, organic matter content, texture, bulk density and aeration (Krümmelbein et al., 2010; Thomson et al., 2012). Soil texture is defined as the composition of the soil from sand, silt and clay. Sand particles range in diameter from 2.0 to 0.05 mm, and silt particles from 0.05 to 0.002 mm, whereas clay particles are smaller than 0.002 mm. Soil texture is related to other soil properties, such as soil porosity, which in turn regulates soil water holding capacity and gas permeability, thereby affecting water movement and gas diffusion in the soil (Upadhyay & Raghubanshi, 2020).

The main soil factors affecting NH_3 volatilization were reported to be clay and sand content, and when urea was applied as fertilizer, soil clay content was negatively correlated with NH_3 volatilization, while sand content of the soil showed a positive correlation coefficient (San Francisco et al., 2011). This may be related to the retention of NH_4^+ by clay minerals through electrostatic attraction, thus hindering NH_3 volatilization (Lu et al., 2019; Padilla et al., 2018). A regression analysis showed that clay percentage was negatively correlated with nitrification in soils maintained at a constant moisture level because, on the one hand, NH_4^+ availability was limited by clay sorption or microbial immobilization and, on the other hand, clay may limit the diffusion of partially decomposed organic matter, hindering N mineralization and nitrification (Sahrawat, 2008; Strong et al., 1999).

The denitrification potential is also highly dependent on soil texture. In general, clay soils leach less NO_3^- than sandy soils due to slower water flow in fine-textured soils, and reduced O_2 diffusion into the soil (van der Weerden et al., 2012), resulting in a higher denitrification potential (Aulakh et al., 1991; Di & Cameron, 2002). However, high denitrification rates may also lead to adverse effects, as some studies found that poorly drained soils with higher soil moisture than well-drained soils showed higher rates of N_2O production (Groffman & Tiedje, 1989; van der Weerden et al., 2012).

Soil properties are closely related to N losses and N use efficiency and therefore influence agricultural productivity and environmental health. The soils of the Lower Rhine Embayment are geologically the youngest loess (Weichsel loess) and are among the best in Germany due to their high productivity potential (personal communication, M. Endenich, RWE AG, Germany). However, lignite mining activities have affected the development of the physical properties and functions of the soils, resulting in a severe disruption of the soil structure (Krümmelbein et al., 2010). This anthropogenic impact has resulted in more or less soil/substrate compaction, and compacted areas tend to exhibit poor soil function, which leads to lower agricultural productivity and negative environmental impacts (Horn et al., 1995; Krümmelbein & Raab, 2012). Therefore, it is necessary to properly restore the mine site to agricultural land to achieve the expected yield of the original soil. The recultivation requires the application of N, P and K fertilizers, and it has been reported that the application of mineral fertilizers on recultivation site increases the concentration of NO_3^-, NH_4^+ and K^+ in the soil solution immediately, but only for a short period of time, whereas the increase in NO_3^- or K^+ by organic fertilizers is long-term (Wilden et al., 1999). In addition, the availability of organic matter increases soil structure formation and aggregate stability, thus increasing permeability to gases and liquids, which can provide additional benefits to soil structure formation and water retention capacity (Eden et al., 2012; Krümmelbein & Raab, 2012; Tester, 1990).

1.3 State of the art

The N cycle is a complex system that is influenced by the interaction of different factors. N losses may occur in different pathways, and mitigating N losses in only one individual pathway may instead lead to higher N losses in other pathways. Therefore, the ultimate approach should be to target the whole system to reduce overall N losses and improve N use efficiency by improving soil health and agricultural sustainability.

As mentioned earlier, organic fertilizers are more beneficial to soil health and long-term sustainability of agriculture than mineral fertilizers. Although the misapplication of organic fertilizers also poses some environmental risks, this challenge is attracting a growing research interest. According to previous studies, high carbon organic soil amendments (HCAs) with a large C:N ratio, such as straw, sawdust, biochar, and lignite, have the potential to alleviate N losses and environmental pollution (Chantigny et al., 2001; J. L. Sun et al., 2016; Taghizadeh-Toosi et al., 2012). The C:N ratio is an important parameter, and a lower C:N ratio leads to rapid mineralization, where N is released to the soil (Watson et al., 2002). When the C:N ratio of HCA is greater than 35, N immobilization is enhanced by releasing labile C to the soil and promoting the activity of soil microorganisms (Brust, 2019). The N in HCA does usually not meet the N requirements for microbial growth, so active microbes have to assimilate N from the soil into their biomass, leading to net immobilization of N and reduced nitrification and denitrification (Chen et al., 2013).

1.3.1 Straw

Wheat straw with C:N ratios between 50 and 100 consists mainly of cellulose, hemicellulose and lignin (Carvalheiro et al., 2009; Reichel et al., 2018). When wheat straw decomposes in the soil, large amounts of organically bound nutrients are released, which are then taken up and used by the crop (Witt et al., 2000). This decomposition process is influenced by the amount of straw, external temperature and moisture, and soil properties (Frouz et al., 2015; Johnson et al., 2007; Melillo et al., 1989).

Incorporation of wheat straw into agricultural fields is a traditional and cost-effective way of providing multiple ecosystem services, such as maintaining soil organic matter content and nutrient cycling, controlling water and wind erosion, and increasing crop yields (Blanco-Canqui, 2013; Ocio et al., 1991).

The incorporation of straw increases the availability of organic C, which is one of the most important factors in increasing N immobilization in soils. In addition, straw application can help reduce NO_3^- leaching losses because it reduces net mineralization in autumn and can also improve N uptake by the crop (Beaudoin et al., 2005; Li et al., 2021; Meng et al., 2021).

The combined application of animal slurry and straw in agricultural soils may be a viable strategy to increase soil microbial biomass (Robertson et al., 1988). Animal slurry contains various important nutrients, especially high concentrations of NH_4^+ (Higgins et al., 2005). Aita et al. (2012) reported that the simultaneous addition of wheat straw and pig slurry promoted N immobilization rates. In addition, there is a synergistic effect between pig slurry and wheat straw. On the one hand, pig slurry can stimulate the decomposition of wheat straw because pig slurry-NH_4^+ stimulates the mineralization of straw-C. On the other hand, the application of straw leads to a temporary immobilization of pig slurry-NH_4^+, by which the production of N_2O can be reduced (Chantigny et al., 2001; Sørensen, 1998).

Conversely, some researchers have found that the application of straw to slurry can have some negative effects. The application of straw to slurry reduces the excessive water content in animal excreta and increases the dry matter content. Application of slurry with this high dry matter content has been shown to enhance NH_3 losses after field application (Vandre et al., 1997). When slurry is applied on recently harvested crop residues, the rate of slurry infiltration into the soil may be slowed down, leading to greater NH_3 volatilization losses compared to application on bare soil (Passera et al., 1991). In addition, some studies have shown that CO_2 losses increase by 23-26% when agricultural soils are amended with pig slurry and straw compared to the application of slurry or straw alone.(Chantigny et al., 2001; Saviozzi et al., 1997).

1.3.2 Sawdust

Sawdust is widely used in the production of particleboards and wood pellets. Sawdust consists mainly of cellulose, lignin, hemicellulose and small amounts (5-10%) of other materials (Horisawa et al., 1999). Compared to wheat straw, sawdust contains more recalcitrant polymers, mainly in the form of lignin, and its decomposition requires white-rot fungi to break the lignified structure and increase the accessibility of cellulose (Reichel et al., 2018; van Kuijk et al., 2017). In addition, the density of sawdust is higher than that of wheat straw, making it difficult for the fungi to penetrate, so making it more difficult to degrade and leading to a lower mineralization rate (Kostov et al., 1991; van Kuijk et al., 2017).

Due to its high water-holding capacity, sawdust can eliminate undesirable odors associated with landfill leachate or other odorous liquids, such as urine (Ruiz et al., 2011). The N content of sawdust is usually very low and not readily biodegradable. Adding slurry-N can help degrade it. In composting, sawdust seems to be an ideal bulking agent for composted pig manure because it has the ability to absorb water, and its structure provides sufficient pore space in the compost (Bhamidimarri & Pandey, 1996). The adsorption of NH_3 by sawdust depends mainly on physical adsorption and biological effects. The former is due to its high surface porosity and the latter is due to the high C content, which may lead to an increase in the C:N ratio of the aqueous phase and increased N retention in the microbial biomass (Hu et al., 2007).

In addition, sawdust has some potential to become an HCA. The addition of C in the form of sawdust has been shown to reduce inorganic N levels, stimulate microbial immobilization of N, and reduce net N mineralization rates (Blumenthal et al., 2003; Cione et al., 2002; Török et al., 2000). Reichel et al. (2018) found that incorporating wheat straw and sawdust into the soil at a high N fertilizer application rate of 150 kg NH_4-N ha^{-1} resulted in rapid immobilization of excess N in the form of microbial biomass N, while sawdust was less effective than wheat straw due to its high lignin content. However, its recalcitrant polymer also hindered microbial decomposition, thus promoting improved temporary C retention. In a grassland restoration experiment, the application of sawdust reduced the N availability in the soil, decreased above-ground biomass, and created voids in the vegetation, which facilitated the establishment of late-seral plant species (Eschen et al., 2007).

1.3.3 Lignite

Due to different ages, lignite can be classified into fibrous lignite, xyloid lignite, and pitchy lignite according to its structure (Annaratone, 2008). Lignite has a high moisture content, so it is inefficient to transport over long distances. Leonardite is a highly oxidized form of lignite, and its suitability as energy source is limited due to its low energy density and low heat content. Due to the inefficiency of leonardite as a fuel, it would be desirable to find some other use, such as a soil amendment, which is potentially beneficial to the environment. Leonardite contains a large amount of humic acids, which can reach 39% to 85% of the total dry weight, and also contains a large amount of nutrients required by plants, such as N, K, sulfur, Ca, Mg, Fe, Zn and Mn, which will be good as HCA to improve soil health and promote plant growth (Chinachanta & Shutsrirung, 2016).

In addition, lignite can be acidic (pH 3.7-4.9) (Chen et al., 2015; Kim Thi Tran et al., 2015; Paramashivam et al., 2016), has a high CEC and contains up to 20% soluble C (Manzoni & Porporato, 2009), which can reduce the volatilization potential of NH_3 and improve the adsorption of NH_3, thus mitigating the emission of NH_3 from the animal slurry (Husted et al., 1991; Sommer et al., 2003; J. L. Sun et al., 2016). Chen et al. (2015) reported applying lignite to cattle excretion can reduce NH_3 emissions by 66% compared to not using lignite. Clouard et al. (2014) found that naturally occurring lignite altered soil organic matter quality and mineralogy and improved some soil properties, such as clay content, organic C, CEC and porosity. Due to its high C content and increased plant biomass (both root and aboveground biomass), the application of lignite humic acid increases the soil organic matter content, which then stimulates microbial activity and ultimately improves soil aggregation by forming and strengthening the bonds between clay domains (Nan et al., 2016). Lignite in anthropogenic soils has also been found to affect pH (Yazawa et al., 2000), mineralogical composition (Ogala et al., 2012), and microbial communities (Rumpel & Kögel-Knabner, 2004). In addition to improving soil properties and enhancing soil fertility, lignite application in soil has been shown to increase P availability (Schefe et al., 2008) and to reduce heavy metal availability (Janoš et al., 2010; Simmler et al., 2013). The improvement of soil properties after lignite application might have a positive impact on plant growth.

1.3.4 Biochar

Biochar is a C-rich material produced by the pyrolysis of biomass at temperatures ranging from 200 to 800°C with limited O_2 supply. The properties of biochar are highly variable and depend on the feedstock, temperature and residence time of the thermochemical process (Kambo & Dutta, 2015). Biochar has received increasing attention from researchers as a soil amendment in the last decades. The addition of biochar to soils can improve crop yields because it improves the physicochemical and biological properties of the soil, such as increased water retention, soil pH, and microbial activity (Ahmad et al., 2014; Kalus et al., 2019; Yaashikaa et al., 2020). The unique properties of biochar, such as large surface area, high porosity, oxygen functional groups, and high CEC, provide additional climate change mitigation benefits. For example, biochar can reduce N_2O emissions by influencing multiple soil processes (i.e. denitrification or N immobilization) and reduce N fertilizer requirements in agricultural soils by increasing the efficiency of N fertilizer use (Borchard et al., 2019; Schmidt et al., 2021). Biochar produced by slow pyrolysis of wood chips and rice husks at 600°C for 10 h could adsorb up to 60% of NH_4^+ from anaerobic pig slurry digestate at an application rate of 30 kg m^{-3} slurry, while its adsorption capacity was related to contact time, pH, NH_4^+ concentration and biochar particle size (Kizito et al., 2015). The application of biochar to animal manure has been shown to have a significant effect on N retention due to the oxygen functional groups on the surface of biochar, such as keto, phenolic hydroxy and carboxy groups (Steiner et al., 2010; B. Wang et al., 2015).

Oxygen functional groups play an important role in the adsorption of heavy metals and organic molecules (Mandal et al., 2017) and have been reported to adsorb NH_3 through proton exchange, resulting in the formation of adduct ions, or through chemical reactions to form amines and amides on the surface of biochar (Seredych & Bandosz, 2007; Spokas et al., 2012). Hydrogen peroxide (H_2O_2) is an effective oxidant that introduces more oxygen functional groups, thereby increasing the adsorption capacity of biochar, while producing only H_2O and O_2, which is environmentally friendly (Chen et al., 2008; Huff & Lee, 2016). B. Wang et al. (2016) treated different biochars with 30% H_2O_2 solution at 30°C for two weeks. The biochar showed a significant fourfold increase in NH_4^+ retention capacity. In addition, Huff and Lee (2016) found that treatment of pine biochar with H_2O_2 increased its CEC.

To improve oxidation efficiency and reduce energy costs, Fenton oxidation is a promising method to activate biochar, which uses H_2O_2 and Fe(II) ions to generate highly reactive HO- radicals in acidic solutions (Bachi et al., 2013). In the Fenton reaction, Fe (II) ions catalyze the decomposition of H_2O_2, producing the powerful oxidant hydroxyl radical (HO·), capable of oxidizing organic and inorganic matter, as in Equations 1.5 and 1.6.

$$\mathrm{Fe(II)} + H_2O_2 \rightarrow Fe(\text{Ш}) + OH^- + {}^{\cdot}OH \qquad \text{(Equation 1.5)}$$

$$\mathrm{Fe(\text{Ш})} + H_2O_2 \rightarrow Fe(\mathrm{II}) + HO_2^{\cdot} + H^+ \qquad \text{(Equation 1.6)}$$

Xu et al. (2020) used the Fenton reaction to modify biochar by adding iron to promote pyrolysis followed by H_2O_2 oxidation. It was found to improve the adsorption of hexavalent chromium and methylene blue. Belete et al. (2021) reported that the Fenton reaction was able to improve the adsorption of NH_4^+ by hydrochar, a material produced by transforming organic matter in an aqueous medium at high temperature and pressure.

1.4 Research objectives

The overall objective of this thesis was to assess the potential of treating slurries with various HCAs for reducing N losses and increasing N use efficiency of slurry N under different conditions by analyzing GHG and NH_3 emissions, N dynamics and retention in soil, as well as crop N uptake. The main questions addressed in this thesis were as follows:

1. Which are the most suitable HCAs that can effectively bind N from different animal slurries?

2. Can oxidation increase the N adsorption capacity of biochar to make it a sustainable and effective HCA?

3. Can oxidized biochar improve N retention in different soils treated with cattle slurry?

4. What are the effects of animal slurry-HCA mixtures on soil fertility and plant growth?

To address these questions, two incubation studies were conducted under laboratory conditions and one lysimeter study under field conditions. The lysimeter is a soil-filled device with a leachate sampling system at its base to collect the leachate (Fig. 1.4), which is between laboratory and field scale, facilitating measurement of the required experimental parameters in studies under field conditions.

Figure 1.4 *Sampling of the soil monoliths for the lysimeter experiment.*

The first incubation study is presented in Chapter 2. Three HCAs as byproducts or waste from agriculture, wood production and lignite mining – wheat straw, sawdust and leonardite – were applied to a silty loam soil together with pig and cattle slurry, using two common application patterns (slurry and HCA mixed overnight and subsequently added to the soil versus sequential direct addition). The experiments were performed in the laboratory at room temperature of 20 °C. The hypothesis was that co-application of animal slurry and HCAs would improve soil N retention and N use efficiency.

The second incubation study was divided into two parts. In the first part (Chapter 3), biochar was oxidized using the Fenton reaction to improve its adsorption capacity as a sustainable and effective HCA. The NH_4^+ adsorption capacity of biochar, oxidized biochar and leonardite was tested in ammonium sulfate [$(NH_4)_2SO_4$] solution, pH-adjusted $(NH_4)_2SO_4$ solution and cattle slurry. It was hypothesized that introduction of more oxygen-rich functional groups in biochar would increase adsorption of NH_4^+ and reduce NH_3 emissions from animal slurry. In the second part (Chapter 4), the effect of biochar and oxidized biochar on N retention in different soils was investigated. Biochar and oxidized biochar were applied to three soils together with cattle slurry and analyzed for GHG and NH_3 emissions, mineral N contents in soil solution and soils, as well as N recovery. The hypothesis was that biochar with more oxygen functional groups would be more effective in improving soil N retention.

Chapter 5 describes a lysimeter study to investigate the effect of HCAs in combination with different crops under field conditions. The lysimeter experiment was conducted with winter wheat and winter barley in a silty loam soil from the recultivation area of a nearby lignite mine, using cattle slurry mixed with wheat straw or leonardite overnight prior to application. It was hypothesized that application of HCAs with animal slurry would not reduce N uptake by crops.

2. High carbon amendments increase nitrogen retention in soil after slurry application – an incubation study with silty loam soil

Based on: Cao, X., Reichel, R., Wissel, H. et al. High Carbon Amendments Increase Nitrogen Retention in Soil After Slurry Application—an Incubation Study with Silty Loam Soil. J Soil Sci Plant Nutr 22, 1277–1289 (2022). DOI: 10.1007/s42729-021-00730-7

2.1 Introduction

Animal slurry, also known as liquid manure, contains large amounts of reactive N, an essential nutrient for plants and microorganisms that enhances metabolic rates and soil respiration when applied to soil. However, excessive N introduced to the environment, for example in the form of NH_3, can be a harmful pollutant of surface water and groundwater, cause biodiversity loss, and endanger human health(Aber et al., 1995). In the form of N_2O it can exacerbate global warming (Nancy N. Rabalais, 2002) and deplete the stratospheric ozone layer (Cowling et al., 1998).

Excessive N in the environment is a serious problem, particularly in areas with intensive livestock production such as northwest Germany, one of the areas with the most intensive livestock production in the world (Zerbe, 2020). The predominant N form in animal slurry is NH_4^+, which accounts for over 50% of total N (TN) in pig and cattle slurry (Jensen, 2013). The calculated global median NH_3 loss from the application of animal slurry amounts to 23%, which is higher than the loss resulting from the application of synthetic N fertilizer (Bouwman et al., 2002). In order to reduce NH_3 emissions, the 2017 German Fertiliser Ordinance aims to gradually ban the application of liquid manure using large spreaders to crop land by 2020 and to grassland by 2025. Once in the soil, NH_3 can rapidly be protonated to NH_4^+ and oxidized to NO_3^- by AOB and AOA. Any NO_3^- that is not taken up by plants is eventually leached into surface water and groundwater. N_2O is formed during both nitrification and denitrification, and is a significant contributor to global warming as a GHG that is 265 times more potent than CO_2 (IPCC, 2013). Therefore, it is important to improve soil N retention and to reduce N pollution from animal slurry.

High-carbon organic soil amendments can immobilize N and reduce GHG emissions and odor due to their composition and structure. Wheat straw, for example, contains considerable amounts of labile organic C, which can stimulate microbial activity and growth, and thus N immobilization in the soil (Zavalloni et al., 2011). Sawdust can eliminate the bad odor of landfills and animal or human excreta due to its high sorption capacity (Hui et al., 2003). Leonardite is a highly oxidized lignite of acidic nature that increases the degree of protonation of NH_3 when applied to slurry or soil, has a high CEC that promotes the adsorption of NH_4^+, and contains up to 20% labile C that can stimulate microbial N immobilization (Manzoni & Porporato, 2009). Furthermore, the addition of HCA, (e.g. straw) during slurry storage increases the amount of volatile fatty acids and may increase net N immobilization after the application of slurry to the soil (Kirchmann et al., 1993; Sørensen, 1998).

HCAs have great potential to reduce N losses from soils, but it is still unclear which HCA (wheat straw, sawdust, leonardite) are best suited to effectively bind N in different types of slurry and whether recovery of N from slurry can be enhanced by the combined application of HCA and slurry to the soil.

We hypothesized that leonardite would be more effective than wheat straw and spruce sawdust in reducing N loss after slurry application due to its combination of properties. We also hypothesized that mixing HCA with slurry prior to application would increase N retention. To put these hypotheses to the test, a laboratory incubation experiment was conducted with leonardite to compare it with sawdust and wheat straw. Pig or cattle slurry was applied to a silt loam soil, either after pre-incubation of the slurry with HCA or directly to the soil amended with the respective HCA. GHG (CO_2, CH_4, and N_2O) and NH_3 emissions were monitored during the 60-day incubation period to quantify the N retention capacity of the HCA in combination with liquid manure.

2.2 Materials and methods

2.2.1 Soil

The soil was obtained from an agricultural field close to Selhausen (Germany) and stored in a dried and 2-mm sieved state until use (Quade et al., 2018). It was classified as an orthic Luvisol with a silt loam soil texture and a pH_{H2O} of 7.1, containing 10.0 ± 0.2 g kg^{-1} total organic carbon (TOC) and 1.07 ±0.05 g kg^{-1} TN.

2.2.2 Slurries

Pig and cattle slurries were obtained from typical animal farms from the Rhineland region (*Rheinisches Revier*) close to Grevenbroich (North Rhine-Westphalia, Germany). Pig and cattle slurry had a density of 1.01 g cm^{-3} and 0.92 g cm^{-3}, a water content of 88% and 91%, a pH of 8.4 and 8.5, and a C/N ratio of 5.9 and 6.3, respectively. Based on dry weight, the pig slurry contained 64 mg g^{-1} TN, of which 45 mg g^{-1} was NH_4^+, 376 mg g^{-1} was TOC, and 193 mg g^{-1} was DOC; the cattle slurry contained 60 mg g^{-1} TN, of which 32 mg g^{-1} was NH_4^+, 378 mg g^{-1} was TOC, and 279 mg g^{-1} was DOC.

2.2.3 HCA

The HCA types used in the experiment were wheat straw, sawdust, and leonardite. The total C content of the HCAs were 43.6%, 44.0%, and 46.3%; the TN content amounted to 0.97%, 0.16%, and 0.92%; and the C:N ratios were 45, 275, and 50, respectively. The average pH in water of the leonardite was 4.2. Before application, wheat straw was cut into pieces that were 2-3 cm in length, and small particles of spruce sawdust without bark were added that were just a few millimeters in size. Leonardite was applied in powder form.

2.2.4 Incubations

Incubations were performed in polyvinyl chloride tubes (150 mm height, 50 mm diameter) containing 390 g of dried soil at a soil bulk density of 1.3 g cm^{-3}. The dry soil was reactivated by pre-incubating at 60% water-holding capacity (WHC, 36 g water per 100 g dry soil) for 10 days. The experiment consisted of 17 treatments with three replicates each - according to the combination of two types of slurry (pig and cattle slurry) - and applied at a rate of 80 kg TN ha^{-1} (corresponding to 4.75 ml pig slurry or 6.22 ml cattle slurry per incubation tube). Three types of HCA (wheat straw, sawdust, leonardite) were applied at a rate of 50 g C L^{-1} slurry (corresponding to 62 kg C ha^{-1} for pig slurry and 73 kg C ha^{-1} for cattle slurry); the application rate of HCA was previously found to be suitable to treat animal slurry with lignite or leonardite for the purpose of maximal nutrient immobilization (German patent DE102016223352A1 by RWE Power AG). Two common agricultural application methods were simulated: either mixing slurry and the respective HCA overnight before application and adding the mixture to the soil on the following day or adding HCA to the soil first and then adding slurry directly to the HCA-amended soil. A factorial design of 2 slurries x 3 HCA x 2 application methods was used, amounting to 12 treatments in total. Five different control groups were established: (1) Soil (S); (2) Soil and Pig slurry (SP); (3) Soil and Cattle slurry (SC); (4) Pig slurry (P); (5) Cattle slurry (C). An overview of all treatments and abbreviations is presented in Table 2.1. Slurry and HCA were incorporated into the first 2 cm of the soil immediately after application. Throughout the 60 days of incubation, the experiment was conducted at a room temperature of 20°C, the tubes were weighed daily, and water loss was compensated by the addition of the corresponding amount of deionized water. Due to the large number of treatments, the experiment was divided into two batches with the pig slurry batch starting 12 days earlier than the cattle slurry batch. To follow the development of the slurry-derived N, we added and mixed 40 mg $(^{15}NH_4)_2SO_4$ (at 1 atom% ^{15}N) each to the 200 ml pig and cattle slurries, respectively, before application.

Table 2.1 *The treatment combinations and their abbreviations.*

	Pig slurry (P)		**Cattle slurry (C)**		**control**
	Mixed overnight	Added directly to soil (+)	Mixed overnight	Added directly to soil (+)	Soil (S)
Wheat straw (W)	SPW	SP+W	SCW	SC+W	Soil + pig slurry (SP)
Sawdust (D)	SPD	SP+D	SCD	SC+D	Soil + cattle slurry (SC)
Leonardite (L)	SPL	SP+L	SCL	SC+L	Pig slurry only (P)
					Cattle slurry only (C)

Note. The abbreviations of the treatments are as follows: S – soil; P – pig slurry; C – cattle slurry; W – wheat straw; D – sawdust; L – leonardite; "+" – direct application of slurry and HCA to soil; no "+" – slurry and HCA mixed overnight before application.

2.2.5 Gas analysis

During the experiment, GHG and NH_3 emissions of the different treatments were measured on Days 1, 2, 3, 5, 7, and 10 of the experiment, and weekly thereafter, until the end of the experiment. An infrared laser gas analyzer (G2508, Picarro, Inc., Santa Clara, CA, USA) with a dynamic chamber (50 mm height, 50 mm diameter) tightly covering each tube was used in closed-loop mode to quantify the emissions of CO_2, N_2O, and NH_3 within 10 min. Gas fluxes were calculated according to Brummer et al. (2008). On the first day of the experiment, the CO_2 emissions data in the P treatment and N_2O and NH_3 emissions data in the P, SPW, and SPD treatments exceeded the calibrated range of the analyzer. An interpretation of this data was ruled out.

2.2.6 Nutrient analysis

After the experiment, soil samples were collected and separated into a top layer (0-5 cm, including slurries and HCA) and a sublayer (5-15 cm). All samples were stored in a freezer at –22 °C before extraction. According to Houba et al. (2000), mineral N fractions (NH_4^+ and NO_3^-) representing the available N were extracted with a 0.01 M $CaCl_2$ solution (soil-to-solution ratio of 1:4 w:v) that had an ionic strength similar to that of the soil solution by 2 h horizontal shaking at 200 rpm and 15 min centrifugation at 3500 rpm. The supernatant was filtrated with 0.45 µm PP-membrane syringe filters (disc size 25 mm; VWR International, Darmstadt, Germany) and then subjected to continuous flow analysis and ion chromatography (Dionex DX-500, ThermoScientific, Massachusetts, USA) for NH_4^+ and NO_3^-, respectively.

2.2.7 Microbial biomass

Soil microbial biomass was extracted using the chloroform-fumigation extraction method (CFE) as described in Reichel et al. (2017). A TOC analyzer (TOC-VcPH + TNM-1 + ASI-V, Shimadzu, Kyoto, Japan) was used to determine the DOC in $CaCl_2$ extracts both without and after chloroform fumigation in order to quantify the microbial biomass C (C_{mic}). C_{mic} and N_{mic} were calculated according to Rainer Georg Joergensen (1996) using the correction factors k_{EC} 0.45 and k_{EN} 0.40.

2.2.8 ^{15}N analysis

For both the top layer and the sublayer of soil samples, 2 g air dry soil were extracted with 50 ml 1 M potassium chloride (KCl) by 1 h horizontal shaking at 200 rpm and 20 min centrifugation at 3,500 rpm. Here, the extraction with 1 M KCl solution was chosen to recover the maximum amount of $^{15}NH_4^+$ from the soil (also including the fraction adsorbed by the soil matrix) in order to analyze of the development of slurry N in soil. The N leaching potential was estimated from the NO_3^- content in the soil solution, which was sampled at a soil depth of 10 cm using MicroRhizon samplers (type 19.21.81, Rhizosphere Research Products, Wageningen, Netherlands) on Days 0 (before application), 4, and 8, and weekly thereafter, until the end of the experiment. All solution samples were stored in a freezer at -22 °C before analysis. For the analysis, each sample (1-2 ml) was diluted to 20 ml with deionized water. ^{15}N isotope signatures of NH_4^+ and NO_3^- in soil extracts and soil solutions were analysed by applying sequential micro-diffusion and liquid-liquid extraction techniques as described in Reichel et al. (2018).

2.2.9 Calculations and statistical analysis

The results are expressed as a mean value of three replicates ± standard deviation on a dry soil basis. After considering the statistical requirements (normal distribution and homogeneity of variance), the differences between treatments were analysed for significance by three-way analysis of variance (ANOVA) with Tukey's HSD used as the post-hoc test at a significance level of $p \leqslant 0.05$ (IBM SPSS Statistics for Windows, Version 25.0, IBM Corp., Armonk, NY, USA).

2.3 Results

The three-way ANOVA (Table A.1) showed that cumulative GHG and NH_3 emissions and ^{15}N recovery responded significantly to the type of slurry (larger in pig than in cattle slurry) and the HCA type. In addition, application methods also affected N_2O, NH_3 emissions, and ^{15}N recovery ($p<0.05$). In the top layer of the soil, the type of HCA significantly affected the DOC, C_{mic}, NO_3^-, and pH ($p<0.05$). In the sublayer, NO_3^- responded to all three factors, while pH only responded to the application method.

2.3.1 pH

The pH values of the topsoil layer of all treatments were lower than in the S control at the end of the incubation period (Table 2.2). Leonardite significantly decreased the pH values of the soil to below 7 for both slurries. There was no significant difference between treatments in the sublayer; the pH of all samples was around 7.6.

Table 2.2 *Soil pH values, NH_4^+ and NO_3^- contents at the end of the experiment.*

		pH		**NH_4^+ (µg N g^{-1} dm)**		**NO_3^- (µg N g^{-1} dm)**	
		Top layer (0-5cm)	Sub layer (5-15cm)	Top layer (0-5cm)	Sub layer (5-15cm)	Top layer (0-5cm)	Sub layer (5-15cm)
Pig slurry treatments	S	7.7 ± 0.0a	7.7 ± 0.0ab	1.0 ± 0.8c	1.0 ± 0.8b	91 ± 7.1c	91 ± 7.1 a
	SP	7.2 ± 0.1b	7.7 ± 0.0ab	4.1 ± 1.9c	1.5 ± 0.3ab	419 ± 145.5ab	82 ± 3.8a
	SP+W	7.1 ± 0.1bc	7.5 ± 0.1c	38.7 ± 15.5a	1.3 ± 0.6ab	362 ± 33.4abc	95 ± 27.6a
	SPW	7.2 ± 0.0b	7.7 ± 0.0a	24.2 ± 7.7ab	3.6 ± 0.5a	307 ± 34.2abc	74 ± 11.9a
	SP+D	7.3 ± 0.0b	7.7 ± 0.1abc	11.5 ± 6.4bc	2.4 ± 1.6ab	487 ± 69.6ab	74 ± 18.1a
	SPD	7.1± 0.0bc	7.7 ± 0.0a	4.6 ± 4.2c	1.9 ± 0.5ab	357 ± 72.5abc	77 ± 12.7a
	SP+L	6.9 ± 0.1d	7.5 ± 0.1bc	9.2 ± 3.7bc	1.9 ± 0.7ab	461 ± 190.0ab	83 ± 19.7a
	SPL	7.0 ± 0.0cd	7.6 ± 0.1abc	4.9 ± 4.3c	1.6 ± 0.9ab	496 ± 189.3ab	92 ± 20.1a
Cattle slurry treatments	S	7.7 ± 0.0a	7.7 ± 0.0a	1.0 ± 0.8a	1.0 ± 0.8a	91 ± 7.1e	91 ± 7.1abc
	SC	7.5 ± 0.1ab	7.5 ± 0.1b	0.0 ± 0.0a	0.0 ± 0.0a	805 ± 118.8a	59 ± 12.5c
	SC+W	7.2 ± 0.2b	7.7 ± 0.0ab	9.3 ± 7.9a	1.0 ± 0.5a	283 ± 82.8de	84 ± 6.7abc
	SCW	7.4 ± 0.2ab	7.6 ± 0.0ab	6.8 ± 1.5a	0.8 ± 0.4a	317 ± 24.0de	101 ± 6.1a
	SC+D	7.6 ± 0.0ab	7.6 ± 0.1ab	8.2 ± 7.4a	0.6 ± 0.3a	375 ± 41.4cde	99 ± 8.8ab
	SCD	7.4 ± 0.0ab	7.6 ± 0.0ab	4.3 ± 4.0a	0.5 ± 0.6a	445 ± 117.8bcd	91 ± 8.9abc
	SC+L	6.8 ± 0.2c	7.6 ± 0.1ab	4.6 ± 4.1a	0.6 ± 0.3a	683 ± 174.8abc	68 ±7.5abc
	SCL	6.7 ± 0.1c	7.6 ± 0.1ab	0.0 ± 0.0a	1.0 ± 0.8a	767 ± 86.9ab	70 ± 7.8abc

Note. The abbreviations of the treatments are as follows: S – soil; P – pig slurry; C – cattle slurry; W – wheat straw; D – sawdust; L – leonardite; "+" – direct application of slurry and HCA to the soil; no "+" – slurry and HCA mixed overnight before application. Values are means ± SD. The different lowercase letters indicate significant differences at the $p<0.05$ level between treatments.

2.3.2 CO_2

The CO_2 emission rates were extremely high on the first day (Fig. A.1). The highest emission rates occurred in SPD (33.7 g C m^{-2} day^{-1}) and SCW (25.7 g C m^{-2} day^{-1}), while SPL (12.8 g C m^{-2} day^{-1}) and SCL (9.8 g C m^{-2} day^{-1}) had the lowest CO_2 emission rates compared with the other HCAs. Comparing the two application methods, the first application method (mixing slurry and HCA overnight followed by application of the mixture on the following day) led to significantly higher CO_2 emission rates for cattle slurry treatments on the first day; this difference then diminished in the following days. The CO_2 emission rates rapidly declined in all treatments after the first day, but remained at an intermediate level for 10 days before levelling off at 1 g C m^{-2} day^{-1} towards the end of the experiment. In this period, the slurry-only treatments P and C always had the lowest CO_2 emission rates.

The cumulative CO_2 emissions of the two application methods were not significantly different from each other, while the wheat straw treatments emitted considerably more CO_2 compared to the other HCA treatments. Adding pig slurry to the soil increased cumulative CO_2 emissions by 39% compared to the S treatment (Fig. 2.1A). The addition of wheat straw increased CO_2 emissions by 15% in the SP+W treatment compared to the SP treatment. Leonardite significantly decreased CO_2 emissions by 16% and 15% in the SP+L and SPL treatments, respectively, compared to the corresponding control (SP). The CO_2 emissions of the SP+D treatment were also reduced by 17% compared to the corresponding control (SP).

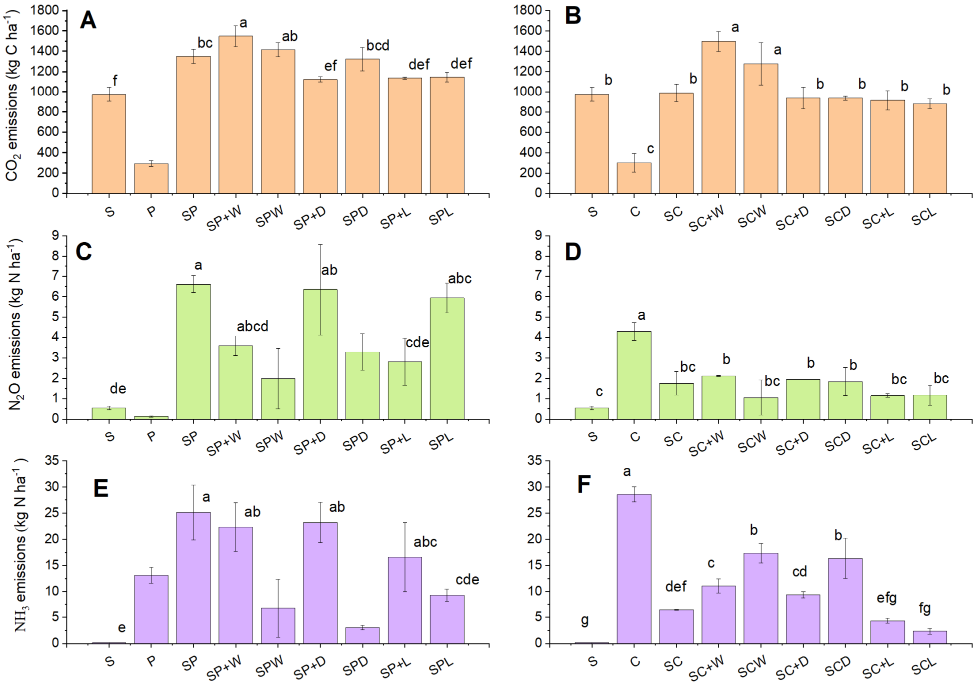

Figure 2.1 *(A) Cumulative CO_2 emissions of pig slurry treatments; (B) cumulative CO_2 emissions of cattle slurry treatments; (C) cumulative N_2O emissions of pig slurry treatments; (D) cumulative N_2O emissions of cattle slurry treatments; (E) cumulative NH_3 emissions of pig slurry treatments; (F) cumulative NH_3 emissions of cattle slurry treatments. The abbreviations of the treatments are as follows: S – soil; P – pig slurry; C – cattle slurry; W – wheat straw; D – sawdust; L – leonardite; "+" – direct application of slurry and HCA to the soil; no "+" – slurry and HCA mixed overnight before application. The error bars show the standard error of the mean of each treatment (n = 3). The different lowercase letters indicate significant differences at the $p<0.05$ level between treatment. The CO_2 emissions of the P treatment are not compared due to the absence of data for the first day. The N_2O emissions of the P, SPW, and SPD treatments are not compared due to the absence of data for the first day. The NH_3 emissions of the P, SPW, and SPD treatments are not compared due to the absence of data for the first day.*

In contrast to pig slurry, the addition of cattle slurry to soil only increased CO_2 emissions by 1% (Fig. 2.1B). In the cattle slurry treatments, wheat straw increased CO_2 emissions by 51% and 29% in SC+W and SCW treatments, respectively, compared to the SC treatment. However, the other HCA types did not significantly reduce the CO_2 emissions in the cattle slurry treatments.

2.3.3 N_2O

On the day of slurry application, the emission rates of N_2O (Fig. A.1) peaked in the C treatment with a maximum emission rate of 813 mg N m^{-2} day^{-1}. Among the HCA substrates tested, only leonardite significantly reduced N_2O emission rates for both slurry treatments. On Day 2 after application, the rates decreased rapidly below 5 mg N m^{-2} day^{-1}. A second peak was reached in the pig and cattle slurry treatments 18 days and 7 days after application, respectively, while it was reached on day 10 in the C (cattle slurry only) treatment. The application of pig slurry together with wheat straw was associated with the lowest N_2O emission rates during the second peak period, in contrast to cattle slurry where this difference was not significant. Thereafter, N_2O emission rates gradually declined to the level of untreated soil.

The application of pig slurry increased cumulative N_2O emissions 11-fold compared to the soil-only (S) treatment. N_2O emissions were reduced by 46% and 58% in SP+W and SP+L, respectively, compared to the SP treatment (Fig. 2.1C). The N_2O emissions of SC was increased by 2-fold compared with the S treatment. The SCW, SC+L, and SCL treatments tended to reduce the N_2O emissions by 40%, 34%, and 33%, respectively, in relation to the SC treatment (Fig. 2.1D).

2.3.4 NH_3

In general, pig slurry treatments had higher NH_3 emissions than cattle slurry treatments (Fig. 2.1E,F). The application of pig slurry to soil was associated with a large NH_3 loss. The total NH_3 emissions in the SP treatment were 3.9 times higher than in the SC treatment. On the first day of slurry application, the NH_3 loss was extremely high, with maximum emission rates of 4,000 mg N m^{-2} day^{-1} and 5,000 mg N m^{-2} day^{-1} in the pig and cattle slurry treatments (Fig. A.1), respectively. One day after slurry application, NH_3 emissions declined considerably to rates below 150 mg N m^{-2} day^{-1}, while in the P treatment emissions remained high at a rate of 565 mg N m^{-2} day^{-1}. NH_3 strongly decreased to below 1 mg N m^{-2} day^{-1} after Day 10, with the exception of P where NH_3 emissions could no longer be detected after Day 25.

The two application methods had different effects on cumulative NH_3 emissions for the two slurries. In the pig slurry treatments, mixing slurry and HCA reduced NH_3 emissions compared to adding slurry and HCA directly to the soil, but the opposite was the case in the cattle slurry.

Leonardite had a similar effect on reducing NH_3 emissions in both slurries compared to the soil + slurry control. In treatments in which leonardite was added directly to the slurry, cumulative NH_3 emissions were reduced by 34% in pig slurry and by 32% in cattle slurry. Leonardite mixed with slurry overnight before application reduced the cumulative NH_3 emissions from pig slurry (SPL) and cattle slurry (SCL) by 63% and 64%, respectively.

In contrast, wheat straw and sawdust increased the NH_3 emissions when mixed with cattle slurry. Compared with the SC treatment, wheat straw significantly increased the NH_3 emissions by 72% (SC+W) and 170% (SCW). Sawdust increased the cumulative NH_3 emissions by 46% (SC+D) and by 154% (SCD) in relation to the SC treatment.

2.3.5 DOC and microbial biomass

In relation to the control S, increased DOC concentrations were found in the top soil layer of all treatments at the end of the incubation period (Fig. 2.2A,B). The addition of pig slurry to the soil increased the DOC concentration by 2.9 times, which was larger than after the addition of the cattle slurry (2.2 times). All the tested HCA types increased the DOC content in relation to the SC treatment: wheat straw and leonardite increased the DOC concentration by 61-68%, while for sawdust the increase was in the range of 23-26%. In the pig slurry treatments, wheat straw increased the DOC by 42% (SP+W) and 18% (SPW). Leonardite increased the DOC by 16% (SP+L) and 30% (SPL). In contrast, the DOC decreased in sawdust treatments with pig slurry (10-12%). In the sublayer of the soil, the DOC concentrations were lower than 80 μg C g^{-1} without any significant difference between the treatments (Fig A.2).

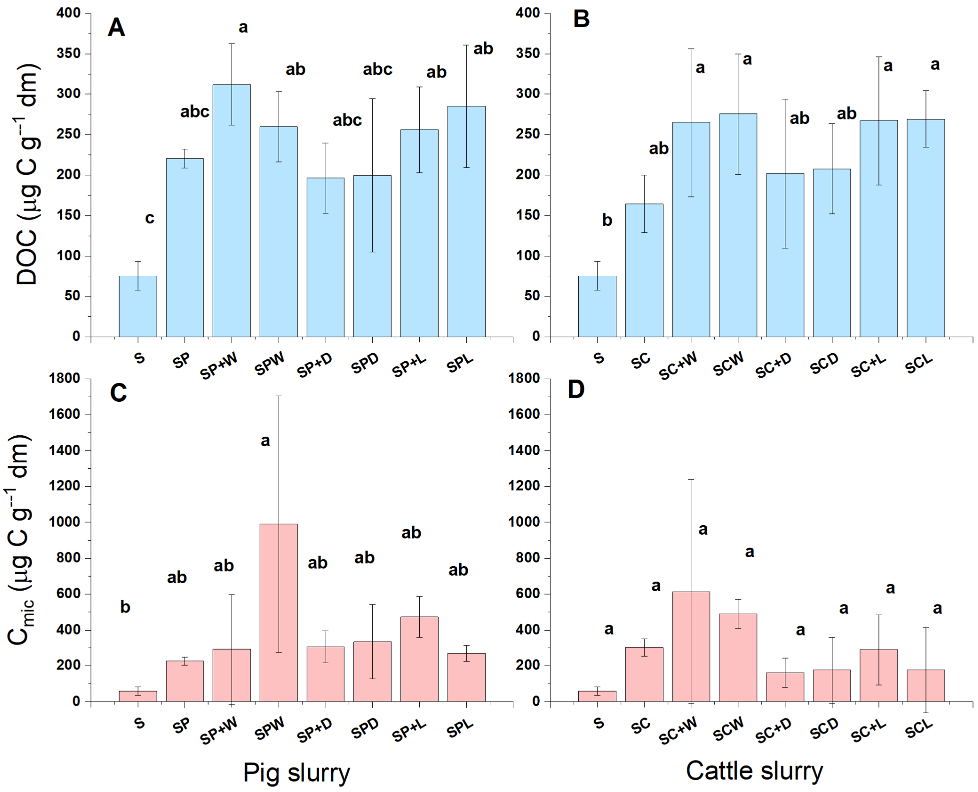

Figure 2.2 *(A) Dissolved organic C (DOC) of pig slurry treatments; (B) DOC of cattle slurry treatments; (C)* C_{mic} *of pig slurry treatments; (D)* C_{mic} *of cattle slurry treatments. S – soil; P – pig slurry; C – cattle slurry; W – wheat straw; D – sawdust; L – leonardite; "+" – direct application of slurry and HCA to the soil; no "+" – slurry and HCA mixed overnight before application. The error bars show the standard error of the mean of each treatment (n = 3). The different lowercase letters indicate significant differences at the* $p<0.05$ *level between treatments.*

Both slurries and the tested HCA types increased the C_{mic} in the top layer (Fig. 2.2C,D). Most HCA treatments with pig slurry tended to have a larger microbial biomass compared to the SP treatment. The C_{mic} of the SP+W treatment was 4.4 times higher than in the SP treatment. The wheat straw treatments with cattle slurry (SC+W and SCW) tended to have a larger C_{mic} compared to the SC treatment. In the sublayer, none of the HCA types appeared to have a significant effect on the C_{mic} of the pig slurry treatments. All the measured C_{mic} concentrations were lower than 65 µg g^{-1}. Most of the C_{mic} of the cattle slurry treatments ranged were below 70 µg g^{-1}, with the exception of the SC+L (114 µg g^{-1} dry soil) (Fig. A.2).

2.3.6 Mineral N in soil

At the end of the experiment, NH_4^+ concentrations reached their minimum level in all treatments. Pig slurry treatments with wheat straw still had the highest NH_4^+ content. Compared to the SP, the NH_4^+ content was 9.4 and 5.9 times higher in the SP+W and SPW treatments. Soil column sublayers contained less than 2 µg NH_4-N g^{-1} except for the SPW treatment, which contained 3.6 µg NH_4-N g^{-1}. In contrast, the HCA had no significant effect in the cattle slurry treatments (Table 2.2).

At the end of the experiment, the NO_3^- concentrations of all treatments were larger than in the S treatment (control). Most of the NO_3^- was retained in the top layer of the soil columns (Table 2.2). The addition of cattle slurry increased the NO_3^- concentration 1.9-fold compared to the treatments with pig slurry. Wheat straw and sawdust decreased NO_3^- in the top layer. However, the decrease of NO_3^- compared to the SC treatment was only significant for the cattle slurry treatments with wheat straw (65% for SC+W and 61% for the SCW treatment) and sawdust (53% for SC+D and 45% for the SCD treatment). In the sublayers of all treatments, NO_3^- was below 105 µg N g^{-1}, but tended to be higher in the sublayer of the cattle slurry treatments with wheat straw and sawdust compared to leonardite treatments.

2.3.7 ^{15}N recovery in soil

Wheat straw and leonardite increased the ^{15}N recovery in the total N fraction ($^{15}N_t$) of both slurry treatments (Fig. 2.3). In the pig slurry treatments, wheat straw increased the $^{15}N_t$ recovery by 58% (SPW) and 111% (SP+W) and leonardite by 106% (SPL) and 91% (SP+L) compared to the SP treatment. In the cattle slurry treatments, wheat straw increased the $^{15}N_t$ recovery by 66% (SCW) and 28% (SC+W) and leonardite by 178% (SCL) and 37% (SC+L), respectively. However, only the increase in the SCL treatment was statistically significant. Sawdust had no apparent effect on the $^{15}N_t$ recovery. Mixing cattle slurry and HCA overnight significantly increased $^{15}N_t$ recovery compared to adding cattle slurry and HCA directly to soil, although not in the pig slurry treatments.

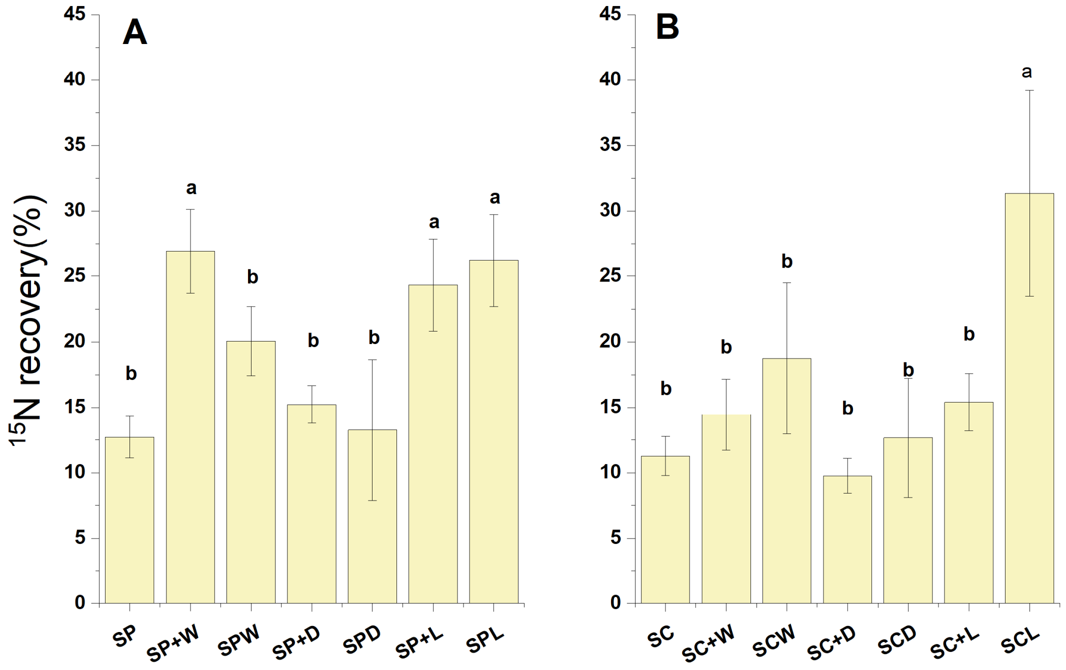

Figure 2.3 *(A) ^{15}N recovery in the pig slurry treatments; (B) ^{15}N recovery in the cattle slurry treatments. The abbreviations of the treatments are as follows: S – soil; P – pig slurry; C – cattle slurry; W – wheat straw; D – sawdust; L – leonardite; "+" – direct application of slurry and HCA to the soil; no "+" – slurry and HCA mixed overnight before application. The error bars show the standard error of the mean of each treatment (n = 3). The different lowercase letters indicate significant differences at the p<0.05 level between treatment.*

2.3.8 Mineral N and δ^{15}N in soil solution

The soil solution volume of all samples was 1-2 ml. Before slurry application, NH_4^+ concentrations in all treatments were <10 µg N ml^{-1} (Fig. 2.4A,B). In pig slurry treatments, the NH_4^+ peaked on Day 8 after slurry application (>10 µg N ml^{-1}) and decreased to values <5 µg N ml^{-1} by Day 29. Most NH_4^+ concentrations of the cattle slurry treatments were below those of the pig slurry treatments. The NH_4^+ concentration of the cattle slurry treatments reached an initial peak on Day 8 after slurry application (~8 µg N ml^{-1}) and declined to around 2 µg N ml^{-1} by Day 22. Interestingly, the highest NH_4^+ concentration in the soil solution was found in the SC+L treatment on Day 22 (11 µg N ml^{-1}), remaining at this level for longer than in all other treatments.

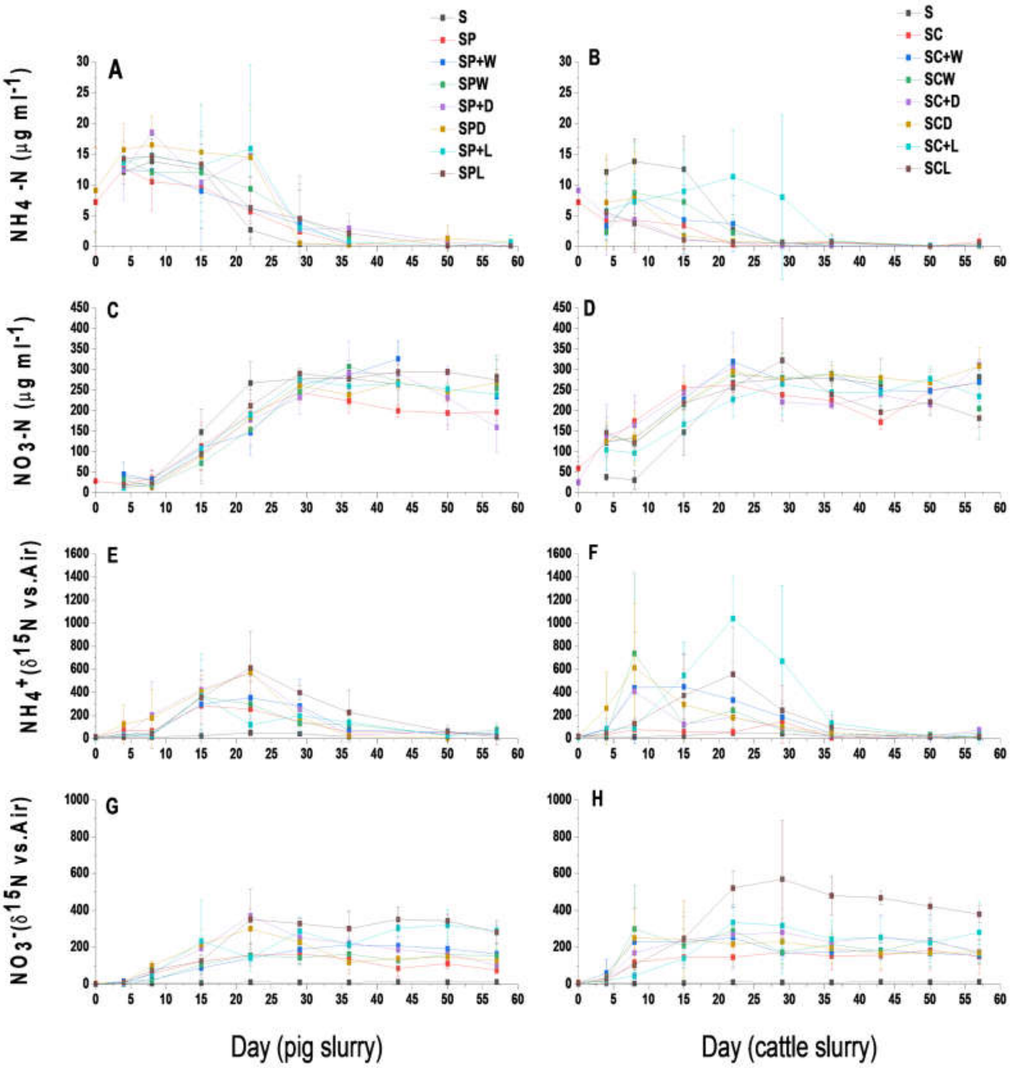

Figure 2.4 *Mineral N concentrations in the soil solution. (A) Ammonium (NH_4^+) content of pig slurry treatments; (B) NH_4^+ content of cattle slurry treatments; (C) NO_3^- content of pig slurry treatments; (D) NO_3^- content of cattle slurry treatments; (E) $^{15}NH_4^+$ of pig slurry treatments; (F) $^{15}NH_4^+$ of cattle slurry treatments; (G) $^{15}NO_3^-$ of pig slurry treatments; (H) $^{15}NO_3^-$ of cattle slurry treatments. The abbreviations of the treatments are as follows: S – soil; P – pig slurry; C – cattle slurry; W – wheat straw; D – sawdust; L – leonardite; "+" – direct application of slurry and HCA to the soil; no "+" – slurry and HCA mixed overnight before application. The error bars show the standard error of the mean of each treatment (n = 3).*

Fig. 2.4E-H show the development of the $\delta^{15}N$ trends over the total incubation time of 60 days. In the pig slurry treatments, the $^{15}NH_4^+$ reached its peak value on Day 22, slightly later than the NH_4^+ concentrations. After 36 days of incubation, $^{15}NH_4^+$ content decreased to its initial level before slurry application. In cattle slurry treatments, $^{15}NH_4^+$ of all HCA treatments reached peak values before Day

15, except for the leonardite treatments which peaked on Day 22. $^{15}NH_4^+$ also declined to its initial level on Day 36.

The NO_3^- concentrations of all pig slurry treatments were <50 µg ml^{-1} and remained at this level until incubation on day 8 before increasing to a peak value on Day 29 (~255 µg N ml^{-1}). There were no significant differences between the NO_3^--N concentrations among treatments. In the cattle slurry treatments, after slurry and/or HCA application, NO_3^- concentrations increased to a maximum concentration between 250 and 300 µg ml^{-1} on Day 22; only the SCL treatment peaked on day 29 (322 µg ml^{-1}).

In contrast to the trend in NO_3^- concentrations, $^{15}NO_3^-$ trends were concurrent with $^{15}NH_4^+$ at the beginning. The $^{15}NO_3^-$ of the leonardite treatments reached its highest value on Day 29, while the other treatments reached their peak on Day 22, remaining at that high level until the end of the experiment.

In all treatments, the NH_4^+ and NO_3^- developed in opposite directions, with the maximum NH_4^+ concentration and minimum NO_3^- concentration in the early incubation period and the lowest and largest concentrations at the end of the incubation, respectively.

2.4 Discussion

In this experiment, the GHG (CO_2 and N_2O) and NH_3 emissions in pig slurry treatments were higher than in cattle slurry treatments. According to Kirchmann et al. (1993), the lower CO_2 emissions in the cattle slurry treatments are related to a lower C mineralization potential in the soil. In contrast to pigs, the high digestive activity in cattle rumen might have removed labile C sources from the slurry, thus lowering its CO_2 emissions potential in soil.

The pig slurry contained more NH_4^+ (70% of TN) than the cattle slurry (53% of TN) and the pig slurry infiltrated into the soil much more slowly than the cattle slurry. A restricted infiltration of the slurry into the soil was found to increase NH_3 emissions (Chen, 1986), as this increases the slurry's time of exposure to the atmosphere and hence the time for NH_3 outgassing. Our experiment also showed that less N_2O was emitted from cattle slurry treatments. The rumen activity of cattle leads to more DOC in the cattle slurry (74% DOC in cattle slurry compared to 51% DOC in pig slurry), which could have resulted in a stronger immobilization of available N in the soil, thus reducing the N_2O emissions potential (Burger & Jackson, 2003). Overall, we can state that the difference in the DOC and the mineral N content in pig and cattle slurries led to the observed differences in gas emission between the treatments with pig and cattle slurries.

Wheat straw treatments emitted more CO_2 than the other HCA treatments with both slurries. The larger fraction of easily available C of wheat straw most likely stimulated the growth of microorganisms after incorporation into the soil. Slurry-NH_4^+ further stimulated the mineralization of wheat straw, which additionally increased CO_2 emissions (Chantigny et al., 2001; M. K. Firestone et al., 1980; Sørensen, 1998). Leonardite also contains sources of labile C, which also significantly increased DOC and C_{mic} concentrations in pig slurry treatments, but without a significant increase in CO_2 emissions. This is in agreement with previous studies, and is also related to the release of proton from acidic leonardite in neutral soils (Schefe et al., 2008; C. K. T. Tran et al., 2015). In general, the high amount of labile C released from wheat straw increased CO_2 emissions, while the acidity of leonardite could have counteracted this effect.

Nitrous oxide emission rates showed two peaks. Similar dynamics have previously been observed in the lab (Velthof et al., 2003) and in the field (Thomsen et al., 2010). The peak on the day of slurry application could have originated from the denitrification of soil NO_3^- stimulated by the input of labile organic C due to slurry application, as assumed by Velthof et al. (2003). This is supported by the findings of Nguyen et al. (2017), who provided a much more detailed insight into the NH_4^+, NO_3^- and O_2 dynamics after slurry application to a grassland soil, and who found N_2O dynamics very similar to those of our findings. They used a planar optode setup to monitor the O_2 concentration in the soil before, during, and after slurry application. In addition, they also implemented a treatment, in which the nitrification inhibitor 3, 4-dimethyl pyrazole phosphate was added to the slurry. Finally, they determined the ^{15}N site preference of the emitted N_2O as an indicator of the N_2O origin (nitrification/fungal denitrification vs. bacterial denitrification). For the first peak, they found no evidence of a significant contribution of nitrification to N_2O emissions despite clearly measurable nitrification activity, which was indicated by the significant difference in oxygen consumption between the slurry treatments with and without the nitrification inhibitor and the much higher NH_4^+ and much lower NO_3^- concentrations in the topsoil at the end of the experiment. Nevertheless, the site preference of N_2O during the first peak was much higher than is typical for bacterial denitrification, which Nguyen et al. (2017) attributed to the fungal denitrification of NO_3^- present in the soil before slurry application in addition to the fact that the nitrification inhibitor did not have an effect on the magnitude of the first N_2O peak. In contrast, during the second N_2O peak, Nguyen et al. (2017) found higher O_2 concentrations, significantly higher N_2O emissions in the treatments without the nitrification inhibitor, and intermediate N_2O site preference, with significantly lower values for the treatment without the nitrification inhibitor, all of which point towards a close connection between nitrification and bacterial denitrification as N_2O source processes. This is also backed up by the N_2O, soil NH_4^+, and NO_3^- dynamics reported by Thomsen et al. (2010), who found increasing concentrations of NO_3^- in the soil coinciding with the second N_2O peak. The oxygen concentration in the soil gradually increases again with the depletion of labile C due to the initially strong respiration activity following slurry application (Nguyen et al., 2017).This enables an increase in nitrification activity and hence an increase in NO_3^- concentration, which in turn serves as a substrate for denitrification. With the build-up of the soil NO_3^- pool, N_2O emissions thus increase again to a second peak due to simultaneous nitrification denitrification (Rochette et al., 2008; Saguer & Gispert, 1996). In short, the two N_2O emission peaks had different causes: while the first peak likely derived from denitrification alone, stimulated by a high soil NO_3^- content, the second N_2O peak was likely due to simultaneous nitrification bacteria denitrification.

Leonardite's mitigating effect on NH_3 emissions was evident for both slurries, but in particular for the pig slurry. When leonardite was mixed with the slurries one day before application, the total NH_3 emissions were reduced by more than 60% compared to the control (soil+slurry). This effect was likely due to the acidic nature and high CEC of leonardite, which led to the protonation of NH_3 and the adsorption of NH_4^+ (Chen et al., 2015; Sommer et al., 2003). The deprotonation of the acid groups on the surface of the lignite decreased the pH of the alkaline slurry, thus enhancing the NH_4^+/NH_3 ratio, and increased the negative charge on the surface of the leonardite, providing more adsorption sites for NH_4^+ (Simmler et al., 2013).

In this experiment, leonardite also reduced N_2O emissions, especially in the SP+L treatment where the reduction amounted to 58%. This was in contrast to the study by J. L. Sun et al. (2016), but they applied lignite, i.e. a less oxidized form than leonardite, directly to the surface of a cattle pen, thereby probably creating a urine-soaked soil cover, in which less cation exchange sites compared to leonardite and micro-anaerobic conditions may have promoted denitrification and N_2O formation.

In contrast to our results, wheat straw applied to fertilized soil without manure was previously found to increase N_2O emissions (J. Wei et al., 2020). The application of slurry may therefore have partly suppressed potential N_2O emission pathways in our study. For example, animal slurry could have stimulated the mineralization of wheat straw, which may have promoted the growth of soil microbial biomass and N immobilization, as indicated by the tendency to higher C_{mic} values in the wheat straw treatments (Fig. 2.2), which subsequently led to a reduction in the availability of N to the nitrifying microorganism (Aita et al., 2012; J. Wei et al., 2020). In contrast, wheat straw and sawdust reduced the infiltration velocity of slurry into the soil and lowered the water content of slurries (Vandre et al., 1997). This can lead to an increase in NH_3 volatilization, as was observed in our experiment. HCAs also significantly affect N in the soil. After the 60 days of incubation, wheat straw and leonardite increased the DOC content of the topsoil layer for both slurry treatments. This is in line with the fact that wheat straw contains more labile organic compounds than sawdust; and lignite was also reported to contain up to 20% of labile C (Chen et al., 2015). The amount of labile OC determines the microbial N immobilization potential by microbial biomass growth. Leonardite therefore clearly has the potential for microbial N immobilization in addition to its physicochemical N retention properties.

Mineral N (NO_3^- and NH_4^+) was mainly retained in the top layer of the soil and was not translocated downward along the soil columns. This might have been due to the fact that the water content was kept constant throughout the experiment by adding small amounts of water every day. This prevented significant vertical water movement in the soil and was therefore different from larger natural precipitation events. Most of the NH_4^+ was oxidized to NO_3^- by the end of the incubation period, although the soil treated with cattle slurry (SC) contained less NH_4^+ and more NO_3^- than the soil treated with pig slurry (SP). The cattle slurry thus seems to be more conducive to nitrification than the pig slurry. One reason for this might be that heavy metals and antibiotic substances are more abundant in pig slurry than in cattle slurry, which affects microbial N transformations in the soil (Sommer et al., 2003). Compared to leonardite, the addition of wheat straw and sawdust led to lower NO_3^- concentration in the top layer of the cattle slurry treatments, which could have resulted from the higher NH_3 loss than in the leonardite treatments (Fig. 2.1F) and the preservation of NH_4^+ by leonardite during the early phase of the incubation. In short, the two different slurries led to significant differences in mineral N dynamics, with a lower nitrification rate in the soil treated with pig slurry compared to the soil amended with cattle slurry. Of the three HCAs tested, leonardite resulted in the highest N retention.

Overall, the application of wheat straw and leonardite was associated with a higher ^{15}N recovery than in the sawdust treatments, i.e. more slurry-N was retained in the soil. The reason for this may very likely be the increase in DOC in the soil due to the application of wheat straw and leonardite, which led to an increase in N retention by stimulating microbial growth. However, compared with straw, leonardite has a more acidic nature and higher CEC, which leads to a stronger ability to adsorb slurry-NH_3 in the form of NH_4^+. As a consequence, leonardite was characterized by lower N_2O and NH_3 emissions compared to the other HCA treatments, leading to a higher N retention in the topsoil layer.

The trend in $\delta^{15}N$ showed the N pathway of the labeled slurry, i.e. NH_4^+ content decreased while NO_3^- increased due to nitrification. It is remarkable that the $\delta^{15}N$ of the NH_4^+ of the leonardite treatments reached higher values, but at a later point in time compared to the other HCA treatments. The reason for this could be that leonardite adsorbed and retained more NH_4^+ in the soil due to its high CEC and its acidic nature and thus its potential negative effect on nitrification activity, thus preserving more NH_4^+ from being nitrified to NO_3^- in the early incubation phase.

The effects of the different slurry application methods were complex in our experiment. The overnight mixing of slurry and HCA increased the CO_2 emission rate on the day of application only for the cattle slurry treatments. This may be due to the conversion of some insoluble organic matter in the cattle slurry to soluble C by fermentation during overnight storage of the slurry with the HCA (Harper & Lynch, 1982). The pig slurry already contained more DOC than the cattle slurry, which is why mixing with HCA and overnight storage did not have a significant effect on the pig slurry treatments.

The most noteworthy result was that leonardite reduced total NH_3 emissions by more than 60% compared to the control when mixed with slurry the day before application. However, when the HCA and slurry were added sequentially, the reduction was only about 33%. Although significant differences were found only in the pig slurry treatments, there was a tendency for mixing the slurries and the HCA before application to reduce NH_3 emissions more than the sequential method for both slurry treatments. Mixing slurries and leonardite overnight before application led to more NH_4^+ adsorption to the leonardite surface (Sommer et al., 2003), while also likely increasing microbial N immobilization due to labile C released from leonardite (Sørensen, 1998).

However, despite the trends described above, the effects of the different application methods for the different slurries and HCAs were not consistent, which was likely due to the short mixing time. Overnight mixing enabled the leonardite to adsorb NH_4^+ through a physicochemical process, but the time was too short to obtain significant effects from biochemical processes. It has been reported in the literature, that this usually takes several weeks or months (Amon et al., 2006; van der Weerden et al., 2014).

2.5 Conclusion

In this laboratory study with silt loam soil, leonardite combined with animal slurry reduced N_2O and NH_3 emissions, increased the retention of slurry-derived N in the soil, and reduced the formation of leachable NO_3^- more effectively than the same amount of wheat straw or sawdust. Overnight mixing of the slurry and the HCA reduced N loss in some treatments, but the effect was not consistent. The type of slurry (pig or cattle slurry) and application methods had a strong influence on the effect of the tested HCA on GHG emissions and N retention. We conclude that leonardite may be a suitable additive for reducing nutrient losses after organic fertilization with animal slurries under similar soil conditions, thus improving the efficiency of agricultural N use.

Our study proves that it is possible to reduce N losses after slurry application by using leonardite. However, since this experiment was conducted under laboratory conditions without plants, further research is required to confirm this under more realistic soil conditions with crops. Future research should also investigate the potential beneficial effects of leonardite on the long-term storage of animal slurries and evaluate whether the positive effects on soil N retention and N cycling can be harnessed in practice.

3. Fenton oxidation of biochar improves retention of cattle slurry nitrogen

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3.1 Introduction

Nitrogen is one of the most essential nutrients for plant growth. Livestock slurry, containing easily available C and NH_4^+, is a traditional organic fertilizer. However, it has been reported that up to 29% of the slurry-N can be emitted to the atmosphere via NH_3 volatilization during the fertilization process (Bouwman et al., 2002). During nitrification, NH_4^+ can be converted to NO_3^-, which is highly mobile in soil and can pollute water bodies through leaching. Part of the N can also be converted to N_2O by nitrification and denitrification, which contributes to global warming (Reay et al., 2012; Zhang et al., 2015).

In addition to agricultural management practices, such as adjusting fertilizer placement and application rates (He et al., 2014; Pan et al., 2016), many studies have attempted to add soil amendments, such as carbonaceous material (CM), to improve N retention (Lehmann et al., 2011; Pitman, 2006; Spokas et al., 2012). Previous studies have shown that leonardite, an oxidized form of lignite, has the potential to mitigate slurry-N loss due to its acidity and high CEC (Cao et al., 2022; Manzoni & Porporato, 2009). However, because leonardite originates from near-surface mining of lignite, it is not a sustainable resource. Therefore, sustainable sources of CM, such as biochar, could provide a suitable alternative and increase acceptance in practice.

Biochar is a readily available and renewable resource, and its benefits as a soil amendment have attracted the attention of a growing number of researchers over the past few decades (Schmidt et al., 2021). The composition and effectiveness of biochar varies depending on the raw material, pyrolysis temperature, and time or rate of heating (Ippolito et al., 2020). Biochar produced by slow pyrolysis of wood cuttings and rice husks at 600 °C for 10 h adsorbed up to 60% of the NH_4^+ from anaerobic pig slurry digestate at an application rate of 30 kg m^{-3} slurry, while its adsorption capacity was related to contact time, pH, NH_4^+ concentration and biochar particle size (Kizito et al., 2015). Biochar produced from corn cobs, grapefruit peels and banana stems by pyrolysis at 200 °C for 21 days retained 90% of NH_4^+ of a $(NH_4)_2SO_4$ solution due to oxygen-rich functional groups (Cai et al., 2016).

It is known that oxygen-containing functional groups, such as carboxylic acid and keto and hydroxyl groups, promote adsorption of heavy metals and organic molecules (Mandal et al., 2017), and can also adsorb NH_3 either by proton exchange, thereby forming adduct ions, or by chemical reactions, thereby forming amines and amides on the surface of biochar (Seredych & Bandosz, 2007). Hydrogen peroxide is an oxidant that can change the properties of biochar by introducing oxygen functional groups, while only producing H_2O and O_2, which are not harmful to the environment (Huff & Lee, 2016). Several studies have shown that the oxidation of biochar with H_2O_2 improves the removal of heavy metals from aqueous solutions (Q. Wang et al., 2018; Zuo et al., 2016). Huff and Lee (2016) used different concentrations of H_2O_2 to oxidize pinewood biochar and showed that high concentrations of H_2O_2 increased the CEC of biochar. However, the efficiency of this modification is usually very low and requires long reaction times and additional heating (B. Wang et al., 2016). Therefore, a faster and more efficient oxidation method would be a great advantage.

Fenton oxidation is a complex chain of reactions between H_2O_2 and Fe(II) ions in acidic solutions, mainly producing the highly reactive HO· radical, which is one of the most powerful oxidants (Bachi et al., 2013). Xu et al. (2020) reported that Fenton modification of biochar, including iron-promoted pyrolysis and H_2O_2 oxidation, improved adsorption of hexavalent chromium and methylene blue. In contrast, the effect of the Fenton reaction on the NH_4^+ adsorption capacity of common biochar has not been studied. To our knowledge there is only one study available that reported a Fenton-mediated enhancement of ammonium adsorption of hydrochar, a material that is produced by high-temperature and high-pressure conversion of organic material in an aqueous medium (Belete et al., 2021).

The objectives of this study were to investigate whether the Fenton reaction can directly and effectively oxidize common biochar and enhance the functional groups on the surface for improving the NH_4^+ adsorption capacity of biochar in aqueous solutions and livestock slurry. In this study, we produced biochar from spruce sawdust in a pyrolysis oven and subsequently oxidized the biochar by Fenton oxidation with a Fe^{2+}:H_2O_2 ratio of 1:1000. Sawdust is a common and abundant byproduct of sawmills and is considered a promising feedstock for biochar and alternative fuels (Beiyuan et al., 2017; Ghani et al., 2013). Then, we compared the NH_4^+ adsorption capacity of biochar, oxidized biochar and leonardite. We hypothesized that Fenton oxidation would introduce oxygen functional groups to the surface of the biochar and increase the NH_4^+ adsorption capacity of the biochar to the same level as that of leonardite.

3.2 Materials and methods

3.2.1 Biochar production

The biochar was produced from small particles of spruce sawdust (no. 823 “Siebgut fein”) from Holz Ruser (Bornhöved, Germany). The spruce sawdust was produced in a custom-made pyrolysis oven (Fig. B.1), and the pyrolysis process was terminated when the flame at the top of the oven changed color from yellow to blue, indicating a change from combustion of organic volatiles to C monoxide (i.e., the completion of wood gasification). The maximum temperature reached during the production process was 610 °C.

3.2.2 Biochar oxidation

Oxidized biochar was produced by applying the Fenton reaction (Fig. B.2). For this purpose, 4 g biochar was added to 40 ml of a solution of 30% H_2O_2 and ferrous sulfate ($FeSO_4 \cdot 7\ H_2O$) with a ratio of Fe^{2+} to

H_2O_2 of 1:1,000. The reaction process was intense with formation of a large amount of foam that lasted for about 10 min. The oxidized biochar was rinsed with deionized water and dried at 65 °C for two days.

3.2.3 Characterization of carbonaceous materials

The properties of the CM were analyzed by a commercial laboratory (Ruhr Lab GmbH, Gelsenkirchen, Germany). Proximate analysis of ash and volatile matter content was performed in line with German standards DIN 51719 (1997) and DIN 51720 (2001), respectively. Elemental analysis included C, N, and H content and molar ratio of H to organic C (H/C_{org}) (performed according to the standard DIN 51732 [2014]); S content (based on the standard DIN 51724-3 [2012]); and oxygen (O) and the molar ratio of O to organic C (O/C_{org}) carried out in line with the standard DIN 51733 (2016), where C_{org} was derived from the total C content minus the inorganic C (CO_2) content in the CM. Solid surface area was determined by Brunauer–Emmett–Teller (BET) multipoint (N_2) surface area analysis based on the standard DIN ISO 9277 (2014). The main elements from the borate digestion of ash, (i.e., Ca, Fe, K, Mg, sodium [Na], P, sulfur and silicon [Si]) were analyzed according to the standard DIN EN ISO 11885 (E22) (2009).

3.2.4 Determination of NH_4^+ retention and release

For the determination of NH_4^+ retention, 500 mg biochar, oxidized biochar or leonardite were added to 40 ml of $(NH_4)_2SO_4$ solution with 100 mg NH_4^+- N L^{-1} (pH 5.55). The solution was shaken at 200 rpm for 20 h and centrifuged at 3,500 rpm for 10 min (20 min for leonardite, which was applied as powder), and the supernatant was filtered through a 0.45 µm syringe filter (ProSense, Oosterhout, Netherlands). The residual sample was rinsed several times with deionized water and then added to 40 ml deionized water to determine the NH_4^+ release of previously retained NH_4^+, shaken at 200 rpm for 20 h, and treated following the same steps as described above for the determination of NH_4^+ retention. All solutions were stored at -22 °C until the NH_4^+ content was analyzed by continuous flow analysis (CFA Analyzer FLOWSYS 3-Kanal, Alliance Instruments, Austria).

3.2.5 Measurement of NH_3 emission

To further investigate the effects of CM on NH_4^+ adsorption, we prepared a pH-adjusted $(NH_4)_2SO_4$ solution containing 0.22% N, corresponding to 2,200 mg NH_4^+-N L^{-1}, and adjusted the pH to 6.8 with 0.01 M sodium hydroxide (NaOH) to resemble the pH and N content of the cattle slurry used below. The different CM (biochar, oxidized biochar, leonardite) were added to the solution at a rate of 50 g C L^{-1} and mixed well, and then NH_3 emission was measured with an infrared laser gas analyzer (G2508, Picarro Inc., Santa Clara. CA, USA) with a dynamic chamber (50 mm high, 50 mm diameter) in closed-loop mode tightly covering each sample for 10 min. The same set of CM was tested in the same way in real cattle slurry with 0.22% N and pH 6.7. After each NH_3 emission test, 10 ml of deionized water was added to the CM+ slurry mixture to measure the pH because the mixture was too thick for direct measurement. The NH_3 emission reduction efficiency was calculated based on the difference in NH_3 emissions from pH-adjusted $(NH_4)_2SO_4$ solution or cattle slurry with and without CM added.

3.2.6 Calculations and statistical analysis

All results are expressed as the mean ± SD of at least three replicates. After accounting for statistical requirements (normal distribution and homogeneity of variance), the significance of the differences between treatments was analyzed by ANOVA and Tukey's HSD as a post-hoc test at a significance level of $p < 0.05$ (IBM SPSS Statistics for Windows, Version 25.0, IBM Corp., Armonk, NY, USA).

3.3 Results

3.3.1 Physicochemical properties of carbonaceous materials

Table 3.1 shows the physicochemical properties of the CM used in this study. The non-oxidized biochar had the highest C content of 72%. Oxidation increased the O content of biochar from 18 to 28% and reduced the pH from 5.3 to 3.2. The BET multipoint (N_2) determination of the specific biochar surface area yielded 193 m^2 g^{-1}, which was 6.7 and 192 times higher than that of oxidized biochar and leonardite, suggesting that the non-oxidized biochar had the largest surface area. Non-oxidized biochar had also the smallest H/C_{org} and O/C_{org} ratios, which are associated with high aromaticity and low degree of oxidation.

***Table 3.1** The physicochemical properties of the organic materials used in this study.*

	Leonardite	**Biochar**	**Oxdized biochar**
pH_{H2O}	4.29	5.27	3.22
Specific surface area (BET) (m^2/g)	1.10	193.04	25.17
C (% w/w_{total})	47.88	72.07	62.12
H (%w/w_{total})	2.93	2.92	3.30
N (%w/w_{total})	0.85	0.15	0.09
S (%w/w_{total})	1.47	0.03	0.01
O (%w/w_{total})	19.37	17.88	28.1
H/C_{org}	0.73	0.48	0.63
O/C_{org}	0.32	0.19	0.35
Volatile matter (% w/w_{total})	41.88	29.96	47.88
Ash (w/w_{total})	15.32	2.54	0.77
Ca as CaO (% w/w_{ash})	20.4	22.0	27.5
Fe as Fe_2O_3 (% w/w_{ash})	5.6	19.2	17.0
K as K_2O (% w/w_{ash})	0.4	8.2	6.2
Mg as MgO (% w/w_{ash})	6.7	3.5	4.9
Na as Na_2O (% w/w_{ash})	3.0	0.8	0.8
P as P_2O_5 (% w/w_{ash})	< 0.1	2.5	3.7
S as SO_3 (% w/w_{ash})	23.6	1.5	4.9
Si as SiO_2 (% w/w_{ash})	28.5	24.1	19.1

Note. The percentages of Ca as CaO, Fe as Fe_2O_3, K as K_2O, Mg as MgO, Na as Na_2O, P as P_2O_5 S as SO_3 and Si as SiO_2 are based on borate-digested biochar ash.

3.3.2 NH_4^+ retention and release

In the non-pH -adjusted $(NH_4)_2SO_4$ solution with 100 mg NH_4-N L^{-1}, the non-oxidized biochar showed the highest NH_4^+ retention capacity of 1.4 mg N g^{-1} biochar, which was significantly higher than that of the oxidized biochar (0.9 mg N g^{-1}) (Fig. 3.1). In contrast, oxidized biochar had the highest exchangeable NH_4^+ content (0.8 mg N g^{-1}) of all CM (i.e., three times higher than that of biochar and 1.6 times higher than that of leonardite).

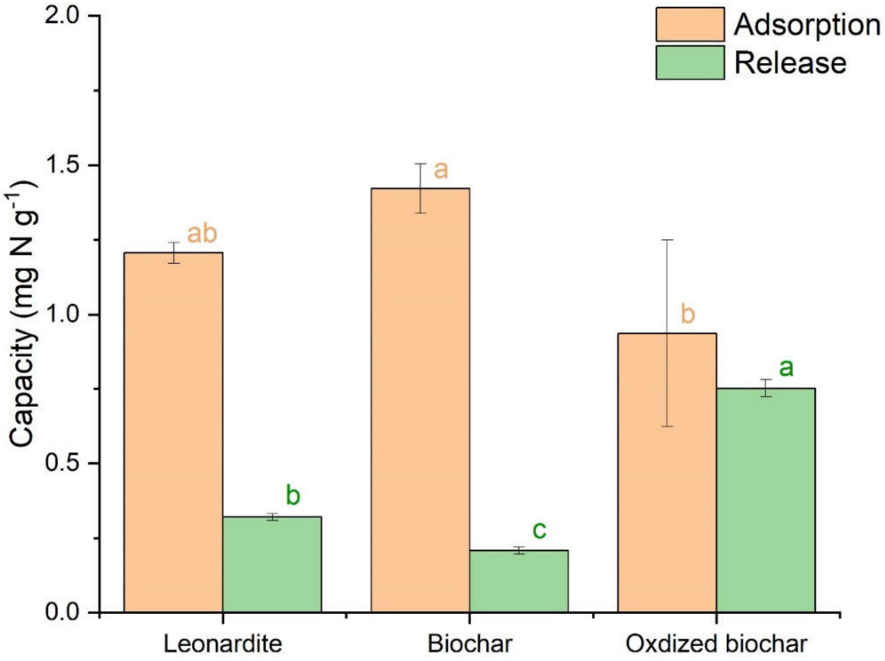

Figure 3.1 *The NH_4^+ retention capacity of carbonaceous materials in aqueous $(NH_4)_2SO_4$ solution and NH_4^+ release in deionized water. The error bars show the standard error of the mean of each treatment ($n \geq 3$). The different lowercase letters indicate significant differences at the $p<0.05$ level between treatment.*

3.3.3 Reduction of NH_3 emission

In the pH-adjusted $(NH_4)_2SO_4$ solution, all CM reduced NH_3 emissions by more than 90%, with the highest reduction efficiency of 99.99% for oxidized biochar (Fig. 3.2). For cattle slurry, the NH_3 emission reduction efficiency was in the following order: leonardite (98%) > oxidized biochar (67%) > biochar (22%) (Fig. 3.2). The pH values of the slurry mixtures with and without CM were in the following order leonardite (6.22) < oxidized biochar (6.69) < biochar (6.92) < cattle slurry (6.95).

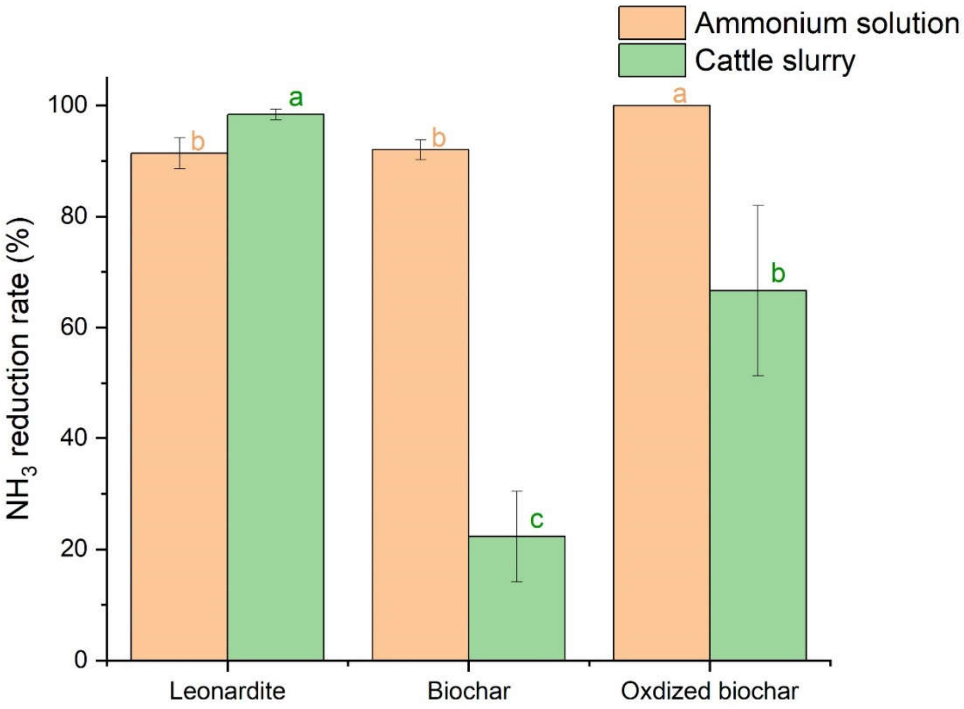

Figure 3.2 *The NH_3 reduction rates of carbonaceous materials in pH-adjusted ammonium solution and cattle slurry ((pH 6.8 and 6.7). The error bars show the SEM of each treatment (n = 3). Different lowercase letters indicate significant differences at the p < .05 level between treatments*

3.4. Discussion

3.4.1 Effect of Fenton oxidation of biochar on NH_4^+ retention and release

Fenton oxidation increased the oxygen content by 10 percentage points and reduced the pH of the biochar from 5.3 to 3.2 (Table 3.1), indicating that oxygen functional groups were introduced to the surface of the biochar (Cheng et al., 2008). However, oxidation did not increase the amount of NH_4^+ retained from the $(NH_4)_2SO_4$ solution compared with biochar. One reason could be that the increasing volatile matter (Table 3.1) in the oxidized biochar blocks the pores and then reduces the surface area (Table 3.1), thus limiting the adsorption of NH_4^+ during the pore filling process (Ambaye et al., 2021; Bourke et al., 2007). Another important reason for the lower NH_4^+ retention rate of oxidized biochar may have been its low pH value. A high degree of protonation of the oxygen functional groups in the acidic $(NH_4)_2SO_4$ solution might have led to a neutral or even positive surface charge that reduced the electrostatic attraction of NH_4^+ (Kizito et al., 2015; Novak et al., 2010). This is supported by studies that have shown that protons and some metals, such as aluminum (Al) and Fe, occupy exchange sites at low pH, which then limit the adsorption of NH_4^+ on biochar (Halim et al., 2013; Sarkhot et al., 2013; B. Wang et al., 2015).

The higher NH_4^+ retention capacity of biochar may be due to its superior BET surface area (Table 3.1), which would be less influenced by pH. The high surface area of biochar may be related to its low H/C_{org} ratio, with values below 0.7 indicating a mostly aromatic structure (Kuhlbusch & Crutzen, 1995). The high degree of aromaticity indicates that the aliphatic alkyl and ester groups shielding the aromatic core are completely destroyed, and the nanopores within the aromatic C structures increase the surface area (Chen et al., 2008; K. Sun et al., 2016; Xiao et al., 2016). Chen et al. (2008) found that the surface area increased significantly when the H/C ratio was below 0.5, and this was confirmed by our results, with a surface area of biochar of 193 m^2 g^{-1} at an H/C_{org} ratio of 0.48. L. Wei et al. (2020) produced a series of biochars from herbal residues at different pyrolysis temperatures and investigated their adsorption mechanisms. They found that when the H/C ratio was lower than 0.5, the number of surface acidic groups was lower than 70 cmol kg^{-1}, and the retention mechanism was dominated by pore filling (i.e., absorption). However, when the H/C ratio was greater than 0.5, the number of surface acidic groups increased with increasing H/C values, and chemical bonding at the surface played the dominant role (i.e., adsorption). In our study, the non-oxidized biochar with an H/C_{org} ratio of 0.48 had a high NH_4^+ retention capacity in acidic solution due to its higher <u>ab</u>sorption capacity (i.e., filling of micro-cavities), compared with leonardite and oxidized biochar, which were characterized by higher <u>ad</u>sorption capacity (i.e., physicochemical bonding at the surface).

In this study, deionized water was used to determine the NH_4^+ release rate of biochars, showing the different NH_4^+retention strengths of different biochars. After shaking for 20 hours, the non-oxidized biochar released the lowest amount of NH_4^+ into deionized water, which further supports the assumption of a strong physical retention of NH_4^+ in the micro-cavities of the biochar (Saleh et al., 2012). In contrast, oxidized biochar exhibited a greater NH_4^+ release in deionized water than non-oxidized biochar and leonardite, indicating that the retention of NH_4^+ by oxidized biochar was not as strong as for biochar due to the more reversible cation–anion interactions (adsorption) of NH_4^+ and negatively charged functional oxygen groups at the surface of the oxidized biochar. This finding suggests that oxidized biochar may be more suitable for increasing the CEC of the soil than non-oxidized biochar, making retained NH_4^+ more easily available to plants and microorganisms in the soil than non-oxidized biochar. In contrast, non-oxidized biochar could be more effective in retaining nitrate by simple absorption of soil solution containing nitrate in the microporous structure of the biochar, which is particularly pronounced in biochar produced at high temperature (especially beyond 600°C) (Ippolito et al., 2020).

3.4.2 Effect of Fenton oxidation on the reduction of NH_3 emission

In the pH-adjusted $(NH_4)_2SO_4$ solution (pH 6.8) all tested CM reduced NH_3 emissions by more than 90%. This is consistent with the study of Kizito et al. (2015), where biochar made from rice husks and woody material adsorbed 80% of the NH_4^+ from ammonium chloride (NH_4Cl) solution at pH values between 6.5 and 7.0. In the pH-adjusted $(NH_4)_2SO_4$ solution, the oxidation of biochar significantly increased the reduction efficiency of NH_3 emissions to 99.99%, which supports our assumption that the acidic $(NH_4)_2SO_4$ solution limited the retention of NH_4^+ by oxidized biochar. In neutral solutions, oxygen functional groups are usually deprotonated, and free ions, such as Al and Fe, are precipitated as oxides, and then more adsorption sites of the oxygen functional groups are available for NH_4^+ adsorption (Brady et al., 2008; B. Wang et al., 2015).

In the cattle slurry, the effect of non-oxidized and oxidized biochar on reducing NH_3 emissions was significantly diminished. The composition of cattle slurry is much more complex than the pure $(NH_4)_2SO_4$ solution. It contains a large number of cations, such as K, Ca, and Al, which can compete with NH_4^+ for adsorption sites, resulting in higher NH_3 emission (Kizito et al., 2015). Although non-oxidized biochar had a much higher BET surface area than oxidized biochar and leonardite, it reduced the NH_3 emissions the least, indicating that it retained the lowest amount of NH_4^+ in the cattle slurry and suggesting that surface area is not a major factor in NH_4^+ adsorption capacity at neutral or even higher pH (Bargmann et al. 2014; Spokas et al. 2012).

Leonardite showed a great effect in reducing NH_3 emissions in both pH-adjusted ammonium solution and cattle slurry, which means that it has sufficient adsorption sites for NH_4^+ and other cations even in cattle slurry. Because oxidized biochar had the highest oxygen content and the lowest pH, we can assume that oxidized biochar had more oxygen functional groups than biochar and leonardite. Nevertheless, the retention of NH_4^+ by leonardite was higher than that of oxidized biochar in cattle slurry. We can only speculate that the reason for this is related to the additional cations in the biochar, which might compete with NH_4^+ for cation exchange sites at the surface of the oxidized biochar. As shown in Table 3.1, oxidized biochar contained more Ca, Fe, and K than leonardite, and these ions can bind to the oxygen functional groups, resulting in fewer vacant adsorption sites for NH_4^+.

The O/C_{org} values of leonardite and oxidized biochar were similar (0.35 and 0.32) and much higher than the O/C_{org} of non-oxidized biochar (0.19). The O/C_{org} values were found to be positively correlated with CEC, because high O/C_{org} ratios indicate a greater abundance of hydroxyl, carbonyl and carboxyl groups, associated with high CEC (Chen et al., 2008; Glaser et al., 2002). Gai et al. (2014) tested 12 types of biochar with different feedstocks and pyrolysis temperatures and confirmed the previous findings that the O/C ratio was positively correlated with CEC and also with the adsorption capacity for NH_4^+ in NH_4Cl solution.

3.5. Conclusions

Our study demonstrated that the Fenton reaction is a rapid and effective method to increase the NH_4^+ adsorption capacity of biochar. Compared with oxidation with H_2O_2 alone, the Fenton reaction has a much higher oxidation capacity and reduces time and energy consumption, providing an economical and environmentally friendly strategy for biochar oxidation. Biochar produced from spruce sawdust and oxidized using the Fenton reaction exhibited significantly higher reversible NH_4^+ adsorption than the other two CM tested (non-oxidized biochar and leonardite). The oxidized biochar caused also the highest NH_3 emission reduction of 99.99% in $(NH_4)_2SO_4$ solution adjusted to pH 6.8, which resembled the pH of cattle slurry. In real cattle slurry, the Fenton-oxidized biochar improved the NH_3 emission reduction effect significantly compared with non-oxidized biochar, although it remained below the performance of leonardite. Although the oxidation with the Fenton reaction could not boost the biochar all the way up to the level of leonardite, it is an important step toward improving the NH_4^+ retention capacity of biochar as a sustainable resource. To achieve the same effect as leonardite, future studies should focus on further increasing the number of adsorption sites by testing different oxidation conditions and on ways of removing excess cations from the produced biochar, to further increase its NH_4^+ ammonium retention capacity.

4. Improving nitrogen retention of cattle slurry with oxidized biochar – an incubation study with three different soils

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4.1 Introduction

As an organic fertilizer, livestock manure or slurry is usually land-applied to increase soil organic matter (SOM) and soil microbial biomass and serves as a source of N for plants (Guo et al., 2022; Ozlu et al., 2019). However, livestock slurry application to agricultural fields accounts for a large proportion of NH_3 emissions, which contribute to environmental and public health problems (Bouwman et al., 2013). Emission and deposition of NH_3 into natural ecosystems can lead to eutrophication and indirect N_2O emissions or NO_3^- leaching (Sutton et al., 2011; Zhang et al., 2015). Ammonia emitted to the atmosphere is also associated with acid rain and the formation of particulate matter (e.g., <2.5 μm), which is a threat to human health (Backes et al., 2016; Walker et al., 2006). Introducing new on-farm management practices, such as slurry injection, is one way to mitigate NH_3 losses but is still expensive, and more slurry-N is left in the soil and under anaerobic conditions, leading to high N_2O emissions due to coupled nitrification-denitrification (Silva et al., 2022; Velthof & Mosquera, 2011).

There are alternative management options for decreasing N loss from animal slurry using HCA, such as biochar, which not only reduce NH_3 emissions when added to the slurry but can also increase soil C storage and the nutrient storage capacity of the soil. Biochar is fine-grained or granular charcoal made from the pyrolysis of biomass and is used as a soil amendment (Guo et al., 2016). The properties of biochar depend on the raw material, the temperature of the thermochemical process, and the residence time of the material (Kambo & Dutta, 2015). Over the past decades, biochar has received increasing attention from researchers as a soil amendment that can improve soil quality, increase microbial activity, and reduce GHG emissions due to its large surface area, high CEC, and abundant functional groups (Guo, 2020; Kalus et al., 2019; Schmidt et al., 2021; Yaashikaa et al., 2020). In addition, the application of biochar to animal manure was demonstrated to have a significant effect on N retention due to the oxygen-containing functional groups on the surface of biochar, such as keto, hydroxyl, and carboxyl groups (Steiner et al., 2010; Z. Wang et al., 2015). Oxidation can increase the number of oxygen functional groups at the surface and thereby increase the CEC of biochar (Chen et al., 2008; Huff & Lee, 2016). B. Wang et al. (2016) oxidized different biochars with a 30% H_2O_2 solution at 30°C for two weeks and found that the treatment significantly increased the NH_4^+ retention capacity of the biochar by up to four times. In Chapter 3, we oxidized biochar through the Fenton reaction, which forms the $HO\cdot$ radical as one of the most powerful oxidants through the reaction between H_2O_2 and Fe^{2+}. The results showed that oxidized biochar was three times more effective than untreated biochar in reducing NH_3 emissions from cattle slurry. However, it remains unclear whether the effect of oxidized biochar on soil N retention is the same in different soils with contrasting properties (pH, CEC, organic C, texture) that may interact with the capacity of biochar to retain slurry-N in soil. Filling this knowledge gap (i.e., determining for which soil properties the application of oxidized biochar is most effective in reducing N losses from the slurry) will help to transfer this method to agricultural practice.

In this study, we examined the effect of oxidized biochar on the fate of cattle slurry N applied to three different soils, and its effectiveness to reduce N loss via NH_3 emission and NO_3^- leaching. For this purpose, we conducted an 86-day laboratory incubation experiment in which untreated or oxidized biochar was co-applied with cattle slurry to three soils with contrasting texture, pH, and organic C. We hypothesized that oxidized biochar would be more effective than untreated biochar in reducing N losses and improving soil N retention when applied to soils along with cattle slurry.

4.2 Materials and methods

4.2.1 Soil and cattle slurry

Three soils with different textures, SOC content and pH (Table 4.1) were tested in this experiment: loamy sand soil (LUFA 2.1, LUFA, Speyer, Germany), loam soil (LUFA 2.4), and a sandy loam soil sampled from a Cambic Luvisol of an agricultural field (54°19′05″ N, 9°58′38″ E) of the experimental farm Hohenschulen of the University of Kiel, Germany. Each soil was a composite sample from the ploughing horizon (0–30 cm; i.e., topsoil). The soils were sieved to 2 mm, air-dried, homogenized, and stored at room temperature before use.

Table 4.1 *Soil properties of the three test soils.*

Soil	Soil texture	Sand (%)	Silt (%)	Clay (%)	TOC (g kg^{-1})	TN (g kg^{-1})	pH $_{CaCl2}$	Maximum WHC (g 100 g^{-1})
LUFA 2.1	loamy sand	87.5	8.7	3.9	6.1±0.5	0.6 ±0.2	4.7±0.1	31.4
Kiel soil	sandy loam	44	35	21	13.0±1.0	1.5 ±0.1	5.7±0.1	35
LUFA 2.4	loam	32.6	42.9	24.5	18.3-2.5	2.3 ±0.2	7.5±0.1	45.6

Note. The abbreviations are as follows: TOC – total organic carbon; TN – total nitrogen; WHC – water holding capacity.

Cattle slurry was obtained from the experimental farm Frankenforst of the University of Bonn, Germany. The slurry had a pH of 6.7 and a density of 0.96 g cm^{-3} and contained 94% water. Based on dry weight, it contained 34 mg g^{-1} TN, of which 10 mg g^{-1} was NH_4^+, and 418 mg g^{-1} TC, of which 70 mg g^{-1} was DOC.

4.2.2 Production and oxidization of biochar

The biochar was produced from spruce [Picea abies (L.) Karst.] sawdust (no. 823 “Siebgut fein”, Holz Ruser, Germany) in a custom-made pyrolysis oven at a maximum temperature of 610 °C with a residence time of about 20 min. The pyrolysis process was manually terminated when the flame color at the top of the furnace changed from yellow to blue. The average biochar yield was about 20%.

The Fenton reaction with a Fe^{2+}:H_2O_2 molar ratio of 1:1000 was used to oxidize the biochar. For this, 4 g biochar was added to a 400-ml beaker to which 40 ml of a 30% H_2O_2 solution with Fe^{2+} was added. After an intense reaction during the first 10 min, the oxidized biochar was cooled to ambient temperature, rinsed with deionized water, and dried at 65 °C for two days.

The TC content of untreated and oxidized biochar was 72 and 62%, TN content was 0.15 and 0.09%, total oxygen content was 18 and 28%, and pH (H_2O) was 5.3 and 3.2, respectively. More parameters can be found in Table 3.1.

4.2.3 Experimental design and incubation

The dry soil substrates were filled into polyvinyl chloride tubes (150 mm height, 50 mm diameter) at their field bulk density: 1.3 g cm^{-3} for the sandy loam (Kiel soil) and the loam (LUFA 2.4) and 1.4 g cm^{-3} for the loamy sand (LUFA 2.1). All soils were pre-incubated at 60% of the maximum WHC for 20 days. For each soil, we had four treatments with three replicates: 1.) soil; 2.) soil with cattle slurry (SC); 3.) soil with cattle slurry and Biochar (SCB); and 4.) soil and cattle slurry with oxidized biochar (SCO). Cattle slurry was applied at a rate of 73 kg TN ha^{-1}, which is equivalent to 35 m^3 ha^{-1}, a typical application rate for organic fertilizers. Biochar and oxidized biochar were mixed with cattle slurry at a rate of 50 kg C m^{-3} overnight and then applied to the surface of the soil columns. During the 86 days of the experiment, the soils were incubated in a thermostatic cabinet (TS 608-G/2-I, WTW, Germany) at 12°C, which is representative of soil temperature in spring in Germany. The polyvinyl chloride tubes were weighed five times per week, and deionized water was added to compensate for water loss whenever a weight loss occurred. Cattle slurry was spiked with ^{15}N-enriched ammonium sulfate ($(NH_4)_2SO_4$, 98 atom% ^{15}N, VWR International, Germany) to a final value of 2 atom% ^{15}N before application.

4.2.4 Analysis of GHG and NH_3

Carbon dioxide (CO_2), N_2O, and NH_3 emissions were measured weekly during the pre-incubation period, and at incubation Days 1, 2, 3, 6, and 9 of incubation before returning to the weekly measurement interval until the end of the incubation experiment (Day 86). Gas fluxes were measured with an infrared laser gas analyzer (G2508, Picarro, Inc., Santa Clara, CA, USA) that measures CO_2, N_2O, and NH_3 with a 1-min precision (1 σ) of <300 ppb, <10 ppb, and <3 ppb within the concentration ranges of 380--5,000 ppm, 0.3--200 ppm, and 0--300 ppb, respectively. For each measurement, the soil column was tightly covered with a dynamic chamber (50 mm high, 50 mm diameter) and connected to the gas analyzer in the closed-loop mode for 10 min. The gas fluxes were calculated according to Brümmer et al. (2008).

4.2.5 Analysis of DOC and mineral N in soil and microbial biomass

After 86 days of incubation, the soil samples were divided into a top layer (0—5 cm, containing cattle slurry and biochar) and a sublayer (5—15 cm), and stored at –22 °C before extraction. Dissolved organic C and mineral N (NH_4^+ and NO_3^-) were extracted with 0.01 M $CaCl_2$ solution (soil/solution ratio of 1:4 w/v), shaken for 2 h at 200 rpm as described in Chapter 2.

Microbial biomass C and microbial biomass N (N_{mic}) were determined with CFE (Vance et al., 1987). The correction factors kEC 0.45 and 0.4 were used to calculate C_{mic} and N_{mic}, respectively (R. G. Joergensen, 1996). Microbial biomass N was measured after pre-extraction of the soil to remove the inorganic N background with a method adopted by Wachendorf and Joergensen (2011). Fresh soil equivalent to 20 g dry matter was added to 80 ml of a 1 M KCl solution, shaken for 1 h at 200 rpm, and centrifuged for 20 min at 3500 rpm, corresponding to a relative centrifugal force of 2684 *g*. The supernatant was filtered through a 0.45 µm membrane filter (Macherey-Nagel, Germany) before ^{15}N analysis.

4.2.6 ^{15}N isotope analysis

To quantify the potentially leachable N, MicroRhizon samplers (type 19.21.81, Rhizosphere Research Products, Wageningen, Netherlands) were installed at 10 cm depth (sublayer). Samples were taken on Day 0 (the day before treatment application), and on Days 2, 4, 8, 15, 29, 57, and 85. Samples contained 0.5—2 ml of the soil solution and were stored at -22 °C before analysis.

The $^{15}NH_4^+$ and $^{15}NO_3^-$ contents in the MicroRhizon sampler solution were analyzed with micro-diffusion and liquid-liquid extraction methods, respectively, before determination of ^{15}N by elemental analyzer isotope ratio mass spectrometry (Flash EA 2000 and Delta V plus; Thermo Fisher Scientific, Germany), as described in Reichel et al. (2018).

4.2.7 Calculation and statistical analysis

The recovery rate of ^{15}N was calculated by dividing the amount of ^{15}N in the soil by the amount of applied slurry-^{15}N by the following equation:

$$^{15}\text{N recovery }\% = \frac{^{15}N_{soil}\,atom\,\%\times TN_{soil}\,\%\times M_{soil}}{^{15}N_{slurry}\,atom\%\times TN_{slurry}\,\%\times M_{slurry}} \qquad \text{(Equation 4.1)}$$

where $^{15}N_{soil}$ *atom%* is the ^{15}N atom percentage in soil, TN_{soil} is th total N in soil (%); M_{soil} is soil dry mass (g), $^{15}N_{slurry}$ *atom%* is the ^{15}N atom percentage in slurry input, TN_{slurry} is the total N in slurry input (%), and M_{slurry} the slurry dry mass input (g).

The Kolmogorov-Smirnov test was used to test for the normal distribution of all the data obtained from the experiment. For normally distributed data, a two-way ANOVA with Tukey's HSD post-hoc test at $p \leq 0.05$ was performed to identify significant differences between treatments. The Games-Howell test was performed for non-normally distributed data (N_2O emissions of the loam soil, DOC and NH_4^+ in the sublayer of the sandy loam, and NH_4^+ in the top layer of the loamy sand) (IBM SPSS Statistics for Windows, Version 25.0, IBM Corp., USA).

4.3 Results

According to the results of the ANOVA (Table C.1), cumulative emissions of CO_2 and NH_3 as well as pH and DOC concentration in the top layer of soil were significantly affected by the treatment. All tested parameters, except NH_3 emission and recovery of microbial biomass ^{15}N, were significantly different between the soil substrates.

4.3.1 GHG and NH_3 emissions

In the loamy sand and the loam, the application SC significantly increased CO_2 emissions by 39 and 30%, respectively, compared with the unfertilized soil treatment (Fig. 4.1A). In contrast, there was no significant increase in CO_2 emissions from the sandy loam after the application of cattle slurry. The addition of biochar or oxidized biochar to the slurry had no effect on CO_2 emissions in all soils compared with the SC treatment. Carbon dioxide emissions were significantly related to the SOC content and increased in the following order: loamy sand < sandy loam < loam.

In the loamy sand, the application of cattle slurry resulted in about 6-fold higher N_2O emissions compared with the unfertilized soil treatment. This pattern was not found for the other soils (Fig. 4.1C). In the loam soil, biochar and oxidized biochar did not significantly reduce N_2O emissions (Fig. 4.1C).

Cumulative NH_3 emissions significantly increased by 28-139 times after slurry application to the three soils (Fig. 4.1B). The oxidized biochar reduced NH_3 emissions by 64-75% in the tested soils compared with the SC treatments. Only in the more acidic loamy sand was a similar effect also found in the treatment with untreated biochar, which led to a 61% reduction in NH_3 emissions.

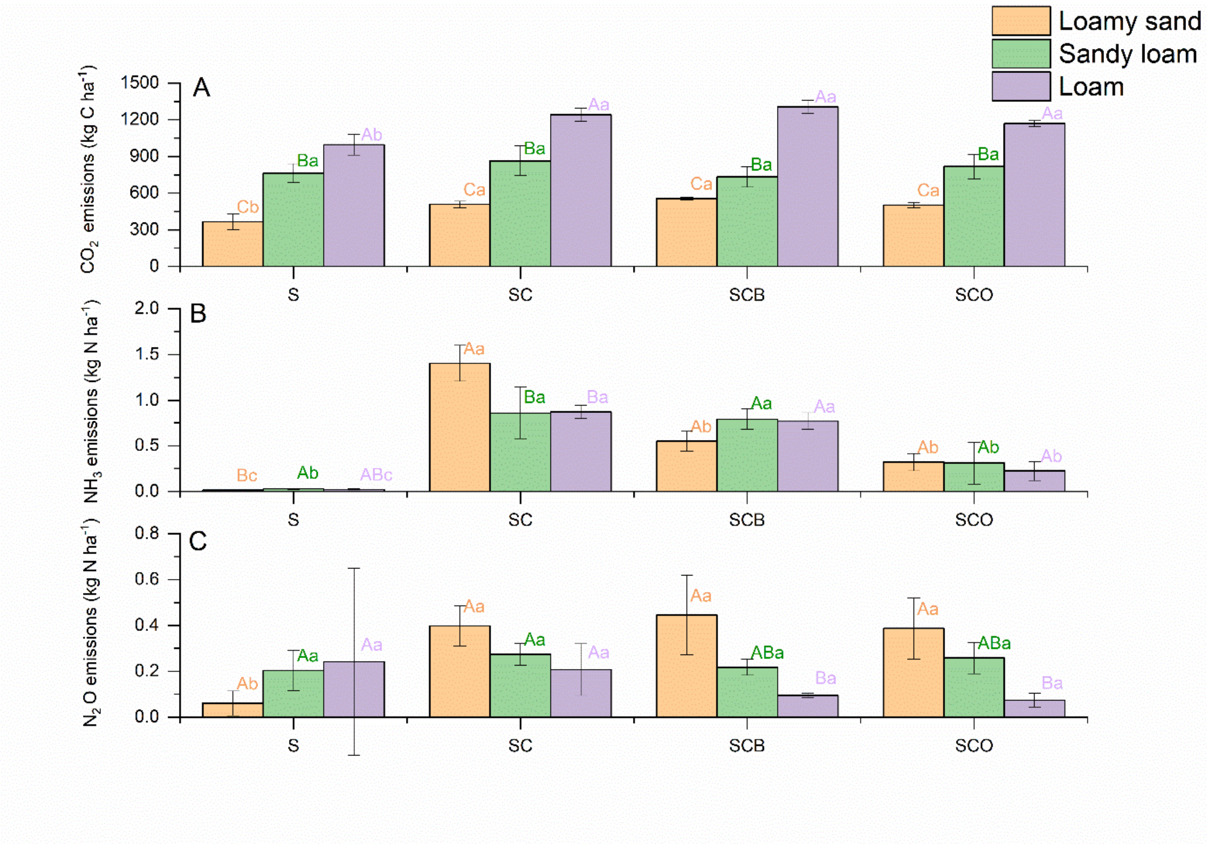

Figure 4.1 *(A) Cumulative CO_2 emissions; (B) cumulative NH_3 emissions; (C) cumulative N_2O emissions. The abbreviations of the treatments are as follows: S – soil; C – cattle slurry; B – biochar; O – oxidized biochar. The error bars show the standard error of the mean of each treatment (n = 3). Different uppercase letters indicate significant differences at the $p<0.05$ level between soils with the same treatment. Different lowercase letters indicate significant differences at the $p<0.05$ level between treatments of the same soil.*

4.3.2 Soil properties after 86 days of incubation

Cattle slurry increased the soil pH from 4.3 to 5.0 in the top layer of the loamy sand, and from 5.0 to 5.4 in the top layer of the sandy loam but not in the loam (Table 4.2). In the sublayer of the soils, pH values were not significantly different between treatments.

Table 4.2 *pH values and ^{15}N and microbial biomass ^{15}N ($^{15}N_{mic}$) recovery of the three tested soils after 86 d of incubation.*

Soil	Treatments	pH		^{15}N recovery	$^{15}N_{mic}$ recovery
		Top layer (0–5 cm)	Sublayer (5–15 cm)		
				– % –	
Loamy sand	S	4.3 ± 0.1b	4.4 ± 0.0a	–	–
	SC	5.0 ± 0.2a	4.4 ± 0.1a	41.5 ± 13.3a	0.3 ± 0.1b
	SCB	5.0 ± 0.2a	4.4 ± 0.0a	61.8 ± 43.4a	1.0 ± 0.4ab
	SCO	4.9 ± 0.0a	4.3 ± 0.0a	54.5 ± 12.9a	1.1 ± 0.2a
Sandy loam	S	5.1 ± 0.1b	5.0 ± 0.1a	–	–
	SC	5.4 ± 0.0a	5.0 ± 0.0a	64.0 ± 12.8a	0.9 ± 0.2a
	SCB	5.5 ± 0.1ab	5.1 ± 0.1a	60.6 ± 19.2a	1.0 ± 0.8a
	SCO	5.3 ± 0.2ab	5.0 ± 0.1a	59.6 ± 11.9a	0.9 ± 0.7a
Loam	S	7.4 ± 0.1a	7.4 ± 0.0a	–	–
	SC	7.5 ± 0.1a	7.4 ± 0.0a	143.3 ± 73.8a	0.7 ± 1.4a
	SCB	7.4 ± 0.0a	7.4 ± 0.0a	119.8 ± 63.6a	1.1 ± 0.4a
	SCO	7.4 ± 0.0a	7.4 ± 0.0a	133.8 ± 2.8a	0.5 ± 0.6a

Note. Values are means ± SD. Different lowercase letters indicate significant differences between treatments in one soil at the $p < .05$ level between treatments. B, biochar; C, cattle slurry; O, oxidized biochar; S, soil.

In the loamy sand, slurry application increased the DOC content of the top layer compared with the unfertilized soil treatment. Especially in the SCO treatment, the DOC content increased significantly by 38% compared with the soil treatment (Fig. 4.2A). In the sublayer, the sandy loam soil contained more than 70 mg C kg^{-1} of DOC in all treatments, whereas the other soils contained less than 25 mg C kg^{-1}. For the same soil, the DOC content of the different treatments was comparable (Fig. 4.2D).

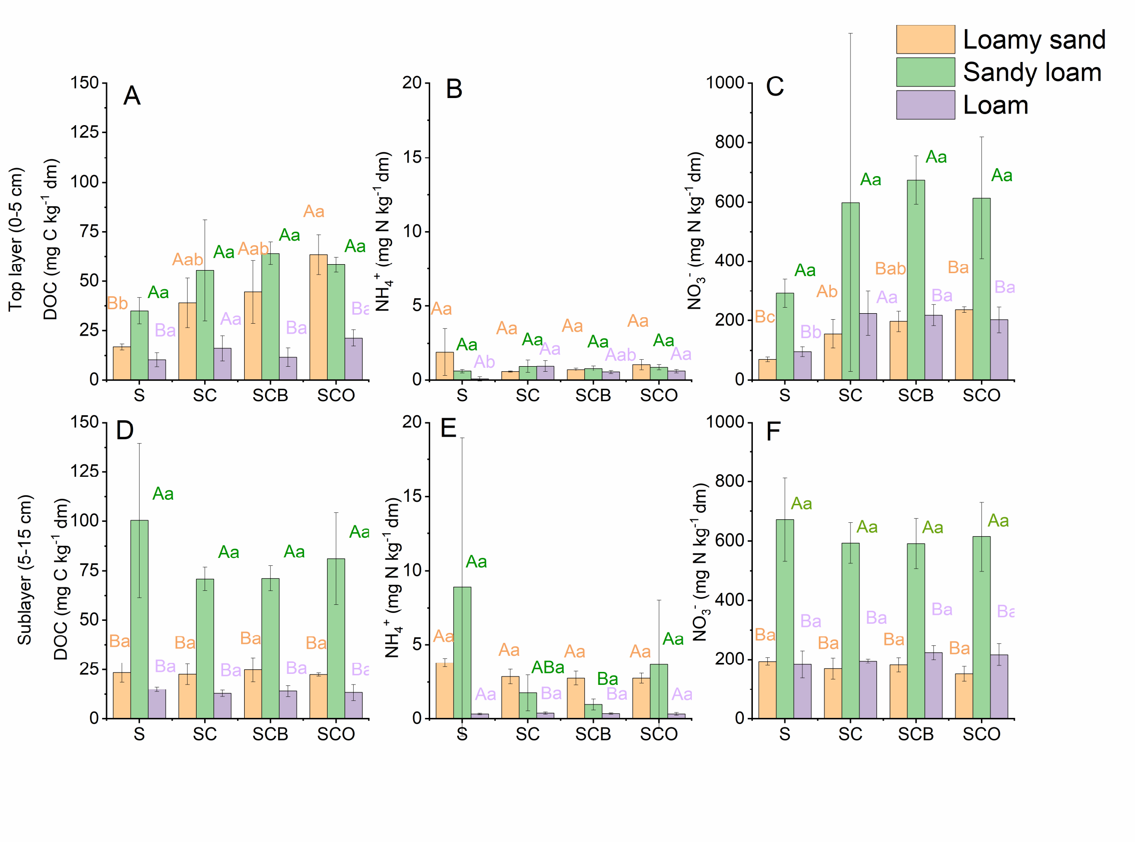

__Figure 4.2__ (A) Dissolved organic C (DOC) content in the top layer; (B) NH_4^+ content in the top layer; (C) NO_3^- content in the top layer; (D) DOC content in the sublayer; (E) NH_4^+ content in the sublayer; (F) NO_3^- content in the sublayer. The abbreviations of the treatments are as follows: S – soil; C – cattle slurry; B – biochar; O – oxidized biochar. The error bars show the standard error of the mean of each treatment (n = 3). Different uppercase letters indicate significant differences at the $p<0.05$ level between soils with the same treatment. Different lowercase letters indicate significant differences at the $p<0.05$ level between treatments of the same soil.

After 86 days of incubation, there were only traces of NH_4^+ left, most of it had been transformed to NO_3^- (Fig. 4.2B,C). In the SC treatment of the loam, the top layer contained 11-times more NH_4^+ than the unfertilized soil treatment, but still less than 1 mg N kg^{-1} (Fig. 4.2B). Concentrations of NH_4^+ in the sublayer were higher than in the top layer but were mostly below 5 mg N kg^{-1} (Fig. 4.2E). Application of cattle slurry (SC) doubled the NO_3^- content in the top layer of loamy sand and loam compared with the unfertilized soil treatment after 86 days of incubation. The addition of SCO further increased the NO_3^- concentration in the loamy sand by 52% in comparison to the corresponding SC treatment (Fig. 4.2C). The sandy loam had the highest NO_3^- content in the sublayer (more than 590 mg N kg^{-1}) in all treatments compared to the other soils (<200 mg of NO_3– N kg^{-1}) (Fig. 4.2F).

The C_{mic} content of the top layer increased in the following order: loamy sand < sandy loam < loam (Fig. 4.3). After 86 days of incubation, there was no significant difference in C_{mic} between the treatments of each soil (Fig. 4.3A). In the sublayer, the loamy sand had the lowest C_{mic} (< 100 mg C kg^{-1}), and the SC and SCB treatment significantly further decreased C_{mic} by 28 and 38%, respectively compared with the unfertilized soil treatment in the sublayer of that soil, whereas it remained unchanged in the other two soils (Fig. 4.3C).

Despite the pre-extraction, some N_{mic} values were still affected by the high initial background N, which likely led to negative values in the top layer of the sandy loam. The loam contained more than 20 mg N_{mic} kg^{-1} in the top layer, and in the sublayer N_{mic} of the sandy loam was higher than the other soils (Fig. 4.3D).

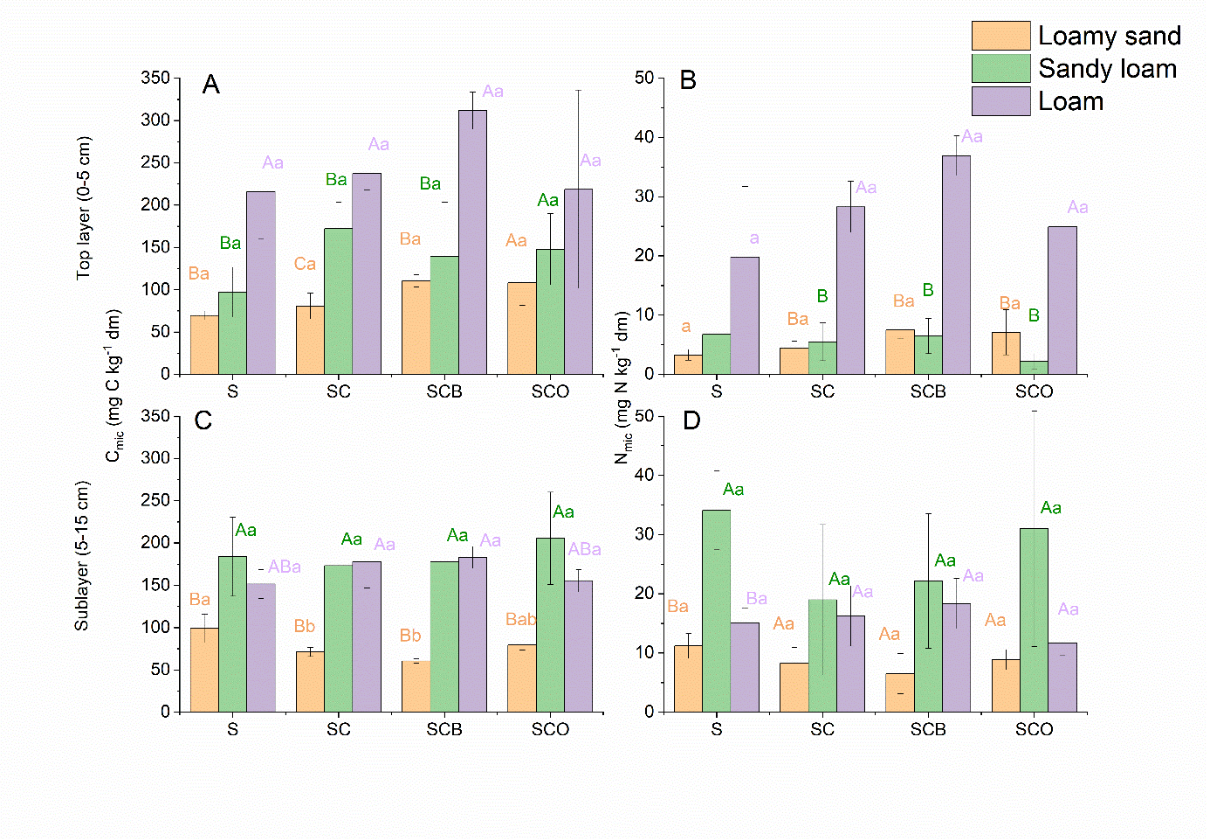

Figure 4.3 *(A) Microbial biomass C (C_{mic}) in the top layer; (B) microbial biomass N (N_{mic}) in the top layer, (C) C_{mic} in the sublayer, (D) N_{mic} in the sublayer. The abbreviations of the treatments are as follows: S – soil; C – cattle slurry; B – biochar; O – oxidized biochar. The error bars show the standard error of the mean of each treatment (n = 3). Different uppercase letters indicate significant differences at the $p<0.05$ level between soils with the same treatment. Different lowercase letters indicate significant differences at the $p<0.05$ level between treatments of the same soil. The significance of differences in the N_{mic} of the sandy loam soil in the top layer could not be determined due to several negative values.*

4.3.3 Mineral N and slurry-^{15}N in the soil solution

In the loamy sand, all treatments had NH_4^+ concentrations in the soil solution of 11-12 µg N ml^{-1} until Day 57 of the incubation experiment, before decreasing to <5 µg N ml^{-1} at Day 86, most significantly in the SCB and SCO treatments (Fig. 4.4A). In the sandy loam, the NH_4^+ content in the soil solution exceeded 30 µg N ml^{-1} on Day 0 but sharply dropped to a steady level of 1 µg N ml^{-1} before Day 29 (Fig. 4.4B). The NH_4^+ content of the soil solution of the loam constantly remained below 1 µg N ml^{-1} (Fig. 4.4C).

The application of cattle slurry increased the δ^{15}N value of NH_4^+ in the soil sublayer solution of all soils (Fig. 4.4D–F). Oxidized biochar increased the $^{15}NH_4$ signal in the loamy sand the most, especially on day 2 of the incubation, when it was significantly higher than the other treatments (Fig. 4.4D). A similar response was found also in the sandy loam for several days (Fig. 4.4E) but not in the loam (Fig. 4.4F).

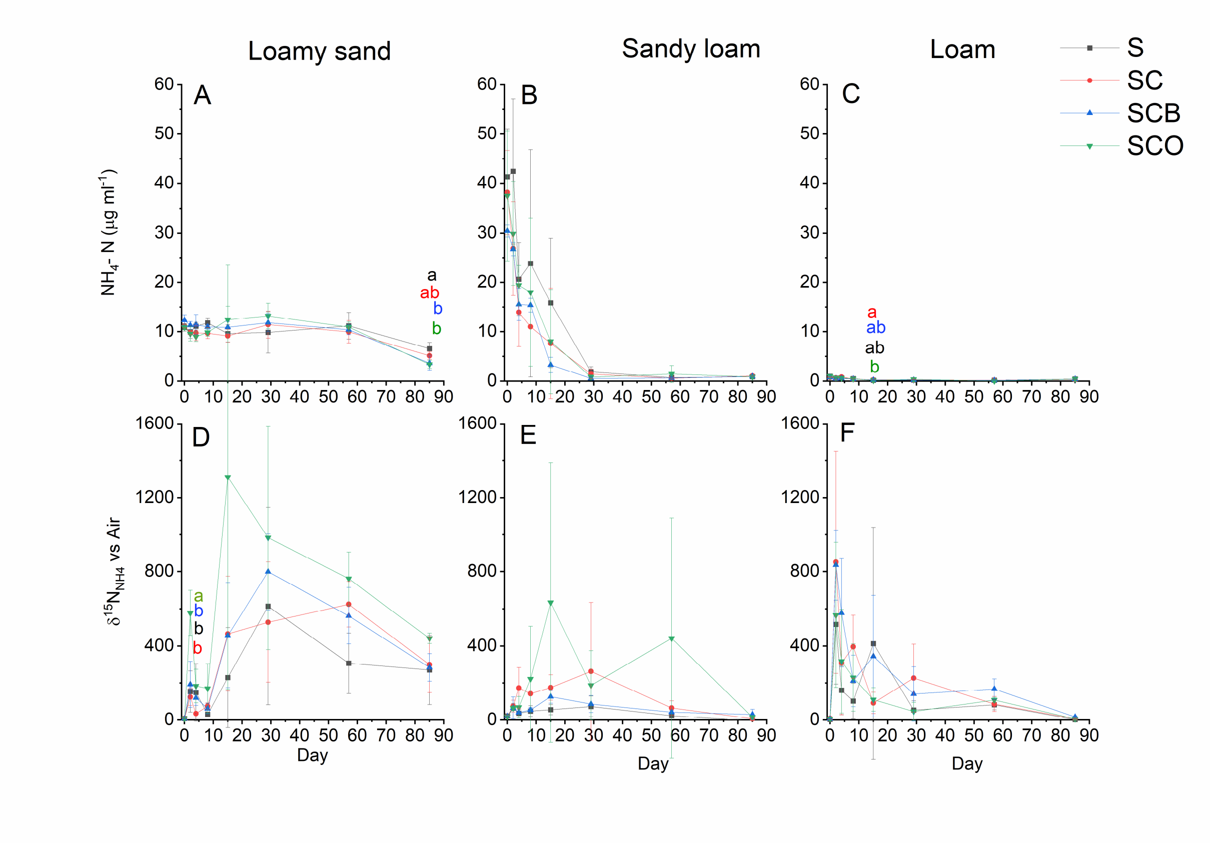

Figure 4.4 *Concentrations of NH_4^+ in the soil solution. (A) Ammonium content of loamy sand; (B) NH_4^+ content of sandy loam; (C) NH_4^+ content of loam; (D) δ$^{15}N_{NH4}$ vs air-N_2 of loamy sand; (E) δ$^{15}N_{NH4}$ vs air-N_2 of sandy loam; (F) δ$^{15}N_{NH4}$ vs air-N_2 of loam. The abbreviations of the treatments are as follows: S – soil; C – cattle slurry; B – biochar; O – oxidized biochar. The error bars show the standard error of the mean of each treatment (n = 3). Different lowercase letters indicate significant differences at the $p<0.05$ level between treatments. Points without lowercase letters indicate no significant differences between treatments.*

The initial NO_3^- content in the soil solution ranged between 120 and 200 µg N ml^{-1} in all three soils, and after the application of cattle slurry, NO_3^- content increased temporarily (at incubation Day 2) (Fig. 4.5A-C). The NO_3^- content decreased in the loamy sand and loam until Day 15 (Fig. 4.5A,C), and in the sandy loam until incubation Day 8 before increasing again (Fig. 4.5B).

The $\delta^{15}N$ values of NO_3^- in the loamy sand and sandy loam peaked at Day 29 (Fig. 4.5E,F). The ^{15}N value of NO_3^- in the SCB treatment of the loam was significantly higher than the other treatments at incubation Day 29 but finally decreased to the level of the SC and SCO treatments (Fig. 4.5F). In contrast, the $\delta^{15}N$ value of NO_3^- in the loamy sand increased significantly after incubation Day 29 until the end of the experiment (Fig. 4.5D).

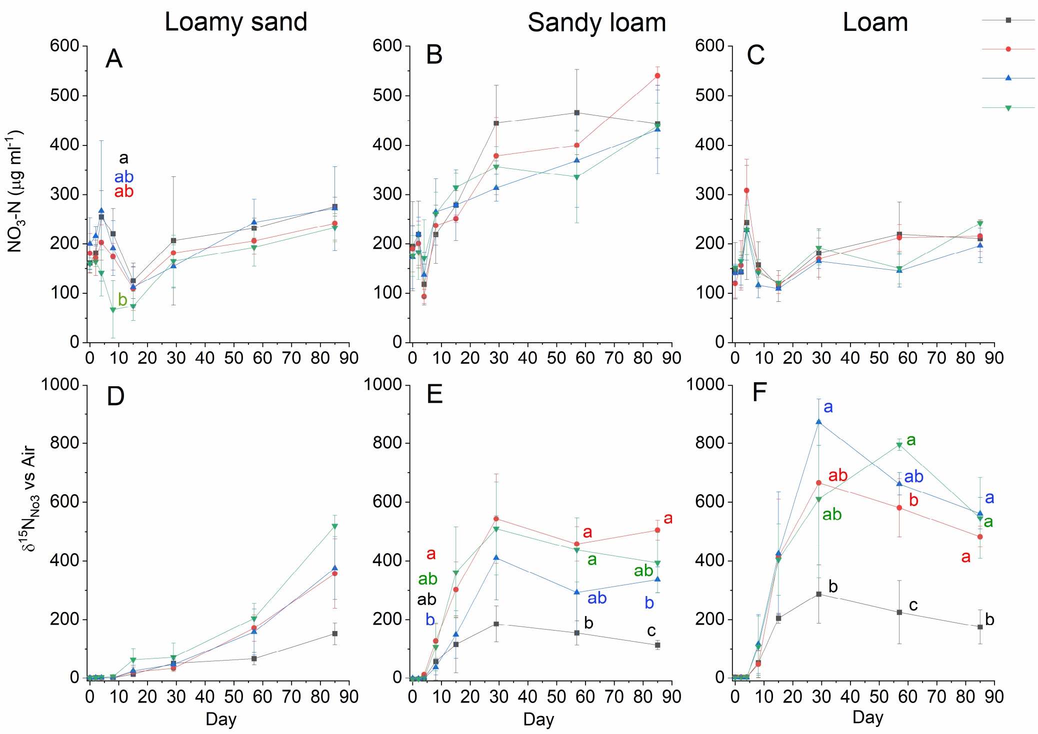

Figure 4.5 *Concentrations of NO_3^- in the soil solution. (A) Nitrate content of loamy sand; (B) NO_3^- content of sandy loam; (C) NO_3^- content of loam; (D) $\delta^{15}N_{NO3}$ vs air-N_2 of loamy sand; (E) $\delta^{15}N_{NO3}$ vs air-N_2 of sandy loam; (F) $\delta^{15}N_{NO3}$ vs air-N_2 of loam. The abbreviations of the treatments are as follows: S – soil; C – cattle slurry; B – biochar; O – oxidized biochar. The error bars show the standard error of the mean of each treatment (n = 3). Different lowercase letters indicate significant differences at the $p<0.05$ level between treatments. Points without lowercase letters indicate no significant differences between treatments.*

4.3.4 ^{15}N recovery in soil

Untreated and oxidized biochar did not increase the ^{15}N recovery in soils compared with the SC treatment. In the sandy loam, the ^{15}N recoveries were about 60% for all treatments (Table 4.2). The ^{15}N recoveries in the loam soil were all above 100%, which likely was the result of a slurry-N underestimation, but without affecting the relative comparison between the treatments.

All $^{15}N_{mic}$ recoveries were below 1.1% (Table 4.2). Oxidized biochar (SCO) significantly increased the $^{15}N_{mic}$ recovery in the loamy sand compared with the SC treatment, whereas in the other soils there was no significant difference between treatments.

4.4. Discussion

4.4.1 Effect of soil type on N retention

In all treatments, CO_2 emission increased with increasing SOC content (Fig. 4.1A). The SOC can act as a source of C for microorganisms in the soil, increasing microbial activity associated with microbial respiration as the main cause of soil CO_2 emission (Soon & Lupwayi, 2012). The use of (oxidized) biochar (SCB and SCO treatments) did not increase CO_2 emissions compared with the use of only cattle slurry treatment (SC), suggesting that both types of biochar did not increase the mineralization of slurry-derived organic C. This may be due to the high porosity and high affinity of (oxidized) biochar for DOC that protects from degradation, which then counteracts the effect of the increase in readily available organic C due to the application of the biochar–slurry mixture (Kasozi et al., 2010; Zimmerman et al., 2011). Following the application of cattle slurry, more N_2O was emitted from loamy sand than from the other soils. This is consistent with Fan et al. (2019), who found that soils with lower pH emitted significantly more N_2O when the same amount of urea-N was added, which might be related to the sensitivity of the N_2O reductase to lower pH at the post-transcriptional level (B. Liu et al., 2010). In addition, the SOM-poor and acidic conditions favor the abiotic formation of N_2O from hydroxylamine released during nitrification (Liu et al., 2017).

The NH_3 emission from the loamy sand was higher than from the other soils after the application of cattle slurry (SC), which may be influenced by soil texture, because high sand content reduces the fixation of NH_4^+ in the soil matrix (Lu et al., 2019; San Francisco et al., 2011). Our data showed that this increase in NH_3 emission can be mitigated by the addition of biochar or oxidized biochar to improve NH_4^+ adsorption (Fig. 4.1B).

Compared with the other soils, the loam soil had the highest C_{mic} and N_{mic} contents in the top layer at the end of the experiment, probably due to its high TOC and TN content, which might have favored the growth of soil microorganisms and increased microbial activity (Gan et al., 2013). The high microbial activity also facilitates N retention in the loam soil through microbial immobilization. In addition, according to a recent meta-analysis, abiotic factors in the loam soil could also contribute to N retention (Wei et al., 2022). Wei et al. (2022) found that abiotic N retention was positively correlated with TOC content and pH, because higher TOC content provided more active adsorption and reaction sites for reactive N intermediates, whereas higher pH reduced the reactivity of nitrite and reduced the activity of the electrophilic functional groups of SOM.

4.4.2 Effect of (oxidized) biochar on soil pH, DOC and microbial biomass

Slurry application mainly affected the soil properties of the top layer (Table C.1). The application of cattle slurry significantly increased the top layer pH of the acidic soils (loamy sand and sandy loam), whereas the slightly alkaline loam soil did not show a significant pH change after slurry applications. The increase in soil pH was attributed to the higher pH (6.7) of cattle slurry partially neutralizing the lower pH of the acidic soils. In addition, the release of basic cations from manure during microbial decarboxylation was reported to contribute to the increase in soil pH (Adekiya et al., 2019).

Application of cattle slurry enriches the organic C pool of the soil, and oxidized biochar can maintain a high DOC content in the top layer through its enhanced adsorption capacity (Bakshi et al., 2016; Banik et al., 2021). In our study, slurry with oxidized biochar increased the DOC content in the SOC-poor, acidic loamy sand, thereby causing significant N_{mic} immobilization and increasing the nitrification of slurry-N (Table 4.2). The loamy sand contained less SOC than the other two soils, and due to its coarser texture, DOC leached more easily. The addition of oxidized biochar can increase the nutrient retention capacity of the soil due to its high CEC, thereby significantly improving soil fertility in sandy soils (Woolf et al., 2010). In addition, the greater contact area of loamy sand with (oxidized) biochar compared with other soils can significantly improve soil aeration, thus enhancing soil microbial respiration and activity, which increased N mineralization (Banik et al., 2021; Liu et al., 2016).

In each of the soils, C_{mic} and N_{mic} did not differ significantly between treatments at the end of the experiment. After 86 days of incubation, the effect of the treatments on microbial biomass may have diminished because the available organic C and other nutrients had been depleted (Zaman et al., 2002). Therefore, multiple additions of easily available C may be required under field conditions to maintain high microbial biomass and high N storage capacity. Furthermore, the soil microbial C and N contents of (oxidized) biochar treatments (SCB and SCO) may have been underestimated due to the strong sorption capacity of (oxidized) biochar for organic compounds.

4.4.3 Effect of (oxidized) biochar on N retention

As we hypothesized, oxidized biochar was more effective than untreated biochar in reducing NH_3 emissions in all the tested soils due to the low pH and high CEC of oxidized biochar. The lower pH of oxidized biochar reduced NH_3 volatilization in slurry-treated soils by promoting NH_4^+ formation. In addition, after Fenton oxidation of biochar, the O content had clearly increased, whereas the pH had steeply decreased, which is indicative of the formation of acidic oxygen functional groups (Cheng et al., 2008). Such functional groups are known to provide adsorption sites for cations, such as NH_4^+, by establishing hydrogen bonds and electrostatic interactions (Cai et al., 2016; Fan et al., 2018). In addition, the oxidized biochar had a higher O/C_{org} molar ratio, indicating that its CEC and thus the ability to absorb NH_4^+ was higher than that of untreated biochar (Al-Saedi et al., 2021; Huff & Lee, 2016; Lee et al., 2010).

Literature reports that the high adsorption capacity of biochar for nutrients and pollutants is related to its large surface area and high CEC (Guo et al., 2020; Kalus et al., 2019; Yaashikaa et al., 2020; Zeng et al., 2013). However, in our experiment, the surface area of biochar was not the decisive factor, because the surface area of the untreated biochar was 6.7 times higher than that of the oxidized biochar, but was associated with a lower NH_4^+ adsorption capacity (Zeng et al., 2013). Our results suggest that the surface area of oxidized biochar is not the main mechanism for NH_4^+ adsorption, which is supported by the findings of Takaya et al. (2016).

In the loamy sand and loam, the application of cattle slurry significantly increased CO_2 emissions, most likely as a result of the frequently reported stimulated C mineralization after cattle slurry application (Cavalli et al., 2017; Troy et al., 2013). In the loamy sand and sandy loam, oxidized biochar increased the $\delta^{15}N_{NH4}$ (Fig. 4.4D,E), indicating a significantly higher proportion of NH_4^+ retained from the slurry than in the other treatments. In contrast, in the loam, there was no obvious difference in the ^{15}N signal between the treatments, probably due to the very low NH_4^+ concentration in the soil solution, which was likely caused by the strong sorption of NH_4^+ to clay particles.

Nitrate was the dominant N form in all soils. The NO_3^- content in the soil solution increased on Day 2 after slurry application, followed by a short-term decline, whereas the proportion of slurry-derived $^{15}NO_3$ increased after about one week (Fig. 4.5). This delay suggests that the increase in NO_3^- content in the first week probably originated from heterotrophic nitrification (i.e., direct conversion of unlabeled organic N to NO_3^-), with the application of slurry leading to a temporary surge in soil microbial activity (Dumale Jr. et al., 2009). In the loamy sand, oxidized biochar temporarily reduced the NO_3^- concentration significantly in the extracted soil water after slurry application (Fig. 4.5A). This could be attributed to increased adsorption of NH_4^+ by oxidized biochar, reducing the concentration of the substrate for nitrification and thus NO_3^- formation (Singh et al., 2010).

Despite the reduced volatilization losses of NH_3 after the co-application of oxidized biochar with slurry, there was no significant difference in soil ^{15}N recovery between treatments at the end of experiment. We attribute this to a potentially too low application rate of (oxidized) biochar with the slurry, which was equivalent to 2.6 t ha^{-1}, compared with a total of 36.9 t slurry plus biochar ha^{-1}, and which was very likely, not sufficient to significantly increase the overall N retention capacity of the soils. This is in accordance with studies that report a minimum application rate of 5 t biochar ha^{-1} for significant effects on soil properties (Haque et al., 2019; Lehmann & Rondon, 2006). In contrast, the SCO treatment significantly increased the $^{15}N_{mic}$ recovery in loamy sand compared with the SC treatment (Table 4.2), indicating that oxidized biochar increased the soil microbial activity and thereby facilitated the utilization of slurry-N by microorganisms in this soil (Banik et al., 2021).

4.5 Conclusions

Among all the soils tested, loamy sand behaved differently compared with the two other soils because of its low pH and low SOC content. Our study showed that oxidized biochar reduced NH_3 volatilization losses up to 75% from cattle slurry, which is the main pathway of N losses during the slurry application, but at the same time did not increase GHG emissions. Furthermore, oxidized biochar has the potential to increase microbial N immobilization in SOC-poor and acidic sandy soils. We conclude that oxidized biochar has the potential to reduce NH_3 during cattle slurry application but without improving the overall N retention capacity of the soil after a single application. Soil organic C content, microbial N immobilization and physicochemical N adsorption capacity of soils will increase if oxidized biochar is applied regularly. However, oxidation of biochar is associated with additional costs. In contrast, the natural weathering of biochar in soils also leads to surface oxidation without additional costs but requires a much longer time. Furthermore, because this surface oxidation of biochar occurs after its application to soil, its effect on reducing NH_3 volatilization during slurry application might be limited. Therefore, further studies should focus on the effect of both multiple combined and separate additions of oxidized biochar and livestock slurry under realistic field conditions.

5. Optimized use of cattle slurry nitrogen in agriculture by co-application of high carbon amendments: An outdoor lysimeter study with ^{15}N-labled slurry

Based on: Cao, X., Reichel, R., Li, Z., Wissel, H., & Brüggemann, N. Optimized use of cattle slurry nitrogen in agriculture by co-application of high carbon amendments: An outdoor lysimeter study with ^{15}N-labled slurry. Manuscript in preparation.

5.1 Introduction

With rapid economic growth and increasing demand for meat and dairy products, global livestock production has increased dramatically, which requires sustainable agricultural strategies to protect the environment. The excess N in animal excreta can be released into the atmosphere as NH_3, leading to acid deposition and eutrophication (Jensen et al., 2000; Sutton et al., 2011). In addition, the use of cattle slurry as fertilizer in agricultural soils can lead to NO_3^- leaching, polluting water bodies and threatening human health (Robertson & Vitousek, 2009). NO_3^- in soil is further converted to N_2O through denitrification, which greatly contributes to GHG emissions from agriculture (N. N. Rabalais, 2002). Compared to other EU countries, Germany has a serious NO_3^- contamination problem in groundwater and has failed to comply with the EC Nitrate Directive. To address this problem, Germany enacted the Fertilizer Ordinance 2020 which stipulates that in areas with high NO_3^- pollution, the fertilizer requirement based on the fertilizer application plan must not exceed 80% (DüV, 2020). Slurry injection is one of the methods that have been developed to effectively reduce odor and NH_3 losses during slurry application, but high costs limit its widespread use due to time and fuel consumption (Silva et al., 2022). High-carbon organic soil amendments with large C:N ratio have been reported to reduce N losses and improve soil N retention when used in combination with fertilizers (Baggs et al., 2000; Spokas et al., 2012). Wheat straw with a C:N ratio of 50-100 contains way more carbon than nitrogen, which stimulates microbial immobilization of available N from soil (Reichel et al., 2018; Zavalloni et al., 2011). Applying lignite to cattle slurry has been reported to reduce N_2O emissions by up to 66% compared to not using lignite due to the its acidity, CEC, and high content of labile carbon of up to 20% (Chen et al., 2015). In a previous soil incubation experiment with pig and cattle slurry, Cao et al. (2022) showed that wheat straw and leonardite (a highly oxidized form of lignite) reduced N_2O emissions by 33-58%. In addition, leonardite reduced NH_3 emissions by 32-64% compared to the control and led to higher soil N retention than wheat straw. However, this incubation experiment was conducted under controlled laboratory conditions without plants. Some studies reported that crop yield could be reduced by 20-30% after HCA application due to excessive N immobilization (Partey et al., 2014; Soon & Lupwayi, 2012). High rates of available C added to the soil can stimulate microbial growth and lead to substantial N immobilization and to N deficiency in the crop (X. Wang et al., 2018). In contrast, other studies have shown that crop yields were unaffected or even increased after HCA application, which might be related to crop-specific effects or differences in soil N content (Kumar & Goh, 2002; Thomsen & Christensen, 1998). In dryland, HCAs have the potential to increase crop yields because they also increase the WHC of the soil and promote nutrient uptake by plants (Khan et al., 2021; Peng et al., 2015; Reichel et al., 2022). Therefore, it is not clear how cattle slurry application in combination with wheat straw and leonardite affect N retention and crop yield under field conditions.

Based on the results of our previous incubation experiment, we hypothesized that application of cattle slurry and HCA would improve soil N retention and N use efficiency under field conditions, and that leonardite would be more effective than wheat straw. A two-year lysimeter trial was conducted with winter wheat and winter barley on silt loam soil. Cattle slurry was used as the sole N fertilizer source, applied with or without wheat straw or leonardite as HCA. The objective of this study was to test the effects of HCAs and cattle slurry on GHG emissions, N leaching and soil properties, as well as on crop yield and crop N uptake.

5.2 Materials and methods

5.2.1 Soil, HCA, cattle slurry and experimental setup

Nine lysimeters with undisturbed soil monoliths (two with 0.5 m^2 and seven with 1 m^2, all 1.1 m deep) were extracted from recultivated soil near Forschungszentrum Jülich, Germany (50°53′0.16″ N, 6°21′55.9″ E) (Fig. 1.4), which usually is cultivated with alfalfa (*Medicago sativa* L.) for three years before being plowed and returning to typical field crops such as winter wheat, winter barley, or sugar beet. The lysimeters were transported and installed on the premises of Forschungszentrum Jülich. The area is subject to oceanic climate, with average temperatures and total precipitation of 10.8°C and 550.1 mm for the wheat season (November 2019-July 2020), and 9.5°C and 679.2 mm for the barley season (October 2020-July 2021), respectively. Detailed climate data during the experiment (October 2019-July 2021) are shown in Fig. D.1. The soil was classified as silt loam and had an initial pH (0.01 M $CaCl_2$) of 7.6. The detailed parameters of the different soil layers are shown in Table 5.1.

***Table 5.1** The initial parameters of soil.*

	Depth (cm)	**Bulk density (g/cm^3)**	**TOC (% dm)**	**TN (% dm)**	**Mineral N (mg/kg)**	**P_2O_5-P (mg/kg)**
Layer 1	0-30	1.51	0.35	0.05	0.60	16.50
Layer 2	30-60	1.55	0.27	0.04	0.49	15.40
Layer 3	60-110	1.54	0.22	0.04	0.38	14.85

Notte. The abbreviations are as follows: TOC – total organic carbon; dm – dry matter; TN – total nitrogen; Mineral N – mineral nitrogen; P_2O_5-P – Phosphorus pentoxide.

The experiment consisted of three treatments with three replicates each: (1) cattle slurry (C), (2) cattle slurry + wheat straw (CW), and (3) cattle slurry + leonardite (CL). To trace the fate of slurry N, we labelled the cattle slurry with $(^{15}NH_4)_2SO_4$ (98 atom-% ^{15}N) before fertilization to achieve a target value of 2 atom-% ^{15}N. Wheat straw was cut into pieces of about 5 cm length, the typical size found in practice, while leonardite was applied as powder. All HCAs were applied at an amount equivalent to 50 kg C m^{-3} slurry, mixed overnight with cattle slurry in a closed vessel the day before each application.

Winter wheat was sown in November 2019 and harvested in July 2020. Cattle slurry was obtained from the experimental farm Frankenforst of the University of Bonn, Germany. The cattle slurry had a pH of 7.04, a density of 1.02 g cm^{-3} and a water content of 95%. It was stored at 4 °C before each fertilization.

During the growth period, three fertilization doses were applied at the rate of 21.2 kg N ha^{-1} each (in total 63.6 kg N ha^{-1}). The total carbon content of wheat straw and leonardite were 43.6% and 46.3%.

Winter barley was sown in October 2020 and was harvested in July 2021. More slurry-N (in total 120 kg N ha^{-1}), and therefore more HCA-C, was applied in the barley compared to the wheat season. In the barley season, we had two slurry fertilization events. The cattle slurry of first fertilization event had a pH of 6.55, a density of 0.96 g cm^{-3} and a water content of 94%, and the application rate was equivalent to 55 kg N ha^{-1}. The cattle slurry of the second fertilization event had a pH of 6.75, a density of 1.04 g cm^{-3} and a water content of 92%, and was applied at a rate equivalent to 65 kg N ha^{-1}. After the first application of HCA-treated slurry, the growth of barley was limited. Thus, we applied only untreated slurry during the second event in all treatments. Both cattle slurries were obtained again from the experimental farm Frankenforst of the University of Bonn, but in two batches. The total carbon content of wheat straw and leonardite was 40.7% and 42.9%, respectively.

5.2.2 Gas analysis

GHG and NH_3 emissions were measured routinely once a week, but the measurement frequency was increased after each fertilization event, with additional emission measurements on days 1, 2 and 3 after fertilizer application. Emissions of CO_2, N_2O and NH_3 were quantified with a portable Fourier Transform Infrared Spectroscopy (FTIR) gas analyzer (DX4015, Gasmet Technologies Oy, Vantaa, Finland), using three polyvinyl chloride tubes (25 cm length, 5 cm diameter) randomly distributed across the surface of each lysimeter and inserted to a soil depth of 15 cm. The three polyvinyl chloride tubes per lysimeter were simultaneously connected to the analyzer in closed-loop mode with gas-tight lids immediately before each gas measurement, and kept closed for 6 min measurement time. Gas fluxes were calculated according to Brummer et al. (2008).

5.2.3 Leachate analysis

Leachate of the lysimeters was collected in a stainless-steel pan below the lysimeters, and was sampled eleven times during the experiment when the leachate reached the minimum collectable volume (5 cm water depth in the collection pan). Leachate samples were pumped out of the collection pans, and filtered through a 0.45 µm membrane filter (Macherey-Nagel, Düren Germany) before measuring the total DOC and total dissolved nitrogen (TDN) content with a TOC/TN analyzer (TOC-VcPH + TNM-1 + ASIV, Shimadzu, Kyoto, Japan), NH_4^+ by continuous flow analysis (CFA Analyzer, FLOWSYS 3-Kanal, Alliance Instruments, Salzburg, Austria), and NO_3^- by ion chromatography (Dionex DX-500, ThermoScientific, Waltham, USA).

The $^{15}NH_4^+$ and $^{15}NO_3^-$ in the leachate were analyzed by micro-diffusion and liquid-liquid extraction as described in Reichel et al. (2018). The determination of the ^{15}N was conducted via an elemental analyzer coupled to an isotope-ratio mass spectrometer (EA-IRMS, Flash EA 2000 and Delta V plus, Thermo Fisher Scientific, Bremen, Germany).

5.2.4 Soil analysis

We conducted in total eight soil samplings: during fall/winter (December 2019 and November 2020), before fertilizer application (March 2020 and February 2021), at crop maturity (June 2020 and May 2021), and post-harvest (August 2020 and August 2021). From each lysimeter, nine randomly distributed soil cores (0-25 cm depth) were taken using a custom-made stainless steel soil auger with 8 mm diameter. The nine soil cores from each lysimeter were mixed to get a representative composite sample. Fresh soil samples were extracted with 0.01 M $CaCl_2$ solution (soil-to-solution ratio of 1:4 w:v) and processed as described in Chapter 2. The extracts were used to determine the DOC, TDN, and mineral N (NH_4^+ and NO_3^-) content with the same methods and analyzers as described in section 5.2.3. The air-dried soil samples were ball-milled (MM2, Retsch, Haan, Germany), treated with 32% hydrochloric acid for 16 h to remove carbonate, dried again, and then analyzed with an elemental analyzer coupled to an EA-IRMS (Flash EA 2000 and Delta V Plus; Thermo Fisher Scientific) to determine the TOC and TN content as well as the ^{15}N content of N.

5.2.5 Plant analysis

Shoots with ears of wheat and barley were cut 1 cm above the ground. The roots (basal, primary, and seminal roots) were extracted from the first 10 cm of soil and washed thoroughly in order to remove adhering rhizosphere soil. All plant samples were dried at 60 °C overnight and ball-milled, and subjected to TN and ^{15}N analysis as described for the soil in section 5.2.4.

5.2.6 Calculation and statistical analysis

The ^{15}N recovery was calculated according to the following equation:

$$^{15}\text{N recovery } \% = \frac{^{15}N_{sp}\ atom\ \% \times TN_{sp}\ \% \times M_{sp}}{^{15}N_{slurry}\ atom\ \% \times TN_{slurry}\ \% \times M_{slurry}} \qquad \text{(Equation 5.1)}$$

where $^{15}N_{sp}$ atom % is the ^{15}N atom percentage in the samples (soil/leachate/plant), %; TN_{sp} is the total N percentage in the samples (soil/leachate/plant), %; M_{sp} is the dry mass of the samples (soil/leachate/plant), g; $^{15}N_{slurry}$ atom % is the input ^{15}N content in slurry, atom %; TN_{slurry} is the input total N content in slurry, %; M_{slury} is the input slurry dry mass, g. For the wheat season, the ^{15}N recovery was calculated based on the cattle slurry N input during the wheat season only, while for the barley season the ^{15}N recovery was calculated based on the cattle slurry N input during the barley season plus the ^{15}N remaining in the soil from the previous wheat season.

Significant differences between treatments were determined by one-way analysis of variance (ANOVA) and Tukey's HSD post-hoc test at ≤ 0.05 after testing normal distribution of the data with the Kolmogorov-Smirnov test (IBM SPSS Statistics for Windows, Version 25.0, IBM Corp., USA).

5.3. Results

5.3.1 GHG and NH_3 cumulative emissions

Throughout the whole experiment over both cropping seasons, cumulative CO_2 emissions were equivalent to 42-64 t C ha^{-1} (Fig. 5.1). However, cumulative CO_2 emissions were much higher in the barley season (31-45 t C ha^{-1}) than in the wheat season (11-19 t C ha^{-1}). Cumulative N_2O and NH_3 emissions ranged between 2.9-3.4- kg N ha^{-1} and 1.2-3.8 kg N ha^{-1}, respectively, for the whole period of two years (Fig. 5.1). Compared to the C treatment, the CW and CL treatments had 34% and 25% lower CO_2 emissions, and 37% and 68% lower NH_3 emissions, respectively. During the wheat season, N_2O emissions from the C treatment were 4.7 and 1.8 times higher than those from the CL and CW treatments, respectively, while they were 1.3 times lower in the C treatment compared to CL and CW, respectively, in the barley season. Compared to the C treatment, leonardite and wheat straw reduced NH_3 emissions by 82% and 92%, respectively, during the wheat season, while wheat straw increased NH_3 emissions by 175% during the barley season. However, there were no statistical differences between the treatments.

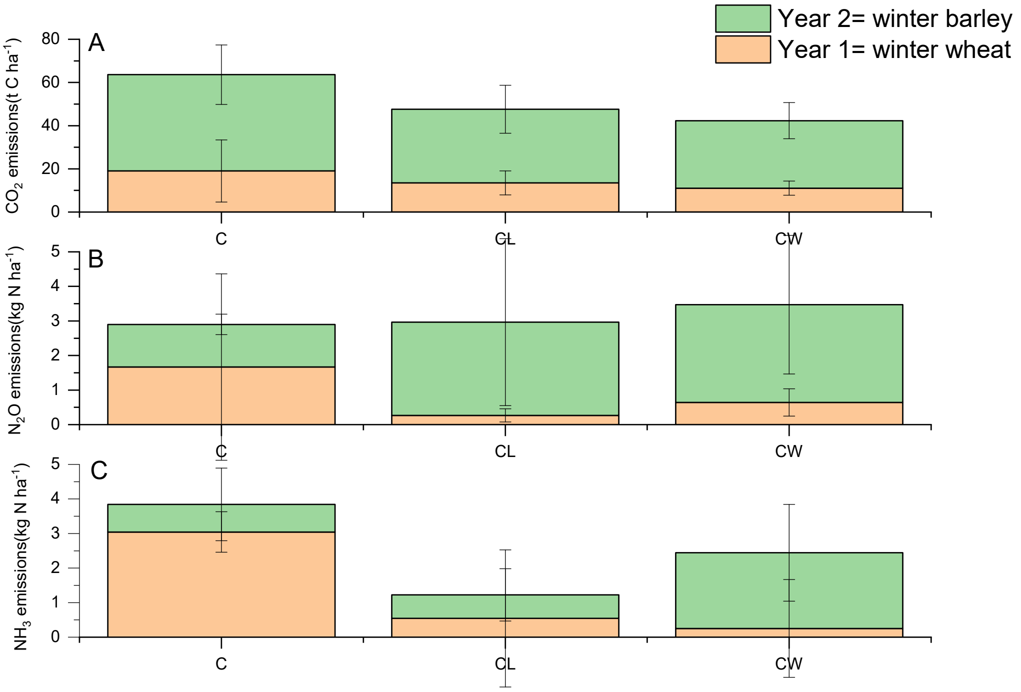

Figure 5.1 *(A) Cumulative CO_2 emissions; (B) cumulative N_2O emissions; (C) cumulative NH_3 emissions. The abbreviations of the treatments are as follows: C – cattle slurry; L – leonardite; W – wheat straw. Year 1 represents the wheat season, from fertilization to the sowing date of the following crop (19 March 2020 - 6 October 2020); Year 2 represents the barley season, from fertilization to the sowing date of the following crop (17 March 2021 - 24 September 2021). The error bars show the standard error of the mean of each treatment (n = 3). There is no significant difference between treatments.*

5.3.2 DOC and mineral N in leachate

The total leachate volume amounted to 2853-2985 m^{-3} ha^{-1} over the entire experimental period (Fig. 5.2). The DOC and mineral N content (NH_4^+ and NO_3^-) of the leachate was highest in the CW treatment, amounting to 30 kg C ha^{-1} and 71 kg N ha^{-1}, and lowest in the CL treatment with 23 kg C ha^{-1} and 46 kg N ha^{-1}, respectively. Most of the mineral N in the leachate was NO_3^--N, with NH_4^+-N accounting for only 0.6-1.6%. During the barley season, the leachate volume was higher by 15% and 45% in the C and CW treatments, respectively, compared to the wheat season, while the change in leachate volume in CL treatment was negligible. During the wheat season, leached DOC was 8.5-8.7 kg C ha^{-1} and mineral N was 6.3-9.9 kg N ha^{-1}, of which NH_4^+-N was 0.11-0.26 kg ha^{-1}; while during the barley season, leached DOC was 14-22 kg C ha^{-1} and mineral N was 39-62 kg N ha^{-1}, of which NH_4^+-N was 0.09-1.02 kg ha^{-1}, i.e., most of the DOC and mineral N was leached during the barley season. Leaching of DOC and mineral N was highest for the CW treatment and lowest for the CL treatment in both seasons.

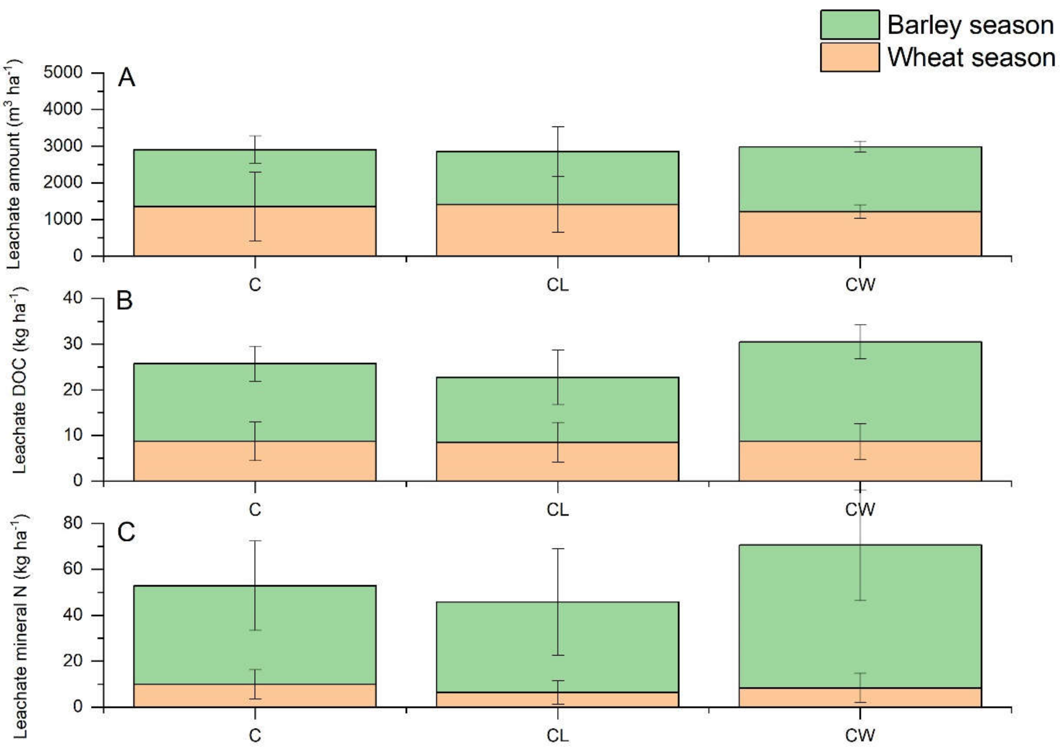

Figure 5.2 *(A) Leachate amounts; (B) DOC contents in leachate; (C) mineral N contents in leachate. The abbreviations of the treatments are as follows: C – cattle slurry; L – leonardite; W – wheat straw. Wheat season indicates leaching between the sowing date of wheat and the sowing date of barley. Barley season indicates leaching between the sowing date of barley and the sowing date of the following crop. The error bars show the standard error of the mean of each treatment (n = 3). There is no significant difference between treatments.*

5.3.3 Soil DOC and mineral N contents

Prior to any fertilization (December 2019), soil DOC was on average 12 and 11 mg C kg^{-1} for the lysimeters of the C and CW treatments, respectively, compared to only 7 mg C kg^{-1} for the lysimeters of the CL treatment, which was significantly lower than the C treatment by 42% (Fig. 5.3). After the first fertilization (June 2020), soil DOC increased to 8 mg C kg^{-1} in the CL treatment and decreased to 5 mg C kg^{-1} in the CW treatment, while the C treatment maintained the same DOC content at 12 mg C kg^{-1}. The highest soil DOC of all treatments occurred after wheat harvest (August 2020) with 14, 19 and 12 mg C kg^{-1} in the C, CL and CW treatments, respectively; however, the differences between treatments were not significant. After barley sowing (November 2020), DOC levels decreased to 5-6 mg C kg^{-1} and increased to 10 mg C kg^{-1} after fertilizer application (May 2021) without any significant difference between treatments. After barley harvest (August 2021), soil DOC decreased slightly to 8 mg C kg^{-1} in the C treatment and remained at 10 mg C kg^{-1} in the other treatments.

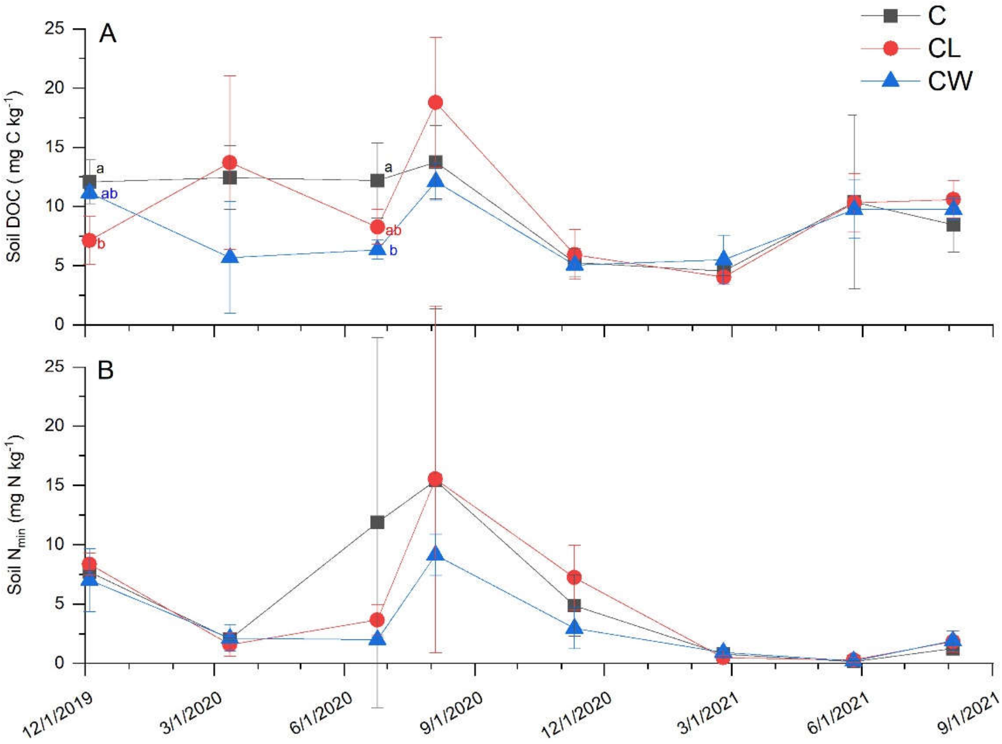

***Figure 5.3** (A) Dissolved organic C (DOC) content in soil (0-25 cm); (B) mineral N content in soil (0-25 cm). The abbreviations of the treatments are as follows: C – cattle slurry; L – leonardite; W – wheat straw. The error bars show the standard error of the mean of each treatment (n = 3). The different lowercase letters indicate significant differences at the p<0.05 level between treatment. The absence of lowercase letters means that there is no significant difference between treatments.*

At the start of the experiment, mineral N in the soil was 7-8 mg N kg^{-1}. In June 2020, slurry application increased mineral N in the C treatment to 12 mg N kg^{-1}, while the CL and CW treatments had much a lower mineral N content of 4 and 2 mg N kg^{-1}, respectively, but this difference was not significant due to high variability between replicates. Mineral N in the C, CL and CW treatments peaked at 15, 16 and 9 mg N kg^{-1} after wheat harvest. The application of slurry in 2021 did not result in an increase in mineral N compared to 2020. Instead, mineral N levels remained below 1 mg N kg^{-1} until they reached 1-2 mg N kg^{-1} after barley harvest.

5.3.4 Yields and TN content of wheat and barley

The aboveground biomass of wheat ranged between 13,300-14,700 kg ha^{-1}, including a grain yield of 5,200-6,200 kg ha^{-1} (Table 5.2). In contrast, the aboveground biomass of barley in the following year was lower than that of wheat, and significantly lower by 43% in the CW treatment than in the C treatment. Grain yields of barley ranged between 4,500-7,900 kg ha^{-1} with no significant differences between treatments. The thousand-grain weight of wheat was lower than that of barley, while the hectoliter (hl) weight of wheat was higher compared to barley.

The highest TN content was found in grains, followed by roots, while the lowest content was found in straw. While the TN content of straw and grains of wheat and barley were comparable, the TN content in wheat roots was clearly lower at 0.31-0.42% than for barley at 0.65%.

Table 5.2 *Yield parameter and TN contents of harvested wheat and barley.*

	Wheat			Barley		
	C	CL	CW	C	CL	CW
Aboveground biomass (100 kg ha^{-1})	147 ± 12a	133 ± 31a	140 ± 20a	110 ± 18a	86 ± 11ab	63 ± 12b
Grain yield (100 kg ha^{-1})	62 ± 3a	52 ± 7a	62 ± 6a	79 ± 19a	61 ± 9a	45 ± 10a
Thousand-grain weight (g)	43 ± 5a	44 ± 4a	42 ± 1a	50 ± 1a	51 ± 2a	53 ± 1a
Hectoliter weight (kg hl^{-1})	73 ± 1a	72 ± 1a	72 ± 0a	61 ± 1a	60 ± 0a	62 ± 1a
Straw TN (%)	0.24 ± 0.03a	0.26 ± 0.13a	0.16 ± 0.02a	0.26 ± 0.05a	0.21 ± 0.05a	0.24 ± 0.02a
Root TN (%)	0.36 ± 0.20a	0.31 ± 0.07a	0.42 ± 0.08a	0.65 ± 0.06a	0.65 ± 0.19a	0.65 ± 0.15a
Grain TN (%)	1.48 ± 0.21a	1.46 ± 0.33a	1.34 ± 0.13a	1.39 ± 0.17a	1.29 ± 0.15a	1.45 ± 0.03a

Note. Values are means ± SD. The abbreviations of the treatments are as follows: C – cattle slurry; CL – cattle slurry with leonardite; CW – cattle slurry with wheat straw. Different lowercase letters indicate significant differences between treatments for the same date at the p<0.05 level.

5.3.5 ^{15}N recovery

Due to low emission rates, the N losses through gaseous emissions were negligible in terms of the total N balance, so ^{15}N recovery in gaseous N losses was not calculated. Only traces of the ^{15}N (less than 0.0001%) applied with cattle slurry were leached during the wheat season, while most of the ^{15}N leaching (0.71-0.82%) occurred during the barley season (Fig. D.2).

Table 5.3 shows soil ^{15}N recovery at six sampling times after the first application of cattle slurry. In June 2020, soil ^{15}N recovery was 51% and 39% for the C and CL treatments, and lowest for the CW treatment at 13%. After wheat harvest, soil ^{15}N recovery increased to 77% and 81% in the C and CL treatments, but only to 31% in the CW treatment, which was significantly lower than in the other two treatments. Before barley harvest, the soil ^{15}N recovery was low at 10-37% for all treatments. After barley harvest, CL had the highest soil ^{15}N recovery of 72%, which was 1.8 times higher than for the CW treatment, while the C treatment had a ^{15}N recovery of 52%.

***Table 5.3** Soil and plant ^{15}N recovery (%) for the six sampling dates of the experiment.*

		C	**CL**	**CW**
Soil	2020-06-24	51 ± 10a	39 ± 14a	13 ± 4b
	2020-08-04	77 ± 6a	81 ± 23a	31 ± 13b
	2020-11-10	34 ± 6a	37 ± 19a	17 ± 4a
	2021-02-23	25 ± 7a	19 ± 4a	23 ± 9a
	2021-05-26	36 ± 13a	21 ± 22a	10 ± 3a
	2021-08-04	52 ± 20ab	72 ± 22a	26 ± 8b
Wheat	Straw	1.2 ± 0.7a	1.2 ± 0.8a	0.5 ± 0.1a
	Grain	8.6 ± 0.5ab	9.0 ± 1.9a	5.7 ± 0.5b
	Root	1.0 ± 1.0a	1.7 ± 0.2a	1.3 ± 0.6a
Barley	Straw	1.5 ± 0.9a	1.2 ± 0.7a	0.3 ± 0.1a
	Grain	17.9 ± 12.9a	19.9 ± 16.9a	4.6 ± 0.2a
	Root	7.0 ± 5.5a	7.0 ± 3.1a	1.8 ± 0.7a

Note. Values are means ± SD. The abbreviations of the treatments are as follows: C – cattle slurry; CL – cattle slurry with leonardite; CW – cattle slurry with wheat straw. Different lowercase letters indicate significant differences between treatments for the same date at the $p<0.05$ level.

The ^{15}N recovery in the whole plant (roots, straw and grains) ranged from 7-12% for wheat and 7-28% for barley, with the CL treatment having the highest ^{15}N recovery, followed by the C and the CW treatment (Table 5.3). In the C and CL treatments, the ^{15}N recovery in the whole plant was 1.4-fold higher in barley compared to wheat, while the CW treatment maintained the same level. Most of the ^{15}N was found in grains, i.e., 68-71% of all ^{15}N in wheat and 76-80% in barley, and the ^{15}N recovery in wheat grains was significantly higher in the CL treatment than in the CW treatment. In the C and CL treatments, root ^{15}N recovery was 6-fold and 3-fold higher in barley compared to wheat, respectively.

5.4. Discussion

5.4.1 Effects of HCA on GHG and NH_3 emission

The cumulative emissions of NH_3 were very low in the two-year trial. In general, there is no guarantee that all transient emission peaks can be captured within the limited temporal coverage of the measurements, even if measurements are taken frequently (daily) after slurry application. However, one possible reason could be that due to application of the cattle slurry in spring, when temperatures were relatively low, NH_3 volatilization was reduced, in addition to higher N uptake by plants due to growth in spring, thus reducing N losses (Sommer et al., 1997). The lower cumulative NH_3 emissions from the CW treatment compared to the C treatment may be related to physical and biological processes. On the one hand, the application of wheat straw might have reduced the airflow through the soil surface, thus reducing NH_3 volatilization; on the other hand, the available C in wheat straw might have promoted microbial activity, which in turn might have increased microbial N immobilization (Gilhespy et al., 2009; Kirchmann & Witter, 1989). However, the effect of wheat straw on NH_3 reduction was not consistent in both years, since NH_3 emissions from CW were higher than from the other treatments during the barley season. A potential reason might be that the addition of a larger amount of wheat straw in the barley growing season reduced the water content of the slurry, decreased slurry infiltration and improved aeration, all favoring the volatilization of NH_3 (Petric et al., 2009).

Leonardite has a high C:N ratio like wheat straw. In addition, leonardite is acidic, which favors NH_3 protonation, and is highly oxidized, which means that the surface contains oxygen-rich functional groups associated with high CEC, thus providing NH_4^+ adsorption sites, which altogether may have contributed to the reduction of NH_3 emissions (Al-Saedi et al., 2021; Chen et al., 2015; Zeng et al., 2013). Similar results have been reported for lignite, which reduced NH_3 emissions from cattle manure by 54% during composting (Bai et al., 2020).

The high N_2O emission rates during the barley season occurred after May (Fig. D.3), which likely was related to the high rainfall amount during the barley growing season. According to the climate station of Forschungszentrum Jülich, the precipitation in 2020 and 2021 were 550 mm and 754 mm, respectively, the main difference being during the crop growing season (March-July), with 195 mm in 2020 and 365 mm in 2021, respectively. The average gravimetric soil water content in 2021 was 18-21%, while it was only 8.8% and 4.7% in June and August 2020 due to the dry summer conditions in that year (Fig. D.4). A global meta-analysis found a significant positive correlation between precipitation and N_2O emissions, regardless of biome, treatment and season, driven primarily by changes in soil moisture and low oxygen conditions in wet soil that favor denitrification (Li et al., 2020). In addition, the application of wheat straw and leonardite with cattle slurry can increase soil DOC content, which can also promote microbially mediated N_2O emission from denitrification (Chen et al., 2013).

Higher CO_2 emissions were recorded during the barley season compared to the wheat season (Fig. 5.1). One reason was very likely that higher amounts of slurry and HCA were applied in the barley season compared to the wheat season. In addition, in dry soils, water limitation inhibits the emission of CO_2 from the soil, while after rainfall, CO_2 emission increases by stimulating microbial growth and increasing microbial activity (Blazewicz et al., 2014; Davidson et al., 2000). Furthermore, since the recultivation soil was rich in carbonate, the dissolution of carbonate can also lead to additional CO_2 emissions (Raza et al., 2021). Although additional carbon was added through wheat straw and leonardite, both treatments were not associated with an increase in CO_2 emissions (Fig. 5.1A). This is in contrast to a previous incubation experiment, in which small pieces of wheat straw (2-3 cm) mixed with slurry significantly increased CO_2 emissions and soil microbial growth after incorporating it into the soil surface (Cao et al., 2021; Li et al., 2022). This effect was not pronounced under field conditions, where large pieces of straw (5 cm) were mixed with slurry and applied to the soil surface, but not further incorporated into the soil. On the contrary, in both laboratory and field conditions, leonardite reduced CO_2 emissions despite its acidic nature, possibly due to the higher adsorption capacity of leonardite reducing DOC availability.

5.4.2 Effects of HCAs on crop yields and ^{15}N recovery

We found that barley grew more slowly in the CW treatment than in the other treatments after the first fertilization (and hence straw application). At the time of harvest, the aboveground biomass of barley was lowest in the CW treatment (Table 5.2), which may be related to the high straw application amount and the increased N immobilization induced by it. Previous studies have shown that soil microorganisms can compete with crops for available N during the decomposition of HCA, thereby reducing crop yield (Cai et al., 2018; Kaye & Hart, 1997; Rashid et al., 2019), which could explain the low productivity of barley in the CW treatment. In addition, wheat straw may have educed soil warming by solar radiation during the early stages of barley growth, and likely reduced soil aeration, impeding root respiration, nutrient uptake and thus barley growth (Linden et al., 2000; Lu et al., 2015).

In addition, the low recovery of ^{15}N by the crops in the CW treatment also supports the previous assumption that N uptake was impeded by the N competition between microorganisms in the topsoil and the crop roots. The application of cattle slurry and wheat straw to the soil can lead to the so-called "priming effect", stimulating microorganisms to mineralize organic matter and increase N immobilization, thereby competing with the crop for N (Baggs et al., 2000; Fontaine et al., 2003). In contrast, leonardite reduced N losses due to its acidity and high CEC by adsorption of NH_4^+ from cattle slurry, while the adsorbed N is still available to the crop and can increase the ^{15}N recovery in the crop (Bai et al., 2020; J. L. Sun et al., 2016), as confirmed by our results (Table 5.3).

5.4.3 Effects of HCAs on soil properties and leachate

Higher precipitation during the barley season compared to the wheat season increased the amount of leachate and concomitantly also the amount of leached DOC and mineral N (Fig. 5.2). This increased DOC and mineral N leaching is reflected by the lower DOC and mineral N contents of the topsoil (0-25 cm) during the barley season. The higher amount of precipitation very likely caused DOC and mineral N to be transferred to the subsoil and leached out, as reported also by (Rosa & Debska, 2018). DOC and mineral N leaching losses were higher in the CW treatment than in the other treatments, but there was no increase in ^{15}N recovery from the CW leachate (Fig. D.2). This implies that the additional N leaching was not from the cattle slurry, but was due to increased mineralization of soil organic matter (positive priming) caused by the addition of wheat straw and cattle slurry (Chantigny et al., 2001).

DOC and mineral N contents peaked in the soil after wheat harvest (Fig. 5.3), very likely due to the decomposition of post-harvest residues (Gregorich et al., 2000). In addition, higher soil temperatures in summer stimulate microbial activity, hence also decomposition of organic matter and release of mineral N (Rosa & Debska, 2018; Worrall et al., 2003). Such stimulated decomposition of slurry and plant residues after harvest could explain the peak post-harvest soil ^{15}N recovery (Table 5.3).

Soil ^{15}N recovery was significantly lower in the CW treatment than in the other treatments after harvest in both years (August 2020 and August 2021) because part of the ^{15}N was likely retained in the unsampled straw material at the soil surface, which may have led to an underestimation. In contrast, the CL treatment had the highest ^{15}N recovery after harvest in both years, implying that leonardite did not only improve N retention, but also increased the use efficiency of N from slurry due to its adsorption capacity (Cao et al., 2021; J. L. Sun et al., 2016).

5.5 Conclusions

In this lysimeter study with winter wheat and winter barley, cattle slurry in combination with wheat straw or leonardite was applied as the only N fertilizer at two different application rates (64 kg N ha^{-1} in the first year, and 120 kg N ha^{-1} in the second year) to a silty loam. Application of leonardite improved N retention in both years by reducing NH_3 emissions and leaching of mineral N. At the same time, leonardite did not reduce N nutrition of the crop and led to the highest ^{15}N recovery in the plants. In contrast, slurry applied with wheat straw reduced crop yield and N uptake from the slurry, with no significant benefit to N retention. At the end of the experiment, soil ^{15}N recovery was highest in the CL treatment at 72% and lowest in the CW treatment at 26%. Despite the field-typical variability, the trends were sufficient to conclude that leonardite has great potential to reduce NH_3 losses, improve N fertilizer efficiency and soil N retention when applied with cattle slurry under field conditions, but that simultaneous application of straw and cattle slurry should be strictly avoided.

6. Synopsis

6.1 Summary

Large amounts of animal manure from livestock production have been used as organic fertilizer for thousands of years; however, losses of gaseous N (e.g., NH_3 and N_2O) and leachate (e.g., NO_3^-) have increased GHG emissions, contaminated surface and groundwater, and threatened human health. HCAs have been reported to have great potential for binding N and reducing N losses, but it is unclear which HCAs are most effective in reducing N losses and improving N use efficiency when applied to soils together with animal slurries. The objective of this thesis was to investigate the potential of HCAs to improve soil N retention when co-applied with animal slurry under different conditions. In addition, we produced and modified biochar to obtain a sustainable and effective HCA.

In the first study, I tested the potential of three different types of HCAs—wheat straw, sawdust, and leonardite (application rate 50 g C L^{-1} slurry for each of the three HCAs)—to mitigate N loss after amendment of soil with pig and cattle slurry using two common application modes (slurry and HCA mixed overnight with subsequent addition to soil vs. sequential addition) at an application rate equivalent to 80 kg N ha^{-1}. Compared to the control with only soil and slurry, the addition of leonardite reduced the NH_3 emissions of both slurries by 32–64%. Leonardite also reduced the total N_2O emissions by 33–58%. Wheat straw reduced N_2O emissions by 40–46%, but had no effect on NH_3 emission. ^{15}N labeling showed that the application of leonardite was associated with the highest N retention in soil (24% average slurry N recovery), followed by wheat straw (20% average slurry N recovery). Mitigation of N loss was also observed for sawdust, although the effect was less consistent compared with leonardite and wheat straw. Mixing the slurry and HCA overnight tended to reduce N losses, although the effect was not consistent across all treatments. In conclusion, leonardite improved soil N retention more effectively than wheat straw and sawdust.

However, leonardite as a byproduct of open-cast lignite mining is not a renewable resource. In order to find a sustainable, but similarly effective substitute for leonardite, we modified biochar by chemical surface oxidation. Biochar was produced from spruce sawdust in a pyrolysis oven at a maximum temperature of 610 °C. Then the biochar was oxidized using the Fenton reaction, with a ratio of Fe^{2+}/H_2O_2 of 1:1,000, as a source of highly reactive HO· radicals to introduce oxygen-rich functional groups to the biochar surface. The NH_4^+ adsorption capacity of biochar, oxidized biochar and leonardite was tested in $(NH_4)_2SO_4$ solution, pH-adjusted $(NH_4)_2SO_4$ solution and cattle slurry. The results showed that biochar had the highest total NH_4^+ adsorption of 1.4 mg N g^{-1} in $(NH_4)_2SO_4$ solution, whereas oxidized biochar had the highest reversible NH_4^+ adsorption of 0.8 mg N g^{-1}. In the pH-adjusted ammonium solution, all materials reduced NH_3 emissions by at least 90%, while oxidized biochar reduced NH_3 emissions completely (99.99%). In contrast, leonardite reduced NH_3 emissions the most in cattle slurry, and oxidation of biochar increased the reduction in NH_3 emissions from 22 to 67%, compared with non-oxidized biochar. In conclusion, biochar oxidized by means of the Fenton reaction greatly decreased NH_3 emission by increased adsorption of NH_4^+ in cattle slurry compared with non-

oxidized biochar, indicating the great potential of oxidized biochar for reducing N losses during slurry application.

To further examine the effect of oxidized biochar on the fate of cattle slurry N applied to three different soils, I investigated the effect of untreated and oxidized biochar (applied at a rate of 50 g C L^{-1} slurry) on reducing N losses in a laboratory experiment with three different soils (loamy sand, sandy loam, loam) amended with cattle slurry at an application rate of 73 kg N ha^{-1}. Oxidized biochar reduced NH_3 emissions by 64-75% in all soils, whereas untreated biochar reduced NH_3 emissions by 61% only in the loamy sand. Oxidized biochar significantly reduced the NO_3^- content in the soil solution of the loamy sand in the early phase of the incubation and led to a significantly higher NO_3^- concentration in the same soil compared with the slurry-only treatment at the end of the experiment, indicating a significant increase in NO_3^- retention in this organic C–poor soil. We conclude that oxidized biochar can reduce N losses, both in the form of NH_3 emission and NO_3^- leaching, from cattle slurry applied to soil, particularly in soil with soil organic carbon content <1% and pH <5 (i.e., oxidized biochar can serve as a means for improving the quality of marginal and acidic soils).

To investigate the effect of wheat straw or leonardite as HCA in combination with cattle slurry fertilization under field conditions, we conducted a two-year lysimeter experiment with winter wheat in the first year and winter barley in the second year using ^{15}N-labeled cattle slurry. Ammonia emissions, DOC leaching and soil mineral N content were lowest in the cattle slurry treatment with leonardite compared with the control without HCA, while they were highest after co-application of slurry and wheat straw. ^{15}N-analysis showed that leonardite, in contrast to the straw treatment, did not reduce grain N content, while it improved the retention of slurry N in soil. In conclusion, compared to wheat straw, leonardite can reduce NH_3 emission and N leaching without reducing crop yield, making it a suitable additive to improve N fertilizer efficiency and soil N retention after slurry application.

6.2 Synthesis

The aim of this thesis was to evaluate the potential of treating slurries in soil with various HCAs under different conditions. HCAs have shown great potential in reducing N losses, and many studies have shown that they can improve soil properties in the long term, thus ultimately increasing the N retention capacity of the soil (Blumenthal et al., 2003; Borchard et al., 2019; Clouard et al., 2014; Firestone & Davidson, 1989). However, to our knowledge, comprehensive studies analyzing the combined effects of different HCAs are still lacking.

In this thesis, I conducted a series of experiments under different conditions to evaluate the potential of treating animal slurry with various HCAs. After finding the ideal HCA(s) in the laboratory experiment, I conducted a lysimeter experiment in combination with crop plants to further investigate the performance of HCAs and their effect on plant nutrient uptake under field conditions. In addition, since leonardite is an unsustainable material of fossil origin, I produced and modified biochar to mimic leonardite as a sustainable alternative. Then their effects were tested with cattle slurry in three different soils.

6.2.1 Identification of the optimal HCA

In Chapter 2, three common HCAs were tested, namely wheat straw, sawdust and leonardite, all of which are byproducts or wastes of agriculture, wood production and mines. The results showed that wheat straw and leonardite had the potential to reduce N_2O emissions, possibly due to N deficiency of nitrifying microorganisms, as the slurry stimulated the mineralization of labile C in HCAs, which then promoted microbial biomass growth and N immobilization (Aita et al., 2012). Since wheat straw contains high levels of available C, which increases microbial growth and activity, the stimulation of straw C mineralization by slurry-N can lead to increased CO_2 emissions (Chantigny et al., 2001; Sørensen, 1998). Compared to wheat straw, leonardite did not increase CO_2 emissions neither in the laboratory nor in the lysimeter experiments, although it also contained 20% labile C (Chen et al., 2015), which is associated with proton release from acidic leonardite in neutral soils, possibly leading to a transient inhibition of microbial respiration (Schefe et al., 2008; C. K. T. Tran et al., 2015). In addition, deprotonation of acidic groups on the leonardite surface reduces the pH of the alkaline slurry, thereby increasing the NH_4^+/NH_3 ratio, and simultaneously increases the negative charge on the leonardite surface, providing more adsorption sites for NH_4^+ and ultimately reducing NH_3 emissions (Chen et al., 2015; Simmler et al., 2013; Sommer et al., 2003). Conversely, wheat straw and sawdust reduced the rate of slurry infiltration into the soil and the water content of the slurry, leading to increased NH_3 emissions. Based on the results of the ^{15}N analysis, the loss of gaseous N dominated under laboratory conditions. The loss of gaseous N was lowest in the leonardite treatment, resulting in the highest soil ^{15}N retention, followed by the wheat straw treatment. Spruce sawdust as an HCA is not as effective as leonardite and wheat straw in mitigating N losses, probably due to its low labile organic matter content and the lack of oxygen-rich functional groups on its surface.

Based on the results in Chapter 2, wheat straw and leonardite were tested as suitable HCAs in the lysimeter experiment (Chapter 5). Under field conditions, weather conditions played an important role in N losses. In the two-year trial, the cumulative emissions of N_2O and NH_3 were very low. This was due to the fact that the cattle slurry was applied in spring, when temperatures were low on the one hand and plant uptake of N was high on the other, thus reducing N losses (Sommer et al., 1997). However, leonardite still showed the potential to further reduce NH_3 emissions. Under controlled laboratory conditions (Chapter 2), we kept the soil WHC at 60%, replenishing only the evaporative water loss, which did not lead to leaching. In contrast, under field conditions, the amount of leachate increased with increasing precipitation, and leonardite reduced the mineral N content of the leachate, very likely due to its oxygen functional groups and high CEC (Chen et al., 2015; Manzoni & Porporato, 2009). They provided adsorption sites for NH_4^+, which then also reduced the NO_3^- content of the soil, as nitrification is inhibited by a lack of substrate (Bai et al., 2020). As in the incubation experiments (Chapter 2), higher $\delta^{15}N$ values for NH_4^+ were found in the leonardite treatment, but at a later time point compared to the other HCA treatments, also providing evidence for the adsorption of NH_4^+ by leonardite in the early incubation phase. Overall, after two years of experiment under field conditions, leonardite reduced NH_3 losses and mineral N leaching losses and thus led to the highest soil ^{15}N retention. In contrast, wheat straw reduced soil ^{15}N recovery, probably because ^{15}N was retained in the straw substrate that was not sampled at the soil surface.

The effects of wheat straw and leonardite on crop yield were different. During the wheat season, the aboveground biomass and grain yield were slightly, but not significantly, lower in the leonardite treatment than in the cattle slurry only treatment. In addition, leonardite increased ^{15}N recovery in wheat grains. During the barley season, the aboveground biomass and grain yield were lowest in the wheat straw treatment, probably because the introduction of large amounts of readily available C increased N retention in microbial biomass. Another reason may be that the high application rate of wheat straw may have prevented soil warming by solar radiation and reduced soil aeration, thus hindering growth in the early barley growing season (Lu et al., 2015). Thus, crop yield was highest in the cattle slurry only treatment, while wheat straw had more adverse effects than leonardite.

Under both laboratory and field conditions, leonardite performed best in reducing N losses and improving soil N retention without reducing crop N supply. Therefore, we consider leonardite to be the best HCA tested and an effective additive for reducing N losses from animal slurries.

6.2.2 The sustainable alternative

As mentioned above, leonardite is an unsustainable material, especially in Germany, where more and more lignite mines are closing. Therefore, it is important to find a sustainable alternative. Biochar is a readily available renewable resource, and its benefits as a soil amendment have attracted the attention of an increasing number of researchers in the last decades. Although spruce sawdust did little to improve N retention in soils (Chapter 2), it can be a useful material for biochar production (Chapter 3). In acidic $(NH_4)_2SO_4$ solution, spruce biochar had the highest NH_4^+ retention capacity compared to oxidized biochar and leonardite due to its superior BET surface area. However, oxidized biochar had the highest NH_4^+ retention capacity in pH-adjusted $(NH_4)_2SO_4$ solution due to the introduction of oxygen-rich functional groups by Fenton oxidation, which increased the CEC of biochar and then promoted its adsorption capacity of NH_4^+. This difference is due to the fact that in acidic $(NH_4)_2SO_4$ solution, the high protonation of the oxygen functional groups may lead to a neutral or even positive surface charge, reducing the electrostatic attraction of NH_4^+ (Kizito et al., 2015; Novak et al., 2010), whereas the high surface area of biochar would be less affected by pH. In the pH-adjusted $(NH_4)_2SO_4$ solution, on the one hand, the surface area of biochar is not the main factor affecting the NH_4^+ adsorption capacity at neutral or even higher pH, and on the other hand, the surface area of the oxidized biochar is less protonated, so that the oxygen functional group had more adsorption sites for NH_4^+ (Bargmann et al., 2014; Spokas et al., 2012). Although oxidized biochar had the highest oxygen content and lowest pH, suggesting that it contained the most oxygen functional groups, it reduced NH_3 emissions less than leonardite. We speculate that the oxidized biochar contained additional cations, such as Ca, Fe and K, which may have competed with NH_4^+ for cation exchange sites on the surface of the oxidized biochar (Kizito et al., 2015).

Oxidized biochar was also more effective in reducing NH_3 emissions than untreated biochar when applied to soils with cattle slurry (Chapter 4), because the oxidized biochar had a lower pH and more oxygen functional groups. Application of oxidized biochar to marginal and acidic loamy sand soil together with cattle slurry increased soil DOC, which stimulated soil microbial activity and increased ^{15}N recovery in the microbial biomass, indicating that microbial utilization of N from cattle slurry was promoted (Banik et al., 2021).

These experimental results validate our hypothesis that the introduction of more oxygen functional groups in biochar improves its ability to adsorb NH_4^+ and reduce NH_3 emissions from animal slurries, thus improving soil N retention more effectively as a sustainable HCA.

6.2.3 Other factors that affect N loss from soils

The N cycle consists of several different processes, and there are many factors, such as the composition of the animal slurry, climate and soil type, that affect N loss from soils.

The composition of animal slurry usually varies depending on the type of animal, feed composition and storage time. In our study (Chapter 2), pig slurry treatments emitted more GHG and NH_3, possibly because cattle slurry had a lower NH_4^+ and a higher DOC content than pig slurry, which may have led to a stronger immobilization of available N in the soil amended with cattle slurry, resulting in the differences in gas emissions from pig and cattle slurry treatments (Burger & Jackson, 2003). Thus, differences in DOC and mineral N content in animal slurries have a significant impact on N content and microbial activity in soils, and ultimately affect N losses.

In the lysimeter experiment (Chapter 5), climatic factors, such as temperature and precipitation, played a very important role. In both years, cattle slurry was applied in spring, when soil temperatures were low, which greatly reduced the rate of mineralization and nitrification; at the same time, the crop was in a vigorous growth phase and was able to rapidly absorb N, so the cumulative gaseous N loss was low (Rahn, 2002; Sommer et al., 1997; Van Den Bossche et al., 2009). However, high rainfall in 2021 resulted in high N_2O emission rates, as the low O_2 conditions in the moist soil favored denitrification and N_2O production (Marinho et al., 2004). During this period, the cattle slurry and HCAs increased readily available C in the soil, stimulating both microbial biomass growth and denitrification-mediated N_2O emissions (Chen et al., 2013).

Soil type is another important factor related to N loss. In Chapter 4, N retention was tested in three soils with different textures after application of cattle slurry and (oxidized) biochar. Our data showed that NH_3 emissions from loamy sand were higher than from the other soils after application of cattle slurry because the high sand content reduced NH_4^+ fixation in the soil matrix (Lu et al., 2019; San Francisco et al., 2011). However, NH_3 emissions could be mitigated by adding biochar or oxidized biochar to improve NH_4^+ adsorption. In general, clay soils have a higher denitrification potential due to the lower gas diffusion in fine-textured soils, which reduces O_2 supply to the soil (Di & Cameron, 2002; van der Weerden et al., 2012) and may lead to higher rates of N_2O production (Groffman & Tiedje, 1989; van der Weerden et al., 2012). However, in our study, N_2O emission from loamy sand was higher after application of cattle slurry than in other soils. This could be due to the lack of significant water movement in all soils due to the maintenance of 60% WHC throughout the experiment. In addition, loamy sand had the lowest pH of 4.7, and significantly more N_2O emissions were reported from acidic than alkaline soils, which may be related to the sensitivity of post-transcriptional N_2O reductase to lower pH, which hampers N_2O reduction during denitrification (Fan et al., 2019; E. Liu et al., 2010).

6.3 Conclusions and outlook

As we hypothesized, HCAs have great potential to reduce N losses and improve N retention in soils treated with animal slurries, and thus can contribute to the protection of the environment and human health by mitigating global warming and ecosystem eutrophication. In addition, applying HCAs to soil is simple and does not require additional equipment, so the convenience of HCAs will make it more attractive to farmers than other methods of mitigating N losses.

Through this work, we were able to find answers to the questions we posed previously. First, we found that leonardite is the most suitable of the HCAs tested in this work that can effectively bind N when applied with animal slurry (pig and cattle slurry), mitigate N loss and improve N retention in the soil. Our results also verified that Fenton oxidation can introduce oxygen-rich functional groups in biochar and improve the adsorption capacity of biochar for NH_4^+, thus reducing NH_3 emissions from cattle slurry. Furthermore, when oxidized biochar was applied together with cattle slurry to three different soils, oxidized biochar reduced gaseous N losses and potentially increased microbial N immobilization, especially in the sandy soil. Finally, under field conditions in silty loam soil with winter wheat and winter barley, leonardite improved N retention in both seasons by reducing NH_3 emissions and leaching of mineral N, while leonardite did not reduce N nutrition of the crop.

Although this thesis clearly demonstrates that HCAs are an effective and feasible strategy for improving soil N retention, several aspects still need attention before large-scale application.

1. Long term field experiments: Although we conducted a two-year lysimeter experiment, the decomposition of organic matter of HCAs and animal slurries may affect the soil over a longer period of time. Therefore, it is of interest to understand the long-term effects of HCAs on soils and plants.
2. Further improvement of biochar adsorption capacity: In our study, the Fenton reaction did improve the NH_4^+ retention capacity of biochar as a sustainable alternative to leonardite. However, it did not bring it to the full level of leonardite. Therefore, future studies should focus on further improving the NH_4^+ adsorption and retention capacity by testing different oxidation conditions and methods to remove excess cations.
3. Oxidized biochar effect on crops: Under laboratory conditions without plants, oxidized biochar had beneficial effects on N retention in soils, but further studies are needed to confirm this effect under more realistic soil conditions with crops.
4. Integrated considerations: The N cycle is strongly influenced by climate, location, soil type, and other natural factors. Therefore, the use of HCAs in practice also requires appropriate planning based on climate, soil characteristics and crop type, such as application timing and application rates, to obtain the maximum benefit to the environment and production.

Appendix

Appendix A: supplemental material for chapter 2

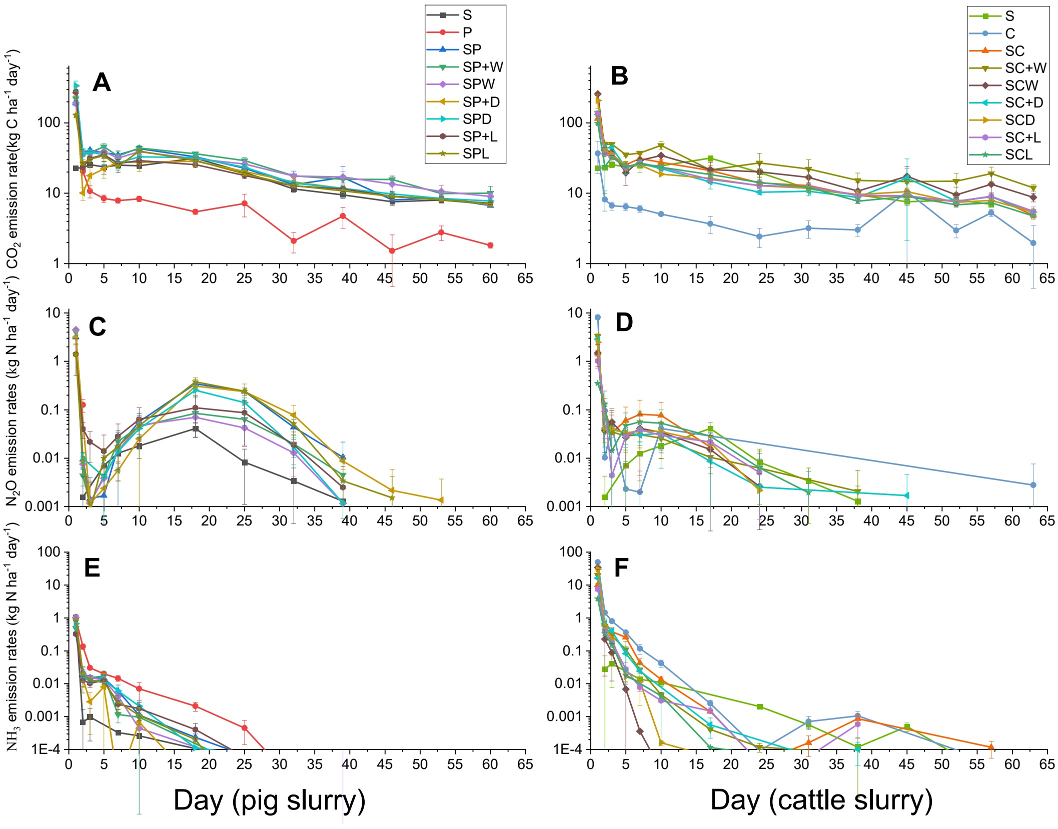

Figure A.1 *(A) Carbon dioxide (CO_2) emissions rates of pig slurry treatments; (B) CO_2 emissions rates of cattle slurry treatments; (C) N_2O emissions rates of pig slurry treatments; (D) N_2O emissions rates of cattle slurry treatments; (E) NH_3 emissions rates of pig slurry treatments; (F) NH_3 emissions rates of cattle slurry treatments. The abbreviations of treatments are: S – soil; P – pig slurry; C – cattle slurry; W – wheat straw; D – sawdust; L – leonardite; "+" – direct application of slurry and HCA to the soil; no "+" – slurry and HCA mixed overnight before application. Error bars show the standard error of the mean of each treatment (n = 3). Different lowercase letters indicate significant differences at the $p<0.05$ level between treatment.*

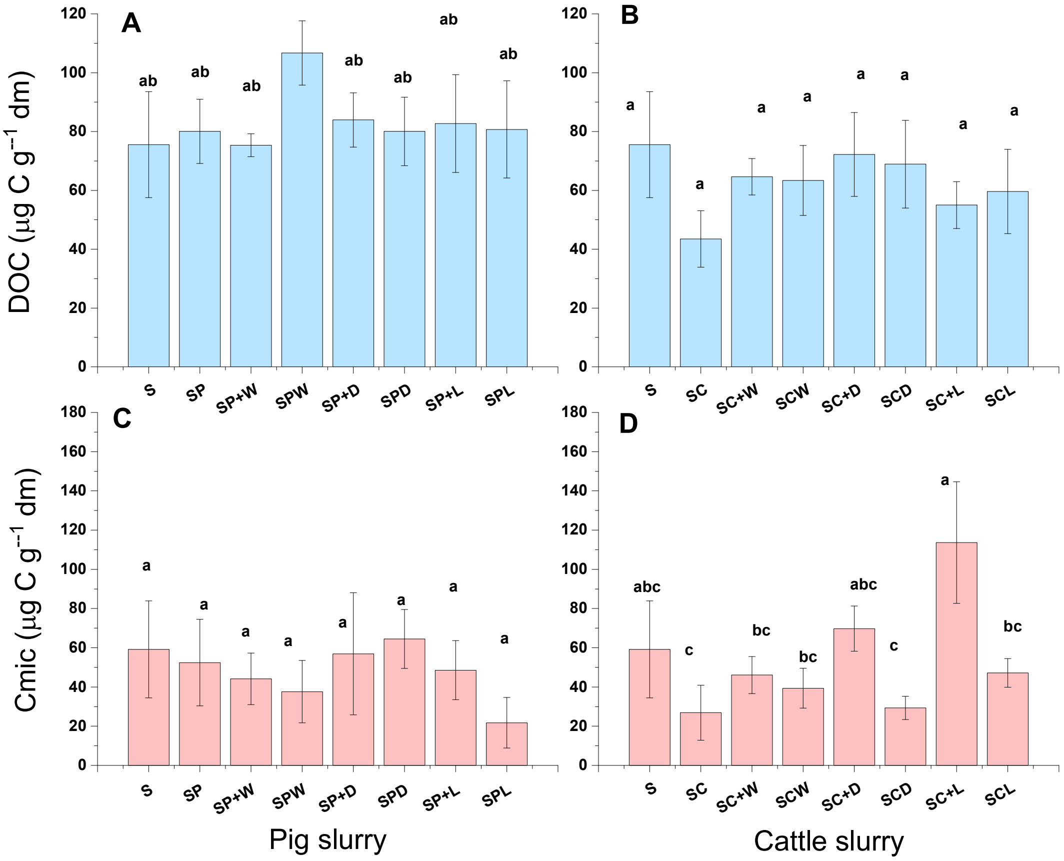

Figure A.2 *(A) Dissolved organic C (DOC) of pig slurry treatments in the sublayer of the soil; (B) DOC of cattle slurry treatments in the sublayer of the soil; (C)* C_{mic} *of pig slurry treatments in the sublayer of the soil; (D)* C_{mic} *of cattle slurry treatments in the sublayer of the soil. The abbreviations of treatments are: S – soil; P – pig slurry; C – cattle slurry; W – wheat straw; D – sawdust; L – leonardite; "+" – direct application of slurry and HCA to the soil; no "+" – slurry and HCA mixed overnight before application. Error bars show the standard error of the mean of each treatment (n = 3). Different lowercase letters indicate significant differences at the* $p<0.05$ *level between treatment.*

Table A.1 *Results of three-way ANOVA showing F values and level of significance for CO_2, N_2O, and NH_3 emissions, DOC, C_{mic} contents in the top layer of the soil, NO_3^- and pH in the top layer and sublayer of the soil, and ^{15}N recovery from the soil.*

Parameters	**Slurry**	**HCA**	**Application**	**Slurry×HCA**	**Slurry×application**	**HCA×application**	**Slurry×HCA×application**
CO_2	70.955^{***}	65.881^{***}	5.769^{*}	2.720^{NS}	1.195^{NS}	6.612^{**}	1.709^{NS}
N_2O	104.479^{***}	6.737^{**}	2.341^{NS}	4.295^{*}	0.285^{NS}	6.841^{**}	5.273^{**}
NH_3	41.263^{***}	11.844^{***}	16.963^{***}	13.309^{***}	54.319^{***}	2.419^{NS}	10.757^{***}
DOC (0-5 cm)	0.185^{NS}	4.400^{*}	0.320^{NS}	0.110^{NS}	0.120^{NS}	0.465^{NS}	0.253^{NS}
Cmic (0-5 cm)	0.855^{NS}	3.656^{*}	0.531^{NS}	0.343^{NS}	0.603^{NS}	1.110^{NS}	1.818^{NS}
NO_3^- (0-5 cm)	3.096^{NS}	14.621^{***}	0.693^{NS}	3.535^{*}	0.476^{NS}	1.344^{NS}	1.153^{NS}
NO_3^- (5-15cm)	12.875^{**}	3.065^{*}	13.805^{**}	1.830^{NS}	9.848^{**}	0.354^{NS}	2.500^{NS}
^{15}N recovery	12.168^{**}	31.771^{***}	0.050^{NS}	1.039^{NS}	4.880^{*}	8.505^{***}	2.307^{NS}
pH (0-5 cm)	2.670^{NS}	44.771^{***}	0.607^{NS}	9.382^{***}	0.142^{NS}	3.925^{*}	0.966^{NS}
pH (5-15 cm)	3.576^{NS}	2.288^{NS}	6.066^{*}	3.137^{*}	0.124^{NS}	0.496^{NS}	7.246^{**}

*Note. NS – not significant. Levels of significance: *$p<0.05$; **$p<0.01$; ***$p<0.001$*

Appendix B: supplemental material for chapter 3

Figure B.1 *Production of biochar.*

Figure B.2 *Oxidation of biochar.*

Appendix C: supplemental material for chapter 4

Table C.1 *Results of two-way ANOVA (soil and treatment) showing F values and level of significance for* CO_2*,* N_2O*,* NH_3*, and* N_2O *emissions, DOC,* NH_4^+*,* NO_3^-*,* C_{mic}*,* N_{mic} *contents,* ^{15}N *and* $^{15}N_{mic}$ *recovery in the top layer and sublayer of the soils.*

	Parameters	**Soil**	**Treatment**	**Soil×Treatment**
GHG emissions	CO_2	310.042^{***}	10.867^{***}	3.460^{*}
	N_2O	3.997^{*}	1.140^{NS}	2.184^{NS}
	NH_3	1.625^{NS}	96.932^{***}	5.579^{**}
	CH_4	44.854^{***}	6.302^{**}	1.620^{NS}
Top layer (0-5 cm)	pH	1414.665^{***}	12.149^{***}	5.373^{**}
	DOC	40.521^{***}	10.250^{***}	2.203^{NS}
	NH_4^+	3.103^{NS}	$.204^{NS}$	2.792^{*}
	NO_3^-	16.932^{***}	2.692^{NS}	0.428^{NS}
	C_{mic}	33.640^{***}	2.441^{NS}	1.087^{NS}
	N_{mic}	29.928^{***}	1.122^{NS}	1.615^{NS}
Sublayer (5-15cm)	pH	11378.607^{***}	1.250^{NS}	0.506^{NS}
	DOC	84.277^{***}	1.122^{NS}	0.986^{NS}
	NH_4^+	3.874^{*}	1.584^{NS}	1.117^{NS}
	NO_3^-	171.268^{***}	0.350^{NS}	0.549^{NS}
	C_{mic}	53.883^{***}	0.116^{NS}	1.399^{NS}
	N_{mic}	14.454^{***}	0.788^{NS}	0.996^{NS}
N recovery	^{15}N recovery	12.453^{***}	0.009^{NS}	0.268^{NS}
	$^{15}N_{mic}$ recovery	0.346^{NS}	1.595^{NS}	1.032^{NS}

Note. NS – not significant. Levels of significance: $^{*}p<0.05$*;* $^{**}p<0.01$*;* $^{***}p<0.001$

Appendix D: supplemental material for chapter 5

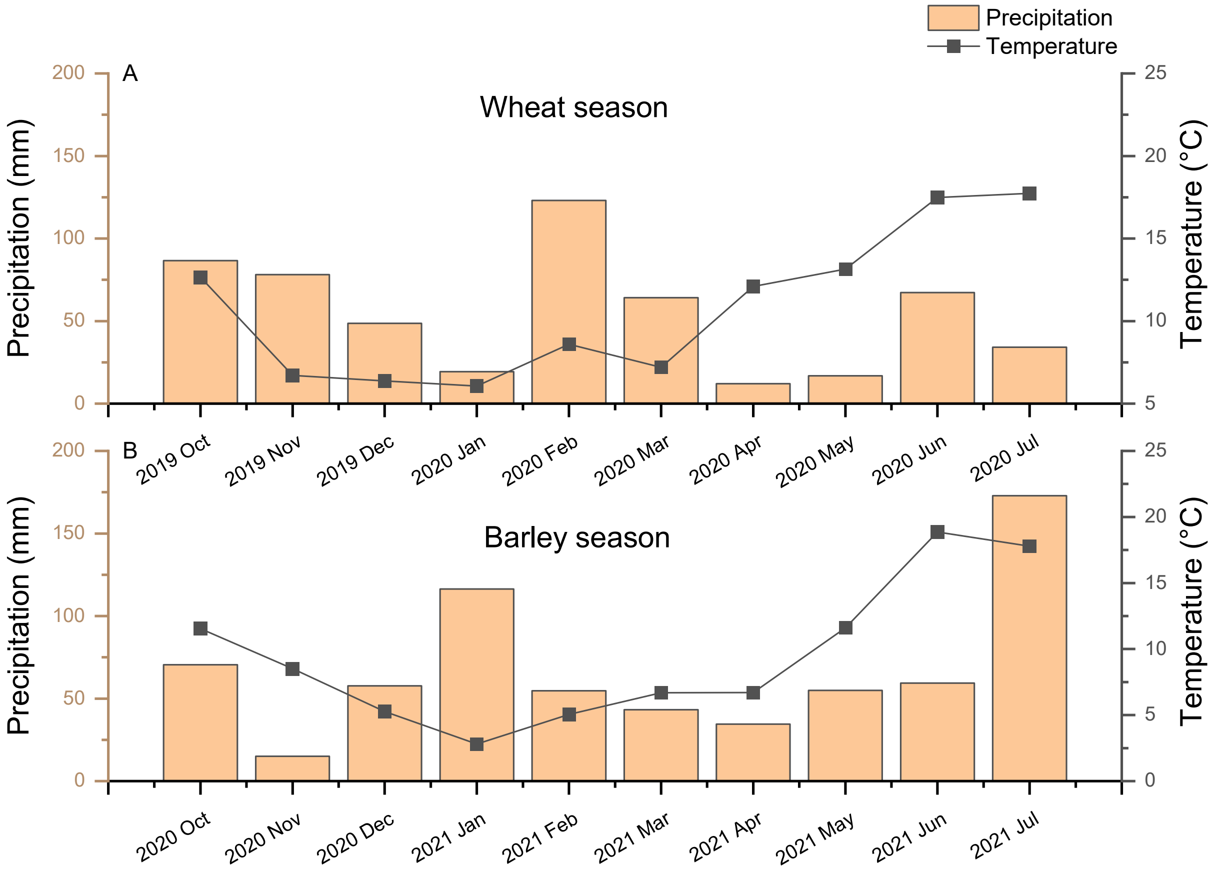

Figure D.1 *(A) The climate data in wheat season (from 2019 October to 2020 July); (B) The climate data in barley season (from 2020 October to 2021 July)*

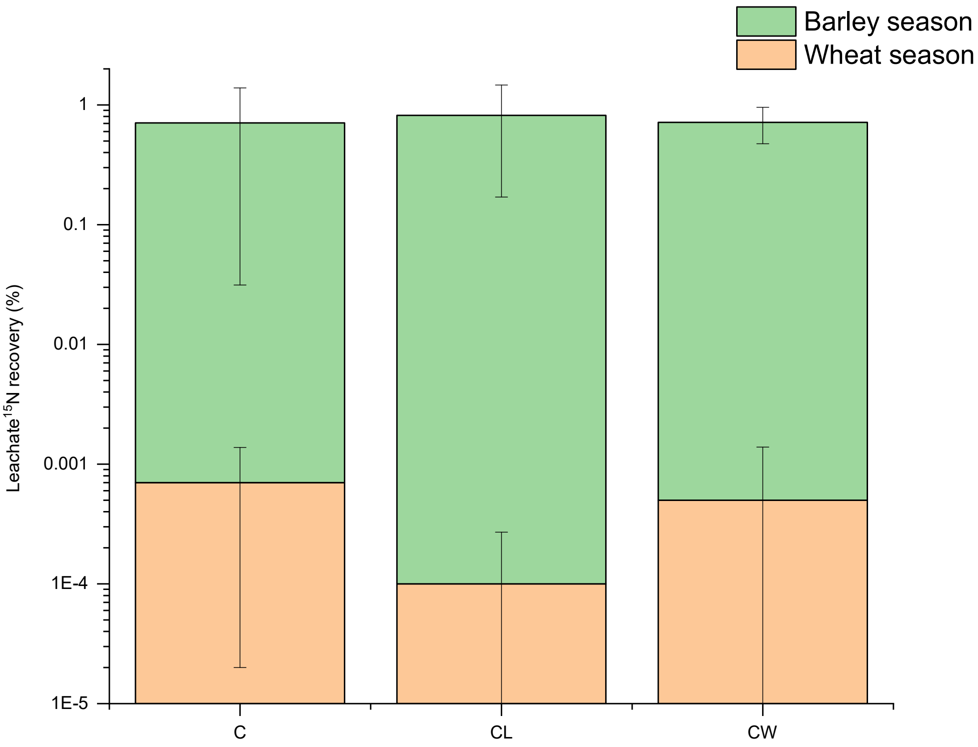

Figure D.2 *Leachate ^{15}N recovery. The abbreviations of the treatments are as follows: C – cattle slurry; L – leonardite; W – wheat straw. The error bars show the standard error of the mean of each treatment (n = 3). There is no significant difference between treatments.*

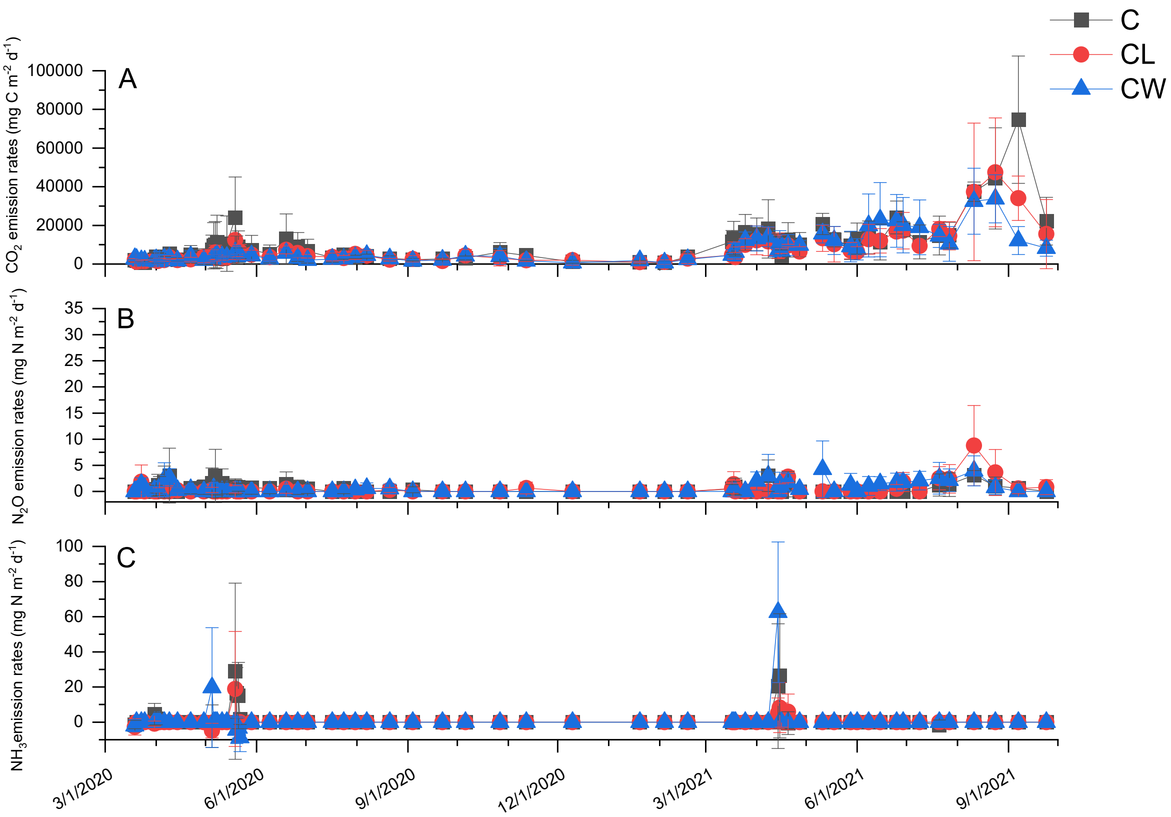

Figure D.3 *(A) Carbon dioxide (CO_2) emissions rates; (B) N_2O emissions rates; (C) NH_3 emissions rates. The abbreviations of the treatments are as follows: C – cattle slurry; L – leonardite; W – wheat straw. The error bars show the standard error of the mean of each treatment (n = 3).*

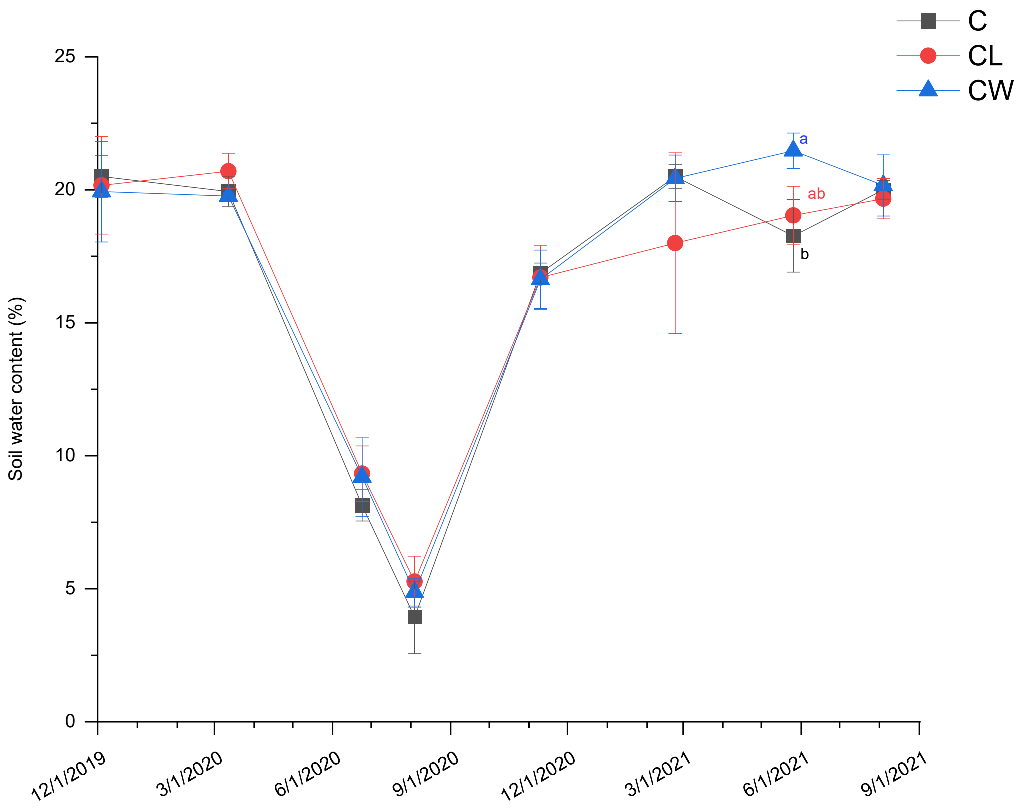

Figure D.4 *Soil gravimetric water contents. The abbreviations of the treatments are as follows: C – cattle slurry; L – leonardite; W – wheat straw. The error bars show the standard error of the mean of each treatment (n = 3). The different lowercase letters indicate significant differences at the p<0.05 level between treatment. The absence of lowercase letters means that there is no significant difference between treatments.*

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