

Effects of activated charcoal and quebracho tannins on the turnover of goat manure in irrigated organic agriculture of the subtropics

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Dedicated to my parents who inspired me to follow this way.

“All in all it was just a brick in the wall.”

The Wall

Pink Floyd, 1979

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Summary

Agriculture in semi-arid and arid regions is constantly gaining importance for the security of the nutrition of humankind because of the rapid population growth. At the same time, especially these regions are more and more endangered by soil degradation, limited resources and extreme climatic conditions. One way to retain soil fertility under these conditions in the long run is to increase the soil organic matter. Thus, a two-year field experiment was conducted to test the efficiency of activated charcoal and quebracho tannin extract as stabilizers of soil organic matter on a sandy soil low in nutrients in Northern Oman. Both activated charcoal and quebracho tannin extract were either fed to goats and after defecation applied to the soil or directly applied to the soil in combination with dried goat manure. Regardless of the application method, both additives reduced decomposition of soil-applied organic matter and thus stabilized and increased soil organic carbon. The nutrient release from goat manure was altered by the application of activated charcoal and quebracho tannin extract as well, however, nutrient release was not always slowed down. While activated charcoal fed to goats, was more effective in stabilising soil organic matter and in reducing nutrient release than mixing it, for quebracho tannin extract the opposite was the case. Moreover, the efficiency of the additives was influenced by the cultivated crop (sweet corn and radish), leading to unexplained interactions. The reduced nutrient release caused by the stabilization of the organic matter might be the reason for the reduced yields for sweet corn caused by the application of manure amended with activated charcoal and quebracho tannin extract. Radish, on the other hand, was only inhibited by the presence of quebracho tannin extract but not by activated charcoal. This might be caused by a possible allelopathic effect of tannins on crops. To understand the mechanisms behind the changes in manure, in the soil, in the mineralisation and the plant development and to resolve detrimental effects, further research as recommended in this dissertation is necessary. Particularly in developing countries poor in resources and capital, feeding charcoal or tannins to animals and using their faeces as manure may be promising to increase soil fertility, sequester carbon and reduce nutrient losses, when yield reductions can be resolved.

Zusammenfassung

Die Landwirtschaft in semi-ariden und ariden Gebieten gewinnt aufgrund des rasanten Bevölkerungswachstums ständig an Bedeutung für die Sicherung der Ernährung der Menschheit. Gleichzeitig sind gerade diese Gebiete durch Bodendegradation, knappe Ressourcen und Extremwetterbedingungen immer stärker bedroht. Ein Ansatz, die langfristige Fruchtbarkeit der Böden unter diesen Bedingungen zu erhalten, ist die organische Substanz im Boden zu erhöhen. In einem zweijährigen Feldversuch wurde daher die Effizienz von Aktivkohle und Quebracho-Tanninen als Stabilisatoren der organischen Bodensubstanz in einem nährstoffarmen sandigen Boden im Norden Omans getestet. Sowohl Aktivkohle als auch Quebracho-Tannine wurden entweder an Ziegen verfüttert und nach der Ausscheidung über den Ziegenkot in den Boden eingearbeitet oder direkt in Kombination mit getrocknetem Ziegenkot appliziert. Beide Zusatzstoffe verringerten unabhängig der Applikationsmethode den Abbau der organischen Substanz im Boden und trugen somit zu einer Stabilisierung und Vermehrung des organischen Kohlenstoffs im Boden bei. Auch die Nährstofffreisetzung aus dem Kot konnte durch den Zusatz der Aktivkohle und der Quebracho-Tannine verändert werden, wobei dies nicht immer zu einer verlangsamten Freisetzung führte. Während verfütterte Aktivkohle wirksamer in der Stabilisierung der organischen Substanz im Boden und der Verlangsamung der Nährstofffreisetzung als direkt auf den Boden applizierte Aktivkohle war, galt für die Quebracho-Tannine das Gegenteil. Die Wirksamkeit der beiden Substanzen wurde zudem von der angebauten Fruchtart (Zuckermais oder Rettich) beeinflusst, was zu untersuchenden Wechselwirkungen führte. Die Verlangsamung der Nährstofffreisetzung durch die Stabilisierung der organischen Substanz könnte ein Grund für die reduzierten Erträge von Zuckermais durch Aktivkohle und Quebracho-Tannine sein. Der Rettich hingegen wurde nur durch die Anwesenheit von Quebracho-Tanninen gehemmt, während Aktivkohle keine Ertragseinbußen verursachte. Dies könnte an einer allelopathischen Wirkung der Tannine liegen. Insbesondere für Entwicklungsländer mit geringen Ressourcen und Kapital könnte das Verfüttern von Kohle und Tannine an Tiere und die anschließende Nutzung deren Kotes als Dünger ein vielversprechendes Mittel zur Verbesserung der Bodenfruchtbarkeit, Kohlenstoffsequestrierung und Reduzierung von Nährstoffverlusten sein. In Langzeitversuchen könnte geklärt werden, ob

langfristig mit Ertragseinbußen zu rechnen ist oder ob die mehrjährige Applikation von Kohle oder Tanninen zu einer deutlichen Verbesserung der Bodeneigenschaften führt, die sich im Ertrag widerspiegelt.

Chapter 1

General introduction, objectives and hypotheses

1.1 Introduction

1.1.1 Agriculture in semi-arid and arid regions

The majority of the population in arid and semi-arid regions, which is about one third of the human population, depend on agriculture and pastoralism for their livelihood (Millennium Ecosystem Assessment 2005). Despite the unfavourable conditions for agriculture, land use is spreading and intensifying on the 41% of dry land areas, as elsewhere in the world, to support the fast growing population. The growing population and the limited available resources create a delicate situation susceptible to production failure and already 10-20% of the world's drylands are degraded (Millennium Ecosystem Assessment 2005). Nevertheless, the millennia old Omani oases proved that sustainable crop-livestock systems are possible even under extreme conditions of a harsh environment. The highly sophisticated irrigation systems and the traditional annual goat manure applications of up to 30 t ha⁻¹ contributed to the sustainability of the multi-storey cultivation of perennial and annual species in Omani oases (Al-Marshudi 2001; Nagieb et al. 2004; Siebert et al. 2007).

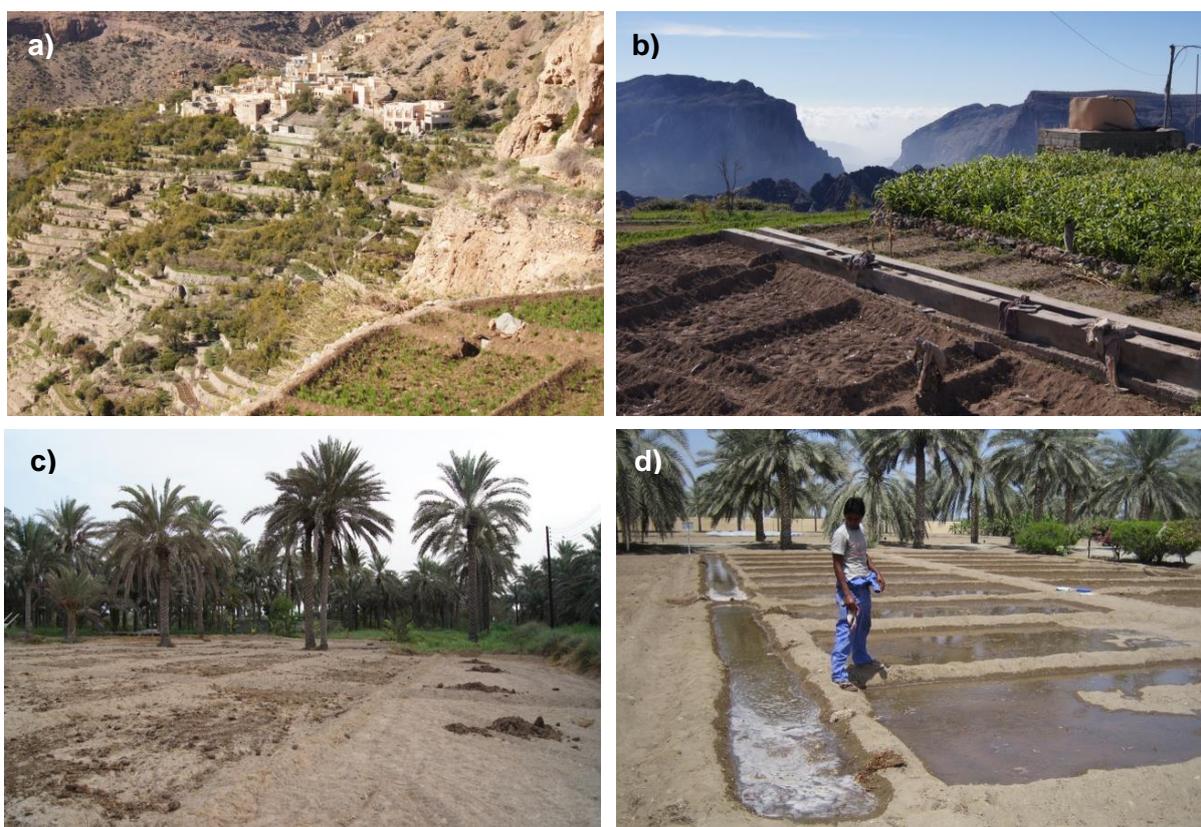


Figure 1.1. a) Traditional terrace oasis in the Al Jabal al Akhdar mountains, b) traditional fields with irrigation channel, c) application of animal manure on a coastal farm, d) traditional flood irrigation in the field experiment in Sohar.

However, with the intensification of agriculture over the last 40 years, major problems regarding soil and water salinity, depletion of soil fertility and overuse of water resources have arisen in Oman (FAO 1993). Despite its poor water use efficiency, surface irrigation is still the major method used in many regions in the semi-arid and arid tropics such as Oman (FAO 1993), because modern irrigation technologies are expensive and more complex in handling. In addition, the soils in semi-arid and arid regions often have low soil fertility characterized by low concentrations of plant available nutrients, such as nitrogen (N), phosphorus (P), and many micronutrients (Bationo et al. 2007). The low soil organic matter (SOM) content of the mainly sandy soils in Oman results in a poor physical soil structure, low moisture holding capacity and cation exchange capacity (CEC; Schjønning et al. 1994; Gao and Chang 1996; Nyamangara et al. 2001; Rasool et al. 2008;), which can only be improved by regular application of organic matter (OM) due to high turnover rates in the Subtropics (Bationo et al. 2007). On cultivated land in the Subtropics, frequent wet-dry cycles induced by flood-irrigation and year-round high soil temperatures cause a high microbial nutrient turnover of organic soil amendments (Austin et al. 2004). This can lead to high nutrient and carbon (C) losses with leaching waters (Jalali 2005) and gaseous emissions (Dalal et al. 2003; Siegfried et al. 2011). Thus, SOM is strongly linked with soil productivity particularly on sandy soils with low clay contents (Micheni et al. 2004; Lal 2006;) and an increase of SOM on degraded soils may consequently increase crop yields and reduce nutrient losses at the same time (Lal 2006; Bationo et al. 2007).

For these reasons, it is particularly important to maintain SOM on a long term basis. The repeated application of OM in the form of animal manure, green manure and compost has proved to increase SOM of subtropical soils in various studies (Nyamangara et al. 2001; Rasool et al. 2008; Sukartono et al. 2011; Schulz and Glaser 2012). However, under the conditions of an arid cultivated soil the residual effect of sheep and goat manure application decreases rapidly within the first five years after the last application (Freschet et al. 2008) and explains the importance of regular inputs of OM in these systems.

Animal manure is one of the major nutrient sources used by farmers particularly in small-scale agro-pastoral systems in semi-arid West Africa and in other dry regions (Williams 1999; Rufino et al. 2007; Freschet et al. 2008; Materechera 2010). Either

farmers keep their own livestock for the generation of food, income and manure or have contractual arrangements with herders to keep animals on harvested fields for browsing and at the same time fertilizing the field with their droppings (Williams 1999). In Oman, 70% of the ruminants that are kept are goats (FAO 2012), because they are adapted to the harsh environmental conditions (Lu 1989; Silanikove 2000). The manure from animals kept in stalls and overnight corrals is an easily available nutrient source for agricultural production. However, the quality of manure varies tremendously depending on the storage conditions (Rufino et al. 2006; Predotova et al. 2010) and fodder quality. Al-Asfoor et al. (2012) reported in a recent study that a high C/N ratio and a high neutral detergent fibre (NDF)/soluble carbohydrate ratio in buffalo diets increased the C/N ratio and NDF concentration of buffalo manure compared to low ratios. The application of this manure resulted in less negative or even positive C balances on an irrigated vegetable field in Oman compared with manure from buffalos fed a diet of low C/N ratio and low NDF/soluble carbohydrate ratio (Siegfried et al. 2011). Another study by Powell et al. (1994) revealed a strong relationship between the forms of N voiding with the N and P concentration, lignin/N ratio, lignin/NDF ratio and polyphenol/N ratio of various forage leaves. Not only the manure composition (the amount and form of C and nutrients) is affected by different diet compositions, but also the excretory pathway of N can be shifted from urine to faeces, reducing possible ammonia losses via volatilization (Powell et al. 1994; Delve et al. 2001). In addition, the faecal microbial community can change significantly in reaction to different diet compositions, which influences N mineralization as well as N₂O emissions from soil applied manure (Jost et al. 2013). Thus, by altering the diet composition to more stable components and higher C/N ratios, it is possible to increase C and nutrient retention in the manure and reduce losses via leaching and volatilization. Two additives which have the potential to reduce OM degradation in the animal digestive system and in soils are introduced in the following.

1.1.2 Charcoal in agriculture – a review

In recent years, the application of charcoal to soils has become the subject of intensive research as it is believed that it sequesters C in soils and thus mitigates climate change. In this context, the charcoal applied to agricultural or forest soils is referred to as “biochar” (Lehmann and Joseph 2009) comprising a group of

heterogeneous carbonized materials. The physico-chemical properties of biochar are highly dependent on the feedstock and the pyrolyzing conditions (temperature and pressure; Joseph et al. 2007; Uchimiya et al. 2011; Cantrell et al. 2012). Biochars made from different feedstock (wood, straw, bone meal, manure etc.) under varying pyrolysis conditions show a high diversity in a great number of parameters, such as ash contents between 4-70%, surface areas between 10-2500 m² g⁻¹, bulk densities between 0.1-2.0 g cm⁻³, pH values between 6-10 and C concentrations ranging from 17-91%, N concentrations from 0.2-8% and C/N ratios from 7-400 or even more (Brewer et al. 2009; Chan and Xu 2009; Downie et al. 2009; Cantrell et al. 2012). A growing number of publications deal with the stability of biochar in soils and the effects of biochar application on greenhouse gas emissions, soil properties, soil biology, soil nutrients and plant response (Van Zwieten et al. 2008; Lehmann et al. 2011; Mukherjee and Lal 2013; Kuzyakov et al. 2014). Under certain conditions, biochar application either as a single soil amendment or in combination with mineral fertilizer, organic manure or compost can improve soil structure, physico-chemical properties and reduce C and nutrient losses (Yamato et al. 2006; Steiner et al. 2007; Laird 2008; Uzoma et al. 2011). However, such beneficial effects were not always observed (Major et al. 2010; Van Zwieten et al. 2010; Lentz and Ippolito 2012) and may differ with biochar properties, soil properties and experimental conditions. The greater number of positive reports leads people to generalize the beneficial effects of biochar applications. However, the majority of biochar research was conducted on infertile acidic soils either in the field or in laboratory experiments (Glaser et al. 2002; Lehmann and Rondon 2006; Steiner et al. 2007). In the few studies conducted on calcareous sandy soils, these beneficial effects are not that apparent (Van Zwieten et al. 2010; Lentz and Ippolito 2012). The major impact of the mostly alkaline biochars on acidic soils seems to result from a liming effect, increasing soil pH, CEC, nutrient availability and reduced aluminium toxicity (Van Zwieten et al. 2010). However, changes in nutrient cycles and soil structure (Steiner et al. 2008) may also be related to modification of soil microbial community and abundance (Pietikäinen et al. 2000). Depending on its properties, biochar can provide improved hydration, greater nutrient availability, higher pH, adsorption of inhibitory compounds and a habitat for soil microorganisms (Lehmann et al. 2011). The fresh application of biochar can stimulate the activity of microbial enzymes in soils, increase mycorrhizal root colonization but decrease saprophytic fungal growth (Quilliam et al. 2012;

Oleszczuk et al. 2014). Thus, the addition of labile C sources by biochar can influence soil microbial biomass, activity and community structure, which alters the mineralization of biochar as well as soil organic carbon (SOC; Lehmann et al. 2011). Even though positive and negative priming effects on mineralization were observed in short term, depending on the properties of biochar (Zimmerman et al. 2011), a long-term accumulation of SOC is reported by most authors (Rogovska et al. 2011; Lentz and Ippolito 2012; Kuzyakov et al. 2014). The higher SOC content in biochar-enriched soils is often combined with a higher water holding capacity (WHC), CEC and nutrient concentrations in soils (Jha et al. 2010; Laird et al. 2010; Uzoma et al. 2011), which can lead to increased crop yields (Yamato et al. 2006; Chan et al. 2008; Zhang et al. 2012). However, the effects on yields also depend on the N supply, as higher SOC leads to an increase in the C/N ratio and greater immobilization of N (Nelson et al. 2011). Schulz and Glaser (2012) showed that a single biochar application of 40 t ha⁻¹ on a sandy soil did not increase oat yields compared to pure sand, but in combination with fertilizer or compost, perceptible yield increases were observed. Nonetheless, the combination of biochar applications with animal manure has scarcely been investigated. A stabilization of manure by biochar application is possible (Laird et al. 2010; Rogovska et al. 2011), but may also result in unchanged or even reduced yields due to higher C/N ratios and N immobilization (Lentz and Ippolito 2012).

In Europe, 90% of the charcoal is used in animal feed, barnyard litter or for slurry treatment prior to soil application (Gerlach 2012). To avoid harmful substances in animal nutrition, AC as a highly purified, pollution-free product is often used. However lately, cheaper non-activated charcoal derived from plant biomass has become available for animal nutrition. Charcoal use in animal production is known to improve animal health, reduce the emissions of greenhouse gases such as methane and deodorize manure. However, scientific proof of the above mentioned effects is limited. Increased growth rates (Van et al. 2006; Leng et al. 2012), the detoxification of bacterial toxins, mycotoxins, plant toxins and herbicides by activated charcoal (Poage et al. 2000; Huwig et al. 2001; Watarai et al. 2008; Wang et al. 2010) and reduction of methane emissions from ruminants (Leng et al. 2012) have, however, been reported by a few authors. The reduced methane production of ruminants fed with charcoal indicates an altered digestion process caused by the ingested

charcoal. As charcoal affects the microbial community composition and activity in soils, it is likely that this is also the case for the microbial community within the gastrointestinal tract of animals. However, up to date no such research is reported in the literature. This is also the case for the effects of charcoal-enriched manure, obtained from feeding charcoal to animals. Due to the high stability of charcoal it is assumed to pass undigested through the gastrointestinal tract of the animals and will enter the soil ecosystem via manure application.

1.1.3 Polyphenols (particularly condensed tannins) in agriculture – a review

The relevance of polyphenols to terrestrial and animal ecosystems derives from the wide distribution of this class of secondary plant metabolites in the plant kingdom, including many browse species in the tropics and subtropics (White 1957; Hättenschwiler and Vitousek 2000; Muir 2011). Within the class of polyphenols, a heterogeneous group of mainly water soluble phenolic polymers, known as tannins, is characterized by a strong ability to bind and precipitate proteins, polysaccharides, metal ions and bacterial cell membranes (Davies et al. 1964; Spencer et al. 1988; Kraus et al. 2003). There are two groups of tannins, hydrolysable tannins and condensed tannins or proanthocyanidins, which can be distinguished by the ability of the first and inability of the second to be broken down by acids or bases (White 1957). Condensed tannins are the main component of the quebracho tannin extract from the bark of *Schinopsis balansae* used in this study.

Oades (1988) summarized some studies about the decomposition rates of ^{14}C and ^{15}N labelled organic substances and stated that polyphenols can persist in soils for years and even protect proteins and polysaccharides by interacting with them in a “tanning” reaction. Since that review was published, several studies discussing tannins from plant litter have revealed their potential in reducing N mineralization, reducing nitrification, and decreasing OM decomposition in soil (Powell et al. 1994; Northup et al. 1998; Bradley et al. 2000; Kraus et al. 2004; Kanerva et al. 2006; Adamczyk et al. 2013a; Adamczyk et al. 2013b). However, these studies mainly focus on tannins and polyphenols from plant litter in forest ecosystems. Palm and Sanchez (1991) and Oglesby and Fownes (1992) showed that in the presence of polyphenols, OM decomposition is not correlated to its C/N ratio, as usually observed, but rather to the substrate’s polyphenol/N ratio. Hättenschwiler and

Vitousek (2000) pointed out two mechanisms by which polyphenols may interact with nutrient cycling: effects on the activity of soil organisms, and physico-chemical effects on nutrient pools. The effects of polyphenols on soil organisms can be inhibitory or stimulating depending on the organisms and the polyphenol type. Saprotrophic fungi and mycorrhizal fungi were found to be inhibited by some polyphenols and stimulated by others, while bacteria seem to be generally unaffected or inhibited (Wu et al. 2003; Mutabaruka et al. 2007). The effects of tannins on the soil macrofauna, however, have scarcely been investigated (Coulis et al. 2009). The physico-chemical effects identified include the reduction of N availability by forming complexes with proteins, increasing CEC by providing negative sorption sites and may also play a role in the reduction of aluminium toxicity by complexation with sesquioxides and preventing phosphate immobilisation (Frazier et al. 2010; Halvorson et al. 2011; Halvorson et al. 2012). However, these effects of polyphenols have mainly been investigated under laboratory conditions and their behaviour in the field seems to be quite complex.

On agricultural soils, the usage of plant biomass as green manure is in conflict with its use as animal fodder. The significance of condensed tannins in animal nutrition is reflected in the numerous publications reporting the effect of tannins on animals. Tanniniferous fodder can have positive effects on animals such as increasing milk production and growth rates, as well as reducing methane emissions, bloat and parasite infections (Aerts et al. 1999; Puchala et al. 2005; Bhatta et al. 2011), but also lead to a reduction of fodder digestibility and toxicity at high concentrations (Makkar 2003). In addition, tannins in animal diets improve N cycling as they shift N excretion from urine to faeces, which reduces volatile N losses (Makkar 2003; Hess et al. 2006). James Muir (2011) summarized the multi-faceted role of condensed tannins in the cutting edge of the plant-animal-environment interface. In his conclusions he addressed the open question if condensed tannins may be an agent delaying faecal OM decay and enhancing C sequestration.

Powell et al. (1999) showed in a comparison of the direct soil application of a variety of browse leaves with faeces derived from sheep fed with the same browse leaves, that N use efficiency of millet and P mineralization was higher in faeces than in the corresponding browse leaves. By binding to proteins and fibre components, tannins can alter manure quality. Feeding different types of tanniniferous fodder

changed N and P concentrations, NDF and acid detergent fibre (ADF) contents and the proportion of insoluble to soluble N of manure (Powell et al. 1994; 2009). However, the fate of tannins in the animal's digestive system is yet unclear. Condensed tannins are not absorbed by the animals (Terrill et al. 1994) and not degraded by rumen microbes (Makkar et al. 1995). However, tannins undergo some conformational changes as only a smaller amount of tannins can be extracted from the faeces (Degen et al. 1995).

The effect of tannins on manure turnover in the soil, either when applied directly or after having passed through an animal's digestive system, has not been investigated. Only a few studies deal with the influence of tannin-enriched manure on fertilizer value (Powell et al. 1994; Tiemann et al. 2009) and none with respect to their C sequestration potential. Tiemann et al. (2009) applied manure from sheep fed with a supplement of different tannin containing tropical shrub legumes on an acidic infertile soil to test its fertilizer value for a *Brachiaria* grass hybrid. Dry matter yield and N uptake by *Brachiaria* were not significantly influenced by feeding tannins. However, it seemed that N was not the limiting nutrient in the study, which might have masked any negative effects on N fertilizer value. Besides, there is an indication from a laboratory incubation experiment that feeding of tanniferous browse reduces NH₃ volatilization from cow slurry applied to soil (Powell et al. 2011). Nevertheless, tannins and other phenolics are potential allelopathic agents and may inhibit the development of crops fertilized with tannin-enriched manure (Stoms 1982; Sinkkonen 2006).

1.2 Research area

The research was conducted on a private farm in Sohar (24.2°N, 56.8°E, 4 m a.s.l.) in the Al-Batinah plain, Northern Oman (Fig. 1.2a), which is one of the most important and intensively cultivated agricultural regions in Oman. Sustainable oasis agriculture has been the economic and cultural backbone of Oman for thousands of years (Korn et al. 2004; Nagieb et al. 2004). In the Al-Batinah plain, 80% of the agricultural area is characterized by a sandy or coarse loamy soil, with low soil fertility, high lime content and low nutrient holding capacity (FAO 1993). The sandy soil of the experimental area was classified as hyperthermic Typic Torrifluent with 82% sand, 16% silt and 2 % clay in the upper 0.5 m layer (Siegfried et al. 2011)

and a pH of 8.7. Despite the intensification of agriculture in Oman, most farmers still use traditional surface irrigation and animal manure as major fertilizer, leading to low water and nutrient use efficiencies (FAO 1993).

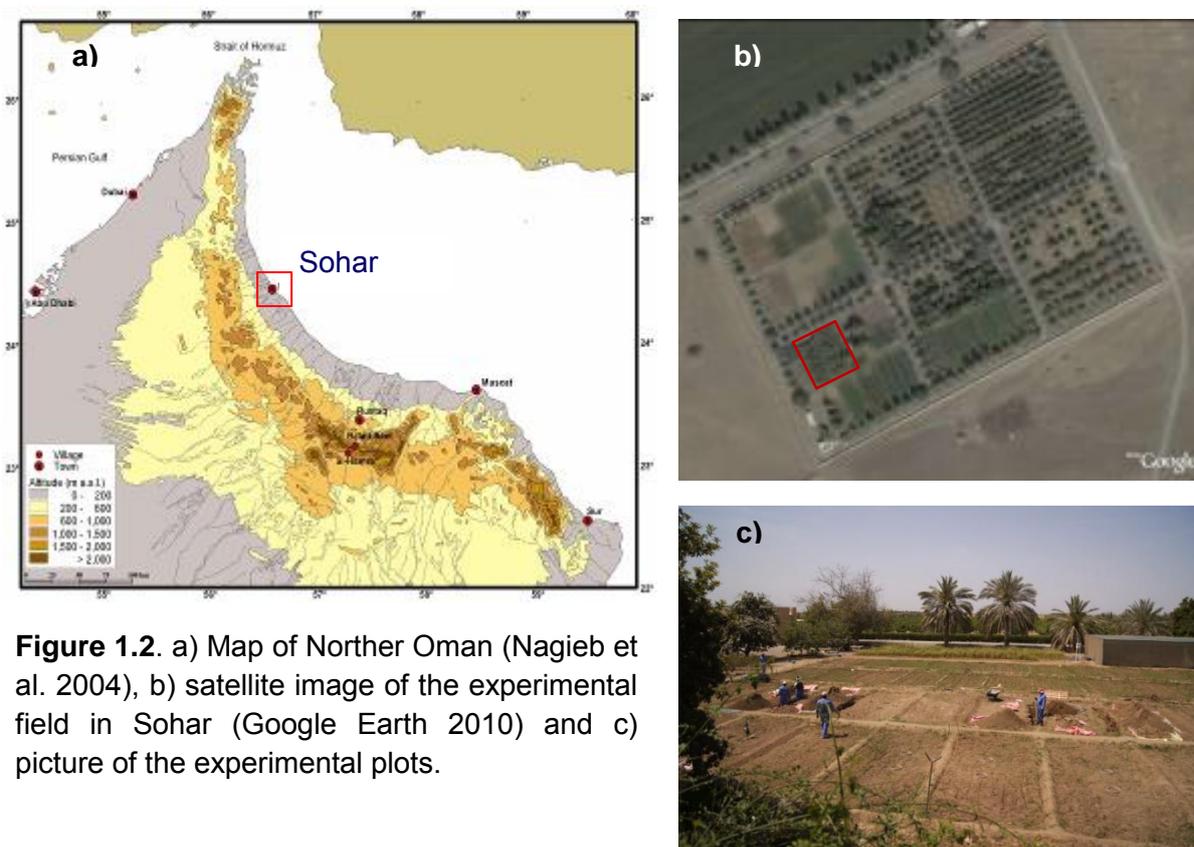


Figure 1.2. a) Map of Northern Oman (Nagieb et al. 2004), b) satellite image of the experimental field in Sohar (Google Earth 2010) and c) picture of the experimental plots.

The climate in Oman is hot with extremely low annual precipitation. In the coastal areas, the year can be divided into two major seasons: a hot and dry summer season and a cooler winter season, with a vegetation period from end of September to mid of May. The average annual precipitation in Sohar over the last 23 years was 109 mm (WMO 2009). The annual average temperature was 27°C with annual mean maximum temperatures of 31°C and annual mean minimum temperatures of 22°C. During the two-year field experiment, the annual precipitation was with 9 and 50 mm in 2010/11 and 2011/12, respectively - both lower than the 30-year-average. Annual average temperature in both years was 28°C with a mean temperature of 24°C during the cropping seasons from October to April. Maximum temperatures reached up to 48°C in May and minimum temperatures between 9-10°C were reached in December to January. Evapotranspiration exceeds precipitation all year round in Northern Oman.

1.3 Overall objective and research question

The overall objective of the research project was to investigate the effect of AC and QT amendments on the quality of manure, the soil properties, and on crop yields under intensive, irrigated vegetable production in Northern Oman. The basic underlying research question was whether AC or QT are useful additives to stabilize SOM and increase nutrient retention in order to improve soil fertility under extreme environmental conditions in the long-run.

1.4 Hypotheses

The following hypotheses were tested in the current research project:

1. Activated charcoal and QT slow down decomposition of goat manure increasing SOM and thus improve soil properties and plant productivity.
2. Activated charcoal and QT affect different pathways to stabilize SOM.
3. Feeding AC and QT is more effective in stabilizing OM in soils than mixing it directly to the soil.

1.5 Experimental setup and thesis outline

A pre-experiment was conducted in Göttingen and Witzenhausen, Germany, to test which concentrations of AC and QT were feasible and most promising to stabilize SOM. Thus, a total of 10 goats were fed with diets containing different concentrations of AC (1.5 and 3% of daily diet) and QT extract (2 and 4%) to collect manure for two climate chamber experiments. One experiment dealt with the effect of the different goat manure types on the early development of radish (*Raphanus sativus* L.), the second with the gaseous emissions of CO₂, N₂O and NH₃ from soils incubated with the different manure types. In this context, the effect of ingested AC and QT was compared with directly application of the amendments to the soil.

To test the hypotheses, a two-year field experiment was conducted in Northern Oman investigating the effects of feeding 2.5% AC and 3.6% QT extract to goats on the composition of their manure and the effects of this amendment-enriched manure (via feeding or direct application) on OM decomposition, soil properties, soil microbial activity and plant development in the field.

The results of the field experiment are discussed in the next three chapters following this introduction. The three chapters are followed up by a general discussion, recommendations and conclusions.

1.6 References

- Adamczyk, B., Kitunen, V. and Smolander A., 2013a. Response of soil C and N transformations to condensed tannins and different organic N-condensed tannin complexes. *Applied Soil Ecology* 64, 163-170.
- Adamczyk, S. Kiikkilä, O., Kitunen, V. and Smolander A., 2013b. Potential response of soil processes to diterpenes, triterpenes and tannins: Nitrification, growth of microorganisms and precipitation of proteins. *Applied Soil Ecology* 67, 47-52.
- Aerts, R.J., Barry, T.N. and McNabb, W.C., 1999. Polyphenols and agriculture: beneficial effects of proanthocyanidins in forages. *Agriculture, Ecosystems and Environment* 75, 1-12.
- Al-Asfoor, H., Schlecht, E., Sundrum, A. and Schiborra, A., 2012. Varying the dietary supply of C and N to manipulate the manure composition of water buffalo heifers in Oman. *Journal of Agriculture and Rural Development in the Tropics and Subtropics* 113, 125-136.
- Al-Marshudi, A.S., 2001. Traditional Irrigated Agriculture in Oman. *Water International* 26, 259-264.
- Austin, A.T., Yahdjian, L., Stark, J.M., Belnap, J., Porporato, A., Norton, U., Ravetta, D.A. and Schaeffer, S.M., 2004. Water pulses and biogeochemical cycles in arid and semiarid ecosystems. *Oecologia* 141, 221-235.
- Bationo, A., Kihara, J., Vanlauwe, B., Waswa, B. and Kimetu, J., 2007. Soil organic carbon dynamics, functions and management in West African agro-ecosystems. *Agricultural Systems* 94, 13-25.
- Bhatta, R., Shinde, A.K., Vaithyanathan, S., Sankhyan, S.K., Enishi, O. and Kurihara, M., 2011. Utilisation of tannin-containing tree leaves in sheep and goat production. Successes and failures with animal nutrition practices and technologies in developing countries, *FAO Electronic Conference Rome, Italy*.
- Bradley, R.L., Titus, B.D. and Preston C.P., 2000. Changes to mineral N cycling and microbial communities in black spruce humus after additions of $(\text{NH}_4)_2\text{SO}_4$ and condensed tannins extracted from *Kalmia angustifolia* and *Balsam fir*. *Soil Biology and Biochemistry* 32, 1227-1240.
- Brewer, C.E., Schmidt-Rohr, K., Satrio, J.A. and Brown, R.C., 2009. Characterization of biochar from fast pyrolysis and gasification systems. *Environmental Progress and Sustainable Energy* 28, 386-396.
- Cantrell, K.B., Hunt, P.G., Uchimiya, M., Novak, J.M. and Ro, K.S., 2012. Impact of pyrolysis temperature and manure source on physicochemical characteristics of biochar. *Bioresource Technology* 107, 419-428.
- Chan, K.Y., Van Zwieten, L., Meszaros, I., Downie, A. and Joseph, S., 2008. Using poultry litter biochars as soil amendments. *Soil Research* 46, 437-444.
- Chan, K.Y. and Xu, Z., 2009. Biochar: Nutrient properties and their enhancement. In: Lehmann, J. and Joseph, S. (Eds.), *Biochar for Environmental Management: Science and Technology*. Earthscan Sterling, VA, USA, pp. 67-84.
- Coulis, M., Hättenschwiler, S., Rapior, S. and Coq, S., 2009. The fate of condensed tannins during litter consumption by soil animals. *Soil Biology and Biochemistry* 41, 2573-2578.
- Dalal, R.C., Wang, W., Robertson, G.P., Parton and W.J., 2003. Nitrous oxide emission from Australian agricultural lands and mitigation options: a review. *Soil Research* 41, 165-195.
- Davies, R.I., Coulson, C.B. and Lewis, D.A., 1964. Polyphenols in plant, humus, and soil III. Stabilization of gelatine by polyphenol tanning. *Journal of Soil Science* 15, 299-309.

- Degen, A.A., Becker, K., Makkar, H.P.S. and Borowy, N., 1995. *Acacia saligna* as a fodder tree for desert livestock and the interaction of its tannins with fibre fractions. *Journal of the Sciences of Food and Agriculture* 68, 65-71.
- Delve, R.J., Cadisch, G., Tanner, J.C., Thorpe, W., Thorne, P.J. and Giller, K.E., 2001. Implications of livestock feeding management on soil fertility in the smallholder farming systems of sub-Saharan Africa. *Agriculture, Ecosystems and Environment* 84, 227-243.
- Downie, A., Crosky, A. and Munroe, P., 2009. Physical properties of biochar. In: Lehmann, J. and Joseph, S. (Eds.), *Biochar for Environmental Management: Science and Technology*. Earthscan Sterling, VA, USA, pp. 13-32.
- FAO, 1993. Soil survey and land classification project: Oman United Nations Development Programme and Food and Agriculture Organization of the United Nations Rome.
- FAO, 2012. FAOSTAT. <http://faostat3.fao.org/faostat-gateway/go/to/download/Q/QA/E>, accessed 20.8.2014
- Frazier, R.A., Deaville, E.R., Green, R.J., Stringano, E., Willoughby, I., Plant, J. and Mueller-Harvey, I., 2010 Interactions of tea tannins and condensed tannins with proteins. *Journal of Pharmaceutical and Biomedical Analysis* 51, 490-495.
- Freschet, G.T., Masse, D., Hien, E., Sall, S. and Chotte, J.L., 2008. Long-term changes in organic matter and microbial properties resulting from manuring practices in an arid cultivated soil in Burkina Faso. *Agriculture, Ecosystems and Environment* 123, 175-184.
- Gao, G. and Chang, C., 1996. Changes in CEC and particle size distribution of soils associated with long-term annual applications of cattle feedlot manure. *Soil Science* 161, 115-120.
- Gerlach, A., 2012. Pflanzenkohle in der Rinderhaltung. *Ithaka Journal* 1, 80-84.
- Glaser, B., Lehmann, J. and Zech, W., 2002. Ameliorating physical and chemical properties of highly weathered soils in the tropics with charcoal: a review. *Biology and Fertility of Soils* 35, 219-230.
- Halvorson, J.J., Gonzalez, J.M., Hagerman, A.E., 2011. Repeated applications of tannins and related phenolic compounds are retained by soil and affect cation exchange capacity. *Soil Biology and Biochemistry* 43, 1139-1147.
- Halvorson, J.J., Gollany, H.T., Kennedy, A.C., Hagerman, A.E., Gonzalez, J.M. and Wuest, S.B., 2012. Sorption of tannin and related phenolic compounds and effects on extraction of soluble-N in soil amended with several carbon sources. *Agriculture* 2, 52-72.
- Hättenschwiler, S. and Vitousek, P.M., 2000. The role of polyphenols in terrestrial ecosystem nutrient cycling. *Trends in Ecology and Evolution* 15, 238-243.
- Hess, H.D., Tiemann, T.T., Stürm, C.D., Carulla, J.E., Lascano, C.E. and Kreuzer, M., 2006. Effects of tannins on ruminal degradation and excretory pattern of N and implications for the potential N emission from the manure. *International Congress Series* 1293, 339-342.
- Huwig, A., Freimund, S., Käppeli, O. and Dutler, H., 2001. Mycotoxin detoxication of animal feed by different adsorbents. *Toxicology Letters* 122, 179-188.
- Jalali, M., 2005. Nitrates leaching from agricultural land in Hamadan, Western Iran. *Agriculture, Ecosystems and Environment* 110, 210-218.
- Jha, P., Biswas, A.K., Lakaria, B.L. and Subba Rao, A., 2010. Biochar in agriculture - prospects and related implications. *Current Science* 99, 1218-1225.
- Joseph, S., Downie, A., Munroe, P., Crosky, A. and Lehmann, J., 2007. Biochar for carbon sequestration, reduction of greenhouse gas emissions and enhancement of soil fertility: A review of the materials science. *Proceedings of the Australian Combustion Symposium*, Sydney, pp. 130-133.
- Jost, D., Joergensen, R. and Sundrum, A., 2013. Effect of cattle faeces with different microbial biomass content on soil properties, gaseous emissions and plant growth. *Biology and Fertility of Soils* 49, 61-70.
- Kanerva, S., Kitunen, V., Kiikkilä, O., Loponen, J. and Smolander, A., 2006. Response of soil C and N transformations to tannin fractions originating from Scots pine and Norway spruce needles. *Soil Biology and Biochemistry* 38, 1364-1374.

- Korn, L., Häser, J., Schreiber, J., Gangler, A., Nagieb, A., Siebert, S. and Buerkert, A., 2004. Tiwi and Wadi Tiwi: the development of an oasis on the north-eastern coast of Oman. *Journal of Oman Studies* 13, 57-90.
- Kraus, T.E.C., Dahlgren, R.A. and Zasoski, R.J., 2003. Tannins in nutrient dynamics of forest ecosystems - a review. *Plant and Soil* 256, 41-66.
- Kraus, T.E.C., Zasoski, R.J., Dahlgren, R.A., Horwath, W.R. and Preston, C.M., 2004. Carbon and nitrogen dynamics in a forest soil amended with purified tannins from different plant species. *Soil Biology and Biochemistry* 36, 309-321.
- Kuzyakov, Y., Bogomolova, I. and Glaser, B., 2014. Biochar stability in soil: Decomposition during eight years and transformation as assessed by compound-specific ¹⁴C analysis. *Soil Biology and Biochemistry* 70, 229-236.
- Laird, D.A., 2008. The Charcoal Vision: A Win-Win-Win Scenario for Simultaneously Producing Bioenergy, Permanently Sequestering Carbon, while Improving Soil and Water Quality. *Agronomy Journal* 100, 178-181.
- Laird, D.A., Fleming, P., Davis, D.D., Horton, R., Wang, B. and Karlen, D.L., 2010. Impact of biochar amendments on the quality of a typical Midwestern agricultural soil. *Geoderma* 158, 443-449.
- Lal, R., 2006. Enhancing crop yields in the developing countries through restoration of the soil organic carbon pool in agricultural lands. *Land Degradation and Development* 17, 197-209.
- Lehmann, J. and Rondon, M., 2006. Bio-Char Soil Management on Highly Weathered Soils in the Humid Tropics. In: Uphoff, N., Ball, A.S., Fernandes, E., Herren, H., Husson, O., Laing, M., Palm, C., Pretty, J., Sanchez, P., Sanginga, N., Thies, J. (Eds.), *Biological Approaches to Sustainable Soil Systems*. Taylor and Francis Group, Boca Raton, pp. 517-530.
- Lehmann, J. and Joseph, S., 2009. *Biochar for Environmental Management: Science and Technology*. Earthscan Sterling, VA, USA.
- Lehmann, J., Rillig, M.C., Thies, J., Masiello, C.A., Hockaday, W.C. and Crowley, D., 2011. Biochar effects on soil biota - A review. *Soil Biology and Biochemistry* 43, 1812-1836.
- Leng, R.A., Preston, T.R. and Inthapanya, S., 2012. Biochar reduces enteric methane and improves growth and feed conversion in local "Yellow" cattle fed cassava root chips and fresh cassava foliage. *Livestock Research for Rural Development* 24, Retrieved August 6, 2014, from <http://www.lrrd.org/lrrd2024/2011/leng24199.htm>.
- Lentz, R.D. and Ippolito, J.A., 2012. Biochar and manure affect calcareous soil and corn silage nutrient concentrations and uptake. *Journal of Environmental Quality* 41, 1033-1043.
- Lu, C.D., 1989. Effects of heat stress on goat production. *Small Ruminant Research* 2, 151-162.
- Major, J., Rondon, M., Molina, D., Riha, S., Lehmann, J., 2010. Maize yield and nutrition during 4 years after biochar application to a Colombian savanna Oxisol. *Plant and Soil* 333, 117-128.
- Makkar, H.P.S., Becker, K., Abel, H.J. and Szegletti, C., 1995. Degradation of condensed tannins by rumen microbes exposed to quebracho tannins (QT) in rumen simulation technique (RUSITEC) and effects of QT on fermentative processes in the RUSITEC. *Journal of the Science of Food and Agriculture* 69, 495-500.
- Makkar, H.P.S., 2003. Effects and fate of tannins in ruminant animals, adaptation to tannins, and strategies to overcome detrimental effects of feeding tannin-rich feeds. *Small Ruminant Research* 49, 241-256.
- Materechera, S., 2010. Utilization and management practices of animal manure for replenishing soil fertility among smallscale crop farmers in semi-arid farming districts of the North West Province, South Africa. *Nutrient Cycling in Agroecosystems* 87, 415-428.
- Micheni, A., Kihanda, F. and Irungu, J., 2004. Soil organic matter (SOM): The basis for improved crop production in arid and semi-arid climates of Eastern Kenya. In: Bationo, A. (Ed.), *Managing Nutrient Cycles to Sustain Soil Fertility in Sub-Saharan Africa*. Academy Science Publishers Nairobi, pp. 239-248.

- Millennium Ecosystem Assessment, 2005. *Ecosystems and Human Well-being: Synthesis*. Island Press, Washington D.C., USA.
- Muir, J.P., 2011. The multi-faceted role of condensed tannins in the goat ecosystem. *Small Ruminant Research* 98, 115-120.
- Mukherjee, A. and Lal, R., 2013. Biochar impacts on soil physical properties and greenhouse gas emissions. *Agronomy* 3, 313-339.
- Mutabaruka, R., Hairiah, K. and Cadisch, G., 2007. Microbial degradation of hydrolysable and condensed tannin polyphenol-protein complexes in soils from different land-use histories. *Soil Biology and Biochemistry* 39, 1479-1492.
- Nagieb, M., Häser, J., Siebert, S., Luedeling, E. and Buerkert, A., 2004. Settlement history of a mountain oasis in northern Oman - Evidence from land use and archaeological studies. *Die Erde* 135, 81-106.
- Nelson, N.O., Agudelo, S.C., Yuan, W. and Gan, J., 2011. Nitrogen and phosphorus availability in biochar-amended soils. *Soil Science* 176, 218-226.
- Northup, R., Dahlgren, R. and McColl, J., 1998. Polyphenols as regulators of plant-litter-soil interactions in Northern California's pygmy forest: A positive feedback? *Biogeochemistry* 42, 189-220.
- Nyamangara, J., Gotosa, J. and Mpfu, S.E., 2001. Cattle manure effects on structural stability and water retention capacity of a granitic sandy soil in Zimbabwe. *Soil and Tillage Research* 62, 157-162.
- Oades, J.M., 1988. The retention of organic matter in soils. *Biogeochemistry* 5, 35-70.
- Oglesby, K.A. and Fownes, J.H., 1992. Effects of chemical composition on nitrogen mineralization from green manures of seven tropical leguminous trees. *Plant and Soil* 143, 127-132.
- Oleszczuk, P., Joško, I., Futa, B., Pasiieczna-Patkowska, S., Pałys, E. and Kraska, P., 2014. Effect of pesticides on microorganisms, enzymatic activity and plant in biochar-amended soil. *Geoderma* 214-215, 10-18.
- Palm, C.A. and Sanchez, P.A., 1991. Nitrogen release from the leaves of some tropical legumes as affected by their lignin and polyphenolic contents. *Soil Biology and Biochemistry* 23, 83-88.
- Pietikäinen, J., Kiiikkilä, O. and Fritze, H., 2000. Charcoal as a habitat for microbes and its effect on the microbial community of the underlying humus. *Oikos* 89, 231-242.
- Poage, G.W., Scott, C.B., Bisson, M.G. and Hartmann, F.S., 2000. Activated charcoal attenuates bitterweed toxicosis in sheep. *Journal of Range Management* 53, 73-78.
- Powell, J.M., Fernández-Rivera, S. and Hörs, S., 1994. Effects of sheep diet on nutrient cycling in mixed farming systems of semi-arid West Africa. *Agriculture, Ecosystems and Environment* 48, 263-271.
- Powell, J.M., Ikpe, F.N. and Somda, Z.C., 1999. Crop yield and the fate of nitrogen and phosphorus following application of plant material and feces to soil. *Nutrient Cycling in Agroecosystems* 54, 215-226.
- Powell, J.M., Broderick, G.A., Grabber, J.H. and Hymes-Fecht, U.C., 2009. Technical note: Effects of forage protein-binding polyphenols on chemistry of dairy excreta. *Journal of Dairy Science* 92, 1765-1769.
- Powell, J.M., Aguerre, M.J. and Wattiaux, M.A., 2011. Dietary crude protein and tannin impact dairy manure chemistry and ammonia emissions from incubated soils. *Journal of Environmental Quality* 40, 1767-1774.
- Predotova, M., Schlecht, E. and Buerkert, A., 2010. Nitrogen and carbon losses from dung storage in urban gardens of Niamey, Niger. *Nutrient Cycling in Agroecosystems* 87, 103-114.
- Puchala, R., Min, B.R., Goetsch, A.L. and Sahlü, T., 2005. The effect of a condensed tannin-containing forage on methane emission by goats. *Journal of Animal Science* 83, 182-186.
- Quilliam, R.S., Marsden, K.A., Gertler, C., Rousk, J., DeLuca, T.H. and Jones, D.L., 2012. Nutrient dynamics, microbial growth and weed emergence in biochar amended soil are influenced by time since application and reapplication rate. *Agriculture, Ecosystems and Environment* 158, 192-199.

- Rasool, R., Kukal, S.S. and Hira, G.S., 2008. Soil organic carbon and physical properties as affected by long-term application of FYM and inorganic fertilizers in maize-wheat system. *Soil and Tillage Research* 101, 31-36.
- Rogovska, N., Laird, D., Cruse, R., Fleming, P., Parkin, T. and Meek, D., 2011. Impact of biochar on manure carbon stabilization and greenhouse gas emissions. *Soil Science Society of America Journal* 75, 871-879.
- Rufino, M.C., Rowe, E.C., Delve, R.J. and Giller, K.E., 2006. Nitrogen cycling efficiencies through resource-poor African crop-livestock systems. *Agriculture, Ecosystems and Environment* 112, 261-282.
- Rufino, M.C., Tiftonell, P., van Wijk, M.T., Castellanos-Navarrete, A., Delve, R.J., de Ridder, N. and Giller, K.E., 2007. Manure as a key resource within smallholder farming systems: Analysing farm-scale nutrient cycling efficiencies with the NUANCES framework. *Livestock Science* 112, 273-287.
- Schjøning, P., Christensen, B.T. and Carstensen, B., 1994. Physical and chemical properties of a sandy loam receiving animal manure, mineral fertilizer or no fertilizer for 90 years. *European Journal of Soil Science* 45, 257-268.
- Schulz, H. and Glaser, B., 2012. Effects of biochar compared to organic and inorganic fertilizers on soil quality and plant growth in a greenhouse experiment. *Journal of Plant Nutrition and Soil Science* 175, 410-422.
- Siebert, S., Nagieb, M. and Buerkert, A., 2007. Climate and irrigation water use of a mountain oasis in northern Oman. *Agricultural Water Management* 89, 1-14.
- Siegfried, K., Dietz, H., Schlecht, E. and Buerkert, A., 2011. Nutrient and carbon balances in organic vegetable production on an irrigated, sandy soil in northern Oman. *Journal of Plant Nutrition and Soil Science* 174, 678-689.
- Silanikove, N., 2000. The physiological basis of adaptation in goats to harsh environments. *Small Ruminant Research* 35, 181-193.
- Sinkkonen, A., 2006. Ecological relationships and allelopathy. In: Reigosa, M.J., Pedrol, N. and González, L. *Allelopathy: A Physiological Process with Ecological Implications*. Springer, Dordrecht, pp. 373-394.
- Spencer, C.M., Cai, Y., Martin, R., Gaffney, S.H., Goulding, P.N., Magnolato, D., Lilley, T.H., Haslam, E., 1988. Polyphenol complexation - some thoughts and observations. *Phytochemistry* 27, 2397-2409.
- Steiner, C., Teixeira, W.G., Lehmann, J., Nehls, T., de Macêdo, J.L.V., Blum, W.E.H. and Zech, W., 2007. Long term effects of manure, charcoal and mineral fertilization on crop production and fertility on a highly weathered Central Amazonian upland soil. *Plant and Soil* 291, 275-290.
- Steiner, C., Glaser, B., Geredes Teixeira, W., Lehmann, J., Blum, W.E.H. and Zech, W., 2008. Nitrogen retention and plant uptake on a highly weathered central Amazonian Ferralsol amended with compost and charcoal. *Journal of Plant Nutrition and Soil Science* 171, 893-899.
- Stoms, D.J., 1982. Effect of polyphenols on shoot and root growth and on seed germination. *Biologia Plantarum* 24, 1-6.
- Sukartono, Utomo, W.H., Kusuma, Z. and Nugroho, W.H., 2011. Soil fertility status, nutrient uptake, and maize (*Zea mays* L.) yield following biochar and cattle manure application on sandy soils of Lombok, Indonesia. *Journal of Tropical Agriculture* 49, 47-52.
- Terrill, T.H., Waghorn, G.C., Woolley, D.J., McNabb, W.C. and Barry, T.N., 1994. Assay and digestion of ¹⁴C-labelled condensed tannins in the gastrointestinal tract of sheep. *British Journal of Nutrition* 72, 467-477.
- Tiemann, T.T., Hincapie, B., Frossard, E., Kreuzer, M. and Hess, H.D., 2009. Effect of supplementing tropical tannin-free and tanniniferous legumes to grass-fed sheep on the utility of their manure as nitrogen fertilizer. *Livestock Research for Rural Development* 21, retrieved August 28, 2014, from <http://www.lrrd.org/lrrd21/3/tiem21041.htm>.
- Uchimiya, M., Wartelle, L.H., Klasson, K.T., Fortier, C.A. and Lima, I.M., 2011. Influence of pyrolysis temperature on biochar property and function as a heavy metal sorbent in soil. *Journal of Agricultural and Food Chemistry* 59, 2501-2510.

- Uzoma, K.C., Inoue, M., Andry, H., Fujimaki, H., Zahoor, A. and Nishihara, E., 2011. Effect of cow manure biochar on maize productivity under sandy soil condition. *Soil Use and Management* 27, 205-212.
- Van, D.T.T., Mui, N.T. and Ledin, I., 2006. Effect of method of processing foliage of *Acacia mangium* and inclusion of bamboo charcoal in the diet on performance of growing goats. *Animal Feed Science and Technology* 130, 242-256.
- Van Zwieten, L., Kimber, S., Morris, S., Chan, K.Y., Downie, A., Rust, J., Joseph, S. and Cowie, A., 2010. Effects of biochar from slow pyrolysis of papermill waste on agronomic performance and soil fertility. *Plant and Soil* 327, 235-246.
- Van Zwieten, L., Kimber, S., Sinclair, K., Chan, K.Y. and Downie, A., 2008. Biochar: Potential for climate change mitigation, improved yield and soil health. 23rd Annual Conference of the Grassland Society Mpumalanga, South Africa
- Wang, H., Lin, K., Hou, Z., Richardson, B. and Gan, J., 2010. Sorption of the herbicide terbuthylazine in two New Zealand forest soils amended with biosolids and biochars. *Journal of Soils and Sediments* 10, 283-289.
- Watarai, S., Tana and Koiwa, M., 2008. Feeding activated charcoal from bark containing wood vinegar liquid (nekka-rich) is effective as treatment for cryptosporidiosis in calves. *Journal of Dairy Science* 91, 1458-1463.
- White, T., 1957. Tannins—their occurrence and significance. *Journal of the Science of Food and Agriculture* 8, 377-385.
- Williams, T., 1999. Factors influencing manure application by farmers in semi-arid west Africa. *Nutrient Cycling in Agroecosystems* 55, 15-22.
- WMO, 2009. World Meteorological Organization, Geneva.
- Wu, T, Sharda, J.N. and Koide, R.T., 2003. Exploring interactions between saprotrophic microbes and ectomycorrhizal fungi using a protein-tannin complex as an N source by red pine (*Pinus resinosa*). *New Phytologist* 159, 131-139.
- Yamato, M., Okimori, Y., Wibowo, I.F., Anshori, S. and Ogawa, M., 2006. Effects of the application of charred bark of *Acacia mangium* on the yield of maize, cowpea and peanut, and soil chemical properties in South Sumatra, Indonesia. *Soil Science and Plant Nutrition* 52, 489-495.
- Zhang, A., Liu, Y., Pan, G., Hussain, Q., Li, L., Zheng, J. and Zhang, X., 2012. Effect of biochar amendment on maize yield and greenhouse gas emissions from a soil organic carbon poor calcareous loamy soil from Central China Plain. *Plant and Soil* 351, 263-275.
- Zimmerman, A.R., Gao, B. and Ahn, M.-Y., 2011. Positive and negative carbon mineralization priming effects among a variety of biochar-amended soils. *Soil Biology and Biochemistry* 43, 1169-1179.

Chapter 2

Effects of activated charcoal and quebracho tannins added to feed or as soil conditioner on manure quality in organic agriculture

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2.1 Abstract

Animal manure is one of the major nutrient and carbon (C) sources in many low to medium input systems of irrigated agriculture in subtropical drylands, particularly if managed under constraints of organic regulations. Under year-round hot and irrigated conditions, high losses of C, nitrogen (N) and other may lead to soil quality deterioration and reduced crop yields. In an effort to develop approaches slowing down decomposition of soil applied manure, activated charcoal (AC) and quebracho tannin extract (QT) were either fed to goats or directly mixed with manure prior to application in a two-year field experiment with sweet corn (*Zea mays* L.) and radish (*Raphanus sativus* L.) in the Batinah Plain of Oman. Sun-dried faeces of goats fed AC had a 15% higher C concentration and a 25% higher C/N ratio than pure goat manure, whereas QT feeding only increased Na concentration. While sweet corn performed best under equivalent mineral fertilization, the addition of AC and QT to goat feed or to goat manure reduced growth and development of sweet corn by 20% and 30%, respectively, compared to pure goat manure, regardless of the application method. Radish yielded highest when fertilized with either pure goat manure or AC amended goat manure, whereas mineral fertilizer and QT amended manure applications inhibited its growth. Activated charcoal may be a promising additive to increase soil organic matter and increase soil fertility, if it does not hamper nutrient supply to crops. Quebracho tannins, however, impaired crop production and further research is needed to evaluate whether tannins from other sources added to agricultural soils have similar detrimental effects on crops.

Keywords: Carbon turnover; Feed additives; Goat manure; Irrigated agriculture; Manure mineralization; Subtropics

2.2 Introduction

Semi-arid and arid environments cover 47% of the global land area (UNEP 1997) and increasingly contribute to feed a growing population. At the same time, soil organic carbon (SOC) depletion, land degradation, and desertification caused by poor management and overuse are endangering these systems (Millennium Ecosystem Assessment 2005). The repeated application of animal manure is a key element for sustainable farming as it recycles nutrients in the system (Rufino et al.

2006), maintains or even improves SOC (Manna et al. 2005), increases soil water storage and soil nutrient availability and finally governs crop yields, particularly in organic agriculture (Aggarwal et al. 1997; Nyamangara et al. 2001). In Omani mountain oases, goat manure is a well-known key element of millennia-old production systems, where goats gather nutrients from large surrounding grazing areas and transfer them to cropped fields (Shankarnarayan et al., 1985; Wichern et al. 2004; Buerkert et al. 2005; Schlecht et al. 2011). However, given low primary biomass production in semi-arid and arid regions, the amount of manure available per unit area is often low and turnover of the applied manure is fast (Materchera 2010). In environments with high temperatures such as Oman, breakdown of organic amendments by termites, and intensive irrigation favour high C and N losses from manure via gaseous emissions and leaching (Siegfried et al. 2013), thereby reducing the efficiency of its application. To limit these losses, it may be appropriate to change manure properties in such a way that organic matter is stabilized. Recent work from subtropical areas has shown that manure properties can be altered by changing fodder composition and quality (Powell et al. 2006; Al-Asfoor et al. 2012), but also the use of feed additives known to stabilize organic matter may be a useful approach.

Increasingly, charcoal - often referred to as biochar - is used as a soil conditioner as many studies have concluded that it improves SOC, pH, water holding capacity (WHC), cation exchange capacity (CEC), and nutrient availability of soils (Glaser et al. 2002; Yamato et al. 2006; Steiner et al. 2007). In addition, large yield increases were reported for a variety of plants (Yamato et al. 2006; Chan et al. 2008; Zhang et al. 2012), but it also seems that the effectiveness of biochar applications depends on several other factors (Van Zwieten et al. 2010; Schulz and Glaser 2012). Positive effects on yields were mainly observed on highly weathered, acidic tropical soils, whereas data regarding other soil types is scarce (Glaser et al. 2002; Yamato et al. 2006). Moreover, a comparison of an acidic Ferrosol and an alkaline Calcarosol resulted in higher radish yields after a biochar application on the Ferrosol, but not on the Calcarosol (Van Zwieten et al. 2010). It seems that particularly the liming effect of charcoals benefits plant development as it increases CEC and can reduce aluminium and manganese toxicities at low pH. At the same time, biochar quality varies enormously with feedstock and pyrolysis conditions (Sukartono et al. 2011) as

well as post-pyrolysis treatments such as steam activation. Depending on feedstock and pyrolysis temperature, Rajkovich et al. (2012) found responses of sweet corn vary from -70% to +50% as compared with a control treatment without biochar application. Finally, the effect of biochar application on plant growth is affected by its application rate and additional nutrient inputs, as the application of a C source can lead to nutrient immobilization, especially of N (Nelson et al. 2011; Schulz and Glaser 2012). As charcoal is used in livestock production to increase intake of phenol-containing forages and detoxify mycotoxins in animal feed (Huwig et al. 2001; Rogosic et al. 2006), the combination of a positive effect on animals with an improvement of manure quality may be a promising approach to increase the efficiency and quality of manures applied to agricultural soils.

The role of condensed tannins on soil properties and nutrient availability has so far mainly been investigated on forest soils, where they can inhibit organic matter degradation and N mineralization by binding to proteins and inhibiting microbial activity (Palm and Sanchez 1991; Northup et al. 1998; Kraus et al. 2004). As secondary plant metabolites, condensed tannins, belonging to the polyphenols, are present in many forage species. In low concentrations, condensed tannins may have positive effects on ruminants, increasing milk production and growth rates, and reducing methane emissions, bloat, and parasite infections (Aerts et al. 1999; Puchala et al. 2005; Bhatta et al. 2011). In addition, condensed tannins ingestion shifts N excretion from urine to faeces (Makkar 2003; Hess et al. 2006), which reduces N volatilisation. Only a few studies deal with the effects of polyphenols in ruminant fodder on manure quality. Powell et al. (1994) found that N release from faeces of goats fed with high polyphenol containing *Acacia trachycarpa* E. Pritz. and *Guiera senegalensis* J. F. Gmel. was lower than that from faeces of goats fed *Vigna unguiculata* L., which has a five-times lower polyphenol content. Yet, the effects of manure derived from tannin-containing fodder on crop development have hardly been studied.

To investigate the effectiveness of activated charcoal and Quebracho (*Schinopsis balansae* Engl.) tannin extract (mainly condensed tannins) as soil conditioners, applied either by enriching the faeces of goats fed with these additives or by mixing the additives with the soil during manure application, a feeding trial and a field experiment were conducted in Northern Oman. On the intensively irrigated sandy

soils of this region, the application of charcoal and tannins was expected to stabilize SOC and increase water and nutrient holding capacities, eventually leading to increased crop yields.

In view of the above the objectives of this study were to (i) determine the effects of addition of activated charcoal and quebracho tannins on manure quality and (ii) to investigate the implications of manure qualities on crop growth and nutrient use efficiencies of two different vegetable crops: sweet corn and radish.

2.3 Materials and methods

2.3.1 Site description

The field experiment was conducted during two consecutive vegetation periods on a private farm with intensive vegetable production near Sohar (24°22' N, 56°34' E), in the Al-Batinah Plain of the Sultanate of Oman. The soil on the farm was categorized as a hyperthermic Typic Torrifluent (US Soil Taxonomy; Al Farsi 2001) with 82% sand, 16% silt, and 2% clay in the upper 0.5 m layer (Siegfried et al. 2011). It had a pH of 8.7 and a carbonate concentration of 6.3% (for more details see Ingold et al. 2015). Given the hot, hyper-arid conditions prevailing in Northern Oman, the vegetation period is limited to the period from October to March, which is cooler than the summer months. Mean annual minimum and maximum temperatures from 1986 to 2009 in Sohar were 21.7°C and 31.3°C, respectively, with a mean annual precipitation of 109 mm (WMO 2009). In both seasons the average temperature from October to March was 24°C with average minima of 14°C and maxima of 34°C (Fig. 2.1). In both periods, average relative humidity was 60%, ranging between 47% and 89% within a day. In 2010/11, a total of 9 mm precipitation occurred in seven rainfall events from November to January, whereas in 2011/12 a total of 50 mm precipitated on ten rainy days from October to March with peaks of 15 mm and 27 mm in single rainfall events in October and November.

2.3.2 Manure collection

A digestibility trial was conducted to evaluate the effects of charcoal and condensed tannins on the fodder digestibility and monitor the animals' development. To this end typical Jabal Akhdar goats were kept in individual crates in an open sided, roofed stockade and offered a basal diet consisting of 50% Rhodes grass hay

(*Chloris gayana* Kunth), 46.5% crushed maize (*Zea mays* L.), and 3.5% soybean (*Glycine max.*) meal. In addition to this basal diet, experimental diets contained 3% steam-activated charcoal (AC) or 4% Quebracho tannin extract (QT). The AC used was a fine powder made from coconut shells (AquaSorb® CP1, Jacobi Carbons GmbH, Frankfurt am Main, Germany) and QT was a water soluble powdered extract of the Quebracho tree (Silva Team S.p.a., San Michele, Italy). Before ingestion crushed maize, soybean meal, AC, and QT, respectively, were mixed and pelleted (Table 2.1). The pellets and hay were divided into two equal portions that were offered to the goats twice a day, in the morning and afternoon. The pelleted mixture and hay were fed separately starting with the pellets, which were usually ingested within 10 minutes. Mineral blocks were provided throughout the experimental period and water was offered *ad libitum*.

Table 2.1. Chemical composition of hay and the different concentrates used for manure collection in a field experiment in northern Oman. Hay and concentrate contributed each 50% to the daily diet.

	OM	NDF	ADF	C	N	P	K	Na	CN
	----- (g kg ⁻¹ DM) -----								ratio
Hay	909	721	399	436	12.9	1.3	10.4	6.77	35.3
Co pellets	979	77	34	439	18.9	3.1	3.4	0.02	23.3
AC _{fed} pellets	976	119	76	463	18.0	3.0	3.7	0.07	25.8
QT _{fed} pellets	975	79	40	447	17.3	3.0	3.3	1.35	25.9
AC				921	1.0	0.3	8.0		
QT				528	1.0	0.1	0.9	24.00	

Co = goat manure; AC_{fed} = manure of goats fed charcoal; QT_{fed} = manure of goats fed quebracho tannin; AC = activated charcoal; QT = quebracho tannin extract

For the field experiment, manure was collected from a total of 60 male goats of which 36 were allocated to a control group and 12 goats each to the AC and QT treatment. The animals were kept under the same conditions and with the same diet as in the digestibility trial. Due to differences in age and size of the goats in the first and second season (36.3 kg ± 3.0 and 23.2 kg ± 2.6, respectively), a daily diet of 1000 g DM of the basal diet per goat and day was fed in the first season, whereas in the second season goats received 600 g DM per goat and day for the first 8 weeks and 700 g DM thereafter, until the end of manure collection. As the weight of goats receiving QT did not increase over the period, the daily diet of this group remained at 600 g DM for the entire experimental period in the second season. AC and QT

extract were added to the feed at rates of 2.7% and 3.7% of daily diet, respectively, in the first season and 2.3% and 3.6% in the second season. Faeces were collected once daily, before morning feeding, from fabric faecal harnesses. Fresh manure was spread on plastic sheets and sun-dried for up to 5 days until weight constancy. Sun-dried manure was thereafter stored in plastic bags under air-conditioned conditions until application to the field.

2.3.3 Setup of the field experiment

The manures originating from the three diets were used in a field experiment with a sweet corn-radish rotation in 2010/11 and 2011/12. In both seasons, sweet corn (*Zea mays* L. var. 'Honey Jean No. 2') was sown at the beginning of November and harvested at milk kernel stage 90 and 84 days after sowing (DAS) in the first and second season, respectively. Due to low germination rates and damage by birds, plant population densities reached only 28,400 and 46,800 plants ha⁻¹, in 2010/11 and 2011/12. Radish (*Raphanus sativus* var. 'Early 40 days') was sown at the beginning of February; post-thinning population density was 90,667 and 125,000 plants ha⁻¹ in the first and second season. Radish was harvested 43 DAS in both seasons.

The application of mineral fertilizer served as NPK control treatment equivalent to that of manure and was based on urea, triple superphosphate and K₂SO₄. The three goat manure types obtained from the feeding trial (Co, AC_{fed}, and QT_{fed}) were analysed for N, P, and K concentrations, and manure application rates were calculated to fit nutrient requirements of sweet corn and radish. Sweet corn was supposed to receive 200 kg N ha⁻¹, 39 and 55.8 kg P ha⁻¹ (in 2010/11 and 2011/12, respectively) and 130 kg K ha⁻¹ in three split applications. Fertilizers, both organic and inorganic, were applied in three steps (one day before sowing, 25 and 45 DAS) at a rate of 20, 50, and 30% of the total N, P, and K fertilizer amount in 2010/11, and at a rate of 40, 40, and 20% in 2011/12, to avoid N deficiency observed in 2010/11. Radish received 135 kg N ha⁻¹, 26 and 38 kg P ha⁻¹ (in 2010/11 and 2011/12, respectively) and 90 kg K ha⁻¹ in a single application. While the organic treatments goat manure was the only source of N, P and K input had to be adjusted with mineral fertilizer additions of 0-17% P and 78-91% K to reach target input levels. Before each manure application, the total of collected faeces was mixed thoroughly to obtain a

homogenous mix of differently aged manure for all plots. Sun-dried manure samples were taken at each manure application step to verify applied nutrient amounts. However, due to heterogeneous nutrient concentrations of manures in the two cropping seasons, application rates of N, P, and K did not always meet the target values (Table 2.2). Activated charcoal and QT were mixed simultaneously with control manure with the soil to achieve two additional manure treatments: AC_{mix} and QT_{mix}. For these two treatments, the amount of amendments was calculated from estimated AC or QT contents in AC_{fed} and QT_{fed} faeces, as charcoal and tannin concentration in faeces could not be analysed prior to field application of the manure (Ingold et al. 2015). The annual application rates amounted to 2 and 1.4 t AC ha⁻¹ and 2 and 1.3 t QT ha⁻¹ in 2010/11 and 2011/12, respectively.

Table 2.2. Application rates of manure DM, C, N, P, and K for the first season in 2010/11 and the second season in 2011/12 in a field experiment in Northern Oman.

	Manure	C	N	P	K
	1 st /2 nd				
----- kg ha ⁻¹ -----					
NPK	0	0.1/0.1	200/200	39/56	130/130
Co	8.7/8.9	3.9/4.0	212/198	56/55	124/129
AC _{fed}	7.8/10.0	4.0/4.9	175/201	47/51	127/127
AC _{mix}	8.7/8.9	4.9/4.8	214/199	57/55	134/136
QT _{fed}	8.8/9.0	4.0/4.1	201/194	50/52	120/123
QT _{mix}	8.7/8.9	4.7/4.6	214/200	57/55	126/130
NPK	0	0.1/0.1	135/135	26/38	90/90
Co	5.6/6.0	2.5/2.8	151/146	39/33	91/86
AC _{fed}	5.5/6.7	2.8/3.3	126/142	35/31	86/88
AC _{mix}	5.6/6.0	3.2/3.3	152/146	40/34	97/90
QT _{fed}	5.8/6.1	2.6/2.8	138/137	36/33	94/82
QT _{mix}	5.6/6.0	3.1/3.1	152/146	39/36	92/86

NPK = mineral fertilizer, Co = goat manure, AC_{fed} = manure of goats fed charcoal, AC_{mix} = goat manure mixed with charcoal, QT_{fed} = manure of goats fed quebracho tannin, QT_{mix} = goat manure mixed with quebracho tannin

The six manure treatments were completely randomized on the field with four replicates. Each plot was laid out in 2.5 m x 6.5 m basins with separate access for irrigation water. Irrigation frequency for sweet corn was every 3.8 and 4.6 days in the

first and second cropping season, respectively, and every 2.2 and 2.4 days for radish, respectively. Several organic plant protection agents were applied at different stages of plant growth to protect plants from aphids, corn borer, and *Pythium* wilt. A mixture of chelated micronutrients (Disper Complex GS, Agrometodos de Alicante, Alicante, Spain) was sprayed twice on sweet corn plants to counteract possible micronutrient deficiencies.

2.3.4 Measurement of growth parameters and sample analysis

During sweet corn and radish cultivation, various growth parameters were measured on a regular basis. Emerging seedlings were counted to calculate germination rate. Plant height from ground to the tip of the highest leaf was measured regularly on five and 10 representative sweet corn plants per plot in the first and second cropping season, respectively. The sweet corn leaf area was estimated by calculating the triangular surface from measures of leaf length and width of two representative plants per plot. To investigate radish growth, the total number of leaves was counted and the length of the longest leaf of 6-8 plants per plot was measured. The chlorophyll status of plants, a commonly used proxy to compare their N status, was estimated with a SPAD chlorophyll meter (Spectrum Technologies Inc., Aurora, IL, USA; Bullock and Anderson 1998). These measurements were made on the youngest fully-grown leaf of 20 sweet corn plants per plot, and on one middle-aged leaf of 20 radish plants per plot. At harvest, sweet corn ears of up to 20 plants per plot were picked and weighed with and without the husk for fresh ear yield. The number of ears per plant was recorded. Shoot fresh matter (FM) and DM, as well as kernel dry matter and thousand kernel weight (TKW) were determined. The harvest index (HI) was calculated as grain yield per unit aboveground DM. For radish, the root and shoot weight of 24 randomly picked plants were determined, and root length and circumference were measured. Nutrient uptake efficiency was calculated as total N, P, and K content in either aboveground DM of sweet corn or total DM of radish, per unit N, P, and K applied to the soil.

Manure, feed, and plant samples were first air-dried and later dried in a ventilated oven to constant weight at 60°C before being ground to 1 mm particle size for analysis. Organic matter (OM) was calculated as the difference between DM and ash after incinerating the sample at 550°C for 4 h in a muffle furnace (Naumann et al.

1997). The neutral detergent fibre (NDF) and acid detergent fibre (ADF) fractions in feed and faecal samples were determined using a semi-automated Ankom 220 Fiber Analyzer (ANKOM Technology, Macedon, NY, USA) following the method of Naumann et al. (1997), without including decalin and sodium sulphite. Residual ash was excluded from the NDF and ADF values. The C and N concentrations were quantified by a CN analyzer (VarioMax[®] CHN, Elementar Analysensysteme GmbH, Hanau, Germany). Phosphorus (P), potassium (K), and sodium (Na) concentrations were determined in an ash solution by spectrophotometry (Hitachi U-2000, Tokyo, Japan) and flame photometry (BWB-XP Technologies, UK), respectively (Naumann et al. 1997).

2.3.5 Statistical analysis

For all data, normal distribution of residuals and homogeneity of variance were tested graphically and with Levenes' test and in case of violation a remark was added to the results as no meaningful transformation could be found. Outliers were winsorised by the 95% confidence interval to prevent overrating of single values. Manure properties as well as nutrient concentrations and harvest parameters of sweet corn and radish were analysed by means of univariate ANOVA, with season and treatment as fixed factors, followed by a Tukey test in case of significance. To examine the effects of differing application rates between the treatments and the two investigated cropping seasons on selected parameters of sweet corn, a stepwise backward linear regression for the organic treatments (NPK excluded) was computed for the following factors as independent variables: plant density (plants m⁻²); soil C (t ha⁻¹), N, P and K stock (kg ha⁻¹) prior to season; and AC and QT application rates (t ha⁻¹) as well as N, P and K application rates (kg ha⁻¹). To compare the different treatments with pure goat manure as a reference, dummy variables were coded to calculate a linear regression including plant population density as well as soil C and nutrient stocks. The other cofactors AC, QT, N, P, and K application rates were excluded as they contributed to the treatment effects.

2.4 Results

2.4.1 Faeces quality parameters

The OM concentration of sun-dried manure was not significantly altered by amendments, though C, N, P, and Na concentrations were significantly different (Table 2.3). Feeding AC increased C concentration by 11% and C/N ratio by 25%, whereas the N and P concentrations were reduced by 11% and 15% compared with pure goat manure. QT feeding increased Na concentration by 126% and reduced P concentration by 18% as compared with pure goat manure. Despite the consistent treatment effects in the two seasons, N, P, and K concentration as well as C/N ratio varied significantly between the two seasons.

Table 2.3. Chemical composition of dry faeces in mg g⁻¹ for the different treatments (n = 9 in first and n = 18 in second cropping season) averaged across the two seasons of a field experiment in Northern Oman.

	Co		AC _{fed}		QT _{fed}		Treatment	Season
	Mean	SD	Mean	SD	Mean	SD	P value	P value
OM	900.14	26.75	912.99	12.14	915.52	9.29	0.35*	0.22
C	449.05 a	10.47	503.75 b	8.71	457.58 a	5.04	<0.000	0.45
N	23.95 b	1.91	21.37 a	1.70	22.75 ab	1.11	<0.05	<0.02
P	6.13 b	0.72	5.16 a	0.85	5.05 a	0.62	<0.010	<0.02
K	2.35	0.53	1.85	0.46	1.99	0.60	0.16	<0.05
Na	1.36 a	0.36	1.49 a	0.56	3.06 b	0.66	<0.001	0.11
CN	18.86 a	1.68	23.68 b	1.58	20.15 a	1.02	<0.001	<0.01

Letters indicate significant differences between treatment means.

*Homogeneity of variances not given

SD= standard deviation

2.4.2 Agronomic parameter

Coefficients of determination (R²) of the stepwise regression models were reached in 6-8 steps and contained 3-5 predictors explaining 34-73% of the parameter variation of sweet corn yield parameters (Table 2.4). Plant density differences across seasons significantly affected aboveground DM (g plant⁻¹) and fresh ear yield (kg ha⁻¹). Soil organic C and total N were important determinants for some of the tested parameters, whereas N and K application rate were not relevant. However, P application rate negatively affected plant DM as well as N, P, and K uptake efficiencies. AC and QT application rate significantly affected all measured parameters. Stepwise regressions for radish resulted in model fits of R² = 0.45-0.62

(Table 2.5). Plant density and soil P stock only affected fresh root yield, whereas SOC significantly affected P and K uptake efficiencies. While N application rate only affected N uptake efficiency, K application rate determined all tested parameters. In addition, P application decreased P and K uptake efficiencies. Whereas QT application rate significantly affected all measured parameters, AC application had no significant influence.

The effects of the different fertilizer treatments on aboveground DM per plant, fresh ear yield per hectare and nutrient uptake efficiencies as tested with dummy variables in a linear regression, yielded highly significant models with $R^2 = 0.70$ ($P < 0.001$) and $R^2 = 0.61$ ($P < 0.001$). Plant density, soil C and nutrient stocks did not significantly affect either parameter. However, compared with the control manure, NPK increased sweet corn yields ($P < 0.001$) by 28% and 98% for aboveground DM, and 33% and 110% for fresh ear yield in the two seasons, with partial correlation coefficients of $r = 0.57$ and $r = 0.53$, respectively (Fig. 2.2 a and b). Nitrogen and K uptake efficiencies in the two seasons were 70 to 100% and 0 to 120% higher compared with the control treatment, respectively ($P < 0.01$; $r = 0.57$ and $r = 0.44$; Fig. 2.3a-c). QT_{mix} negatively affected aboveground DM, N, P, and K uptake efficiencies, decreasing them between 27% and 59% ($P < 0.03$; $r = -0.46, -0.41, -0.41$ and -0.37 , respectively).

In radish, total DM per plant was significantly affected by the covariate plant population density ($P < 0.01$, $r = -0.42$), but soil C and nutrient stocks did not have any significant effect, whereas fresh marketable root yield was significantly affected by soil N stock ($P < 0.05$; $r = 0.32$). Nutrient uptake efficiencies of radish were not influenced by plant density, soil C or nutrient stocks. Overall model fits were highly significant with R^2 ranging from 0.53 to 0.68 ($P < 0.001$). NPK decreased total DM and fresh marketable root yield significantly ($P < 0.001$; $r = -0.55$ and -0.52 , respectively; Fig. 2.2c and d)) by 40 to 58% and nutrient uptake efficiencies by 12 to 55% ($r = -0.32$ - 0.55 ; Fig. 2.3d-f) compared with goat manure. Mixing tannins reduced DM and fresh marketable root yield by 25 to 34% ($P < 0.05$; $r = -0.38$) and 30 to 45% ($P < 0.01$; $r = -0.46$), respectively, compared with goat manure with stronger effects during the second cropping season. Feeding tannins only affected fresh marketable root yield with 20 to 47% yield reductions ($P < 0.05$; $r = -0.32$). QT_{fed} and QT_{mix}

decreased uptake efficiency of N by 20 and 37% and 35 to 33% and of K by 27 to 38% and 23 to 29% ($r = -0.39$ and -0.34 for QT_{fed} ; $r = -0.46$ and -0.35 for QT_{mix}).

Table 2.4. Multiple linear regression analysis of several harvest parameters of organically fertilized sweet corn including plant population density (plant m^{-2}), soil C (t ha^{-1}), N, P, and K contents (kg ha^{-1}), charcoal and tannin application rates (t ha^{-1}) as well as N, P, and K application rates (t ha^{-1}) as covariates of a field experiment in Northern Oman.

	B	Std. Error	β	<i>P</i> value	Partial correlation	<i>R</i> ²	<i>P</i> value
Aboveground DM (g plant ⁻¹)						0.36	0.003
Constant	252.45	67.06		0.001			
Plant density	-6.55	2.99	-0.32	0.035	-0.35		
AC	-25.31	9.55	-0.54	0.012	-0.41		
QT	-29.44	6.90	-0.84	0.000	-0.59		
P input	-2.30	1.13	-0.30	0.051	-0.32		
Fresh ear yield (t ha^{-1})						0.34	0.008
Constant	1.42	1.40		0.315			
Plant density	-0.87	0.33	-0.62	0.013	-0.42		
Soil N	0.01	0.00	0.69	0.008	0.44		
AC	-1.78	0.67	-0.54	0.013	-0.42		
QT	-1.24	0.47	-0.50	0.013	-0.42		
N uptake efficiency						0.51	0.000
Constant	0.47	0.15		0.004			
Soil N	0.00	0.00	0.31	0.025	0.37		
AC	-0.07	0.02	-0.55	0.002	-0.49		
QT	-0.06	0.02	-0.73	0.000	-0.59		
P input	-0.01	0.00	-0.31	0.023	-0.37		
P uptake efficiency						0.73	0.000
Constant	1.14	0.26		0.000			
SOC	-0.02	0.01	-0.39	0.002	-0.50		
Soil N	0.00	0.00	0.70	0.000	0.73		
AC	-0.09	0.04	-0.37	0.011	-0.42		
QT	-0.09	0.03	-0.48	0.001	-0.53		
P input	-0.02	0.00	-0.39	0.000	-0.55		
K uptake efficiency						0.38	0.001
Constant	0.88	0.25		0.001			
AC	-0.12	0.04	-0.62	0.002	-0.49		
QT	-0.12	0.03	-0.83	0.000	-0.62		
P input	-0.01	0.00	-0.29	0.049	-0.32		

Table 2.5. Multiple linear regression analysis of several harvest parameters of organically fertilized radish including plant population density (plant m⁻²), soil C (t ha⁻¹), N, P, and K contents (kg ha⁻¹), charcoal and tannin application rates (t ha⁻¹) as well as N, P, and K application rates (t ha⁻¹) as covariates of a field experiment in Northern Oman.

	B	Std. Error	β	P value	Partial correlation	R ²	P value
Total DM (g plant ⁻¹)						0.45	0.000
Constant	-18.91	7.32		0.014			
QT	-3.00	0.76	-0.48	0.000	-0.54		
K input	0.33	0.08	0.50	0.000	0.56		
Fresh root yield (t ha ⁻¹)						0.53	0.000
Constant	-28.05	9.94		0.008			
Plant density	0.00	0.00	0.45	0.006	0.45		
Soil P	-0.02	0.01	-0.25	0.046	-0.33		
QT	-2.94	0.65	-0.54	0.000	-0.61		
K input	0.34	0.09	0.58	0.001	0.54		
N uptake efficiency						0.62	0.000
Constant	0.09	0.11		0.446			
QT	-0.08	0.01	-0.75	0.000	-0.77		
N input	-0.00	0.00	-0.24	0.056	-0.31		
K input	0.00	0.00	0.34	0.008	0.42		
P uptake efficiency						0.58	0.000
Constant	0.32	0.18		0.088			
SOC	-0.01	0.00	-0.24	0.043	-0.33		
QT	-0.08	0.02	-0.47	0.000	-0.57		
P input	-0.02	0.00	-0.74	0.000	-0.62		
K input	0.01	0.00	0.48	0.004	0.46		
K uptake efficiency						0.51	0.000
Constant	0.60	0.50		0.240			
SOC	-0.02	0.01	-0.22	0.084	-0.29		
QT	-0.25	0.05	-0.58	0.000	-0.63		
P input	-0.03	0.01	-0.48	0.007	-0.43		
K input	0.02	0.01	0.40	0.024	0.37		

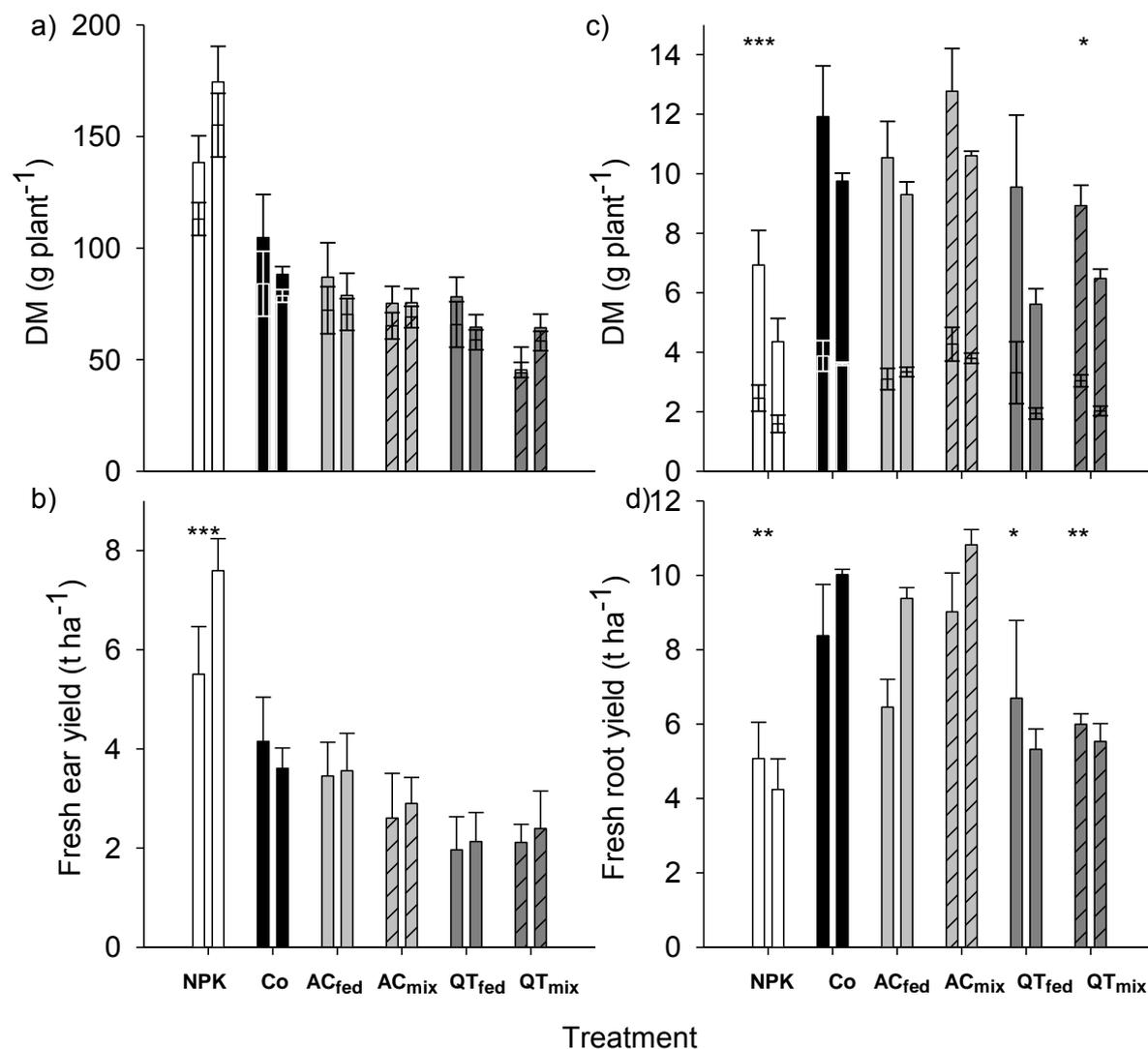


Figure 2.2. Aboveground and total DM of sweet corn (a and b) and radish (c and d) for the first (left bars) and second cropping season (right bars) in a field experiment in northern Oman. Error bars indicate \pm one standard error of the mean. Grey shades indicate goat manure with amendments, pattern indicates feeding application, no pattern mixed application. Stars indicate significant difference from control treatment (Co) * $P < 0.05$, ** $P < 0.01$ and *** $P < 0.001$.

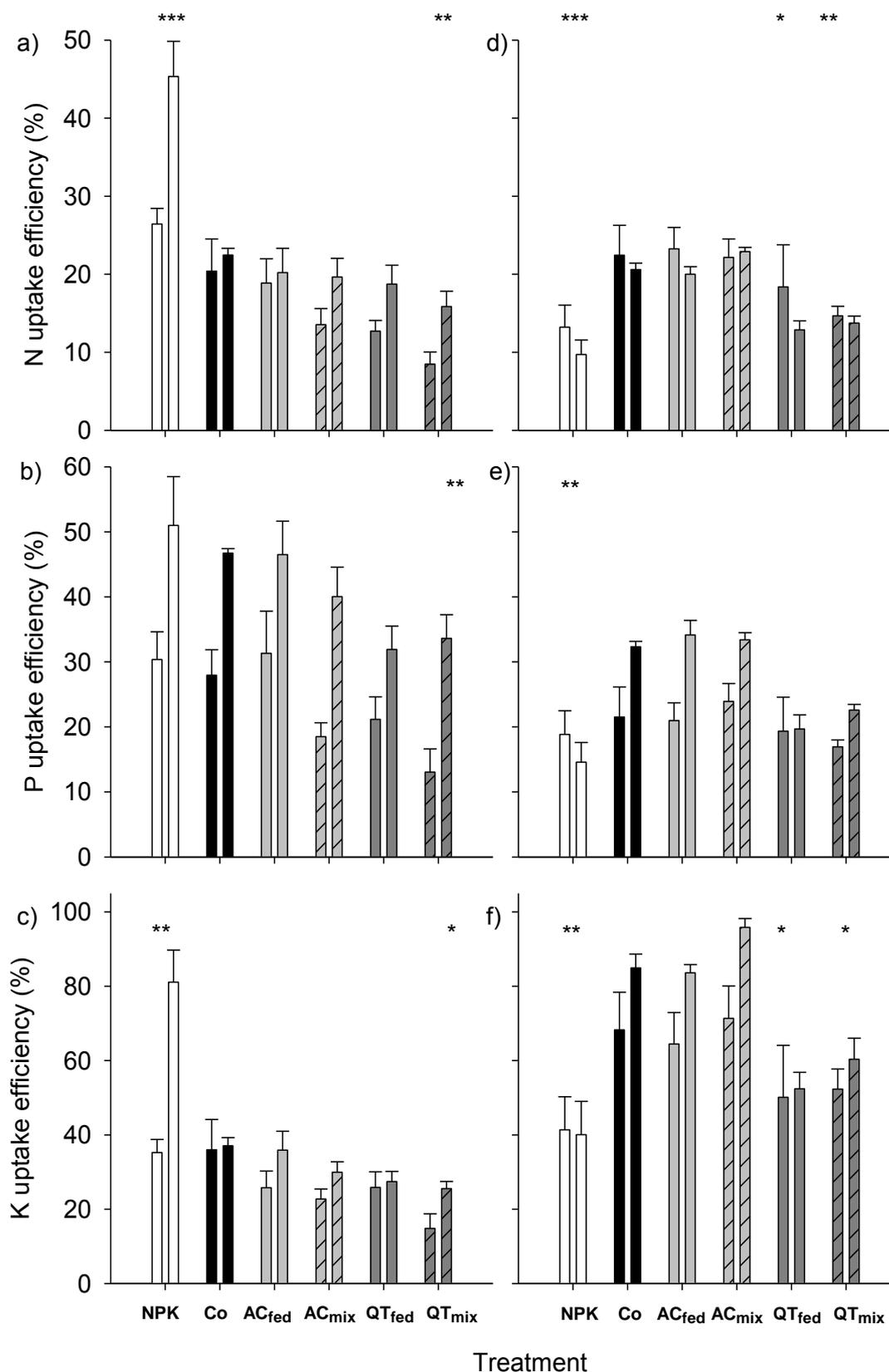


Figure 2.3. N, P, and K uptake efficiencies of sweet corn (a-c) and radish (d-f) for the first (left bars) and second cropping season (right bars) in a field experiment in northern Oman. Error bars indicate \pm one standard error of the mean. Grey shades indicate goat manure with amendments, pattern indicates feeding application, no pattern mixed application. Stars indicate significant difference from control treatment (Co) * $P < 0.05$, ** $P < 0.01$ and *** $P < 0.001$.

Germination of sweet corn and radish was unaffected by treatments in either cropping season. Generally, the germination of sweet corn was low, especially in the first season (60%) as compared with the second season (71%). For radish, the germination rate was higher in the first season (88%) than in the second season (79%).

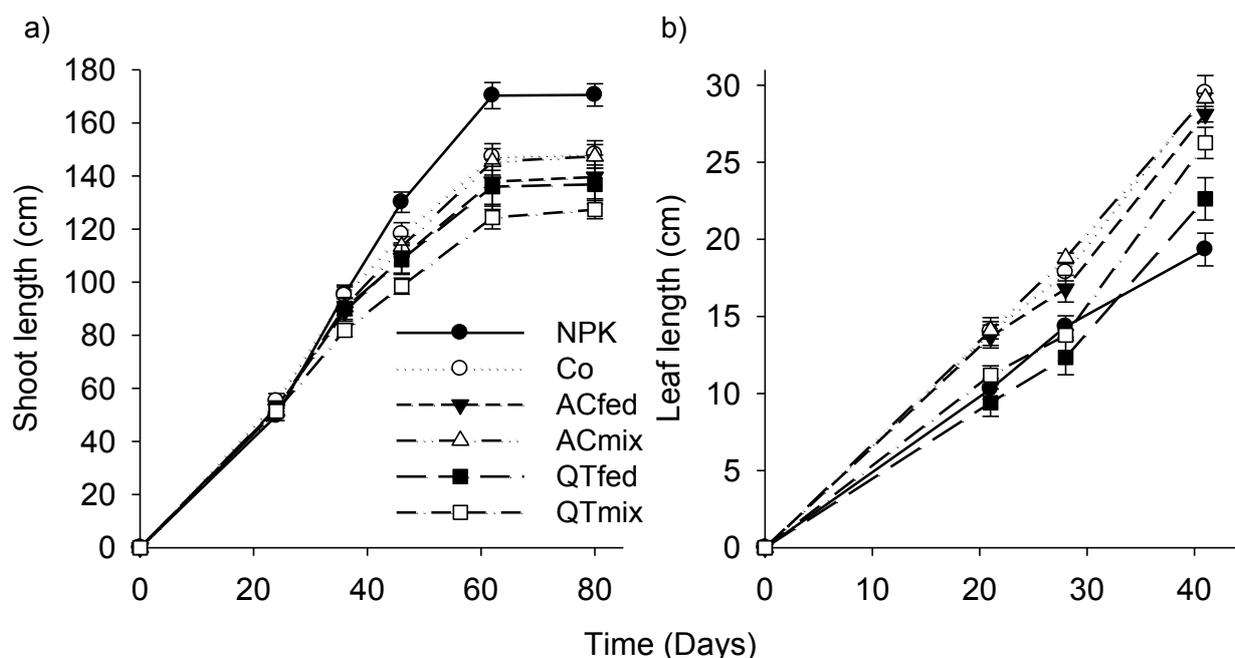


Figure 2.4. Plant height of sweet corn from ground to tip of highest leaf (a) and radish leaf length (b) in the course of the second cropping season of a field experiment in Northern Oman. Symbols represent mean averages, whiskers indicate \pm one standard error of the mean. Stars indicate significant difference from control treatment (Co) * $P < 0.05$, ** $P < 0.01$ and *** $P < 0.001$.

Growth parameters of sweet corn and radish basically showed similar tendencies in both cropping seasons. In sweet corn, NPK resulted in significantly higher growth parameters compared with goat manure treatments; effects due to additives were only significant for shoot length. Treatment effects on total shoot length in sweet corn were significant as of 46 DAS until harvest at 81 DAS (Fig. 2.4a), with significant differences between NPK and the three manure treatments (AC_{fed} , QT_{fed} and QT_{mix}). Other measured growth parameters such as total leaf area are not shown because they showed similar treatment effects. In radish, NPK reduced leaf length and in the second cropping season, radish already had significantly shorter leaves in NPK and QT_{fed} treatments after 21 DAS and this difference remained until harvest at 43 DAS (Fig. 2.4b). In addition, number of leaves, root length, and circumference in radish

were significantly reduced by NPK and tannin application compared with pure goat manure application in both seasons (data not shown).

During the two cropping seasons, SPAD readings of sweet corn showed different patterns reflecting differences in season-specific splitting of manure application. Nevertheless, in both cropping seasons, SPAD chlorophyll values were significantly higher for the NPK treatment (+20%) and lower for the tannin treatments (-10 to 15%) after only 35 DAS as compared with pure goat manure (data not shown). These differences increased between 45 and 60 DAS, resulting in up to 40% higher SPAD values for NPK, and then declined until harvest. Carbon and nutrient concentrations in shoot DM of sweet corn were similar for both seasons averaging 422 mg C g⁻¹, 9.6 mg N g⁻¹, 5.3 mg P g⁻¹ and 11.9 mg K g⁻¹ (Table 2.6). In kernels, these values were around 571 mg C g⁻¹, 28.9 mg N g⁻¹, 5.2 mg P g⁻¹ and 10.5 mg K g⁻¹. Only C and P concentrations showed significant treatment effects in the shoot and kernel of sweet corn at harvest. NPK-fertilized plants had significantly higher C concentrations in the shoot and kernels and 50% lower P concentrations in the shoot than control plants. In the kernel, QT_{fed} resulted in significantly higher P concentrations as compared with AC_{mix}. For radish, in contrast significantly lower SPAD chlorophyll values were measured for NPK and QT treatments during both seasons until 32 DAS (data not shown). At 41 DAS in the second cropping season, no treatment effects were observed. In addition, C as well as N, P and K concentrations remained unaltered by any treatment in either cropping season (Table 2.7).

Table 2.6. Carbon and nutrient concentrations in shoot and kernel of sweet corn after harvest at 81 DAS (first cropping season in 2010 and second season in 2011) in a field experiment in Northern Oman. Letters indicate significant differences between treatment means.

	C		N		P		K				
	mg g ⁻¹										
	2010	2011	2010	2011	2010	2011	2010	2011			
Sweet corn shoot											
NPK	430	b	426	9.4	10.8	2.6	a	3.2	a	12.2	13.2
Co	419	a	418	10.6	8.7	5.4	b	6.4	b	12.4	11.7
AC _{fed}	419	a	419	10.5	9.2	5.9	b	6.6	b	11.9	12.5
AC _{mix}	422	ab	420	9.2	9.5	4.5	ab	6.4	b	10.5	11.7
QT _{fed}	424	ab	425	8.8	10.1	4.7	ab	5.5	b	12.3	11.2
QT _{mix}	422	ab	420	10.0	8.8	5.8	b	6.3	b	12.1	11.1
<i>P</i> - <i>value</i>	<0.05		0.07	0.40	0.46	<0.01		<0.001		0.67	0.07
Sweet corn kernels											
NPK		474	c		31.7			5.1	ab		10.2
Co		470	abc		28.2			5.1	ab		10.4
AC _{fed}		471	abc		27.0			5.3	ab		10.6
AC _{mix}		470	bc		27.8			4.9	a		10.0
QT _{fed}		473	ab		31.6			5.5	b		10.8
QT _{mix}		468	a		27.0			5.0	ab		10.9
<i>P</i> - <i>value</i>		<0.01			0.22			<0.05			0.05

Table 2.7. Carbon and nutrient concentrations in shoot and root of radish at 43 DAS (first cropping season in 2010/11 and second season in 2011/12) in a field experiment in Northern Oman.

	C		N		P		K	
	2010	2011	2010	2011	2010	2011	2010	2011
Radish root								
NPK	363	366	21.3	19.8	7.3	9.6	73.5	96.5
Co	358	370	23.8	21.2	6.9	7.9	75.5	80.7
AC _{fed}	359	367	24.2	21.0	7.2	8.1	76.3	80.7
AC _{mix}	357	369	23.5	23.0	7.4	8.3	76.8	85.6
QT _{fed}	362	363	22.1	23.5	7.3	7.8	67.8	82.6
QT _{mix}	364	369	20.2	21.7	7.4	8.3	75.1	85.7
<i>P-value</i>	<i>0.23</i>	<i>0.74</i>	<i>0.47</i>	<i>0.98</i>	<i>0.81</i>	<i>0.07</i>	<i>0.50</i>	<i>0.27</i>
Radish shoot								
NPK	352	328	31.4	28.3	8.1	11.2	49.4	51.3
Co	355	332	34.5	28.8	8.0	10.2	48.2	52.7
AC _{fed}	365	331	33.4	28.7	7.9	10.6	40.4	60.0
AC _{mix}	351	335	31.9	28.6	8.6	9.3	51.1	59.8
QT _{fed}	352	331	32.2	28.3	8.2	10.9	46.3	55.8
QT _{mix}	356	334	31.3	28.0	8.8	10.6	50.7	59.6
<i>P-value</i>	<i>0.48</i>	<i>0.24</i>	<i>0.42</i>	<i>0.43</i>	<i>0.83</i>	<i>0.43</i>	<i>0.68</i>	<i>0.55</i>

For sweet corn, the number of grain-bearing cobs per plant, average cob weight, kernel DM per cob and per plant, as well as HI were generally higher in the first season compared with the second season, indicating a better development due to the lower plant population density (Table 2.8). NPK treatment plants developed 50% and 90% more cobs per plant in the first and second season, respectively. Average cob weight and DM kernel DM weight per cob and per plant were 15, 21, and 41% lower in the second season compared with the first one. All harvest parameters were highest for the NPK treatment followed by those of Co, AC_{fed}, AC_{mix} and they were lowest for the two QT treatments. TSW, only measured in the second season, was lowest for NPK and highest for Co. Average HI as grain yield per unit aboveground DM was by 73% higher in the first as compared with the second season, but did not show any significant treatment effect in either season.

Table 2.8. Harvest parameters of sweet corn at 81 DAS in 2010/11 and 2011/12 in a field experiment in Northern Oman. Letters indicate significant differences between treatment means.

	Pollinated cobs per plant		Average cob weight (g)		Kernel DM per cob (g)		Kernel DM per plant (g)		TSW (g)		HI	
	2010	2011	2010	2011	2010	2011	2010	2011	2010	2011	2010	2011
NPK	1.3 a	1.1 a	153	148 a	20.2	16.1	25.3	19.4 a		50.7	0.18	0.11
Co	0.9 b	0.7 ab	162	115 ab	22.7	12.3	20.7	9.6 b		63.4	0.19	0.11
AC _{fed}	0.9 b	0.7 ab	133	106 ab	16.0	10.4	14.8	8.6 b		58.6	0.16	0.10
AC _{mix}	0.9 b	0.6 b	134	112 ab	16.2	10.3	12.5	6.4 c		56.4	0.13	0.08
QT _{fed}	0.8 b	0.5 b	116	96 b	14.8	12.7	10.1	5.7 d		51.9	0.17	0.09
QT _{mix}	0.7 b	0.5 b	100	99 b	14.2	9.8	10.1	5.9 d		57.5	0.17	0.09
<i>P-value</i>	<i><0.01</i>	<i><0.01</i>	<i>n.s.</i>	<i>0.04</i>	<i>n.s.</i>	<i>n.s.</i>	<i>n.s.</i>	<i>0.001</i>		<i>n.s.</i>	<i>n.s.</i>	<i>n.s.</i>

2.5 Discussion

The heterogeneous quality of applied manure resulted from differences in feed quality, climatic conditions and age of goats. Moreover, the long collection period of manure might have caused an adaptation of goats to the feed additives, changing the faeces composition within the season. Due to their higher feed intake the heavier goats from the first season quantitatively excreted more faeces than the younger ones. Yet, given the higher digestibility of feed in the older animals, the faecal concentration of the indigestible AC and QT was higher leading to an overall higher quantity of these amendments in the first cropping season. However, even with such seasonal and treatment-related differences in manure nutrient concentrations and thus total application rates of AC, QT, C and nutrients, some significant amendment effects were noticed.

2.5.1 Faeces quality

The quality of goat manure can vary considerably ranging from 25 to 49% for C, 0.9 to 2.3% for N, 0.2 to 0.7% for P, and 9-38 for the C/N ratio (Somda et al., 1995; Mafongoya et al., 2000; Maerere et al., 2001; Wichern et al., 2004; Azeez and Van Averbek, 2010). These differences depend on diet composition, animal age, and management, as well as storage conditions of the manure itself. In our study, quality parameters of sun-dried manure were in the upper third of these ranges with 45 with 50% C, 2.1 to 2.4% N, 0.5 to 0.6% P, and C/N ratios ranging from 19 to 24.

Feeding AC to goats increased the C concentration and the C/N ratio in their manure. In contrast to the vast literature on the effects of ruminant-fed AC on their growth, productivity and methane emissions (Leng et al. 2012), feed intake (Van et al. 2006; Rogosic et al. 2009), detoxification (Poage et al. 2000; Huwig et al. 2001) as well as on parasite infection (Van et al. 2006; Watarai et al. 2008), little data is available on the quality of manure of animals fed with this amendment. In a digestibility trial with goats, using a similar concentration of AC but a different basal diet, Al-Kindi et al. (unpublished) observed that compared with the control, C, NDF and ADF concentrations of manure increased by 15, 8, and 14%, respectively, while N concentrations decreased by 8%. In their study, the lower manure N was explained by a 13% higher excretion of organic matter paired with unchanged

excretion of faecal N. This result is similar to ours and indicates that AC can increase stable components in the organic matter fraction of faeces.

In contrast, feeding QT did not significantly alter most proximate components in the dry faeces. Studies dealing with the effects of feeding polyphenols such as QT focus mainly on their impact on animal health, productivity, methane emissions, and their digestibility or toxicity, effects to evaluate forage values (Silanikove et al. 1996; Puchala et al. 2005; Bhatta et al. 2011; Novobilský et al. 2011). The influence of polyphenol-containing fodder on the manure quality of the excreted faeces is largely ignored. However, from digestibility trials it is known that the ingestion of leaves containing different amounts and types of polyphenols can lead to higher C and N concentrations in goat faeces and to higher C/N ratios (Mafongoya et al. 2000). In addition, it has been shown that polyphenol-rich legumes fed to lambs reduced protein digestibility in the rumen and thus lead to a shift in N excretion from urine to faeces (Hess et al. 2006). In the digestibility trial of Al-Kindi et al. (unpublished), total C and N as well as ADF contents in faeces increased by 5, 9 and 4%, respectively, when QT was fed to goats, while NDF was reduced by 4%. In addition, the daily excretion of organic matter, C, and N per goat increased by 35, 40, and 50%. Therefore, it seems that feeding QT increases the amount of nutrients excreted by goats rather than changing their concentrations.

2.5.2 Agronomic parameters

In our field experiment, sweet corn yields were reduced by AC and QT amendments, regardless of the application method and cropping season, while radish was only negatively affected by QT. Yields of fresh sweet corn ears were low in treatments fertilized with goat manure (2.0 to 4.1 t ha⁻¹ and 2.1 to 3.6 t ha⁻¹ in the first and second cropping season, respectively) compared with yields of plants fertilized with mineral fertilizer (5.5 t ha⁻¹ and 7.6 t ha⁻¹ first and second season, respectively) and with fresh ear yields reported in the literature for semi-arid environments (3 to 15 t ha⁻¹; Oktem et al. 2003; Rivera-Hernández et al. 2010; Ertek and Kara 2013). Despite the foliar application of micronutrients, our low sweet corn yields may have resulted from micronutrient deficiencies of zinc or iron on the alkaline soil as indicated by chlorotic leaves. Early season SPAD chlorophyll values, a good indicator of corn's N status (Bullock and Anderson 1998), were lower in

organically fertilized sweet corn than in plants receiving mineral fertilizer. Nitrogen uptake efficiency of latter plants reached up to 45% in the second season and produced up to 50% higher fresh ear yields compared with goat manure, whereas plants treated with goat manure only reached N uptake efficiencies of 9 to 22%.

In contrast, radish growth did not seem to be limited by lower nutrient availability in goat manure treatments as yields were higher compared with NPK treated plots. For radish fertilized with goat manure – alone or amended with AC or QT – fresh root yields ranged between 6 to 9 and 5 to 11 t ha⁻¹ in the first and second season, while radish receiving mineral fertilizer only yielded 5 and 4 t ha⁻¹, respectively. These marketable root yields were substantially lower compared with those of a previous study conducted with the same radish variety under flood irrigation in Northern Oman (Siegfried et al. 2013).

2.5.3 Charcoal effects

In contrast to many reports for different crops (Glaser et al. 2002), yields of sweet corn and radish were unaffected or even reduced by AC application. In a study by Yamato et al. (2006) the application of 37 t ha⁻¹ charcoal in combination with mineral fertilizer lead to an increase of maize yields by 50% on highly weathered soils in Indonesia. However, if charcoal application is not combined with sufficient amounts of nutrients, N immobilization can lead to yield reductions (Nelson et al. 2011). In a greenhouse experiment by Schulz and Glaser (2012), the application of 40 t ha⁻¹ biochar only increased oat (*Avena sativa*) yields compared with oat grown on pure sand in combination with fertilizer or compost. Even though Zhang et al. (2012) reported yield increases of 16% when 20 t ha⁻¹ biochar was applied without additional N, the N input via biochar amounted to 120 kg ha⁻¹. It is likely that in the present study, where AC had low nutrient concentrations, a very high C content and C/N ratio even at its low application rate may have led to partial immobilization of manure N and thus negatively affected yields.

Radish, a crop much lower in N demand compared with sweet corn, did not exhibit the same yield depressions. At the low application rates of 0.8 to 1.3 t AC ha⁻¹ on the alkaline sandy soil of our study, SOC and WHC were significantly increased compared with pure goat manure (Ingold et al. 2015).

In a pot experiment conducted by Van Zwieten et al. (2010) the effects of two types of paper mill waste-based biochars on radish yields were studied on an acidic Ferrosol and an alkaline Calcarosol. In combination with a mineral fertilizer, the application of 10 t ha⁻¹ of either two biochars led to higher yields on the Ferrosol but lower yields on the Calcarosol compared with the unamended control. Most studies observing positive effects of charcoal application on plant yields were conducted on highly weathered and acidic soils (Yamato et al. 2006; Van Zwieten et al. 2010), where charcoal application typically increases pH, CEC and nutrient availability and also reduces aluminium toxicity (Glaser et al. 2002; Yamato et al. 2006; Steiner et al. 2007). On alkaline soils, however, the application of biochar is unlikely to change soil properties such as pH, CEC, and nutrient availability (Van Zwieten et al. 2010; Ingold et al. 2015). In addition feed and pyrolysis conditions strongly influence charcoal properties (Chan et al. 2008; Bruun et al. 2012). In our study, steam activated charcoal with low nutrient concentrations, but high pH and pore space was used. As SOC significantly increased after two cropping seasons even at this low AC application rate (Ingold et al. 2015), positive effects on yields can be expected on the alkaline soil with accompanying nutrient inputs and a longer experimental duration.

2.5.4 Tannin effects

QT inhibited plant growth regardless of crop or application method. So far the effects of tannins on soils have been mainly investigated on forest soils, where tannins from leaf litter inhibited organic matter degradation and N mineralization by binding to proteins and inhibiting microorganisms (Palm and Sanchez 1991; Kraus et al. 2004). Studies dealing with their effects on animals mainly focused on the effects tannins-containing browse species on animal health and productivity and the digestibility of such forages (Aerts et al. 1999; Makkar 2003; Bhatta et al. 2011). In a greenhouse study on millet growth conducted by Powell et al. (1999), the effects of a variety of crop residues and browse leaves containing polyphenols were compared with faeces derived from these feeds. Even though faeces composition, N, and P concentrations varied and insoluble and soluble N was altered (Powell et al. 1994) millet yield remained unaffected by faeces obtained from different polyphenol-containing diets without additional N application. Moreover, the reported changes in faecal composition could not be clearly attributed to the polyphenol content of

browse leaves, but may have been caused by other secondary metabolites contained in the browse or cell wall constituents such as lignin.

In our study, both QT applications increased N deficiency of sweet corn, as indicated by a 7% reduction in SPAD values at 25 DAS in QT_{mix} and QT_{fed} plants, compared with pure goat manure fertilized plants. SPAD values in these plants remained lower until harvest. As total soil N increased by 36% QT_{mix} for after the two-year experimental period (Ingold et al. 2015) it is likely that N mineralization was inhibited by QT when mixed directly to the soil. However, low concentrations of condensed tannins can inhibit microbial enzyme activity and slow down N mineralization (Kraus et al. 2004; Kanerva et al. 2006; Joannis et al. 2007). Interestingly, when QT was fed to goats, total soil N increased as well, but only by 19%, and SOC was slightly reduced (Ingold et al. 2015). It is well known that tannins ingested by ruminants may undergo conformational changes (Degen et al. 1995; Makkar 2003), and thus affect N binding in the soil. Al-Kindi et al. (unpublished) reported a 56% increase in the soluble N concentration of faeces when goats fed a diet containing 4% QT. However, tannins and other phenolics are potential allelopathic agents, which may inhibit the development of crop species (Sinkkonen 2006). As the tannin source - *Schinopsis balansae* - does not naturally grow in the same ecosystems as sweet corn or radish, confronting these crops with tannins may thus have resulted in unintended, negative allelopathic effects (Stoms 1982). Further research is thus necessary to examine whether tannins from other plant species, applied to other crops or on different soil types lead to similarly negative effects and how these can be potentially reduced.

2.6 Conclusions

Manure properties resulting from AC feeding to goats may stabilize soil organic matter and thus contribute to increased soil fertility in the long run. However, the likely immobilization of N by AC, supported by the high C/N ratio of AC manure, negatively affected sweet corn, whereas radish benefitted from the improvement of soil properties by addition of organic matter via goat manure and AC. To fully benefit from AC-related improvement of soil properties, N supply needs to be enhanced. This may lead to improved yields on alkaline sandy soils even at low AC application rates, particularly when low AC application rates are applied repeatedly.

In contrast, QT feeding hardly changed faeces properties, but reduced growth and development of sweet corn and radish. This points to a direct inhibition of crop development by tannins, and is of particular importance for many subtropical and tropical regions where tannin containing forage contributes to overcome feed shortages. As animal manure is often the only nutrient source in resource poor farming systems, the detrimental effect of tannin-enriched manure on plant growth may be of economic relevance. Therefore, further research is needed to evaluate the inhibitory potential of other tannin sources, and how such deleterious effects can be counteracted.

2.7 Acknowledgements

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2.8 References

- Aerts, R.J., Barry, T.N. and McNabb, W.C., 1999. Polyphenols and agriculture: beneficial effects of proanthocyanidins in forages. *Agriculture, Ecosystems and Environment* 75, 1-12.
- Aggarwal, R.K., Praveen-Kumar and Power, J.F., 1997. Use of crop residue and manure to conserve water and enhance nutrient availability and pearl millet yields in an arid tropical region. *Soil and Tillage Research* 41, 43-51.
- Al-Asfoor, H., Schlecht, E., Sundrum, A. and Schiborra, A., 2012. Varying the dietary supply of C and N to manipulate the manure composition of water buffalo heifers in Oman. *Journal of Agriculture and Rural Development in the Tropics and Subtropics* 113, 125-136.
- Al-Farsi, S.A.I., 2001. Classification of soils from an alluvial fan and coastal plain near Sohar. Sultan Qaboos University, Sultanate of Oman.
- Azeez, J.O. and Van Averbek, W. 2010. Nitrogen mineralization potential of three animal manures applied on a sandy clay loam soil. *Bioresource Technology* 101, 5645-5651.
- Bhatta, R., Shinde, A.K., Vaithyanathan, S., Sankhyan, S.K., Enishi, O. and Kurihara, M., 2011. Utilisation of tannin-containing tree leaves in sheep and goat production. Successes and failures with animal nutrition practices and technologies in developing countries, *FAO Electronic Conference Rome, Italy*.
- Bruun, E.W., Ambus, P., Egsgaard, H. and Hauggaard-Nielsen, H. 2012. Effects of slow and fast pyrolysis biochar on soil C and N turnover dynamics. *Soil Biology and Biochemistry* 46, 73-79.
- Buerkert, A., Nagieb, M., Siebert, S., Khan, I. and Al-Maskri, A. 2005. Nutrient cycling and field-based partial nutrient balances in two mountain oases of Oman. *Field Crop Research* 94, 149-164.
- Bullock, D.G. and Anderson, D.S., 1998. Evaluation of the Minolta SPAD-502 chlorophyll meter for nitrogen management in corn. *Journal of Plant Nutrition* 21, 741-755.

- Chan, K.Y., Van Zwieten, L., Meszaros, I., Downie, A. and Joseph, S., 2008. Using poultry litter biochars as soil amendments. *Soil Research* 46, 437-444.
- Degen, A.A., Becker, K., Makkar, H.P.S. and Borowy, N. 1995. *Acacia saligna* as a fodder tree for desert livestock and the interaction of its tannins with fibre fractions. *Journal of the Science of Food and Agriculture* 68, 65-71.
- Ertek, A. and Kara, B., 2013. Yield and quality of sweet corn under deficit irrigation. *Agricultural Water Management* 129, 138-144.
- Glaser, B., Lehmann, J. and Zech, W., 2002. Ameliorating physical and chemical properties of highly weathered soils in the tropics with charcoal: a review. *Biology and Fertility of Soils* 35, 219-230.
- Hess, H.D., Tiemann, T.T., Stürm, C.D., Carulla, J.E., Lascano, C.E. and Kreuzer, M., 2006. Effects of tannins on ruminal degradation and excretory pattern of N and implications for the potential N emission from the manure. *International Congress Series* 1293, 339-342.
- Huwig, A., Freimund, S., Käppeli, O. and Dutler, H., 2001. Mycotoxin detoxication of animal feed by different adsorbents. *Toxicology Letters* 122, 179-188.
- Ingold, M., Dietz, H., Sradnick, A., Joergensen, R., Schlecht, E. and Buerkert, A., 2015. Effects of activated charcoal and quebracho tannin amendments on soil properties in irrigated organic vegetable production under arid subtropical conditions. *Biology and Fertility of Soils* 51, 367-377.
- Joanisse, G.D., Bradley, R.L., Preston, C.M. and Munson, A.D., 2007. Soil enzyme inhibition by condensed litter tannins may drive ecosystem structure and processes: the case of *Kalmia angustifolia*. *New Phytologist* 175, 535-546.
- Kanerva, S., Kitunen, V., Kiiikkilä, O., Lojonen, J. and Smolander, A., 2006. Response of soil C and N transformations to tannin fractions originating from Scots pine and Norway spruce needles. *Soil Biology and Biochemistry* 38, 1364-1374.
- Kraus, T.E.C., Zasoski, R.J., Dahlgren, R.A., Horwath, W.R. and Preston, C.M., 2004. Carbon and nitrogen dynamics in a forest soil amended with purified tannins from different plant species. *Soil Biology and Biochemistry* 36, 309-321.
- Leng, R.A., Preston, T.R. and Inthapanya, S. 2012. Biochar reduces enteric methane and improves growth and feed conversion in local "Yellow" cattle fed cassava root chips and fresh cassava foliage. *Livestock Research for Rural Development* 24. <http://www.lrrd.org/lrrd2024/2011/leng24199.htm>. Accessed 6 August 2014.
- Maerere, A.P., Kimbi, G.G. and Nonga, C.L.M. 2001. Comparative effectiveness of animal manures on soil chemical properties, yield and root growth of *Amaranthus (Amaranthus cruentus L.)*. *African Journal of Science and Technology* 1, 14-21.
- Mafongoya, P.L., Barak, P. and Reed, J.D. 2000. Carbon, nitrogen and phosphorus mineralization of tree leaves and manure. *Biology and Fertility of Soils* 30, 298-305.
- Makkar, H.P.S., 2003. Effects and fate of tannins in ruminant animals, adaptation to tannins, and strategies to overcome detrimental effects of feeding tannin-rich feeds. *Small Ruminant Research* 49, 241-256.
- Manna, M.C., Swarup, A., Wanjari, R.H., Ravankar, H.N., Mishra, B., Saha, M.N., Singh, Y.V., Sahi, D.K. and Sarap, P.A., 2005. Long-term effect of fertilizer and manure application on soil organic carbon storage, soil quality and yield sustainability under sub-humid and semi-arid tropical India. *Field Crops Research* 93, 264-280.
- Materechera, S., 2010. Utilization and management practices of animal manure for replenishing soil fertility among smallscale crop farmers in semi-arid farming districts of the North West Province, South Africa. *Nutrient Cycling in Agroecosystems* 87, 415-428.
- Millennium Ecosystem Assessment, 2005. *Ecosystems and Human Well-being: Synthesis*. Island Press, Washington D.C.
- Naumann, C., Bassler, R., Seibold, R. and Barth, C. 1997. *Methodenbuch. Band III, Die chemische Untersuchung von Futtermitteln*, 3rd edn. VDLUFA, Darmstadt, Germany.
- Nelson, N.O., Agudelo, S.C., Yuan, W. and Gan, J., 2011. Nitrogen and phosphorus availability in biochar-amended soils. *Soil Science* 176, 218-226.

- Northup, R., Dahlgren, R. and McColl, J., 1998. Polyphenols as regulators of plant-litter-soil interactions in Northern California's pygmy forest: A positive feedback? *Biogeochemistry* 42, 189-220.
- Novobilský, A., Mueller-Harvey, I. and Thamsborg, S.M., 2011. Condensed tannins act against cattle nematodes. *Veterinary Parasitology* 182, 213-220.
- Nyamangara, J., Gotosa, J. and Mpfu, S.E., 2001. Cattle manure effects on structural stability and water retention capacity of a granitic sandy soil in Zimbabwe. *Soil and Tillage Research* 62, 157-162.
- Oktem, A., Simsek, M. and Oktem, A.G., 2003. Deficit irrigation on sweet corn (*Zea mays saccharata* Sturt) with drip irrigation system in a semi-arid region: I. Water-yield relationship. *Agricultural Water Management* 61, 63-74.
- Palm, C.A. and Sanchez, P.A., 1991. Nitrogen release from the leaves of some tropical legumes as affected by their lignin and polyphenolic contents. *Soil Biology and Biochemistry* 23, 83-88.
- Poage, G.W., Scott, C.B., Bisson, M.G. and Hartmann, F.S., 2000. Activated charcoal attenuates bitterweed toxicosis in sheep. *Journal of Rangeland Management* 53, 73-78.
- Powell, J.M., Fernández-Rivera, S. and Hörs, S., 1994. Effects of sheep diet on nutrient cycling in mixed farming systems of semi-arid West Africa. *Agriculture, Ecosystems and Environment* 48, 263-271.
- Powell, J.M., Ikpe, F.N. and Somda, Z.C., 1999. Crop yield and the fate of nitrogen and phosphorus following application of plant material and feces to soil. *Nutrient Cycling in Agroecosystems* 54, 215-226.
- Powell, J.M., Wattiaux, M.A., Broderick, G.A., Moreira, V.R. and Casler, M.D., 2006. Dairy Diet Impacts on Fecal Chemical Properties and Nitrogen Cycling in Soils. *Soil Science Society of America Journal* 70, 786-794.
- Puchala, R., Min, B.R., Goetsch, A.L. and Sahl, T., 2005. The effect of a condensed tannin-containing forage on methane emission by goats. *Journal of Animal Science* 83, 182-186.
- Rajkovich, S., Enders, A., Hanley, K., Hyland, C., Zimmerman, A. and Lehmann, J., 2012. Corn growth and nitrogen nutrition after additions of biochars with varying properties to a temperate soil. *Biology and Fertility of Soils* 48, 271-284.
- Rivera-Hernández, B., Carrillo-Ávila, E., Obrador-Olán, J.J., Juárez-López, J.F. and Aceves-Navarro, L.A. 2010. Morphological quality of sweet corn (*Zea mays* L.) ears as response to soil moisture tension and phosphate fertilization in Campeche, Mexico. *Agricultural Water Management* 97, 1365-1374.
- Rogosic, J., Pfister, J.A., Provenza, F.D. and Grbesa, D., 2006. The effect of activated charcoal and number of species offered on intake of Mediterranean shrubs by sheep and goats. *Applied Animal Behaviour Science* 101, 305-317.
- Rogosic, J., Moe, S.R., Skobic, D., Knezovic, Z., Rozic, I., Zivkovic, M. and Pavlicevic, J., 2009. Effect of supplementation with barley and activated charcoal on intake of biochemically diverse Mediterranean shrubs. *Small Ruminant Research* 81, 70-84.
- Rufino, M.C., Rowe, E.C., Delve, R.J. and Giller, K.E., 2006. Nitrogen cycling efficiencies through resource-poor African crop-livestock systems. *Agriculture, Ecosystems and Environment* 112, 261-282.
- Schlecht, E., Dickhoefer, U., Predotova, M. and Buerkert, A., 2011. The importance of semi-arid natural mountain pastures for feed intake and recycling of nutrients by traditionally managed goats on the Arabian Peninsula. *Journal of Arid Environments* 75, 1136-1146.
- Schulz, H. and Glaser, B., 2012. Effects of biochar compared to organic and inorganic fertilizers on soil quality and plant growth in a greenhouse experiment. *Journal of Plant Nutrition and Soil Science* 175, 410-422.
- Shankarnarayan, K.A., Bohra, H.C. and Ghosh, P.K., 1985. The goat: an appropriate animal for arid and semi-arid regions. *Economic and Political Weekly* 20, 1965-1972.
- Siegfried, K., Dietz, H., Schlecht, E. and Buerkert, A., 2011. Nutrient and carbon balances in organic vegetable production on an irrigated, sandy soil in northern Oman. *Journal of Plant Nutrition and Soil Science* 174, 678-689.

- Siegfried, K., Dietz, H., Amthauer Gallardo, D., Schlecht, E. and Buerkert, A., 2013. Effects of manure with different C/N ratios on yields, yield components and matter balances of organically grown vegetables on a sandy soil of northern Oman. *Organic Agriculture* 3, 9-22.
- Silanikove, N., Gilboa, N., Perevolotsky, A. and Nitsan, Z., 1996. Goats fed tannin-containing leaves do not exhibit toxic syndromes. *Small Ruminant Research* 21, 195-201.
- Sinkkonen, A., 2006. Ecological relationships and allelopathy. In: Reigosa, M.J., Pedrol, N. and González, L. *Allelopathy: A Physiological Process with Ecological Implications*. Springer, Dordrecht, pp. 373-394.
- Somda, Z.C., Powell, J.M., Fernández-Rivera, S. and Reed, J., 1995. Feed factors affecting nutrient excretion by ruminants and the fate of nutrients when applied to soil. In: Powell et al. *Livestock and Sustainable Nutrient Cycling in Mixed Farming Systems of Sub-Saharan Africa*, Addis Ababa, Ethiopia, pp. 227-243.
- Steiner, C., Teixeira, W.G., Lehmann, J., Nehls, T., de Macêdo, J.L.V., Blum, W.E.H. and Zech, W., 2007. Long term effects of manure, charcoal and mineral fertilization on crop production and fertility on a highly weathered Central Amazonian upland soil. *Plant and Soil* 291, 275-290.
- Stoms, D.J., 1982. Effect of polyphenols on shoot and root growth and on seed germination. *Biologia Plantarum* 24, 1-6.
- Sukartono, Utomo, W.H., Kusuma, Z. and Nugroho, W.H., 2011. Soil fertility status, nutrient uptake, and maize (*Zea mays* L.) yield following biochar and cattle manure application on sandy soils of Lombok, Indonesia. *Journal of Tropical Agriculture* 49, 47-52.
- UNEP, 1997. *World atlas of desertification*. Nairobi.
- Van, D.T.T., Mui, N.T. and Ledin, I., 2006. Effect of method of processing foliage of *Acacia mangium* and inclusion of bamboo charcoal in the diet on performance of growing goats. *Animal Feed Science Technology* 130, 242-256.
- Van Zwieten, L., Kimber, S., Morris, S., Chan, K.Y., Downie, A., Rust, J., Joseph, S. and Cowie, A., 2010. Effects of biochar from slow pyrolysis of papermill waste on agronomic performance and soil fertility. *Plant and Soil* 327, 235-246.
- Watarai, S., Tana and Koiwa, M., 2008. Feeding activated charcoal from bark containing wood vinegar liquid (nekka-rich) is effective as treatment for cryptosporidiosis in calves. *Journal of Dairy Science* 91, 1458-1463.
- Wichern, F., Mueller, T., Joergensen, R.G. and Buerkert, A., 2004. Effects of manure quality and application forms on soil C and N turnover of a subtropical oasis soil under laboratory conditions. *Biology and Fertility of Soils* 39, 165-171.
- WMO, 2009. *World Meteorological Organisation*, Geneva, Switzerland.
- Yamato, M., Okimori, Y., Wibowo, I.F., Anshori, S. and Ogawa, M., 2006. Effects of the application of charred bark of *Acacia mangium* on the yield of maize, cowpea and peanut, and soil chemical properties in South Sumatra, Indonesia. *Soil Science and Plant Nutrition* 52, 489-495.
- Zhang, A., Liu, Y., Pan, G., Hussain, Q., Li, L., Zheng, J. and Zhang, X., 2012. Effect of biochar amendment on maize yield and greenhouse gas emissions from a soil organic carbon poor calcareous loamy soil from Central China Plain. *Plant and Soil* 351, 263-275.

Chapter 3

Effects of activated charcoal and quebracho tannin amendments on soil properties in irrigated organic vegetable production under arid subtropical conditions

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3.1 Abstract

In many arid and semi-arid regions, irrigated vegetable production leads to major carbon (C) and nitrogen (N) losses owing to high turnover rates. The goal of this experiment was therefore to test two amendments, activated charcoal and quebracho tannins, in their ability to stabilize soil organic carbon (SOC) from goat manure application in order to enhance nutrient and water retention. A two-year field experiment was conducted on a sandy alluvial soil in Northern Oman investigating the effects of the two amendments either by mixing them to goat manure in the soil (AC_{mix} and QT_{mix}) or by applying manure from goats fed 2.5% charcoal (AC_{fed}) or 3.6% tannin (QT_{fed}) of their daily diet. Mineral fertilizer (NPK) and pure goat manure (M) served as controls. Application rates amounted to $335 \text{ kg N ha}^{-1} \text{ a}^{-1}$ and $6.4\text{--}8.2 \text{ t C ha}^{-1} \text{ year}^{-1}$ (depending on N and C concentrations) and 2.0 and $1.4 \text{ t activated charcoal ha}^{-1} \text{ year}^{-1}$ and, 2.8 and $1.7 \text{ t quebracho tannin ha}^{-1} \text{ year}^{-1}$ (in 2010 and 2011, respectively). Goat manure applications, in general, increased SOC, total N, and basal respiration compared with mineral fertilizer. Mineral fertilizer reduced SOC by -25.5% and total N by -20% , whereas organic treatments increased SOC up to 21% and total N by 19 to 48% . Charcoal amendments increased SOC by 10.6% when charcoal was fed to goats and 21.3% when charcoal was mixed to manure and reduced net C losses, whereas pure goat manure did not change it significantly. Tannins mixed to manure did not have any effects on soil parameters, whereas tannins fed to goats, showed opposite effects to the other goat manure treatments on pH and SOC.

Keywords: Basal respiration; Irrigated Agriculture; Oman; Soil organic carbon and nitrogen

3.2 Introduction

Agricultural production in arid regions, such as Northern Oman, is limited by high temperatures, water scarcity and low soil organic carbon (SOC) and nutrient concentrations in the largely sandy alluvial soils. From the often intensively irrigated, high input systems dominating the market-oriented production systems, Siegfried et al. (2011) reported high nitrogen (N) losses via volatilization and leaching, and negative carbon (C) balances. Under these conditions any increase or even

maintenance of SOC affects crop production by improving soil structure and water and nutrient availability for plants while reducing water and nutrient losses (Emerson 1995; Craswell and Lefroy 2001; Nyamangara et al. 2001; Lal 2006). While recent global estimates (Lal 2006) claim that food-grain production in developing countries can be increased by 24-39 Mio t yr⁻¹ by enhancing SOC, sources for organic matter (OM) inputs are scarce given competing uses as food, fodder, fuel or more recently as a substrate for the production of gaseous or liquid biofuels. Additionally, the yield efficiency of OM applications to soil is often low due to low nutrient stocks or unpredictable soil moisture (Bationo and Buerkert 2001).

The multiple positive effects of organic manure application on soil fertility are widely known (Schjønning et al. 1994; Aggarwal et al. 1997). Animal manure, especially from ruminants such as sheep and goat, is a readily available fertilizer in many arid regions. The manure composition and thus manure quality is strongly affected by the animals' diet. Recent experiments have confirmed that the C/N ratio and neutral detergent fiber (NDF) concentration in manure can be modified by feeding fodder with high C/N ratios and a high fiber concentration (Al-Asfoor et al. 2012; Jost et al. 2013).

Charcoal is a beneficial compound known to improve soil properties (Steiner et al. 2007; Laird et al. 2010; Abel et al. 2013). As a stable C source it can persist in soils for a long time (Bolan et al. 2012). Soil application of charcoal can increase its SOC, pH, water holding capacity (WHC), cation exchange capacity (CEC) and nutrient concentrations (Glaser et al. 2002; Yamato et al. 2006; Steiner et al. 2007), but this is not always the case (Van Zwieten et al. 2010; Brewer et al. 2011). Given its porosity the huge surface area binds nutrients and water, but can also provide a habitat for soil microorganisms (Jones et al. 2012), which by itself could trigger decomposition of easily degradable OM. In animal nutrition, activated charcoal (AC) is used to increase intake of phenol-containing fodder or to protect animals from toxins (Huwig et al. 2001; Rogosic et al. 2006). Thus, in small concentrations, AC may benefit the animal and improve manure quality as a soil amendment at the same time.

As a naturally occurring secondary metabolite in many plant species browsed by goats (Muir 2011), tannins can shift N excretion from urine to faeces and from soluble to insoluble forms therein (Makkar and Becker 1997; Makkar 2003; Hess et al. 2006) while simultaneously increasing milk yield of goats and dairy cows,

avoiding bloat, reducing parasitic infections, and reducing methane emissions during digestion (Aerts et al. 1999; Puchala et al. 2005; Bhatta et al. 2011). The protein-binding and antimicrobial properties of condensed tannins can also retard OM degradation by microorganisms (Palm and Sanchez 1991; Kraus et al. 2003) and could – if added to metabolisable substrates during feeding or after defecation – contribute to stabilizing SOC in irrigated agriculture of arid regions.

The objective of this experiment was to investigate whether AC or quebracho tannin extract (QT), added either to the goat's diet or directly to the soil, can increase soil organic matter content and improve soil properties even with small application rates on a sandy irrigated soil. Especially the effect of the amendments after the passage through the goat's digestive system on the mineralization in the soil is lacking sufficient information.

3.3 Materials and methods

3.3.1 Site description

The field experiment was conducted on a private farm near Sohar (24°22' N, 56°34' E) in the Al-Batinah Coastal Plain of the Sultanate of Oman. The semi-arid climate is characterized by two seasons, a hot and dry summer, and a moderate winter with only occasional rainfall. Under these conditions the local cropping season lasts from September to May. The average temperature during the vegetation periods in 2010/11 and 2011/12 were similar and ranged from 19.7-29.8°C. Precipitation varied between the two seasons, a total of 9 mm in 2010/11 and 50 mm in 2011/12. During the hot season between the two cropping seasons, average temperature was 33.4°C with a maximum of 48°C and 0.4 mm of precipitation. The mean annual minimum and maximum temperature from 1986 to 2009 in Sohar accounted to 21.7°C and 31.3°C, respectively, with a mean annual precipitation of 109 mm (WMO 2009). The soil is characterized as a hyperthermic Typic Torrifluvent (US Taxonomy; Al-Farsi 2001), with 82% sand, 16% silt, 2% clay in the upper 0.5 m layer, a bulk density of 1.44 g cm⁻³ (Siegfried et al. 2011), CaCO₃ of 6.3% and a pH of 8.7. Initial mean SOC concentration was 7.8 mg g⁻¹, with 0.4 mg g⁻¹ total N and a C/N ratio of 19.4. CEC ranged between 91-108 μmol_c kg⁻¹ and WHC averaged 33%. P_{olsen} and K_{CAL} amounted to 18.1 and 59.2 μg g⁻¹, respectively.

3.3.2 *Experimental setup*

To test the effect of activated charcoal and condensed tannins on the soil, a total of six amendment types were randomly arranged in the field with four replications. Activated charcoal was used to avoid potentially harmful effects on goats from carcinogenic substances or heavy metals. The charcoal powder was manufactured from coconut shells followed by steam activation (AquaSorb[®] CP1, Jacobi Carbons Service GmbH, Premnitz, Germany). During the production process, the coconut shells pass three phases physically located in different zones of the furnace (zone 1: 900-950°C, zone 2: 870-920°C and zone 3: 780-850°C) in which residence time varies from 18-40 hours. The charcoal had a particle size of 44 µm, a surface area of 1050 m² g⁻¹, a tamped density of 510 kg m⁻³ and a total pore volume of 0.62 cm³ g⁻¹. Total C concentration was 92.1% with 0.1% N, 0.03% P, 0.8% K, and a pH of 9.1.

As tannin source, a water soluble powdered extract of the quebracho tree (*Schinopsis balansae*; Silva Team S.p.a., San Michele, Italy) was used. It had a total phenol concentration of 75%, of which 95% are total tannins. The C concentration was estimated to 52.8%, as well as 0.1% N, 0.01% P, 0.09% K, and 2.4% Na; pH was 4.65 in a 1:2.5 water solution. A mineral fertilizer treatment containing equivalent NPK levels as the goat manure treatments and consisting of urea, triple super phosphate, potassium sulfate (in the diagrams referred to as NPK), and pure goat manure (Co) served as control. The goats were fed a daily ration of 50% hay, 47% maize, and 3% soybean cake. Two manure treatments were obtained from goats which received either an addition of 2.5% activated charcoal (AC_{fed}) or 2.6% quebracho tannin (QT_{fed}) to their normal daily diet. After a two week adaptation phase, manure was collected directly from goats on a daily basis and sun-dried on plastic sheets for about 5 days until weight constancy. A quantification of charcoal and tannins in the faeces was not possible. Assuming that the two additives leave the goats' digestive system unaltered (Makkar et al. 1995), the charcoal and total tannin concentration in the faeces was estimated at 15% charcoal in 2010 and 8% in 2011, and at 14.5% total tannins in 2010 and 8% in 2011; the calculation was based on the amount of charcoal and quebracho tannins, respectively, in the goats' daily diet divided by the daily amount of faeces excreted. The different concentrations in the two years result from altered faeces output of the goats and therefore different accumulation rates of AC and QT in the manure, and an underestimation of the

moisture concentration of AC and QT powder in calculations. Another two treatments resulted from mixing pure goat manure with either charcoal (AC_{mix}) or tannins (QT_{mix}) at the same concentrations. Carbon and nutrient concentrations for the different manure treatments can be seen in Table 3.1.

Table 3.1. Charcoal, total tannin, C and nutrient concentrations of the different fertilizer treatments.

	Charcoal	Total tannin	C	N	Total P	K	Na	C/N	
	2010/2011	2010/2011							
	----- % -----		----- mg g ⁻¹ -----						ratio
NPK	0	0	200	460.0	197.00	430.00		0.4	
Co	0	0	448	24.3	6.19	2.27	1.34	19.5	
AC _{fed}	15.5 / 8.0	0	503	21.7	5.24	1.79	1.45	22.2	
AC _{mix}	13.5 / 9.0	0	495	20.7	4.75	3.24	1.22	23.9	
QT _{fed}	0	14.5 / 8.5	457	22.7	5.00	1.96	3.09	20.2	
QT _{mix}	0	14.5 / 8.0	458	20.1	4.60	2.46	1.48	22.8	

NPK = mineral fertilizer, Co = goat manure, AC_{fed} = manure from goats fed with charcoal, AC_{mix} = manure mixed with charcoal, QT_{fed} = manure from goats fed with tannin, QT_{mix} = manure mixed with tannin.

Amounts of total nutrients applied with manure were balanced for nitrogen (N), phosphorus (P), and potassium (K) to annual levels of 335 (N), 66 / 94 (P in 2010 / 2011), and 220 (K) kg ha⁻¹, whereby the target N level was given by the different manure types and P and K was supplemented with mineral fertilizers as required. Due to the different N and C concentrations in manures, application rates of C ranged between 6.4-8.2 t C ha⁻¹ year⁻¹ in organic treatments. Annual application of charcoal was 2 and 1.4 t ha⁻¹ in 2010 and 2011, respectively, for AC_{fed} and AC_{mix}, and 2 and 1.3 t ha⁻¹ total tannins in 2010 and 2011, respectively, for QT_{fed} and QT_{mix}. To compensate for possible confounding effects of different sulfate supply from mineral fertilizers, all treatments received 200 kg CaSO₄ ha⁻¹ yr⁻¹.

On the experimental field a sweet corn-radish crop rotation was followed in both years whereby the field was flood-irrigated in small basins as required. For sweet corn, average irrigation frequency was 3.8 and 4.6 days with a mean of 67 mm and 50 mm during the first and second cropping seasons, respectively, whereas for radish, it was 2.2 and 2.4 days with 41 mm and 45 mm. Manure application for sweet corn was split into three installments. In 2010, the application steps were 20-50-30% of the total fertilizer amount. In 2011, these steps were changed to 40-40-20% to better meet plant nutrient demands. The first application was carried out one day

before sowing (-1 DAS), the second application 25 DAS, and the third application 45 DAS. For radish, the total amount of fertilizer and manure was applied in one step -1 DAS. At each application manure was distributed homogeneously on the plots, incorporated into the soil by rototiller in a depth up to 12 cm and irrigated to reduce N losses. Sweet corn roots and stover as well as radish leaves after the first season were incorporated by rototiller as harvest residues.

3.3.3 Soil sampling and analysis

Four separate soil samples were taken from each plot before the start of the field experiment in August 2010 at 0-10 cm depth and cooled at 4°C for soil microbial analysis. Thereafter sampling occurred after the first (April 2011) and the second cropping season (April 2012) and again in August 2011. Subsamples were sieved (<2 mm), wetted to 50% WHC, and pre-incubated at 22°C for one week before measuring basal respiration (Öhlinger 1993). Evolved CO₂ was trapped in 0.5 M NaOH over 7 days, and unreacted NaOH was back-titrated with 0.5 M HCl after addition of saturated BaCl₂ solution. The metabolic quotient $q\text{CO}_2$ was calculated as $\mu\text{g CO}_2\text{-C d}^{-1}$ divided by g microbial biomass C analyzed by Sradnick et al. (2014). Another subsample was air-dried and sieved to 2 mm. Dried and ball-milled subsamples were analyzed for total C and N by means of a VarioMax[®] CHN analyzer (Elementar, Hanau, Germany). Carbonate was measured with a Scheibler apparatus (Schaller 2000) and SOC concentrations were calculated by subtracting carbonate C from total C. For the analysis of pH, dry samples were pooled plot-wise to reduce sample number. Soil pH was measured in water (1:2.5 ratio).

3.3.4 Statistical analysis

Results are presented as arithmetic means with their respective standard errors. In some cases, statistical analysis was conducted on absolute changes of parameters between two sampling dates to avoid masking treatment effects by differences in initial values. To identify significant changes within a treatment over time, one-sided t tests were conducted comparing means with zero. Treatment effects were tested by one-way ANOVA for the fertilizer treatments (NPK, Co, AC_{fed}, AC_{mix}, QT_{fed}, and QT_{mix}) as a main factor. Homogeneity of variance was tested with the Levene test and in case of heterogeneous variance the Welsh test was used instead of ANOVA. Means were separated by defining contrasts comparing NPK

fertilizer with goat manure treatments, Co with charcoal treatments, Co with tannin treatments, and feeding versus mixing treatments. All statistical analyzes were conducted with SPSS Statistics 17.0. A linear regression was calculated to analyze correlations between SOC and basal respiration.

3.4 Results

3.4.1 Soil chemical properties

The soil pH varied around 8.7 and decreased in most organic fertilizer treatments by roughly 0.1 pH units, even though changes were only significant for AC_{mix}; NPK increased pH slightly by 0.08 pH units (Fig. 3.1).

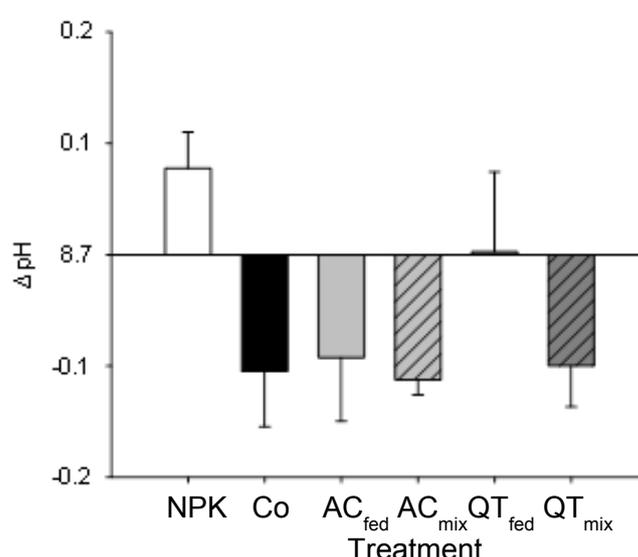


Figure 3.1. Changes of pH of the experimental field in Sohar, Northern Oman after two cropping seasons. Error bars indicate standard error of mean. * represent significant difference of means from 0: * $p < 0.05$.

SOC ranged initially from 7.1 to 8.4 mg g⁻¹ (Fig. 3.2). After the first cropping season, a 10-40% increase in SOC was detected, but this change was only significant in QT_{mix}. During the hot fallow period between cropping seasons, SOC concentrations decreased by 36% for NPK, by 18% for AC_{fed}, and by 29% for QT_{mix}. The other treatments showed a by 20-34% reduced SOC concentration, but these changes were not significant due to the high variability between replicates. After the second cropping period, SOC increases were only significant for Co, AC_{mix} and QT_{mix} with 26, 11, and 15%, respectively. Considering both cropping seasons separately,

treatment effects were not significant. Overall, mean comparison yielded significant differences between mineral fertilizer and organic manures ($P < 0.01$), Co and charcoal treatments ($P < 0.02$), and feeding and mixing ($P < 0.04$). Mineral fertilizer reduced SOC concentrations by 25.5% after two cropping seasons, whereas organic treatments increased concentrations by an average of 7.2% (-6 to 21%).

Initial total N concentrations ranged from 360 to 480 $\mu\text{g g}^{-1}$. Similar to SOC, changes in total N concentration varied between the two cropping seasons (Fig. 3.2). After the first season, total N was higher by 36-87% across treatments without any treatment effect. N losses during the hot fallow period ranged from 40-180 $\mu\text{g g}^{-1}$ (6-27%) and were for NPK, AC_{mix} , QT_{fed} , and QT_{mix} significantly higher than for the control. After the second cropping season N concentrations were either unchanged or slightly reduced for organic treatments, whereas NPK reduced N concentration by 21%. Mean comparison showed significant effects of goat manure treatments ($P < 0.01$), charcoal treatments ($P < 0.02$), and application method ($P < 0.01$). Over the total experimental period, NPK reduced total N contents by 20% ($P < 0.02$), whereas organic manure treatments led to increased topsoil N (19-48%). NPK had a significantly different effect on total N concentrations than organic treatments.

The C/N ratio varied initially from 17.5-20.8 and was reduced for all treatments after the first cropping season due to increasing N concentrations. After the hot fallow period C/N ratio decreased for NPK, Co, and AC_{fed} , whereas for the other treatments it remained constant. After the second cropping period C/N ratios increased for NPK, Co, AC_{fed} , and AC_{mix} , whereas tannin treatments were unchanged compared with initial values. Mean comparisons showed significant effects of organic treatments ($P < 0.01$) and application method ($P < 0.01$). Overall, the C/N ratio was significantly reduced for Co, but tended to be also lower in the other treatments.

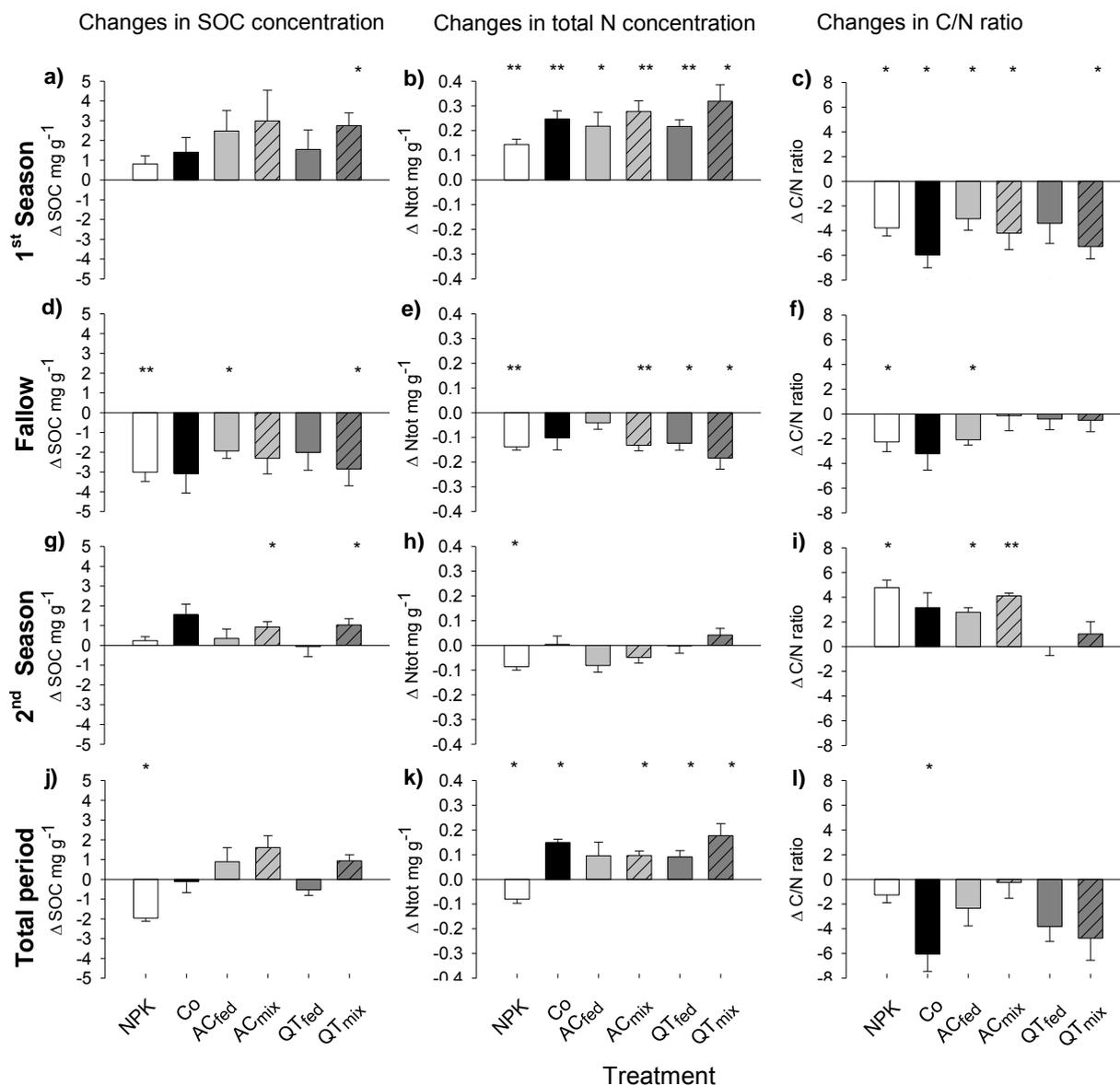


Fig. 3.2. Changes in SOC, total N and C/N ratio after a-c) 1st season, d-f) fallow, g-i) 2nd season, j-l) total period. Error bars indicate standard error of mean. * represent significant difference of means from 0: * p<0.05; ** p<0.01.

3.4.2 Microbial activity

After the two cropping seasons (April 2011 and April 2012) values ranged between 5.3-8.5 and 4.1-7.4 $\mu\text{g CO}_2\text{-C d}^{-1} \text{g}^{-1}$ soil, respectively (Fig. 3.3). A significant treatment effect could only be observed after the first cropping season. Compared with the goat manure treatments, NPK showed significantly lower basal respiration. The same tendency was apparent after the second cropping season, but due to high variation within the treatments this difference was not significant. After the first season, $q\text{CO}_2$ varied between 30 and 62 $\mu\text{g CO}_2\text{-C g}^{-1} \text{biomass C d}^{-1}$ and after the second season between 25 and 49 $\text{mg CO}_2\text{-C g}^{-1} \text{biomass C d}^{-1}$, but no significant treatment effect was observed. The two charcoal and two tannin treatments were combined for regression analysis because no significant treatment effect could be observed for measured parameters (Fig. 3.4). Both NPK (not shown) and Co did not show significant correlations between SOC and basal respiration. But AC and QT treatments significantly increased basal respiration with increasing SOC for both seasons. The constants in the regression equations are not significant.

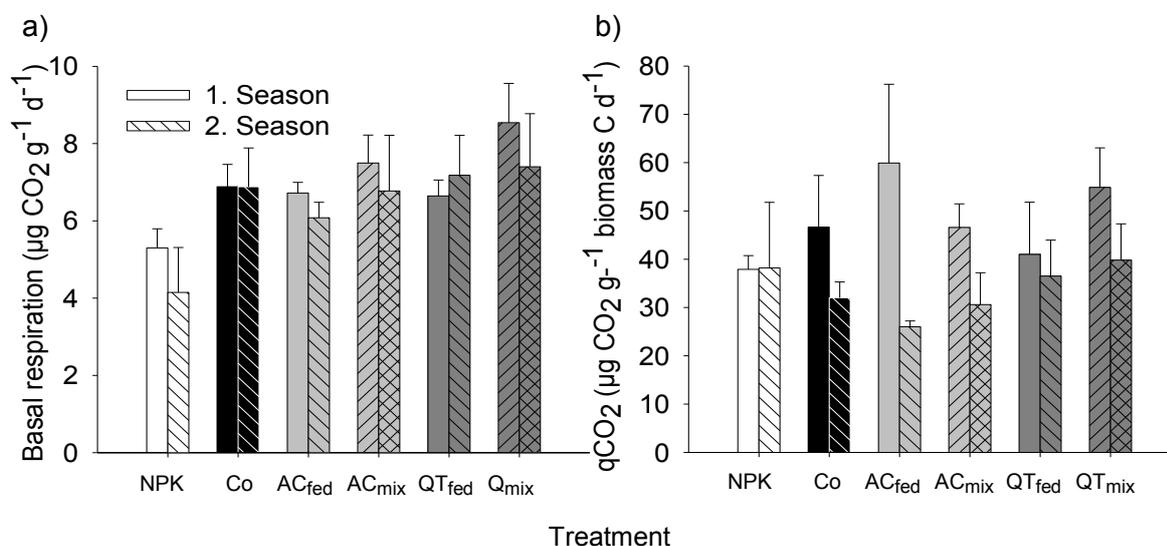


Figure 3.3. Basal respiration (a) and $q\text{CO}_2$ (b) after first and second cropping season. Error bars indicate standard error of mean.

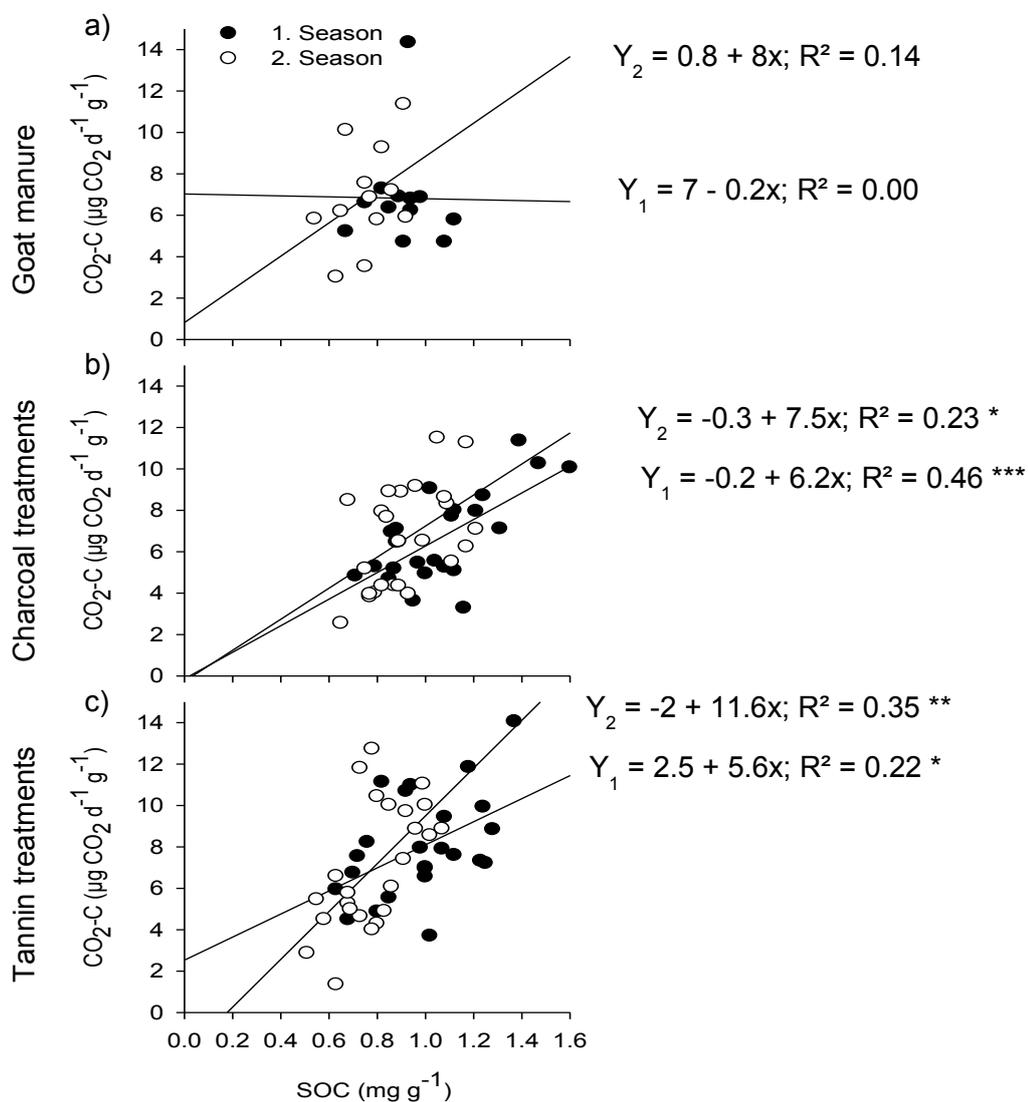


Figure 3.4. Correlations between SOC and basal respiration, for a) Co, b) charcoal treatments (AC_{fed} and AC_{mix}), and c) tannin treatments (QT_{fed} and QT_{mix}). Y_1 and Y_2 in equations stand for 1st and 2nd season. * $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$.

3.5 Discussion

3.5.1 *Organic manure treatments increase soil fertility compared to mineral fertilizer*

After two cropping seasons, goat manure had positive effects on several soil parameters compared with the control treatment of mineral fertilizer application (NPK). SOC concentration increased or remained unchanged for the goat manure treatments (-1 to 21%), whereas NPK reduced SOC concentrations. Compared with organic treatments, the negative C balance for NPK mainly resulted from the 8.6-times lower C input from fertilizer. Considering SOC stock before and after the experiment plus the C input, a total of 5.1 t C ha⁻¹ was lost from the top 12 cm soil layer (assuming unchanged bulk density) for NPK, which represents three times higher losses than the C input and lies within the range of 5 to 7 t ha⁻¹ gaseous C losses reported by Siegfried et al. (2011) in a similar time period. This loss might be even higher considering the C input from root biomass of sweet corn, which was estimated to around one t ha⁻¹ for the two cropping seasons and is two-times higher than for the organic treatments. For organic treatments, C losses varied from 13.6-15.9 t ha⁻¹ (83%-106% of input), which is higher than gaseous C losses of 9 to 12 t ha⁻¹ from fields fertilized with buffalo manure at similar rates (Siegfried et al. 2011). Under irrigated subtropical conditions C losses are typically high, owing to the hot climatic conditions and repeated wet-dry-cycles (Austin et al. 2004). However, some of the goat manure treatments allowed maintaining C stocks. The high rates of pure goat manure application led even to an increase in SOC content by 1.4 mg g⁻¹ and 1.6 mg g⁻¹ after the first and second cropping season compared with only 0.8 mg g⁻¹ and 0.2 mg g⁻¹ for NPK, respectively. Against our expectations C disappearance during hot fallow period exceeded this seasonal accumulation by a factor of two. Even if in the long run goat manure is returning high amounts of C to the soil, under these hot irrigated conditions it can only slow down SOC depletion.

Total N content showed seasonal changes similar to those of SOC. In contrast to C, N inputs were balanced for all treatments. Unfortunately, N contents in manure varied during the season, which could not be accounted for in the application rates. In the first season N application surpassed the targeted 335 kg ha⁻¹ by 8.5% for Co, AC_{mix}, and QT_{mix}, whereas AC_{fed} was undersupplied by 10%. In the second season all treatments were undersupplied with N by 1.7 to 2.4%, except for QT_{fed} with a

5.8% shortage. Total N disappearance from the top 12 cm soil layer were estimated to amount to 858 kg N ha⁻¹ for NPK (119% of added N), whereas N disappearance in organic manure treatments varied between 435-574 kg N ha⁻¹ (59-78% of added N). N removal via crop yield amounted to 614-27 kg N ha⁻¹ and 27-47 kg ha⁻¹ in the first and second cropping season, respectively, which cannot explain the high N disappearance from top soil. Volatilization and leaching of N is known to be high on sandy soils and high pH (Clay et al. 1990; Gioacchini et al. 2002), but Siegfried et al. (2011) reported only losses around 70 kg ha⁻¹ via the two pathways during the cropping season on an irrigated sandy soil in Oman. In their study Siegfried et al. (2011) identified volatilization as the major pathway with 2.5-times higher N losses compared to leaching of mineral N. But it might be very likely that N losses via volatilization are much higher, when measurement frequency is based on irrigation and fertilization events. Another often underestimated factor is leaching of dissolved organic C (DOC) and N (DON), which can reach up to 83% of the total N leachate on a sandy soil covered with turf grass and high N application rates (Barton et al. 2006). High irrigation frequency combined with high N application rates on a sandy soil, as in our study, led to high DOC and DON loads of 200 kg DOC ha⁻¹ and 125 kg DON ha⁻¹ in a 12-week greenhouse study (Willich et al. unpublished). The high disappearance of 3.4-5.3 t SOC ha⁻¹ and 71-317 kg total N ha⁻¹ during fallow is surprising since temperature and soil moisture were non-favorable for microbial activity. One possible explanation may be a priming effect caused by incorporation of radish leaves as a labile C pool leading to quick mineralization of SOC and soil N stocks within the short period after harvest when soil moisture was still available. Bell et al. (2003) showed in an incubation experiment at 25°C on a silt-loam from a semi-arid region that the addition of wheat straw at a rate of 1.5 mg g⁻¹ soil in three steps led to cumulative C losses via CO₂ evolution of up to 2.5 mg g⁻¹ soil in a period of 40 days. At each application step freshly incorporated wheat straw caused a CO₂ flush of which 10% came from residual C in the soil. The higher SOC and total N contents after the first season may result from the freshly incorporated radish leaves, while after the second seasons this input is missing. This is supported by the higher qCO₂ after the first season and the lower microbial biomass C to SOC ratio reported by Sradnick et al. (2014), indicating dynamic changes in microbial biomass and a high metabolic rate at the end of the first season and lower labile organic matter at the end of the second season (Fernandes et al. 2005). Physical degradation processes

as well as the activity of termites and ants which are known to be major surface litter decomposers under arid conditions, and whose omnipresence was observed at the site, may be another explanation (Cepeda-Pizarro 1993; Formowitz et al. 2007). The subterranean termites in the field were identified as *Microcerotermes diversus* Silvester (personal communication Dr. Magdy) the most abundant termite species in Oman and important pest of date palms, which were located close the experimental field. Nash and Whitford (1995) reported a highly significant negative correlation ($r = -0.97$) between subterranean termite abundance and SOC in the Chihuahuan Desert, leading to the conclusion that low SOC contents in semi-arid regions may largely result of termite activity. But termites are prone to moisture as well, causing a decline of straw disappearance by 50% during dry season in a litterbag experiment in Burkina Faso (Mando and Brussaard 1999). The fate of the disappearing SOC and total N cannot be clarified and it must be considered that the reduction of SOC and total N content may result from dilution of the soil in sampling depth due to compaction of the soil during fallow.

3.5.2 Charcoal effects on soil properties

In our study there were a few distinct differences between the application of the two charcoal treatments and the unamended goat manure (Co). In contrast to the literature from acid soils (Yamato et al. 2006; Novak et al. 2009; Schulz and Glaser 2012) charcoal addition did not alter pH on our alkaline soil. Charcoals with high pH, such as used in our study, might have a liming effect on acid soils, but have been found pH ineffective on alkaline soils even at 10 times higher application rates (Lentz and Ippolito 2012). After two cropping seasons, charcoal treatments showed 1.2 times higher SOC contents than pure goat manure. The difference seems to result mainly from lower losses during fallow in charcoal treatments. In total, Co lost 100% of the applied organic C, whereas AC_{fed} lost 90% and AC_{mix} 80%. The low application rate and the high soil pH may explain the missing beneficial effects of charcoal on total N observed in other studies (Jha et al. 2010; van Zwieten et al. 2010; Lentz and Ippolito 2012). After two seasons only 24% of added N was found in the top soil for charcoal treatments compared to 35% for Co, despite lower plant uptake. Charcoal must have enhanced either N leaching or volatilization. Contrary to expectations feeding charcoal did not enhance the positive effects on SOC. On the contrary, AC_{mix} seemed to have a slightly stronger effect on pH reduction, increase in

SOC accumulation. This may result from a homogenous distribution of charcoal in the top soil. Although feeding AC did not have positive effects in our study, it may still have beneficial effects on the animals or on plant growth.

3.5.3 Tannin effects on soil properties

Contradicting to previously reported results, the two tannin treatments did not significantly affect pH, SOC, and total N compared to pure goat manure. This may reflect the incongruous results obtained for QT_{fed} and QT_{mix}. Unlike QT_{fed}, QT_{mix} did not have any additional effects on measured parameters as compared to Co. Condensed tannins, the major phenolic compound in the quebracho extract, have a high binding affinity to organic matter and can thus stabilize labile soil C and N (Halvorson et al. 2011; Adamczyk et al. 2013), thereby slowing down organic matter degradation (Kraus et al. 2004; Kanerva et al. 2006). Already low contents of condensed tannins can inhibit enzyme activity and slow down mineralization (Joanisse et al. 2007). Although soils treated with QT_{mix} showed higher SOC and total N contents than pure goat manure treated soils after two seasons, this difference was not significant. Regarding the total C disappearance from top soil, pure goat manure lost 101% of incorporated C while QT_{mix} only lost 90%. Total N disappearance was also by 6% lower for QT_{mix}, and the soil C/N ratio was reduced showing an immobilization of N. The tannin content in the soil may have been too low for significant effects on mineralization, but a considerable amount of the water-soluble QT may also have been leached with frequent irrigation events.

When QT was fed to goats, the total polyphenol content in the manure was estimated at 14% and 8.5% (first and second cropping season, respectively – see materials and methods section). Due to the higher content of total tannins in the thus derived manure and the direct interaction of tannins with feed and microbial protein as well as other feed components in the animals' intestines, a stronger stabilization of manure derived C and N was expected. In composted cattle manure Hao et al. (2011) found higher total C and N concentrations, when the diet of cattle contained condensed tannins from *Acacia*. Surprisingly, SOC and total N concentrations were lower for QT_{fed} compared to Co and QT_{mix}. Total SOC disappearance was 14.5 t ha⁻¹ for QT_{mix} and Co, and 15.9 t ha⁻¹ for QT_{fed}, which represents roughly 100% of the C input. Compared with Co and QT_{mix}, N disappearance was 1.2-1.3 times higher for

QT_{fed} as well. Also for the soil pH, QT_{fed} yielded different effects than the other goat manure treatments as it did not change soil pH. The differing effects of mixing or feeding tannins may either come from different content and location of tannins in the manure applied, or from conformational changes of the tannins during passage through the goat's digestive system (Terrill et al. 1994). Even though the tannins could not be extracted from faeces of sheep and goats fed with tannin-rich *Acacia saligna* leaves (Degen et al. 1995), Makkar et al. (1995) state that extractable condensed tannins from fodder are not degraded, but bound to fiber fractions and proteins in the digestive system of ruminants. Thus, condensed tannins reduce the digestibility of carbohydrates and proteins in the gastrointestinal tract (Muir 2011), but tannin-protein or tannin-carbohydrate complexes may be mineralized by soil microorganisms under the changed environmental conditions in the soil (different pH, aerobic environment). Furthermore, animals as well as their gastrointestinal microorganisms exhibit protective mechanisms to tolerate high tannin levels in feed, such as increased mucous production to protect the intestinal wall from damage, and release of extracellular polysaccharides and other components (Smith et al. 2005). When tannin-rich manure is applied to the soil, these substances might be quickly mineralized and lead to a priming effect. However, at the end of the cropping season no significant effect of tannin treatments on microbial biomass C and N (Sradnick et al. 2014) as well as on basal respiration and $q\text{CO}_2$ could be observed. Leaching of soluble tannin-protein complexes and the role of termites in this ecosystem need to be investigated to better understand the fate of SOC and total N in soils treated with QT_{fed}.

3.6 Conclusions

Even though C and N losses were high for all amendments, goat manure could stabilize or even increase the highly dynamic soil C and N stocks. Compared to mineral fertilizer the regular application of organic manures significantly increased the basal respiration. Especially during fallow the distinct reduction in SOC and total N is unanticipated and cannot be explained in this study. Compared to pure goat manure, AC addition helped to maintain soil C. With higher application rates or annually repeated applications, the observed effect could be even larger. Feeding AC did not bring any additional effects on SOC and total N as well as basal respiration compared to mixing AC. Quebracho tannin extract mixed to soil did not

have any improving effects on soil parameters except for SOC. Soil organic C losses were reduced by mixing, but increased by feeding QT. It seems that the addition of QT to goat feed increased mineralization or enhances leaching losses of soluble C and N. The mechanisms behind these effects are still unclear. Although feeding the two amendments did not benefit the soil in this study, there may be positive effects on different soil types as well as on the animals and plant growth supporting the use of charcoal and tannins as feed additives.

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3.8 References

- Abel, S., Peters, A., Trinks, S., Schonsky, H., Facklam, M. and Wessolek, G., 2013. Impact of biochar and hydrochar addition on water retention and water repellency of sandy soil. *Geoderma* 202-203, 183-191.
- Adamczyk, B., Kitunen, V. and Smolander, A., 2013. Response of soil C and N transformations to condensed tannins and different organic N-condensed tannin complexes. *Applied Soil Ecology* 64, 163-170.
- Aerts, R.J., Barry, T.N. and McNabb, W.C., 1999. Polyphenols and agriculture: beneficial effects of proanthocyanidins in forages. *Agriculture, Ecosystems and Environment* 75, 1-12.
- Aggarwal, R.K., Praveen-Kumar and Power, J.F., 1997. Use of crop residue and manure to conserve water and enhance nutrient availability and pearl millet yields in an arid tropical region. *Soil and Tillage Research* 41, 43-51.
- Al-Asfoor, H., Schlecht, E., Sundrum, A. and Schiborra, A., 2012. Varying the dietary supply of C and N to manipulate the manure composition of water buffalo heifers in Oman. *Journal of Agriculture and Rural Development in the Tropics and Subtropics* 113, 125-136.
- Al-Farsi, S.A.I., 2001. Classification of soils from an alluvial fan and coastal plain near Sohar, Sultanate of Oman, Sultan Qaboos University, Muscat, Sultanate of Oman.
- Austin, A.T., Yahdjian, L., Stark, J.M., Belnap, J., Porporato, A., Norton, U., Ravetta, D.A. and Schaeffer, S.M., 2004. Water pulses and biogeochemical cycles in arid and semiarid ecosystems. *Oecologia* 141, 221-235.
- Barton, L., Schipper, L.A., Barkle, G.F., McLeod, M., Speir, T.W., Taylor, M.D., McGill, A.C., van Schaik, A.P., Fitzgerald, N.B. and Pandey, S.P., 2005. Land application of domestic effluent onto four soil types: plant uptake and nutrient leaching. *Journal of Environmental Quality* 34, 635-643.
- Bationo, A. and Buerkert, A., 2001. Soil organic carbon management for sustainable land use in Sudano-Sahelian West Africa. *Nutrient Cycling in Agroecosystems* 61, 131-142.
- Bell, J.M., Smith, J.L., Bailey, V.L. and Bolton, H.J., 2003. Priming effect and C storage in semi-arid no-till spring crop rotations. *Biology and Fertility of Soils* 37, 237-244.
- Bhatta, R., Shinde, A.K., Vaithyanathan, S., Sankhyan, S.K., Enishi, O. and Kurihara, M., 2011. Utilisation of tannin-containing tree leaves in sheep and goat production.

- Successes and failures with animal nutrition practices and technologies in developing countries, FAO Electronic Conference Vol. 11, Rome, Italy.
- Bolan, N.S., Kunhikrishnan, A., Choppala, G.K., Thangarajan, R. and Chung, J.W., 2012. Stabilization of carbon in composts and biochars in relation to carbon sequestration and soil fertility. *Science of the Total Environment* 424, 264-270.
- Brewer, C., Unger, R., Schmidt-Rohr, K. and Brown, R., 2011. Criteria to select biochars for field studies based on biochar chemical properties. *Bioenergy Research* 4, 312-323.
- Cepeda-Pizarro, J.G., 1993. Litter decomposition in deserts: an overview with an example from coastal arid Chile. *Revista Chilena de Historia Natural* 66, 323-336.
- Clay, D.E., Malzer, G.L. and Anderson, J.L., 1990. Ammonia volatilization from urea as influenced by soil temperature, soil water content, and nitrification and hydrolysis inhibitors. *Soil Science Society of America Journal* 54, 263-266.
- Craswell, E.T. and Lefroy, R.D.B., 2001. The role and function of organic matter in tropical soils. *Nutrient Cycling in Agroecosystems* 61, 7-18.
- Degen, A.A., Becker, K., Makkar, H.P.S. and Borowy, N., 1995. *Acacia saligna* as a fodder tree for desert livestock and the interaction of its tannins with fibre fractions. *Journal of the Sciences of Food and Agriculture* 68, 65-71.
- Emerson, W.W., 1995. Water-retention, organic-C and soil texture. *Australian Journal of Soil Research* 33, 241-251.
- Fernandes, S.A.P., Bettiol, W. and Cerri, C.C., 2005. Effect of sewage sludge on microbial biomass, basal respiration, metabolic quotient and soil enzymatic activity. *Applied Soil Ecology* 30, 65-77.
- Formowitz, B., Schulz, M.-C., Buerkert, A. and Joergensen, R.G., 2007. Reaction of microorganisms to rewetting in continuous cereal and legume rotation soils of semi-arid Sub-Saharan Africa. *Soil Biology and Biochemistry* 39, 1512-1517.
- Gioacchini, P., Nistri, A., Marzadori, C., Giovannini, C., Vittori Antisari, L. and Gessa, C., 2002. Influence of urease and nitrification inhibitors on N losses from soils fertilized with urea. *Biology and Fertility of Soils* 36, 129-135.
- Glaser, B., Lehmann, J. and Zech, W., 2002. Ameliorating physical and chemical properties of highly weathered soils in the tropics with charcoal: a review. *Biology and Fertility of Soils* 35, 219-230.
- Halvorson, J.J., Gonzalez, J.M., Hagerman, A.E., 2011. Repeated applications of tannins and related phenolic compounds are retained by soil and affect cation exchange capacity. *Soil Biology and Biochemistry* 43, 1139-1147.
- Hao, X., Benke, M.B., Li, C., Larney, F.J., Beauchemin, K.A. and McAllister, T.A., 2011. Nitrogen transformations and greenhouse gas emissions during composting of manure from cattle fed diets containing corn dried distillers grains with solubles and condensed tannins. *Animal Feed Science and Technology* 166-167, 539-549.
- Hess, H.D., Tiemann, T.T., Stürm, C.D., Carulla, J.E., Lascano, C.E. and Kreuzer, M., 2006. Effects of tannins on ruminal degradation and excretory pattern of N and implications for the potential N emission from the manure. *International Congress Series* 1293, 339-342.
- Huwig, A., Freimund, S., Käppeli, O. and Dutler, H., 2001. Mycotoxin detoxication of animal feed by different adsorbents. *Toxicology Letters* 122, 179-188.
- Jha, P., Biswas, A.K., Lakaria, B.L. and Subba Rao, A., 2010. Biochar in agriculture - prospects and related implications. *Current Science India* 99, 1218-1225.
- Joanisse, G.D., Bradley, R.L., Preston, C.M. and Munson, A.D., 2007. Soil enzyme inhibition by condensed litter tannins may drive ecosystem structure and processes: the case of *Kalmia angustifolia*. *New Phytologist* 175, 535-546.
- Jones, D.L., Rousk, J., Edwards-Jones, G., DeLuca, T.H. and Murphy, D.V., 2012. Biochar-mediated changes in soil quality and plant growth in a three year field trial. *Soil Biology and Biochemistry* 45, 113-124.
- Jost, D., Joergensen, R. and Sundrum, A., 2013. Effect of cattle faeces with different microbial biomass content on soil properties, gaseous emissions and plant growth. *Biology and Fertility of Soils* 49, 61-70.

- Kanerva, S., Kitunen, V., Kiikkilä, O., Loponen, J. and Smolander, A., 2006. Response of soil C and N transformations to tannin fractions originating from Scots pine and Norway spruce needles. *Soil Biology and Biochemistry* 38, 1364-1374.
- Kraus, T.E.C., Dahlgren, R.A. and Zasoski, R.J., 2003. Tannins in nutrient dynamics of forest ecosystems - a review. *Plant and Soil* 256, 41-66.
- Kraus, T.E.C., Zasoski, R.J., Dahlgren, R.A., Horwath, W.R. and Preston, C.M., 2004. Carbon and nitrogen dynamics in a forest soil amended with purified tannins from different plant species. *Soil Biology and Biochemistry* 36, 309-321.
- Laird, D.A., Fleming, P., Davis, D.D., Horton, R., Wang, B. and Karlen, D.L., 2010. Impact of biochar amendments on the quality of a typical Midwestern agricultural soil. *Geoderma* 158, 443-449.
- Lal, R., 2006. Enhancing crop yields in the developing countries through restoration of the soil organic carbon pool in agricultural lands. *Land Degradation and Development* 17, 197-209.
- Lentz, R.D. and Ippolito, J.A., 2012. Biochar and manure affect calcareous soil and corn silage nutrient concentrations and uptake. *Journal of Environmental Quality* 41, 1033-1043.
- Makkar, H.P.S., Becker, K., Abel, H.J. and Szegletti, C., 1995. Degradation of condensed tannins by rumen microbes exposed to quebracho tannins (QT) in rumen simulation technique (RUSITEC) and effects of QT on fermentative processes in the RUSITEC. *Journal of the Science of Food and Agriculture* 69, 495-500.
- Makkar, H.P.S. and Becker, K., 1997. Nutrients and antiquality factors in different morphological parts of the *Moringa oleifera* tree. *Journal of Agricultural Sciences* 128, 311-322.
- Makkar, H.P.S., 2003. Effects and fate of tannins in ruminant animals, adaptation to tannins, and strategies to overcome detrimental effects of feeding tannin-rich feeds. *Small Ruminant Research* 49, 241-256.
- Mando, A. and Brussaard, L., 1999. Contribution of termites to the breakdown of straw under Sahelian conditions. *Biology and Fertility of Soils* 29, 332-334.
- Muir, J.P., 2011. The multi-faceted role of condensed tannins in the goat ecosystem. *Small Ruminant Research* 98, 115-120.
- Nash, M.H. and Whitford, W.G., 1995. Subterranean termites: regulators of soil organic matter in the Chihuahuan Desert. *Biology and Fertility of Soils* 19, 15-18.
- Novak, J.M., Busscher, W.J., Laird, D.L., Ahmedna, M., Watts, D.W. and Niandou, M.A.S., 2009. Impact of biochar amendment on fertility of a southeastern coastal plain soil. *Soil Science* 174, 105-112.
- Nyamangara, J., Gotosa, J. and Mpofu, S.E., 2001. Cattle manure effects on structural stability and water retention capacity of a granitic sandy soil in Zimbabwe. *Soil and Tillage Research* 62, 157-162.
- Öhlinger, R., 1993. Bestimmung der Bodenatmung im Laborversuch, In: Schinner, F. et al. (Eds.). *Bodenbiologische Arbeitsmethoden*. 2nd edition. Springer, Berlin, pp. 86-90.
- Palm, C.A. and Sanchez, P.A., 1991. Nitrogen release from the leaves of some tropical legumes as affected by their lignin and polyphenolic contents. *Soil Biology and Biochemistry* 23, 83-88.
- Puchala, R., Min, B.R., Goetsch, A.L. and Sahl, T., 2005. The effect of a condensed tannin-containing forage on methane emission by goats. *Journal of Animal Sciences* 83, 182-186.
- Rogosic, J., Pfister, J.A., Provenza, F.D. and Grbesa, D., 2006. The effect of activated charcoal and number of species offered on intake of Mediterranean shrubs by sheep and goats. *Applied Animal Behaviour Science* 101, 305-317.
- Schaller, K., 2000. *Praktikum zur Bodenkunde und Pflanzenernährung*. 7th ed. Gesellschaft zur Förderung der Forschungsanstalt Geisenheim, Geisenheim.
- Schjønning, P., Christensen, B.T. and Carstensen, B., 1994. Physical and chemical properties of a sandy loam receiving animal manure, mineral fertilizer or no fertilizer for 90 years. *European Journal of Soil Science* 45, 257-268.

- Schulz, H. and Glaser, B., 2012. Effects of biochar compared to organic and inorganic fertilizers on soil quality and plant growth in a greenhouse experiment. *Journal of Plant Nutrition and Soil Science* 175, 410-422.
- Siegfried, K., Dietz, H., Schlecht, E. and Buerkert, A., 2011. Nutrient and carbon balances in organic vegetable production on an irrigated, sandy soil in northern Oman. *Journal of Plant Nutrition and Soil Science* 174, 678-689.
- Smith, A., Zoetendal, E. and Mackie, R., 2005. Bacterial mechanisms to overcome inhibitory effects of dietary tannins. *Microbial Ecology* 50, 197-205.
- Sradnick, A., Ingold, M., Marold, J., Murugan, R., Buerkert, A. and Joergensen, R., 2014. Impact of activated charcoal and tannin amendments on microbial biomass and residues in an irrigated sandy soil under arid subtropical conditions. *Biology and Fertility of Soils* 50, 95-103.
- Steiner, C., Teixeira, W.G., Lehmann, J., Nehls, T., de Macêdo, J.L.V., Blum, W.E.H. and Zech, W., 2007. Long term effects of manure, charcoal and mineral fertilization on crop production and fertility on a highly weathered Central Amazonian upland soil. *Plant and Soil* 291, 275-290.
- Terrill, T.H., Waghorn, G.C., Woolley, D.J., McNabb, W.C. and Barry, T.N., 1994. Assay and digestion of ¹⁴C-labelled condensed tannins in the gastrointestinal tract of sheep. *British Journal of Nutrition* 72, 467-477.
- Van Zwieten, L., Kimber, S., Morris, S., Chan, K.Y., Downie, A., Rust, J., Joseph, S. and Cowie, A., 2010. Effects of biochar from slow pyrolysis of papermill waste on agronomic performance and soil fertility. *Plant and Soil* 327, 235-246.
- Willich, M., Padilla Vega, J. and Buerkert, A. (unpublished). Effects of charcoal enriched goat manure on mineralization and leaching of carbon and nutrients from a subtropical sandy soil - A comparison between suction plates and ion exchange resins.
- WMO, 2009. World Meteorological Organisation, Geneva.
- Yamato, M., Okimori, Y., Wibowo, I.F., Anshori, S. and Ogawa, M., 2006. Effects of the application of charred bark of *Acacia mangium* on the yield of maize, cowpea and peanut, and soil chemical properties in South Sumatra, Indonesia. *Soil Science and Plant Nutrition* 52, 89-95.

Chapter 4

Effects of activated charcoal and quebracho tannin as feed additive on decomposition of goat manure

4.1 Abstract

Animal manure is the major fertilizer used in many semi-arid and arid regions; however, its application is often inefficient due to low manure quality and high turnover rates leading to nutrient losses. To investigate possible mitigation strategies a litterbag experiment was conducted examining the effects of activated charcoal (AC) and quebracho tannin extract (QT) on turnover and nutrient release from goat manure on an irrigated sandy soil in the intensively farmed, arid lowlands of Northern Oman. Both additives were either added to the goats' feed or mixed to manure before field application. Samples of pure goat manure (control) and the four types of amended goat manure (AC_{fed} , AC_{mix} , QT_{fed} , QT_{mix}) were buried in the soil at 10 cm depth one day after sowing of each crop in a sweet corn-radish rotation followed by recovery of litterbags after 2, 4, 6, 8, 12 and 20 during sweet corn cultivation and after 2, 4, and 6 weeks under radish cultivation. Organic matter (OM) disappearance was 70% after 12 weeks of sweet corn cultivation and 60% after 6 weeks of radish cultivation. Results indicate that AC and QT were able to stabilize OM in goat manure by up to 22% compared with the unamended control treatment. However, under sweet corn there was no stabilization of OM by QT amendment. While under sweet corn AC reduced relative carbon (C), nitrogen (N) and potassium (K) release by 25, 25 and 10% compared with the control, under radish primarily phosphorus (P) release was reduced by 28%. On the other hand, QT reduced C, N, P and K release under radish, while mixing QT even increased N and P release under sweet corn. Feeding QT reduced N release under both crops by 36-63% compared with the control. The differences in OM disappearance and nutrient release patterns under the two crops combined with the observation of treatment dependent differences in termite and fungal colonization of manure led to the conclusion that different groups of soil microbes and soil fauna dominated mineralization processes under sweet corn and radish cultivation and that AC and QT are affecting these soil organisms in different ways. The application of charcoal or tannins to soil has the potential to stabilize soil OM and reduce nutrient losses, however, the slower N release from manure needs attention to avoid its deficiency for crop production.

Keywords: Activated Charcoal; Irrigated agriculture; Manure mineralisation; Nutrient losses; Subtropics; Tannins

4.2 Introduction

Animal manure is an important nutrient source in agriculture in general, but particularly in organic and low input agriculture where farmers often rely on it as the principle source of nutrients and organic carbon (C; Williams 1999). Not only the amount of applied manure, but also the timing of nutrient release is an important factor determining crop development and yield. In addition, animal manure, like all organic soil amendments, contributes to soil fertility as it improves soil structure, water and nutrient retention capacities (Schjønning et al. 1994; Aggarwal et al. 1997; Rasool et al. 2008). However, its efficiency largely depends on the mineralization rate which is a function of manure composition, environmental conditions and soil microbial community (Knacker et al. 2003). Quick mineralization releases nutrients that can benefit plant development, but also makes them prone to leaching or volatilization, and reduces the effect of manures as soil conditioners. Slow mineralization may help building up higher levels of soil organic matter (SOM), which improves soil fertility, but can lead to an under-supply of plant nutrients. In intensive irrigated agriculture of semi-arid and arid regions such as Oman, mineralization is particularly fast and C and nutrient losses can be severe (Siegfried et al. 2011). However, literature on mineralization and nutrient release patterns of manure under subtropical conditions are scarce and studies on the effects of manure amendments to its mineralization are particularly lacking.

Litterbags are a simple but effective tool to investigate the decomposition of organic material under field conditions (Bocock and Gilbert 1957). In this experiment litterbags were used to measure the effect of activated charcoal (AC) and quebracho tannin extract (QT) on mineralization of goat manure under hot climatic conditions combined with regular irrigation. Charcoal, often also referred to as biochar, is receiving growing attention as a soil conditioner, able to stabilize soil organic carbon (SOC) for a long time (Bolan et al. 2012; Lentz and Ippolito 2012; Schulz and Glaser 2012). On the other hand, by providing microorganisms a favourable habitat (Jones et al. 2012), it may also enhance microbial degradation of labile organic matter. We used AC to test whether charcoal amendments, either by feeding it to goats or mixing it with goat manure before application, can reduce C and nutrient losses by stabilizing organic matter (OM) and enhancing soil fertility. As a second amendment, QT was added in a similar manner as charcoal, to examine whether the protein

binding and anti-microbial properties of tannins can provide similar stabilizing effects. Tannins are secondary plant metabolites, ubiquitous in the plant kingdom and present in many browse species for small ruminants in dry climates. Thus, feeding of tannin containing fodder may not only benefit the ingesting animal (Aerts et al. 1999; Puchala et al. 2005; Bhatta et al. 2011), but also enhance manure quality.

The hypotheses of this study were that (i) AC and QT stabilize OM leading to slower disappearance of goat manure from the litterbags and lower nutrient release and (ii) feeding AC and QT is more effective than manure coating with AC or QT due to direct changes in manure composition.

4.3 Materials and methods

4.3.1 Site description

A litterbag experiment was conducted in the second year of a two-year field experiment on a private farm in Sohar (24°22' N, 56°34' E) in the Al-Batinah Plain of the Sultanate of Oman. The mean annual minimum and maximum temperature from 1986 to 2009 in Sohar accounted to 21.7°C and 31.3°C, respectively, with a mean annual precipitation of 109 mm (WMO 2009). Litterbags were buried in experimental plots in two periods from November 2011 to January 2012 under sweet corn (*Zea mays* L., var. Honey Jean No. 2) and from February 2012 to April 2012 under radish (*Raphanus sativus*, var. Early 40 days). The daily average air temperature during both periods was 22°C with minimum and maximum temperatures of 9°C and 36°C, respectively (Fig. 4.1a). During the first cropping period, at the beginning of the cropping season, initial monthly mean temperatures were high with 25°C and declined thereafter to 20°C, whereas during the second period, temperatures were low at the beginning (21°C) and rose until the end of the experiment (24°C). Precipitation was low during the experimental period with one bigger rain event of 33 mm. Evaporation measured in an class A evaporation pan was relatively constant around 100 mm per month during the first period and rose up to 180 mm at the end of the second period.

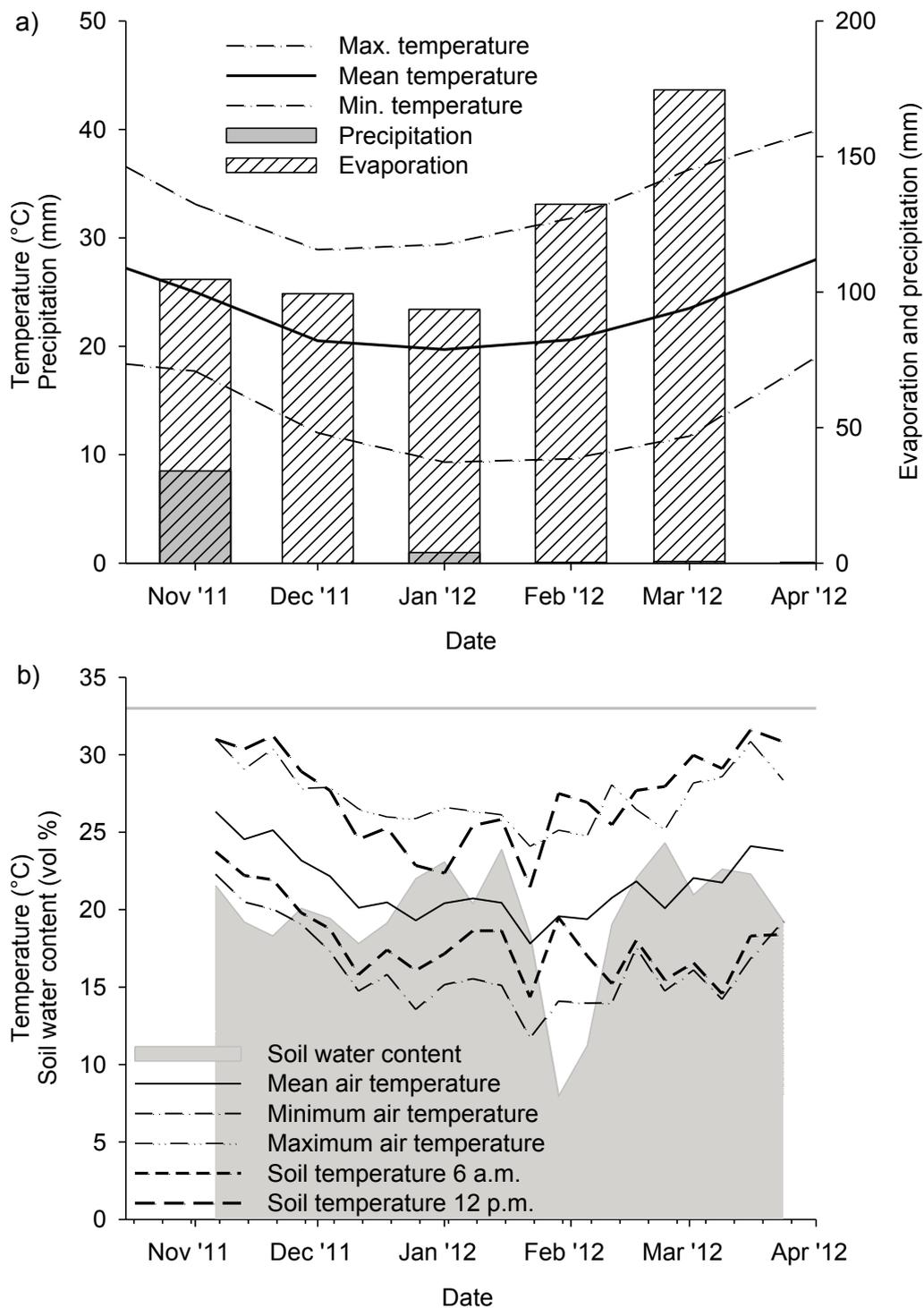


Figure 4.1 a) Monthly mean, maximum and minimum temperature, precipitation and cumulative evaporation at the experimental field near Sohar (Oman) from September 2011 to March 2012. b) Weekly volumetric water content, mean, minimum and maximum air temperature and average soil temperature at 6 a.m. and 12 p.m. representing the coolest and hottest daytime at the experimental site near Sohar (Oman). The gray line at 33% soil water content indicates the water holding capacity of the soil.

The sandy soil of the flood-irrigated field is classified as a hyperthermic Typic Torrifuvent (US Taxonomy; Al-Farsi 2001) with a pH of 8.7, a SOC content of 8 mg g⁻¹, a total N content of 0.4 mg g⁻¹ and a C/N ratio of 19 (Ingold et al. 2015). The weekly average soil temperatures in 6 cm depth were high at the beginning of the experiment with 24°C in the morning at 6 am and 31°C at 12 pm and declined thereafter until the end of the first period to 14 and 21°C, respectively (Fig. 4.1b). At the beginning of the second period soil temperatures were 17 and 28°C and rose to 18 and 32°C in the morning and afternoon. The daily fluctuation of the soil temperature was 8°C on average during the first period and 13°C during the second period.

4.3.2 Manure treatments

Two treatments contained AC (AquaSorb[®] CP1, Jacobi Carbons, Service GmbH, Premnitz, Germany), either coated on goat manure (AC_{mix}) or admixed to manure through digestion by goats (AC_{fed}). Two additional treatments contained QT extract (*Schinopsis balansae*, Silva Team S.p.a., San Michele, Italy) with the same application methods mentioned above (QT_{mix} and QT_{fed}). An unamended goat manure (Co) served as control. The manure types resulting from different diets were collected on a daily basis from goats and dried in the sun for 5 days. Starting one week prior to manure collection goats were fed a daily ration of 50% hay, 47% maize and 3% soybean cake. Two groups of goats received additionally to this basic diet either 2.5% charcoal (AC_{fed}) or 3.6% quebracho tannin extract (QT_{fed}). The charcoal and tannin concentrations in manure were estimated assuming that amendments were not digested nor absorbed by the goats. The calculation resulted in 8.2% AC and 11.4% QT in the collected manure. For the coated types, dry pure goat manure (Co) was mixed with a water suspension of either AC or QT and sun-dried again. The AC and QT amount used to coat the manure was calculated to mimic the levels in manure of goats that were fed either AC or QT. As the AC powder was not sticky as the QT extract, a considerable amount of charcoal was lost after drying, and resulted in lower AC content in AC_{mix}. The addition of AC, with a high K concentration, also added a certain amount of K to the manure, but analysis of the AC_{mix} treatment revealed 20% less K than estimated. This indicates that some of the attached AC powder was lost during processing. However, QT_{mix} contained 28% less

Na than estimated from the addition of QT extract, which may indicate some heterogeneity in the distribution of the QT extract.

Application rates of manure were adjusted to 200 kg N ha⁻¹ for sweet corn and 135 kg ha⁻¹ for radish. Calculations were based on nutrient concentrations measured prior to the cropping season (Tab. 4.1). Due to varying N and C concentrations in manures, application rate of C ranged between 7.6-9.1 t C ha⁻¹ a⁻¹.

Table 4.1. Organic matter, C and nutrient concentrations and, C/N ratio of the different manure types. Co = Control, AC_{fed} = manure from goats fed with activated charcoal, AC_{mix} = manure coated with activated charcoal, QT_{fed} = manure from goats fed with quebracho tannin extract, QT_{mix} = manure coated with quebracho tannin extract in the experimental field near Sohar (Oman).

		Co	AC _{fed}	AC _{mix}	QT _{fed}	QT _{mix}
OM	mg g ⁻¹	917.3	910.5	906.5	913.1	901.5
C	mg g ⁻¹	453.6	496.4	462.8	461.9	460.2
N	mg g ⁻¹	23.8	21.5	23.2	22.3	23.4
P	mg g ⁻¹	6.1	5.1	5.8	4.8	5.4
K	mg g ⁻¹	2.1	1.8	2.1	1.8	2.0
Na	mg g ⁻¹	1.3	1.5	1.3	3.0	2.8
C/N	ratio	19.1	23.1	20.0	20.7	19.7

4.3.3 Experimental setup

To examine the effect of the five above mentioned manure treatments on the turnover of goat manure, litterbags were installed in the second year of a two-year field experiment with a sweet corn-radish rotation in each year. In the field experiment, the five manure treatments were set in a completely randomized design with four replicate plots wet up as basins with separate water access for flood irrigation. Crops were fertilized in three split applications for sweet corn (-1, 25 and 45 days after sowing) and one single application prior to sowing of radish. Applied manure was incorporated by rototiller into the top 12 cm of the soil prior to sowing or with rakes after emergence of sweet corn plants. Litterbags of 1 mm mesh and 15 cm x 20 cm size containing the five different goat manure types were buried horizontally in 10 cm depth within the corresponding plots two days after sowing of crops in two separate areas within the 2.5 m x 6.5 m plots, at distances of 10-20 cm between

litterbags and planting rows. During sweet corn cultivation 12 litterbags containing 27-29 g manure DM per litterbag were installed in each plot (48 litterbags in each of the five treatments) resulting in a total of 240 samples followed by the recovery of two litterbags per plot after 2, 4, 6, 8, 12 and 20 weeks (S2, S4, S6, S8, S12 and S20). During radish cultivation 6 litterbags containing 18-20 g manure DM per litterbag were installed in each plot (24 litterbags per treatment) resulting in 120 samples collected after 2, 4, and 6 weeks (R2, R4, and R6). During sweet corn cropping, the plots were irrigated every 4.6 days with 50 mm, while during radish cultivation plots were irrigated every 2.4 days with 46 mm.

4.3.4 Litterbag sampling and analysis

At each sampling date two litterbags per plot were picked randomly and pooled prior to analysis. Samples were cleared of bigger soils particles, roots and termites, and placed in paper bags before drying to constant weight at 60°C. As soil contamination of samples could not be avoided because it was impossible to separate soil particles from small manure particles, AC and QT powder, results are based on ash-free dry matter or OM. As mineral soils contain only a small portion of OM, which is burned during the ashing process, ash content is often set equivalent to soil contamination accepting a slight underestimation (Potthoff and Lofffield 1998; Esse et al. 2001; Ke et al. 2005). For the small amounts of remaining root parts and dead termites in the samples no such correction could be made and may have led to slight overestimations of remaining DM and nutrients. As all treatments were affected by roots and termites in a similar way, a comparison between the treatments is considered to still be admissible. As the presence of the subterranean termite *Microcerotermes diversus* Silvestri in the experimental field was unknown prior to the experiment, no measures of termite activity, such as number of termites in the litterbags, were taken. Only the presence or absence of termites and foraging signs were noted. To give an estimation of the impact of termite activity on OM disappearance, samples showing signs of the presence of termites were statistically compared with samples without any termite activity, regardless of the treatment.

Dried manure samples were weighed, grinded, ashed and extracted with 32% HCl for the determination of P, K and Na. Phosphorus was measured colorimetrically (Gericke and Kurmies 1952; Hitachi U-2000 spectrophotometer, Tokyo, Japan), K

and Na by means of a flame photometer (Instrument Laboratory 543, Bedford, MA, USA). Total C and N concentrations were measured by a CN analyzer (VarioMax® CHN, Elementar Analysesysteme GmbH, Hanau, Germany). All results are relate to OM contents, calculated as ash content subtracted from the DM:

$$OM (g) = DM (g) - ash (g)$$

The daily OM disappearance rate was calculated as the difference between the remaining OM (kg ha^{-1}) of a sampling date (OM_t) and the remaining OM (kg ha^{-1}) of the previous sampling date (OM_{t-1}) divided by sampling interval in days (d):

$$OM \text{ disappearance rate } (\text{kg ha}^{-1} \text{d}^{-1}) = \frac{OM_t - OM_{t-1}}{d}$$

Nutrient content from soil contamination was calculated multiplying ash content with nutrient concentration of adjacent soil and subtracted from nutrient content in samples to estimate nutrient content of manure only. Relative C and nutrient releases were calculated relating its amount in the litterbag samples to the initial C and nutrient contents.

4.3.5 Statistics

Results are presented as arithmetic means with standard errors. The parameters were statistically analysed with an ANOVA separating the data for sampling date and crop with fertilizer treatments (Co , AC_{fed} , AC_{mix} , QT_{fed} , QT_{mix}) as the main factor. Comparison of means was done by means of planned contrasts comparing Co with amended treatments, AC treatments *versus* QT treatments, and feed *versus* mixed treatments (AC_{fed} *versus* AC_{mix} and QT_{fed} *versus* QT_{mix}). Prior to the statistical analysis, data was screened for outliers and winsorised with the 95% confidence interval. Thereafter, the data were analysed for homogeneity of variances and normal distribution of residuals. In the few cases where variances were not homogenous, contrasts were conducted for unequal variances. Pearson correlation coefficients were also calculated whereby SPSS Statistics 17.0 was used for all computations.

4.4 Results

4.4.1 Remaining organic matter

At almost all sampling dates, there were significant treatment effects under sweet corn with $F(4,15) = 4.0-15.6$ and $P < 0.0001-0.02$ and radish with $F(4,15) = 15.6-24.6$ and $P < 0.001$. The comparison of treatments by planned contrasts revealed significantly higher remaining OM (up to 22%) for amended manure compared with Co at most sampling dates ($P < 0.001-0.05$). While under sweet corn cultivation, the remaining OM in litterbags was 4-25% higher in AC treatments compared to QT treatments (non-significant for S8 and S12; $P < 0.01$), under radish cultivation their effect was reverse (-5 to -15%; $P < 0.01$). In addition, feeding AC led to significantly higher remaining OM at some sampling dates compared with mixing AC (S6, S20; $P < 0.05$), while feeding QT had a stronger impact only under radish cultivation ($P < 0.01$). Across all treatments, the OM disappearance was highest during the first two weeks after litterbag burial, with about 40% OM disappearing under both sweet corn and subsequent radish cultivation (Figure 2). Similarly, the high initial daily OM disappearance rates of 198 and 141 kg OM ha⁻¹ d⁻¹, representing 2.2-2.4% of applied OM strongly declined after 4 weeks (Table 2). The daily OM disappearance rates under sweet corn and radish were only significantly affected by the treatments during the initial 2-4 weeks ($P < 0.05$). Within the first two weeks under sweet corn, AC_{fed} had a by 13% lower OM disappearance rate compared with AC_{mix}, whereas under radish it was by 17% higher. Coating QT, however, reduced OM disappearance rate by 42-45% compared with QT_{fed} within the same time period. After six weeks, up to 55% of the OM had disappeared under both crops and up to 70% after 12 weeks under sweet corn.

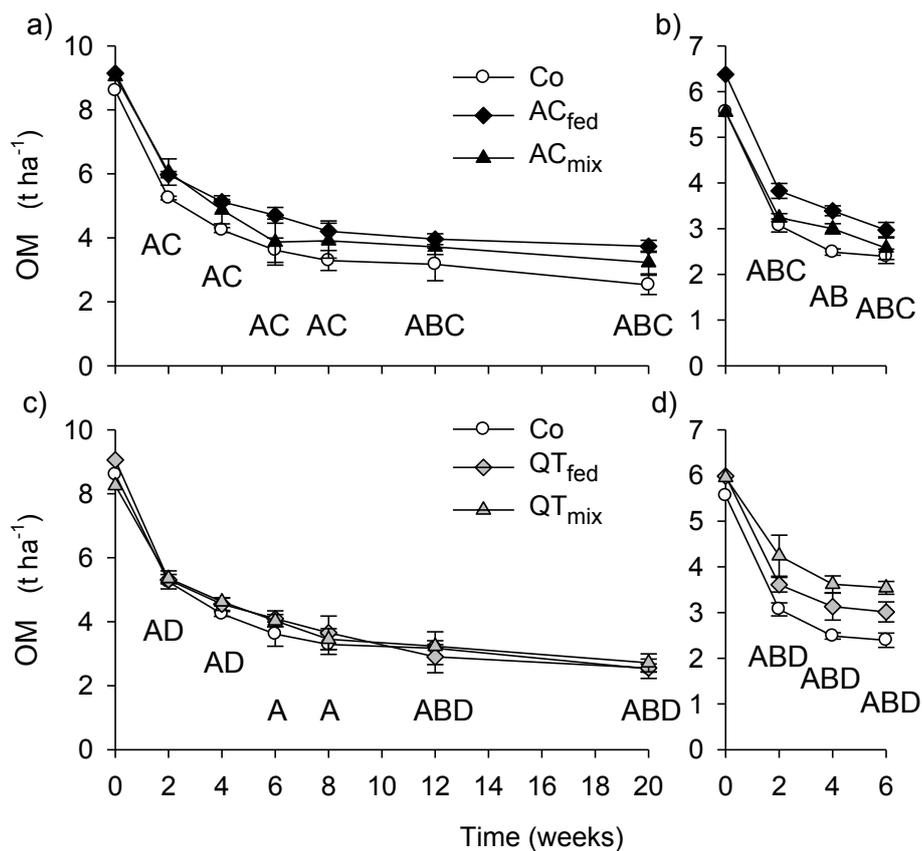


Figure 4.2. Remaining ash-free dry matter of manure in litter bags ($t\ ha^{-1}$) during the cultivation of sweet corn (a + c) and radish (b + d). Symbols represent means, whiskers represent standard error and capital letters indicate significant treatment differences. Comparison of means by contrasts: A: Co *versus* amended; B: AC *versus* QT; C: AC_{fed} *versus* AC_{mix}; D: QT_{fed} *versus* QT_{mix}.

4.4.2 Carbon and nutrient concentrations and CN ratio

The overall manure C and nutrient concentrations during sweet corn and radish cropping were similar for the different nutrients (Fig. 4.3). C concentrations were roughly 10-times higher than P concentrations and 20-times higher than N, K and Na concentrations. While C and P concentrations increased within the first two to four weeks by 20-26% and 47-50%, respectively, and declined slightly thereafter, the concentration of N rose continuously (up to 60-80%) until the end of sampling (12 and 6 weeks in sweet corn and radish, respectively). Potassium and Na concentrations dropped strongly within the first two weeks (60-70%) and stayed relatively constant until the end of each sampling period. Initial C and nutrient concentrations varied between the two cropping periods, but this difference was only distinct for P (18% higher under sweet corn).

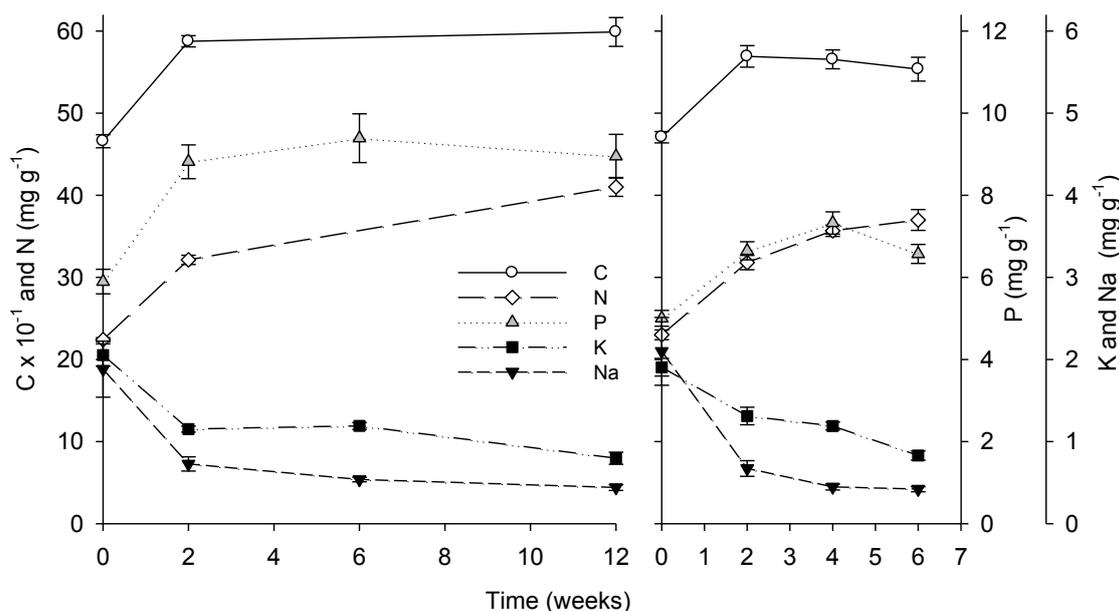


Figure 4.3. Carbon and nutrient concentrations of litterbag samples during a) sweet corn and b) radish cultivation averaged across all treatments in the experimental field near Sohar (Oman). Symbols represent means with standard errors. (n=20). White symbols refer to the left axis, gray on the first right axis and black on the second right axis.

The C/N ratio varied significantly between treatments on all sampling dates, except at R² (Fig. 4.4). On average, amended manures (AC_{fed}, AC_{mix}, QT_{fed} and QT_{mix}) had 17% higher C/N ratios during sweet corn cultivation compared with control, while during radish cultivation this difference was only 6-12%. Feeding AC increased the C/N ratio by 30% on average of both cultivation periods compared with mixing AC ($P < 0.001$). Conversely, feeding QT reduced C/N ratio by 12% on average of both cultivation periods, compared with its mixed application ($P < 0.001$).

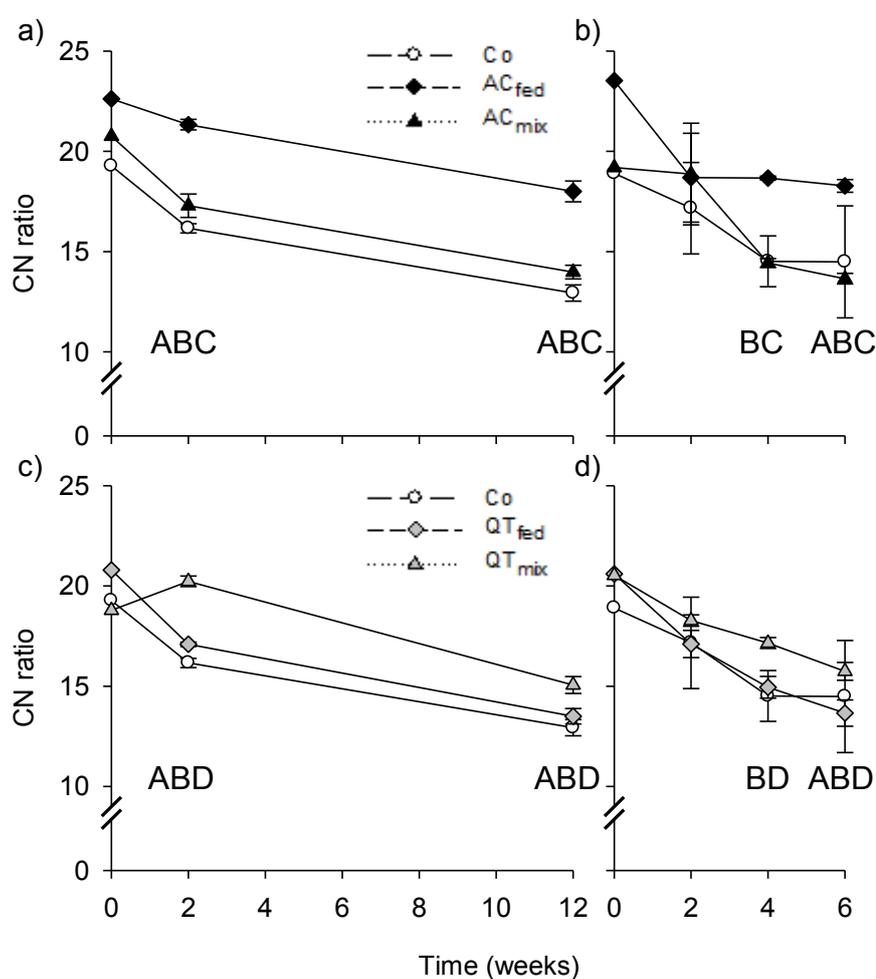


Figure 4.4. C/N ratios of manure in litter bags ($t\ ha^{-1}$) during sweet corn cultivation (a + c) and radish cultivation (b + d) in the experimental field near Sohar (Oman). Symbols represent means, whiskers represent standard error and capital letters indicate significant treatment. Comparison of means by planned contrasts: A: Co *versus* amended; B: AC *versus* QT; C: AC_{fed} *versus* AC_{mix}; D: QT_{fed} *versus* QT_{mix}.

4.4.3 Carbon and nutrient release

In general, relative C and nutrient release were significantly altered during the cultivation periods of both crops by the two amendments (Fig. 4.5). Generally, less C was released from amended manure than from control ($P = 0.000-0.02$), except at R6. While C release from AC amended manure was significantly higher than that from QT amended manure at S2 ($P = 0.03$; Fig. 4.5a and b) and at R2, R4, and R6 ($P = 0.000-0.01$; Fig. 4.5c and d), the opposite relation was observed at S12 ($P = 0.004$). Significant differences in C released by AC_{mix} and AC_{fed} manures were only observed under radish ($P = 0.03-0.05$; Fig. 4.5c), however, during both cropping periods more C tended to be released by AC_{mix} . In contrast, mixing QT with manure reduced C release during sweet corn and radish cropping compared with AC_{fed} , but this difference was only significant at S2 and R4 ($P = 0.01$ and 0.05 , respectively; Fig. 4.5b and d). A treatment effect of amendments compared with control was only observed for R4 ($P < 0.001$). Feeding QT reduced N release compared with QT_{mix} ($P < 0.000$ and $P = 0.05$ at S2 and R2, respectively; Fig. 4.5f and h), and under radish cultivation generally less N was released from QT than from AC treatments ($P < 0.01$). Only at S2, AC and QT treatments had significantly higher relative P release than the control (Fig. 4.5i and j). Thereafter, only the amount released from QT_{mix} was significantly different from QT_{fed} ($P < 0.01$), which also resulted in higher P release for QT treatments in general compared with AC treatments for S2 and S12 ($P = 0.001$ and $P < 0.001$, respectively). However, during radish cultivation, both AC and QT reduced P release compared with control (Fig. 4.5k and l). A significant difference between feeding and mixing QT was only detectable at R6 ($P=0.05$). Potassium release tended to be reduced by amendments (Fig. 4.5m-p), but this difference was only significant for S6 ($P = 0.001$). Feeding AC reduced K release at S2, S6, and S12 as well as at R4 and R6 compared with AC_{mix} ($P = 0.001-0.02$ and $0.03-0.05$, respectively).

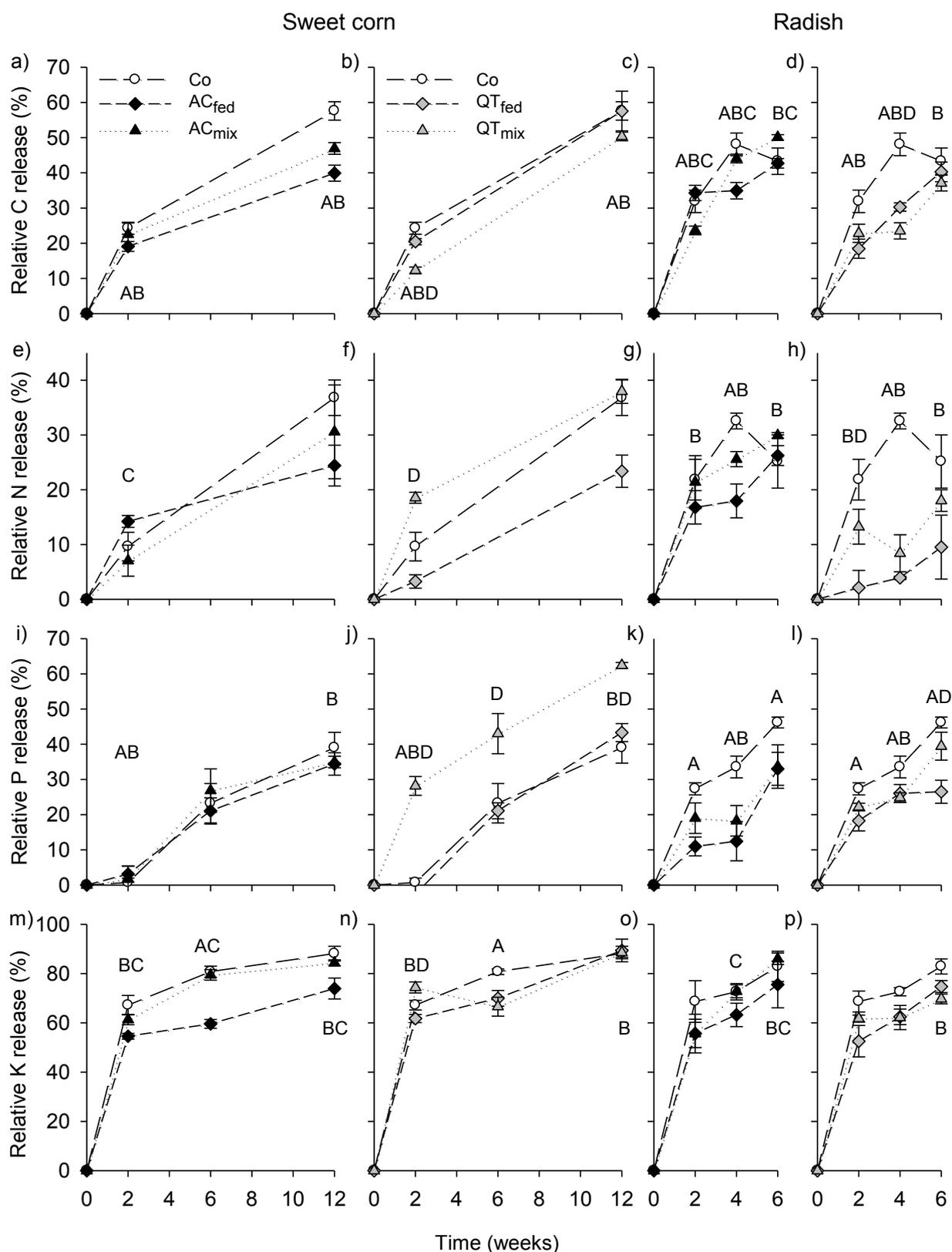


Figure 4.5. Relative C (a-d), N (e-h), P (j-l) and K release (m-p) from litterbag samples under sweet corn (two left columns) and radish (two right columns) in the experimental field near Sohar (Oman). Symbols represent means, whiskers represent standard error and capital letters indicate significant treatment. Comparison of means by planned contrasts: A: Co *versus* amended; B: AC *versus* QT; C: AC_{fed} *versus* AC_{mix}; D: QT_{fed} *versus* QT_{mix}.

Table 4.3. Means and standard error (SE) of total C and nutrient release from goat manure in kg ha⁻¹ until crop harvest (n=4) in the experimental field near Sohar (Oman) and results from statistical analysis of variances (ANOVA) followed by a comparison of means by planned contrasts.

	C		N		P		K		Na	
	Mean	SE	Mean	SE	Mean	SE	Mean	SE	Mean	SE
	Sweet corn									
Co	2220	101	73.6	6.5	22.5	2.5	17.3	0.3	10.4	0.4
AC _{fed}	1805	103	48.8	7.5	18.0	1.7	11.0	0.3	12.0	0.2
AC _{mix}	1948	69	61.2	17.0	20.4	1.0	15.5	0.2	9.4	0.1
QT _{fed}	2393	235	46.8	5.9	19.9	1.2	15.6	0.8	24.7	0.2
QT _{mix}	1892	46	76.0	4.4	28.6	0.4	17.5	0.5	19.2	0.2
	Radish									
Co	1245	88	45.8	1.1	14.3	0.5	8.9	0.3	6.7	0.0
AC _{fed}	1356	43	35.4	2.4	9.5	1.4	9.9	0.6	7.5	0.2
AC _{mix}	1298	20	40.4	0.7	9.6	1.8	10.6	0.3	7.2	0.1
QT _{fed}	1121	78	14.2	7.2	7.3	0.9	7.6	0.2	17.6	0.2
QT _{mix}	1028	62	24.3	2.7	12.1	1.2	6.8	0.2	17.1	0.2
Sweet corn										
<i>P-value</i>	<0.05		0.14		<0.01		<0.001		<0.001	
Co vs. amended	<0.05		ns		ns		<0.001		<0.001	
AC vs. QT	ns		ns		<0.01		<0.001		<0.001	
AC _{fed} vs. AC _{mix}	ns		ns		ns		<0.001		<0.001	
QT _{fed} vs. QT _{mix}	<0.05		ns		<0.01		<0.05		<0.001	
Radish										
<i>P-value</i>	<0.01		<0.001		<0.01		<0.001		<0.001	
Co vs. amended	ns		<0.001		<0.01		ns		<0.001	
AC vs. QT	<0.01		<0.01		ns		<0.001		<0.001	
AC _{fed} vs. AC _{mix}	ns		ns		ns		ns		ns	
QT _{fed} vs. QT _{mix}	ns		ns		<0.01		<0.05		<0.05	

Total C and nutrient release under sweet corn and radish significantly depended on treatments for all measured elements, except for N under sweet corn (Tab. 4.2). However, the patterns of these changes were different under sweet corn and radish. While under sweet corn, C release from control manure was 10% higher compared with that of amended manures, under radish C release was highest for AC treatments. On average, AC treatments released 23% more C compared with QT treatments. The distinct difference in C release between QT_{fed} and QT_{mix} (+26%) under sweet corn was not apparent under radish (+9%). While N release under sweet corn was insignificant, control manure released 60% more N under radish

cultivation. AC treatments released two-times more N compared with QT treatments, but no effects of the application method were observed. Phosphorus release from control manure under radish was significantly greater, whereas under sweet corn it was highest for QT_{mix}. While K release under sweet corn was significantly lower for AC treatments compared with QT treatments (-20%), the opposite was observed under radish (+40%). In both crop cultivation periods, Na release was lower for control compared with amended treatments, with significantly higher total release for QT treatments and highest values for QT_{fed}.

4.5 Discussion

On the irrigated sandy soil of Northern Oman, OM disappearance was high in the control treatment with 70% after 12 weeks of sweet corn cultivation and 60% after 6 weeks of radish cultivation. The comparison of these results with the literature is quite difficult as litterbags are mainly used to investigate the decomposition of leaf litter or harvest residues, with a focus on forest and grassland soils in temperate regions (Knacker et al. 2003; Kampichler and Bruckner 2009). Nevertheless, Esse et al. (2001) reported 28% OM disappearance of a mixture of sheep and goat manure from surface applied litterbags on a sandy soil in Niger after 10 weeks. Ouédraogo et al. (2004) reported OM disappearances from cattle dung of 25-95% after 12 weeks to depend on mesh size, presence of mesofauna and on application mode of the dung (applied to the soil surface *versus* burial at 30 cm) on an Eutric Cambisol in southern Burkina Faso. On the same soil and under similar conditions as in this study, Rottmann et al. (2011) found C losses of 69-94% from maize, alfalfa (*Medicago sativa* L.), wheat (*Triticum aestivum* L.) and canola (*Brassica napus* L.) leaves and straw after 81 days. The differences in decomposition rates between these studies may have several reasons, as they are governed by the physico-chemical environment, the initial organic matter quality and the decomposer community (Knacker et al. 2003). The litterbags in this study were placed at 10 cm depth in an irrigated vegetable field, which provided a permanently moist environment (>45% of water holding capacity) with moderate daily temperature fluctuations, compared with surface placed litterbags on rainfed fields by Esse et al. (2001). The moist environment with soil temperatures between 14-32°C, likely provided an ideal environment for the decomposer community, which also led to the high C disappearance from plant residues in the study of Rottmann et al. (2011). The

study of Ouédraogo et al. (2004) showed that the presence of meso- and macrofauna, such as termites, can play a crucial role in organic matter decomposition.

In the current study, subterranean termites of the species *M. diversus* were observed in litterbag samples of all manure treatments from different sampling dates across the field. By comparing the remaining OM of litterbags showing termite activity with unaffected samples across all treatments, we estimate that termites reduced OM by only 6% across all sampling dates during sweet corn cultivation. During radish termite activity was very low and only visible in a few samples. Despite their key role in many arid ecosystems (Cepeda-Pizarro 1993; Brussaard et al. 2007), termites' effects on cropping systems have rarely been investigated (Black and Okwakol 1997; Kampichler and Bruckner 2009). When mesofauna, such as termites, are allowed to access manure in litterbags, the OM disappearance on arable land may be 1.4 to 3-times higher than with exclusion of meso-fauna by smaller mesh size or pesticide treatment (Esse et al. 2001; Ouédraogo et al. 2004). While termite activity seems to be influenced by application depth and quality of organic material, under the irrigated conditions of this study, termites did not seem to play a major role in OM decomposition.

Organic matter disappearance and C and nutrient release showed clear effects of AC and QT. Generally, AC and QT stabilized OM and slowed down C and nutrient release with some exceptions. This confirms our initial hypotheses that both amendments slow down OM disappearance as well as C and nutrient release, and thus stabilize OM in manure.

4.5.1 Effects of activated charcoal

Feeding AC to goats at 2-3% of their daily DM intake results in an increase of C, neutral detergent fibre (NDF) and acid detergent fibre (ADF) concentrations of the excreted faeces and a reduction of N concentration leading to a higher C/N ratio (Al-Kindi et al. unpublished). Kyvsgaard et al. (2000) reported that N mineralization from manure is negatively correlated with the NDF concentration of feed. The addition of 2.6% AC to the feed increased feed NDF by 55%, so it is likely that AC stabilizes OM in the soil and reduces nutrient release rates. The stabilization of goat manure applied to the soil by AC amendments was accompanied by higher C/N ratios in

litterbag samples during both crop cultivation periods. AC_{fed} exhibited higher C/N ratios than AC_{mix} at almost all sampling dates, which correlates with higher absolute but also relative remaining OM. This corresponds to the general view that higher C/N ratios lead to a slower decomposition of organic material (Janssen 1996). When AC was mixed to manure it increased the remaining OM by an average of 9% under sweet corn and 11% under radish. This roughly corresponds to the percentage of AC added to the manure (10%). Hence, it might be that AC application did not stabilize the manure, but led to lower OM disappearance rates due to its own recalcitrance. This is in agreement with Lentz and Ippolito (2012) who reported an increase of SOC by charcoal application but there was no synergistic effect with simultaneous manure application. However, feeding AC resulted in an average of 16 and 12% more OM remaining under sweet corn and radish, while the AC concentration in the manure was estimated at 9%. Therefore it seems that feeding AC might stabilize OM within the manure, but there are no comparable studies to support this conclusion.

In addition, AC_{fed} reduced relative C, N and K release during both crop cultivation periods to different extents. The stabilization was more distinct during sweet corn cultivation, which may be due to the longer exposure of manure to the soil or to an adaptation of the soil microbial community to the AC application in the subsequent cultivation of radish. Many studies reported an increase of SOC, total N and cation exchange capacity in the soil after the application of charcoal to the soil (Laird et al. 2010; Uzoma et al. 2011). However, no significant increase of SOC and total N in the soil of the two-year field experiment, which ran parallel to this litterbag experiment, was observed, though SOC was numerically higher in AC amended soil compared with the control (Ingold et al. 2015). As the AC application rate was low and the experiment ran for only two years, the stabilizing effect of AC on manure might be moderate at the plot level. At higher application rates, Uzoma et al. (2011) found an increase of total C, total N and P_{Olsen} in a sandy soil treated with up to 20 t of cow manure charcoal after only three month in a greenhouse experiment. While C and N release from AC treatments were more strongly reduced under sweet corn than under radish, P release was unaffected under sweet corn, but significantly reduced under radish. There are indications that AC application can affect the microbial community structure (Jones et al. 2012, Al-Kindi et al. unpublished data), which may also alter the nutrient release patterns from manure. In addition, interactions

between cultivated crop and/or the accompanying differences in soil temperature and irrigation frequency, as well as AC application method may play a role in regulating the microbial community structure or its activity and the resulting nutrient release.

The total nutrient release from goat manure at the end of each cropping period showed that sweet corn was undersupplied with N compared to mineral fertilized plants. Nitrogen uptake of well-developed mineral fertilized sweet corn was 112 kg ha⁻¹ while N release from pure goat manure was only 74 kg ha⁻¹ and even less from AC-enriched manure with 50-61 kg ha⁻¹. Furthermore, P release from goat manure was insufficient as well, with 33 kg ha⁻¹ taken up by plants compared to 18-22 kg ha⁻¹, though AC did not intensify the deficiency. However for radish, nutrient supply from goat manure was sufficient, though AC application reduced total N and P release while K release was slightly increased. Depending on the crop, AC application can intensify N deficiency (Nelson et al. 2011) in the short term, however on the long run improvement of the soil properties and an accumulation of slowly mobilized nutrients might increase crop yields.

4.5.2 Effect of quebracho tannins

Organic matter was stabilized by feeding and mixing QT to different extents. However, the stabilization of OM by QT addition differed for sweet corn and radish. Tannin addition (QT) led to only 5% more remaining OM under sweet corn and 24% under radish. In contrast to our expectations, manure-mixing with QT was more efficient in stabilizing OM (29% more than control) than feeding it to animals (13%). This is also reflected in the higher SOC and total N found in the soil when QT was mixed directly to the soil than when it was fed to the goats after the two-year field experiment (Ingold et al. 2015). Joannis et al. (2007) state that tannins inactivate enzymes by binding them and thus inhibit mineralization. As tannins which passed the digestive system are difficult to extract, but are not absorbed by the ruminants (Terrill et al. 1994), it is likely that they bound to undigested feed particles and were thus inactivated (Makkar 2003). The direct application of QT to the soil may have been more efficient in stabilizing OM by inactivating microbial enzymes.

The different efficiency of QT application on OM stabilization during sweet corn and radish cultivation can have several reasons. There is evidence that the soil

microbial community structure is influenced by different crop species, as the released root exudates differ in their composition (Garbeva et al. 2004; Rottmann et al. 2011). By comparing the contents of ergosterol (an indicator of saprotrophic fungi) and muramic acid (a bacterial residue; Joergensen and Wichern 2008) in the rhizosphere of *Brassicaceae* and *Poaceae*, Appuhn and Joergensen (2006) found that under *Brassicaceae*, the ergosterol concentration is significantly higher and that of muramic acid is significantly lower than under *Poaceae*. This indicates that the microbial communities under *Brassicaceae* and *Poaceae* differ significantly, with the *Brassicaceae* rhizosphere seeming to encourage the growth of fungi, to the detriment of bacteria, compared with *Poaceae*. Other factors influencing the soil microbial community structure or its activity may be the higher irrigation frequency during radish cultivation, lower soil temperatures at the beginning of its cultivation or residual effects of the previous sweet corn. Tannins are known for their antimicrobial properties (Scalbert 1991; Mutabaruka et al. 2007) and may thus more strongly inhibit mineralization in soils with bacterial dominance. In addition, tannins may even favour fungal development as higher fungal C concentrations were found in manure from goats fed with QT (Al-Kindi et al., unpublished data) and higher ergosterol concentrations in soil fertilized with QT-enriched manure (Sradnick et al. 2014). At the same time, QT seemed to affect termite preference for goat manure. Tian et al. (1993) observed a preference of termites for certain tanniniferous prunings (*Acioa barteri*) while others (*Leucaena leucocephala*, *Gliricidia sepium*) are avoided in mulch layers. Under sweet corn, 60% of QT_{mix} samples were affected by termite foraging, while for the other four treatments only 32 to 42% showed foraging signs. However, the reasons for this remain unclear.

Nutrient release from manure could be reduced to different degrees by QT application depending on the application method, the cultivated crop and the nutrient in question. While under radishes, relative C, N, P and K release were reduced by QT_{fed} and QT_{mix}, the effect under sweet corn was more complicated. QT_{fed} only reduced N release by 36% compared with the control, while the release of C, P and K was not significantly affected. As stated before, the tannins might be bound to fodder residues during passage of the goats' digestive system and thus inactivated for their antimicrobial activity. However, the reduction of N release indicates that N containing fodder components such as proteins are not only protected from microbial

degradation within the animals' digestive system (Waghorn et al. 1997), but even after 12 weeks in the soil, which is in agreement with Powell et al. (1994). This is of major importance as it may help reducing N losses via leaching and volatilization in intensive agricultural systems. In a composting experiment with manure from cattle fed with *Acacia mearnsii* as a tannin source, total C, total N and ammonia were higher in the final compost compared with a tannin-free control (Hao et al. 2011). However, in our study, when QT was mixed directly to manure, it only reduced C release under sweet corn, while the release of P and N was greater than that in the control. Studies with tannins from leaf litter, which are mainly unbound, reported either no effect on or a reduction of N mineralization and mineral N in soils (Kraus et al. 2004; Kanerva et al. 2006). Based on the data available, it is not possible to explain this unexpected release pattern observed, but it may well be that the presence of termites and/or fungi in the samples may play a role.

4.6 Conclusions

OM decomposition in the irrigated vegetable production system in Northern Oman is fast and thus may lead to major losses of soil organic matter and nutrients. However, the addition of either AC or QT to goat manure via feed additives or directly mixed to the manure stabilizes manure after application to the soil and reduces relative carbon and nutrient release. While feeding AC seemed more efficient in stabilizing OM than mixing it with manure, for QT the opposite was true. There are indications that during the cultivation of sweet corn and radish, different groups of soil microbes and soil fauna dominated the mineralization processes, which may be caused by direct effects of the crop's root exudates. Different soil temperatures and moisture content may also have provided different environmental conditions, affecting the meso- and microfauna of the soils. AC and QT may influence different soil organisms in different ways, which could explain the contrasting effects under sweet corn and radish cultivation. Activated carbon stabilized OM and reduced nutrient release under both cultivated crops; however, its efficiency was highest under sweet corn. In contrast, QT was only efficient in radish, while under sweet corn cultivation N and P release increased. However, the stabilization of OM by AC and QT may also lead to nutrient deficiencies of crops which needs consideration before application to soils.

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4.8 References

- Aerts, R.J., Barry, T.N. and McNabb, W.C., 1999. Polyphenols and agriculture: beneficial effects of proanthocyanidins in forages. *Agriculture, Ecosystems and Environment* 75, 1-12.
- Aggarwal, R.K., Praveen-Kumar and Power, J.F., 1997. Use of crop residue and manure to conserve water and enhance nutrient availability and pearl millet yields in an arid tropical region. *Soil and Tillage Research* 41, 43-51.
- Al-Farsi, S.A.I., 2001. Classification of soils from an alluvial fan and coastal plain near Sohar, Sultanate of Oman. Sultan Qaboos University.
- Appuhn, A. and Joergensen, R.G., 2006. Microbial colonisation of roots as a function of plant species. *Soil Biology and Biochemistry* 38, 1040-1051.
- Bhatta, R., Shinde, A.K., Vaithyanathan, S., Sankhyan, S.K., Enishi, O. and Kurihara, M., 2011. Utilisation of tannin-containing tree leaves in sheep and goat production. Paper presented at the Successes and failures with animal nutrition practices and technologies in developing countries, FAO Electronic Conference Rome, Italy,
- Black, H.I.J. and Okwakol, M.J.N., 1997. Agricultural intensification, soil biodiversity and agroecosystem function in the tropics: the role of termites. *Applied Soil Ecology* 6, 37-53.
- Bocock, K.L. and Gilbert, O., 1957. The disappearance of leaf litter under different woodland conditions. *Plant and Soil* 9, 179-185.
- Bolan, N.S., Kunhikrishnan, A., Choppala, G.K., Thangarajan, R. and Chung, J.W., 2012. Stabilization of carbon in composts and biochars in relation to carbon sequestration and soil fertility. *Science of The Total Environment* 424, 264-270.
- Brussaard, L., Pulleman, M.M., Ouédraogo, E., Mando, A. and Six, J., 2007. Soil fauna and soil function in the fabric of the food web. *Pedobiologia* 50, 447-462.
- Cepeda-Pizarro, J.G., 1993. Litter decomposition in deserts: an overview with an example from coastal arid Chile. *Revista Chilena de Historia Natural* 66, 323-336.
- Esse, P.C., Buerkert, A., Hiernaux, P. and Assa, A., 2001. Decomposition of and nutrient release from ruminant manure on acid sandy soils in the Sahelian zone of Niger, West Africa. *Agriculture, Ecosystems and Environment* 83, 55-63.
- Garbeva, P., van Veen, J.A. and van Elsas, J.D., 2004. Microbial diversity in soil: Selection of microbial populations by plant and soil type and implications for disease suppressiveness. *Annual Review of Phytopathology* 42, 243-270.
- Hao, X., Benke, M.B., Li, C., Larney, F.J., Beauchemin, K.A. and McAllister, T.A., 2011. Nitrogen transformations and greenhouse gas emissions during composting of manure from cattle fed diets containing corn dried distillers grains with solubles and condensed tannins. *Animal Feed Science and Technology* 166-167, 539-549.
- Ingold, M., Dietz, H., Sradnick, A., Joergensen, R., Schlecht, E. and Buerkert, A., 2015. Effects of activated charcoal and quebracho tannin amendments on soil properties in irrigated organic vegetable production under arid subtropical conditions. *Biology and Fertility of Soils* 51, 367-377.
- Janssen, B.H., 1996. Nitrogen mineralization in relation to C:N ratio and decomposability of organic materials. *Plant and Soil* 181, 39-45.

- Joanisse, G.D., Bradley, R.L., Preston, C.M. and Munson, A.D., 2007. Soil enzyme inhibition by condensed litter tannins may drive ecosystem structure and processes: the case of *Kalmia angustifolia*. *New Phytologist* 175, 535-546.
- Joergensen, R.G. and Wichern, F., 2008. Quantitative assessment of the fungal contribution to microbial tissue in soil. *Soil Biology and Biochemistry* 40, 2977-2991.
- Jones, D.L., Rousk, J., Edwards-Jones, G., DeLuca, T.H. and Murphy, D.V., 2012. Biochar-mediated changes in soil quality and plant growth in a three year field trial. *Soil Biology and Biochemistry* 45, 113-124.
- Kampichler, C. and Bruckner, A., 2009. The role of microarthropods in terrestrial decomposition: a meta-analysis of 40 years of litterbag studies. *Biological Reviews* 84, 375-389.
- Kanerva, S., Kitunen, V., Kiikkilä, O., Loponen, J. and Smolander, A., 2006. Response of soil C and N transformations to tannin fractions originating from Scots pine and Norway spruce needles. *Soil Biology and Biochemistry* 38, 1364-1374.
- Ke, X., Winter, K. and Filser, J., 2005. Effects of soil mesofauna and farming management on decomposition of clover litter: a microcosm experiment. *Soil Biology and Biochemistry* 37, 731-738.
- Knacker, T., Förster, B., Römbke, J. and Frampton, G.K., 2003. Assessing the effects of plant protection products on organic matter breakdown in arable fields - litter decomposition test systems. *Soil Biology and Biochemistry* 35, 1269-1287.
- Kraus, T.E.C., Zasoski, R.J., Dahlgren, R.A., Horwath, W.R. and Preston, C.M., 2004. Carbon and nitrogen dynamics in a forest soil amended with purified tannins from different plant species. *Soil Biology and Biochemistry* 36, 309-321.
- Kyvsgaard, P., Sørensen, P., Møller, E. and Magid, J., 2000. Nitrogen mineralization from sheep faeces can be predicted from the apparent digestibility of the feed. *Nutrient Cycling in Agroecosystems* 57, 207-214.
- Laird, D.A., Fleming, P., Davis, D.D., Horton, R., Wang, B. and Karlen, D.L., 2010. Impact of biochar amendments on the quality of a typical Midwestern agricultural soil. *Geoderma* 158, 443-449.
- Lentz, R.D. and Ippolito, J.A., 2012. Biochar and manure affect calcareous soil and corn silage nutrient concentrations and uptake. *Journal of Environmental Quality* 41, 1033-1043.
- Makkar, H.P.S., 2003. Effects and fate of tannins in ruminant animals, adaptation to tannins, and strategies to overcome detrimental effects of feeding tannin-rich feeds. *Small Ruminant Research* 49, 241-256.
- Mutabaruka, R., Hairiah, K. and Cadisch, G., 2007. Microbial degradation of hydrolysable and condensed tannin polyphenol-protein complexes in soils from different land-use histories. *Soil Biology and Biochemistry* 39, 1479-1492.
- Nelson, N.O., Agudelo, S.C., Yuan, W. and Gan, J., 2011. Nitrogen and phosphorus availability in biochar-amended soils. *Soil Science* 176, 218-226.
- Ouédraogo, E., Mando, A. and Brussaard, L., 2004. Soil macrofaunal-mediated organic resource disappearance in semi-arid West Africa. *Applied Soil Ecology* 27, 259-267.
- Potthoff, M. and Lofffield, N., 1998. How to quantify contamination of organic litter bag material with soil? *Pedobiologia* 42, 147-153.
- Powell, J.M., Fernández-Rivera, S. and Hös, S., 1994. Effects of sheep diet on nutrient cycling in mixed farming systems of semi-arid West Africa. *Agriculture, Ecosystems and Environment* 48, 263-271.
- Puchala, R., Min, B.R., Goetsch, A.L. and Sahlü, T., 2005. The effect of a condensed tannin-containing forage on methane emission by goats. *Journal of Animal Science* 83, 182-186.
- Rasool, R., Kukal, S.S. and Hira, G.S., 2008. Soil organic carbon and physical properties as affected by long-term application of FYM and inorganic fertilizers in maize-wheat system. *Soil and Tillage Research* 101, 31-36.
- Rottmann, N., Siegfried, K., Buerkert, A. and Joergensen, R., 2011. Litter decomposition in fertilizer treatments of vegetable crops under irrigated subtropical conditions. *Biology and Fertility of Soils* 47, 71-80.

- Scalbert, A., 1991. Antimicrobial properties of tannins. *Phytochemistry* 30, 3875-3883.
- Schjønning, P., Christensen, B.T. and Carstensen, B., 1994. Physical and chemical properties of a sandy loam receiving animal manure, mineral fertilizer or no fertilizer for 90 years. *European Journal of Soil Science* 45, 257-268.
- Schulz, H. and Glaser, B., 2012. Effects of biochar compared to organic and inorganic fertilizers on soil quality and plant growth in a greenhouse experiment. *Journal of Plant Nutrition and Soil Science* 175, 410-422.
- Siegfried, K., Dietz, H., Schlecht, E. and Buerkert, A., 2011. Nutrient and carbon balances in organic vegetable production on an irrigated, sandy soil in northern Oman. *Journal of Plant Nutrition and Soil Science* 174, 678-689.
- Sradnick, A., Ingold, M., Marold, J., Murugan, R., Buerkert, A. and Joergensen, R., 2014. Impact of activated charcoal and tannin amendments on microbial biomass and residues in an irrigated sandy soil under arid subtropical conditions. *Biology and Fertility of Soils* 50, 95-103.
- Terrill, T.H., Waghorn, G.C., Woolley, D.J., McNabb, W.C. and Barry, T.N., 1994. Assay and digestion of ¹⁴C-labelled condensed tannins in the gastrointestinal tract of sheep. *British Journal of Nutrition* 72, 467-477.
- Tian, G., Brussaard, L. and Kang, B.T., 1993. Biological effects of plant residues with contrasting chemical compositions under humid tropical conditions: Effects on soil fauna. *Soil Biology and Biochemistry* 25, 731-737.
- Uzoma, K.C., Inoue, M., Andry, H., Fujimaki, H., Zahoor, A. and Nishihara, E., 2011. Effect of cow manure biochar on maize productivity under sandy soil condition. *Soil Use and Management* 27, 205-212.
- Waghorn, G.C., Reed, J.D. and Ndlovu, L.R., 1997. Condensed tannins and herbivore nutrition. *International Grassland Congress Winnipeg, Manitoba*.
- Williams, T., 1999. Factors influencing manure application by farmers in semi-arid west Africa. *Nutrient Cycling in Agroecosystems* 55, 15-22.
- WMO, 2009. *World Meteorological Organisation, Geneva*.

Chapter 5

General discussion, conclusions and recommendations

5.1 Evaluation of the methodology

5.1.1 Experimental set-up

The previously described controlled field experiment was conducted to test the effect of AC and QT added to the goats' feed or directly to manure on: manure quality, crop yield, crop nutrient use efficiencies, soil properties, and turnover of OM and nutrients. Field experiments have the advantage that they are conducted under natural conditions with the impact of all environmental factors, which are difficult to reproduce under laboratory conditions. However, even in so called controlled field experiments, not all factors can be accounted for and evaluating the experimental outcome can be quite complex. Thus, to avoid bias, the randomization of the treatments on the field plots is a very important step, in particular on heterogeneous sites. In this experiment a completely randomized block design comprising the six fertilization treatments with four replicates in each of two blocks was used and the plots were located in a field in which two years earlier a fertilization experiment had been conducted. The treatments of the previous experiment proved to still have an effect on initial SOC and total N concentrations in the soil. Though the variation of the initial soil parameters was considered in the statistical analyses of treatment effects, it may have partly masked treatment effects. The selection of an experimental area should be done very carefully and sites with plots of heterogeneous prior use or treatment should be avoided whenever possible. However, combining plots with a similar prior treatment into blocks and randomizing the new experimental treatments within these blocks may help reducing the experimental variance. This approach could not be used in the present study, however, as the number of plots within a block did not match the number of treatments.

Another factor which varied within the two-year experimental period was the composition of manure collected for the field experiment. The composition of manure varied considerably within and between the seasons, leading to deviations in applied C, nutrients, AC, and QT. The variation of nutrient concentrations in manure was high with N concentrations ranging from 20.4-24.3 mg g⁻¹, P concentrations from 4.6-6.6 mg g⁻¹ and K concentrations from 1.7-3.4 mg g⁻¹ within a treatment. To obtain enough manure for the two blocks, manure was collected over a period of 5-6 months.

in each season. This long period resulted in large variations of climatic conditions as monthly average temperature declined from 33°C in August to 20°C in January. It is well known that goats under heat stress (at temperatures up to 40°C) reduce their feed intake by 40-50% compared with goats under moderate conditions (20-22°C; Hirayama et al. 2004; Maloiy et al. 2008), while water intake increases by 30%. Though Maloiy et al. (2008) did not find that OM digestibility was affected by heat stress, Hirayama et al. (2004) reported an increase in crude protein digestibility. The digesta passage rates of sheep and goats were found to be reduced under heat stress as well (Hirayama et al. 2004; Bernabucci et al. 2009).

In addition, the feed quality changed within the collection period despite the similar diet composition of 50% Rhodes grass hay and 50% pellets (47% crushed maize and 3% soybean cake). Particularly N concentrations of hay varied from 12-19 mg g⁻¹ within a season, resulting in C/N ratios between 22 and 36. An increase in crude protein of feed from 15% to 18% improves digestibility of crude protein and non-structural carbohydrates by goats (Arieli et al. 2005) and thus changes manure excretion and composition. The total daily crude protein intake of goats was calculated from N concentrations in the hay and pelleted feed used, and variations between 9-12% crude protein were observed within the season.

The age of the goats is another likely factor affecting the quality and daily excretion of manure used in this study. In the first season, manure was collected from almost fully grown male goats (37.4 kg on average), while in the second season, manure was collected from growing male goats of 23.2 kg. To meet their energy demand, the heavier, older goats in the first season were fed a daily ration of 1000 g DM compared with 600 g DM fed to the younger, lighter goats in the second season. The total faecal DM excretion per goat and day amounted to 170-196 g DM d⁻¹ goat⁻¹ and 142-193 g DM d⁻¹ goat⁻¹, in the first and second season, respectively. That is 17-20% of the intake was excreted by older goats, while younger goats excreted 24-32%. As the digestion of younger goats is less efficient and they excrete a greater portion of their ingested feed than do older goats, the estimated AC and QT (assuming that AC and QT is not digested) concentration in manure from these goats was likely lower than that of the older goats.

In conclusion, climatic conditions, fodder quality, and animal age need to be considered when planning and evaluating feeding experiments and alterations in

these manure quality modifying factors should be avoided. In case of inevitable changes, manure quality should be analyzed regularly to adjust rates of manure application, though this may be difficult to implement, depending on cost and time constraints.

5.1.2 Litterbag methodology

The litterbag method is a simple method to investigate the turnover of organic material under field conditions originally introduced by Bockock and Gilbert (1957). Organic material is enclosed in bags of 15-600 cm² made of non-degradable, inert material with mesh sizes between 2 µm and 10 mm, placed on the soil surface or buried in the soil to examine the decomposition of litter or crop residues, the effects of plant protection products on the breakdown of OM (Knacker et al. 2003) or the role of microarthropods in terrestrial decomposition (Kampichler and Bruckner 2009). Typically, different mesh sizes are used to include or exclude specific soil organisms allowing the differentiation of the role of microorganisms, meso- and macrofauna in decomposition of OM in soils (Kampichler and Bruckner 2009). Despite its ease of application and low cost, the litterbag approach brings along some challenges. The litterbag method is designed to examine the decomposition of organic material under natural conditions. However, by enclosing organic material in the litterbags, it is inevitable that the microclimate within the bag also changes, depending on the material used and the mesh size (Bradford et al. 2002). Very fine mesh sizes will interrupt contact with the surrounding soil and thus colonization by soil organisms and water infiltration is hampered, reducing leaching of mineral components. In addition, the exclusion of soil meso- and macrofauna also affects the presence of bacterivorous, fungivorous and nematophagous organisms as well as their predators (Vreeken-Buijs and Brussaard 1996) and thus affects the soil microbial community structure. On the other hand, big mesh sizes need to be handled carefully as small particles of the organic material are easily lost when retrieving the litterbags from the soil. To reduce the effects of artificial microclimates within the litterbags and to compare the results with those of other studies, the often used mesh size of 1 mm was chosen for this study. Even though the focus of the study was to estimate the effects of soil microorganisms and microfauna on the decomposition of organic material, a fraction of the meso-fauna was able to enter the litterbags.

The quantification of OM remaining in the litterbags at the sampling point is difficult because of contamination from the surrounding material. Particularly litterbags buried in soils are prone to contamination by soil particles. If contamination cannot be avoided, a common method to estimate the soil contamination is to analyse the ash content of a subsample as a marker for soil contamination (Potthoff and Lofffield 1998). As mineral soils contain only a small portion of OM, which is burned during the ashing process, ash content is often set equivalent to soil contamination accepting a slight underestimation. Authors then often refer to the ash-free DM - which represents the OM content of the litterbag sample (Kaneko and Salamanca 1999; Esse et al. 2001; Georgieva et al. 2005, Ke et al. 2005). By this approach, SOM and ash content of the organic material are not accounted for. In the equation by Malkomes (1980) the ash concentration of the initial organic material (9% in this study) and the surrounding soil (95%) is considered for the calculation of the soil contamination (Fig. 5.1).

$$DW_{SC} = \frac{A_{LB} - A_{OM}}{A_S}$$

Figure 5.1. Equation by Malkomes (1980) for the calculation of soil contamination in litterbag samples, with a slight simplification by Potthoff and Lofffield (1998). DW_{SC} = dry weight of soil contamination; A_{LB} = ash of litterbag sample; A_{OM} = ash of initial organic matter; A_S = ash of surrounding soil.

This approach assumes that the ash content in the organic material does not change in the course of the experiment, but it is likely that mineral components of the applied organic material are removed by leaching or root uptake. A comparison of the ash-free DM with the DM calculated with the Malkomes equation resulted in slightly lower values for the ash-free DM approach, but higher variances for the Malkomes approach (data not shown). Potthoff and Lofffield (1998) recommend the use of other markers for soil contamination such as aluminium or lead, as their concentration in soil is 40-100 times higher than in straw. However, the analysis of these elements is more complicated and expensive than a simple estimation of ash. In their study, straw was mixed with a predefined amount of soil, to test which internal markers can be used to estimate soil contamination. The measured ash content and the predefined soil contamination showed a good correlation ($R^2 = 0.99$) when the whole sample was ground before taking a subsample for ash determination. For these reasons, in this study the entire litterbag sample was removed from the bag, carefully cleaned from soil, roots and other contaminants as

far as possible without losing any sample material (manure particles attached to roots, small loose particles in the soil), ground and sub-sampled for analysis. In most cases, the removal of soil was impossible without losing small fragments of the decomposed manure leading to highly variable soil contamination of samples (17-89% ash concentrations). The difficulty of taking homogenous subsamples for analysis as result of the varying degrees of contamination was met by repeating the analysis two to four times. The quantification of contamination by organic material from plant roots, fungal hyphae or termite bodies is difficult as there is no standard method. In this study roots and termites were carefully removed from samples prior to analysis. A slight distortion of the results cannot, however, be ruled out.

5.2 Efficiency of AC as soil amendment

Activated charcoal slowed down decomposition of goat manure in the alkaline, sandy soil and increased SOC in the two-year field experiment even at the low annual application rates of 1.4-2.1 t ha⁻¹. The litterbag experiment (Chapter 4) showed that AC defecated by goats or directly mixed with dry faeces reduced OM decomposition and nutrient release. The half-life of OM from the AC_{fed} treatment, calculated from the logarithmic decay equation fitted to the OM loss from litterbags, increased by almost 20 days under sweet corn, while AC_{mix} extended it by six days compared to the control treatment (Fig. 5.2 and Table 5.1). Under radish, both AC treatments prolonged half-life by 10 days compared with the unamended control. Particularly on poor sandy soils, the accumulation of SOC and the accompanying improvement of soil properties (such as soil aggregate stability, pore space, CEC, and WHC) promise to increase crop productivity (Lal 2006; Bationo et al. 2007). Despite the heterogeneity of the soil in the field experiment, the relatively low AC application rates, and the short experimental period of two years, SOC concentration was higher in AC treated soils compared to pure goat manure, while other measured soil parameters remained unchanged.

$$\frac{DW_t}{DW_0} = 1 - k \times \ln(t + 1)$$

Figure 5.2. Logarithmic decay equation fitted to the OM loss from litterbags in an irrigated organic field in Northern Oman. DW_t = dry weight of litterbag sample at time t ; DW_0 = dry weight of initial litterbag sample; k = decay constant; t = time in days of incubation.

Table 5.1. Constant k , p-value and coefficient of determination R^2 of the logarithmic decay equation fitted to the OM loss from litterbags under sweet corn and radish cultivation in an irrigated organic field in Northern Oman.

	Constant k	P-value	R^2	Half-life (days)
Sweet corn				
Co	0.148	<0.001	0.98	28
AC _{fed}	0.130	<0.001	0.99	47
AC _{mix}	0.140	<0.001	0.94	34
QT _{fed}	0.149	<0.001	0.98	27
QT _{mix}	0.139	<0.001	0.99	36
Radish				
Co	0.157	<0.001	0.99	23
AC _{fed}	0.141	<0.001	0.99	33
AC _{mix}	0.141	<0.001	0.98	33
QT _{fed}	0.137	<0.001	0.97	38
QT _{mix}	0.111	<0.001	0.95	90

Contrary to our expectations, the application of AC in combination with goat manure did not increase sweet corn or radish yields. The regression analysis presented in Chapter 2 revealed a negative effect of AC application on sweet corn yield and nutrient uptake, irrespective of the application method. In the literature, positive effects of charcoal on yields were mainly observed when high charcoal application rates improved soil properties such as neutralization of an acidic pH, or added considerable amounts of nutrients to the soil (Yamato et al. 2006; Chan et al. 2008; Zhang et al. 2012). Other studies, where these beneficial effects were lacking, similar results as in our study were observed (Van Zwieten et al. 2010; Lentz and Ippolito, 2012; Schulz and Glaser, 2012). It is likely that the pre-existing N deficiency in the control treatment was amplified by AC application. The N release from AC-enriched manure in the litterbag study was 17-34% less than that of the control manure. Considering the N uptake by the cultivated crops, 70% of the N released by pure goat manure is found in the sweet corn and radish biomass, while 80-100% of the N released by AC-enriched manure is theoretically utilized. Even if such a calculation is not completely true, as the crops may also use N released from soil N pools, it gives an indication how AC may improve N use efficiency. Slowing down N release and thus reducing losses via leaching and gaseous emissions (Yao et al. 2012; Zheng et al. 2013; Nelissen et al. 2014;) can lead to a long-term accumulation of slowly available N in the soil. However, for optimal crop production a sufficient supply of plant nutrients is necessary. Particularly in the first years after initial

charcoal application, nutrient immobilization may cause yield reductions for some crops.

Feeding AC to goats was more effective in stabilizing OM and reduced nutrient release compared to mixing it directly to the soil. The C, ADF and NDF concentrations of faeces from goats fed AC were higher compared with control goats indicating a stabilization of the OM in goat manure. The different impact of AC on nutrient release under sweet corn and radish may indicate diverse effects on the microbial community. Under *Brassicaceae*, such as radish, fungi are stimulated (Appuhn and Jörgensen 2006). The slighter inhibition of OM decomposition, C and P release under radish indicated that the application of AC inhibited bacteria more than fungi. However, on the same soil Sradnick et al. (2014) did not find any changes on microbial community structure of the experimental soil in response to the application of AC, which contradicts the findings of Pietikäinen et al. (2000), Quilliam et al. (2012) and Oleszczuk et al. (2014). Charcoal can favour bacteria under some conditions, as it provides a habitat for soil microorganisms, improves hydration and stimulates microbial enzyme activity in soils (Lehmann et al. 2011; Oleszczuk et al. 2014), whereas saprotrophic fungi can be inhibited by biochar application according (Quilliam et al. 2012). The effect of AC application on the microorganisms within the manure and the soil fauna is unclear. Under certain conditions, charcoal fed to goats can stabilize OM more efficiently than direct soil application of charcoal. Moreover, the daily N excretion by AC fed goats was not reduced compared to control goats, while C excretion increased by 20-30%. Thus, feeding AC at a rate of 2.5% of the daily diet to goats not only provided a more stable C source but also increased the amount of C applied to the soil at similar N application rates. The application of charcoal to soils by letting it first pass through the digestive tract of animals may be a way to improve the efficiency of charcoal application and at the same time provide health benefits to the animals (Huwig et al., 2001; Van et al. 2006; Leng et al. 2012).

5.3 Efficiency of QT as soil amendment

In most cases, the application of QT in combination with goat manure was able to reduce decomposition of OM and slow down nutrient release. While OM decomposition in the litterbag experiment (Chapter 4) was clearly reduced under radish, this effect was less pronounced under sweet corn. Under sweet corn, QT_{mix}

increased the half-life of the OM by 8 days (1.3 times longer) compared with the control, whereas QT_{fed} did not affect half-life at all. However under radish, half-life was prolonged by 15 days (1.7 times longer) in QT_{fed} treatment and by as much as 67 days (3.9 times longer) in the QT_{mix} treatment (Fig. 5.2 and Table 5.1). In soil samples, no significant effect on SOC was observed at the end of the two-year field experiment. This is very surprising, but might be explained by the higher C disappearance from the top soil during the hot fallow period. As microbial activity in the soil was not affected by the treatments and was expected to be low during the hot and dry period, termites might have been the driving force of the C disappearance. Termites play a key role in many arid ecosystems and contribute greatly to OM decomposition (Cepeda-Pizarro 1993; Brussaard et al. 2007). During the cropping season, the impact of termites on OM decomposition seemed to be low, but a preference for tannin-enriched manure was observed (personal observation). However, the role of termites in the irrigated agriculture of Oman and the impact of tannins on their foraging activity is not yet understood and calls for further research.

The application of tannin-enriched manure, either by feeding QT to goats or mixing it directly with the manure, resulted in DM yield reductions of sweet corn and radish by 25-60 and 25-40%, respectively, compared to control treatment. Contrary to this, pearl millet yields were not reduced in a greenhouse study in Niger when fertilized with manure from sheep fed with a variety of polyphenol containing browse leaves (Quilliam et al. 2012). In a similar pot experiment in Colombia, using manure from sheep fed with condensed tannin-containing legumes, no clear effect of the tannin treatment could be observed on *Brachiaria* grass (Powell et al. 1999). This raises the question why polyphenol- or tannin-enriched manure leads to yield reductions only in some cases depending on the soil type and plant species used.

The OM decomposition, C, N, P and K release under sweet corn and radish were significantly affected by QT application in the litterbag experiment. Sradnick et al. (2014) found a significant change in the microbial community structure in soil samples from the same field experiment. Similar to Mutabaruka et al. (2007), they found that tannins favour fungal colonization and inhibit bacterial growth. A change in microbial community structure is likely to influence turnover rates of OM in soils and thus nutrient mineralization. However, the effect of tannins on mineralization depended on the cultivated crop, the application method (fed or mixed) and the

nutrient in question. The reason for this seemed to be the different microbial community structure under *Brassicaceae* and *Poaceae* reported by Appuhn and Jørgensen (2006). Tannins might influence different groups of soil organisms and soil fauna in different ways, inhibiting or favouring their activity in decomposition and mineralization. The reactivity of tannins was also altered by digestion, as QT mixed directly to the soil inhibited OM decomposition and nutrient release more strongly than QT defecated by goats. The C and nutrient composition of manure was not altered by feeding goats a dietary supplement of 3.5% QT extract in this study, though an increase of C and N concentrations in manure was reported in other studies (Mafongoya et al. 2000). It is likely that tannins from different sources have different impacts on manure properties as they have different chemical compositions, size and reactivity. However, N release was inhibited more after feeding, as N might be protected by covalent binding to tannins not only during digestion, but also later in the soil. One reason for the observed yield reductions is likely the lowered amount of N released from manure. Some tannins might even have allelopathic effects on particular crop species, directly inhibiting their development (Li et al. 2010). This negative impact on crop production might be particularly problematic in small-scale farming in humid and semi-arid tropics and subtropics where tanniniferous browse species often form part of ruminant diets, especially during the dry seasons.

Nevertheless, feeding QT to almost fully grown male goats (first season) or growing male goats (second season) increased the daily faecal excretion by 15 and 36%, respectively compared to the control. Consequently, faecal N excretion per goat increased by 6 and 34%, compared to control. This higher N excretion likely results from a better utilization of the ingested N by ruminants fed tannins and a shift of N excretion from urine to faeces (Makkar 2003; Hess et al. 2006; Al-Kindi et al., unpublished). By feeding tannins to growing male goats, the annual faecal N excretion of 1000 tropical livestock units (TLU) can be increased from 12.7 t to 16.9 t. To sum up, there are indications that feeding tannins has a positive effect on the composition of manure. However, the enhanced excretion of OM and nutrients in faeces may be of even more importance. To assess the fertilizer value of tannin-enriched manure, further research is necessary, especially to understand the yield reduction observed in this study and to find countermeasures for these types of detrimental effects.

5.4 Conclusions and recommendations

The soil application of AC and QT in combination with goat manure slowed down the turnover of goat manure on the irrigated sandy soil in Northern Oman. Activated charcoal and QT seemed to inhibit different groups of the soil microbial community and soil fauna leading to diverse effects under sweet corn and radish. Used as feed additives, both agents affected the excretion and composition of goat manure. Activated charcoal and QT after defecation by goats exhibited different effects on manure turnover than direct mixing with the soil. Under our experimental conditions, the efficiency of OM stabilization was higher when AC was fed to goats, making this application method advantageous compared to direct application to soils, especially when potentially beneficial effects on the animals are considered. Feeding charcoal to goats can improve positive effects of manure and charcoal application to soils at low rates, which is particularly interesting in regions low in resources and high in OM turnover. However, as AC is too expensive for an extensive use, non-activated charcoal produced from plant material as feedstock in small pyrolysis units should be considered.

Conversely, QT stabilized OM more strongly when directly mixed to the soil than after defecation. It seemed that tannins are inactivated during digestion possibly by forming complexes with proteins, though the fate of tannins during digestion is unclear. The litterbag revealed diverse effects of defecated and directly mixed QT under sweet corn and radish, indicating different impacts on bacteria and fungi. In addition, tannins also seemed to affect foraging activity of termites. Thus, under certain conditions, OM decomposition may be increased with tannin application, however, N release was always reduced. The enhanced N excretion by goats fed with tannins may be a promising way to reduce N losses via urine and improve N cycling. However, detrimental effects of tannin-enriched manure on crops need to be understood in order to avoid them. The combined application of tannins and charcoal as feed additives may be a possible solution for detrimental effects of tannins, which already proved to benefit animals feeding on tanniferous browse (Van et al. 2006).

The experimental difficulties encountered in this controlled field experiment demonstrated the importance of avoiding changing conditions as much as possible. The effects of changing feed quality, climatic conditions and animal age can greatly alter study outcomes and complicate their evaluation. To further understand the

diverse effects of AC and QT on the turnover of goat manure and their interactions with the application method and the cultivated crop observed in this study, laboratory incubation and pot experiments should be conducted. Particularly long-term field experiments are needed to evaluate positive effects of SOC accumulation, which can generally only be observed after several years of regular application.

- To understand the effects of AC and QT on the microbial community, ergosterol and amino acids in litterbag samples should be analysed. In addition, ¹⁵N labelled manure should be used to track the N brought in by manure in the soil.
- As the role of termites on agriculture in Oman is poorly understood, on-field litterbag experiments with two different mesh sizes, including or excluding termites, should be conducted. In regard to the considerable SOC disappearance observed after the hot fallow period, termite foraging activity should be investigated.
- A screening of the effect of tannins from a variety of browse species should be conducted on a variety of crops with or without additional mineral fertilizer applications, to test whether the inhibitory effect of tannins on crops resulted from induced nutrient deficiencies or from direct allelopathy. This is particularly important as tanniniferous browse is regularly used as animal fodder and might affect crop productivity, when tannin-enriched manure is used as fertilizer.
- The effects of different charcoals on soil and plants have been screened previously, however, information on the effect of different ingested charcoals on animals and on the composition of manure have yet to be investigated.
- For the evaluation of AC and QT as manure additives, the quantification of C and nutrient losses via leaching and gaseous emissions need to be considered in order to examine C and nutrient balances.

5.5 References

- Appuhn, A. and Joergensen, R.G., 2006. Microbial colonisation of roots as a function of plant species. *Soil Biology and Biochemistry* 38, 1040-1051.
- Arieli, A., Sasson-Rath, R., Zamwel, S. and Mabjeesh, S.J., 2005. Effect of dietary protein and rumen degradable organic matter on milk production and efficiency in heat-stressed goats. *Livestock Production Science* 96, 215-223.
- Bationo, A., Kihara, J., Vanlauwe, B., Waswa, B. and Kimetu, J., 2007. Soil organic carbon dynamics, functions and management in West African agro-ecosystems. *Agricultural Systems* 94, 13-25.
- Bernabucci, U., Lacetera, N., Danieli, P.P., Bani, P., Nardone, A. and Ronchi, B., 2009. Influence of different periods of exposure to hot environment on rumen function and diet digestibility in sheep. *International Journal of Biometeorology* 53, 387-395.
- Bocock, K.L. and Gilbert, O., 1957. The disappearance of leaf litter under different woodland conditions. *Plant and Soil* 9, 179-185.
- Bradford, M.A., Tordoff, G.M., Eggers, T., Jones, T.H. and Newington, J.E., 2002. Microbiota, fauna, and mesh size interactions in litter decomposition. *Oikos* 99, 317-323.
- Brussaard, L., Pulleman, M.M., Ouédraogo, E., Mando, A. and Six, J., 2007. Soil fauna and soil function in the fabric of the food web. *Pedobiologia* 50, 447-462.
- Cepeda-Pizarro, J.G., 1993. Litter decomposition in deserts: an overview with an example from coastal arid Chile. *Revista Chilena de Historia Natural* 66, 323-336.
- Chan, K.Y., Van Zwieten, L., Meszaros, I., Downie, A. and Joseph, S., 2008. Using poultry litter biochars as soil amendments. 46, 437-444.
- Esse, P.C., Buerkert, A., Hiernaux, P. and Assa, A., 2001. Decomposition of and nutrient release from ruminant manure on acid sandy soils in the Sahelian zone of Niger, West Africa. *Agriculture, Ecosystems and Environment* 83, 55-63.
- Georgieva, S., Christensen, S., Petersen, H., Gjelstrup, P. and Thorup-Kristensen, K., 2005. Early decomposer assemblages of soil organisms in litterbags with vetch and rye roots. *Soil Biology and Biochemistry* 37, 1145-1155.
- Hess, H.D., Tiemann, T.T., Stürm, C.D., Carulla, J.E., Lascano, C.E. and Kreuzer, M., 2006. Effects of tannins on ruminal degradation and excretory pattern of N and implications for the potential N emission from the manure. *International Congress Series* 1293, 339-342.
- Hirayama, T., Kato, K. and Obara, Y., 2004. Effects of heat exposure on nutrient digestibility, rumen contraction and hormone secretion in goats. *Animal Science Journal* 75, 237-243.
- Huwig, A., Freimund, S., Käppeli, O. and Dutler, H., 2001. Mycotoxin detoxication of animal feed by different adsorbents. *Toxicology Letters* 122, 179-188.
- Idol, T.W., Holzbaur, K.A., Pope, P.E. and Ponder, F., 2002. Control-Bag Correction for Forest Floor Litterbag Contamination. *Soil Science Society of America Journal* 66, 620-623.
- Kampichler, C. and Bruckner, A., 2009. The role of microarthropods in terrestrial decomposition: a meta-analysis of 40 years of litterbag studies. *Biological Reviews* 84, 375-389.
- Kaneko, N. and Salamanca, E., 1999. Mixed leaf litter effects on decomposition rates and soil microarthropod communities in an oak-pine stand in Japan. *Ecological Research* 14, 131-138.
- Ke, X., Winter, K. and Filser, J., 2005. Effects of soil mesofauna and farming management on decomposition of clover litter: a microcosm experiment. *Soil Biology and Biochemistry* 37, 731-738.
- Knacker, T., Förster, B., Römbke, J. and Frampton, G.K., 2003. Assessing the effects of plant protection products on organic matter breakdown in arable fields - litter decomposition test systems. *Soil Biology and Biochemistry* 35, 1269-1287.

- Lal, R., 2006. Enhancing crop yields in the developing countries through restoration of the soil organic carbon pool in agricultural lands. *Land Degradation and Development* 17, 197-209.
- Lehmann, J., Rillig, M.C., Thies, J., Masiello, C.A., Hockaday, W.C. and Crowley, D., 2011. Biochar effects on soil biota - A review. *Soil Biology and Biochemistry* 43, 1812-1836.
- Leng, R.A., Preston, T.R. and Inthapanya, S., 2012. Biochar reduces enteric methane and improves growth and feed conversion in local "Yellow" cattle fed cassava root chips and fresh cassava foliage. *Livestock Research for Rural Development* 24, retrieved August 6, 2014, from <http://www.lrrd.org/lrrd2024/2011/leng24199.htm>.
- Lentz, R.D. and Ippolito, J.A., 2012. Biochar and manure affect calcareous soil and corn silage nutrient concentrations and uptake. *Journal of Environmental Quality* 41, 1033-1043.
- Li, Z.-H., Wang, Q., Ruan, X., Pan, C.-D. and Jiang, D.-A., 2010. Phenolics and plant allelopathy. *Molecules* 15, 8933-8952.
- Mafongoya, P.L., Barak, P. and Reed, J.D., 2000. Carbon, nitrogen and phosphorus mineralization of tree leaves and manure. *Biology and Fertility of Soils* 30, 298-305.
- Makkar, H.P.S., 2003. Effects and fate of tannins in ruminant animals, adaptation to tannins, and strategies to overcome detrimental effects of feeding tannin-rich feeds. *Small Ruminant Research* 49, 241-256.
- Malkomes, H.-P., 1980. Strohhrotteversuche zur Erfassung von Herbizid-Nebenwirkungen auf den Strohumsatz im Boden. *Pedobiologia* 20.
- Maloiy, G.M.O., Kanui, T.I., Towett, P.K., Wambugu, S.N., Miaron, J.O. and Wanyoike, M.M., 2008. Effects of dehydration and heat stress on food intake and dry matter digestibility in East African ruminants. *Comparative Biochemistry and Physiology - Part A: Molecular and Integrative Physiology* 151, 185-190.
- Mutabaruka, R., Hairiah, K. and Cadisch, G., 2007. Microbial degradation of hydrolysable and condensed tannin polyphenol-protein complexes in soils from different land-use histories. *Soil Biology and Biochemistry* 39, 1479-1492.
- Nelissen, V., Saha, B.K., Ruyschaert, G. and Boeckx, P., 2014. Effect of different biochar and fertilizer types on N₂O and NO emissions. *Soil Biology and Biochemistry* 70, 244-255.
- Oleszczuk, P., Joško, I., Futa, B., Pasieczna-Patkowska, S., Pałys, E. and Kraska, P., 2014. Effect of pesticides on microorganisms, enzymatic activity and plant in biochar-amended soil. *Geoderma* 214-215, 10-18.
- Pietikäinen, J., Kiikkilä, O. and Fritze, H., 2000. Charcoal as a habitat for microbes and its effect on the microbial community of the underlying humus. *Oikos* 89, 231-242.
- Pothoff, M. and Lofffield, N., 1998. How to quantify contamination of organic litter bag material with soil? *Pedobiologia* 42, 147-153.
- Powell, J.M., Ikpe, F.N. and Somda, Z.C., 1999. Crop yield and the fate of nitrogen and phosphorus following application of plant material and feces to soil. *Nutrient Cycling in Agroecosystems* 54, 215-226.
- Quilliam, R.S., Marsden, K.A., Gertler, C., Rousk, J., DeLuca, T.H. and Jones, D.L., 2012. Nutrient dynamics, microbial growth and weed emergence in biochar amended soil are influenced by time since application and reapplication rate. *Agriculture, Ecosystems and Environment* 158, 192-199.
- Schulz, H. and Glaser, B., 2012. Effects of biochar compared to organic and inorganic fertilizers on soil quality and plant growth in a greenhouse experiment. *Journal of Plant Nutrition and Soil Science* 175, 410-422.
- Sradnick, A., Ingold, M., Marold, J., Murugan, R., Buerkert, A. and Joergensen, R., 2014. Impact of activated charcoal and tannin amendments on microbial biomass and residues in an irrigated sandy soil under arid subtropical conditions. *Biology and Fertility of Soils* 50, 95-103.
- Van, D.T.T., Mui, N.T. and Ledin, I., 2006. Effect of method of processing foliage of *Acacia mangium* and inclusion of bamboo charcoal in the diet on performance of growing goats. *Animal Feed Science and Technology* 130, 242-256.

- Van Zwieten, L., Kimber, S., Morris, S., Chan, K.Y., Downie, A., Rust, J., Joseph, S. and Cowie, A., 2010. Effects of biochar from slow pyrolysis of papermill waste on agronomic performance and soil fertility. *Plant and Soil* 327, 235-246.
- Vreeken-Buijs, M.J. and Brussaard, L., 1996. Soil mesofauna dynamics, wheat residue decomposition and nitrogen mineralization in buried litterbags. *Biology and Fertility of Soils* 23, 374-381.
- Yamato, M., Okimori, Y., Wibowo, I.F., Anshori, S. and Ogawa, M., 2006. Effects of the application of charred bark of *Acacia mangium* on the yield of maize, cowpea and peanut, and soil chemical properties in South Sumatra, Indonesia. *Soil Science and Plant Nutrition* 52, 489-495.
- Yao, Y., Gao, B., Zhang, M., Inyang, M. and Zimmerman, A.R., 2012. Effect of biochar amendment on sorption and leaching of nitrate, ammonium, and phosphate in a sandy soil. *Chemosphere* 89, 1467-1471.
- Zhang, A., Liu, Y., Pan, G., Hussain, Q., Li, L., Zheng, J. and Zhang, X., 2012. Effect of biochar amendment on maize yield and greenhouse gas emissions from a soil organic carbon poor calcareous loamy soil from Central China Plain. *Plant and Soil* 351, 263-275.
- Zheng, H., Wang, Z., Deng, X., Herbert, S. and Xing, B., 2013. Impacts of adding biochar on nitrogen retention and bioavailability in agricultural soil. *Geoderma* 206, 32-39.

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Witzenhausen, den 28.8.2014

Mariko Nadine Ingold