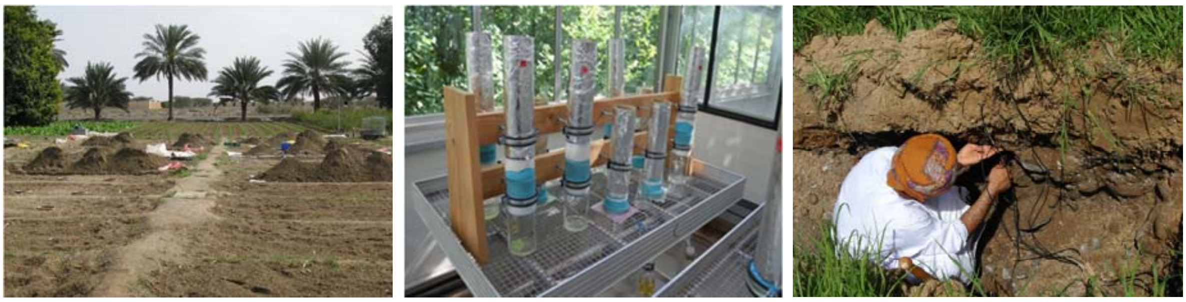
Leaching of Carbon and Nutrients on a Subtropical Sandy Soil from Northern Oman - A Comparison of Methods and Amendments



by Melanie Willich

organicagriculturalsciences UNI KASSEL

Organic Plant Production and Agroecosystems Research
in the Tropics and Subtropics

DFG - Research Training Group 1397
'Regulation of Soil Organic Matter and Nutrient Turnover
in Organic Agriculture'

Leaching of Carbon and Nutrients on a Subtropical Sandy Soil from Northern Oman - A Comparison of Methods and Amendments

Dissertation
Submitted to the Faculty of Organic Agricultural Sciences
of the University of Kassel to fulfill the requirements for the degree of
Doktor der Agrarwissenschaften (Dr. agr.)

by Melanie Willich

Witzenhausen, July 2014

This work has been accepted by the Faculty of Organic Agricultural Sciences of the University of Kassel as a thesis for acquiring the academic degree of Doktor der Agrarwissenschaften (Dr. agr.).

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Defense date: 12th September, 2014

Die vorliegende Arbeit wurde vom Fachbereich Agrarwissenschaften der Universität Kassel als Dissertation zur Erlangung des akademischen Grades eines Doktors der Agrarwissenschaften (Dr. agr.) angenommen.

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Tag der mündlichen Prüfung: 12. September, 2014

This work is dedicated to my grandparents,
Anni and Hans Römer.

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Acknowledgments

First of all, I would like to thank my first supervisor, Prof. Dr. Andreas Bürkert for the opportunity to conduct my PhD thesis in his working group. I appreciated the trust he put in me and the freedom I had to conduct my research. I am also very grateful for the patience and scientific discussions with my second supervisor, Prof. Dr. Bernard Ludwig. I want to thank the DFG for funding my research as part of the Research Training Group 1397 'Regulation of Soil Organic Matter and Nutrient Turnover in Organic Agriculture'.

I would like to thank Eva Wiegard, Claudia Thieme, Elsa Zwicker, Sabine Ahlers, Gabi Dormann, Anja Sawallisch, Margit Rode, Rainer Braukmann, Manfred Kunick, and Christian Wagner for laboratory assistance, joyful breaks, and technical discussions. I also thank Frau Haber for her often relieving answers to all administrative questions, for her time, and for a memorable raclette dinner at her home. Very special thanks go to José Padilla Vega for working with me on one of the experiments during the summer 2013, during which time he became a good friend. His engagement lasted in my mind even during the hard times of thesis writing. I also want to thank my student workers and project students Julia Voss, Charlotte Gründler, Manuel Toledo Hernandez, Raymond Kofi Sakyi, Leo Kenmoe, Ulla Rosskopf, Usman Asghar, and Katharina Fischer. I acknowledge their work attitude, independence, and individual characters. Thank you very much!

Unfortunately, my time in the field was short. However, I spent it well together with my colleague Mariko Ingold and her husband Paul Becke, who I wish to thank at this point. I greatly acknowledge the help of Narendra Bahadur Singh in organizing all kind of work supplies, Dr. Mohamed Al Rawahi for his arabic translation efforts and kindness, and especially Mr. Manoj Shan from Sealand Oman for accompanying me through the major challenge of shipping almost three tons of soil from Oman to Germany. For scientific advice and administrative support, I want to thank Dr. Herbert Dietz from Royal Court Affairs, Sultanate Oman, as well as Prof. Dr. Osman Mahgoub, and Dr. Malik Al-Wardy from the College of Agricultural and Marine Sciences, Sultan Qaboos University, Al Khod, Oman.

Working in a big group brings more than just scientific dynamics, it enriched my life with wonderful people who I was blessed to share my time with. I want to particularly thank Dr. Martin Wiehle, Francesca Beggi, Dr. Rajasekaran Murugan, Thin Nwe Htwe, Noromalala Jessica Andriamparany, Takuya Soma, Dr. Zampaligre Nouhoun, Greta Jordan, and Dr. Sven Gönster. Many thanks also to Dr. Anne Schiborra, Dr. Alexandra zum Felde, Dr. Martina Predotova, Dr. Katja Brinkmann, Dr. Regina Rößler, and my colleagues from the Research Training Group 1397. Very special thanks to the hospitality of Prof. Dr. Eva Schlecht and her family.

I would like to thank my parents for their unconditional love and support. My father in particular taught me early that with discipline and passion for "something", one creates a path. Forever indebted I am to my friend Michael Müller. Thank you for everything! Last, but not least, the immeasurable backing of Mary Lee Moody helped me to go through this phase; she often reminded me that there is still a world beyond the computer, and lifted me up during all difficult times of the PhD process. Many thanks!

Summary

Leaching of carbon and nutrients on a subtropical sandy soil from Northern Oman - A comparison of methods and amendments

It has been shown that carbon and nutrient losses via leaching are high under hot-wet conditions that support a rapid microbial turnover of organic matter such as it is the case on heavily fertilized, irrigated sandy subtropical soils. However, little quantitative data exists for Oman's intensively managed soils, because the measurement of leaching losses under field conditions remains difficult. Furthermore, only little is known about the effects of filter materials on the composition of leachate samples. One study therefore addressed on a sandy model substrate (i) how filter materials (glass or polyethylene, PE) affect the concentrations of dissolved organic carbon (DOC), mineral nitrogen (NO_3-N), and potassium (K) in the percolates, and (ii) whether ion exchange resins and suction plates of different materials are equally suited to capture dissolved inorganic nutrients (NO_3-N, K). In order to answer these questions, we developed an experimental setup which allowed us to collect samples from all initiated leaching events. Two fertilizer amendments were compared, one consisted of goat manure (ORG), the other of mineral fertilizer (MIN). The amount of nutrients applied was equivalent to 150-65-59 kg N-P-K ha^{-1}. Over a period of seven weeks, soil water was collected weekly at -100 hPa after simulated irrigation events, whereas the ion exchange resin method represented cumulative measurements. The different materials of the suction plate filters did not affect NO_3-N leaching concentrations from the ORG treatment (Glass: 28 ± 5 kg ha^{-1}; PE: 23 ± 2 kg ha^{-1}), whereas from the MIN treatment significantly less ($P = 0.012$) NO_3-N leaching was detected by ion exchange resins (142 ± 13 kg ha^{-1}) than by PE suction plates (211 ± 17 kg ha^{-1}). DOC leaching from both fertilizer amendments was significantly higher (MIN: $P = 0.015$; ORG: $P < 0.001$) from PE suction plates (MIN: 25 ± 1.9 kg ha^{-1}; ORG: 24 ± 1.3 kg ha^{-1}) than from glass suction plates (MIN: 13 ± 0.2 kg ha^{-1}; ORG: 13 ± 0.8 kg ha^{-1}). Both plate types yielded similar results for K leaching: MIN-Glass: 5.5 ± 0.1 kg ha^{-1}, MIN-PE: 4.9 ± 0.6 kg ha^{-1}; ORG-Glass: 3.4 ± 0.4 kg ha^{-1}, ORG-PE:

2.9 ± 0.2 kg ha^{-1}. In contrast, K leaching from ion exchange resins was 25-times higher (131 ± 6 kg ha^{-1}; $P < 0.001$) for MIN and 47-times higher (147 ± 14 kg ha^{-1}; $P < 0.001$) for ORG than the averaged K leaching across both suction plate types. We concluded that particularly glass suction plates and ion exchange resins are appropriate for determining NO_3-N in leachate, while for DOC measurements glass suction plates were the only suitable option. The significantly higher K leaching results from ion exchange resins merit further research.

Additions of biochar (BC) or activated charcoal (AC) to mainly tropical and to a lesser extent temperate soils are known to increase nutrient and water retention capacities, and may thereby decrease leaching losses. Although AC is commonly used in animal diets, data about the effects of AC-enriched manure used as a soil amendment on carbon and nutrient leaching are scarce and little is known about the effects of AC addition on nutrient leaching from subtropical sandy soils. In two experiments, we therefore investigated (i) how AC-enrichment affects manure mineralization and leaching of dissolved organic carbon (DOC), dissolved organic and inorganic nitrogen (DON, NO_3-N), dissolved organic and inorganic phosphorus (DOP, PO_4-P), and dissolved K, and compared (ii) whether ion exchange resins and suction plates are equally suited to capture dissolved mineral nutrients (NO_3-N, PO_4-P, K) on a sandy subtropical soil from Northern Oman using the previously described experimental setup. To this end AC-enriched manure was collected from a goat feeding trial where goats were fed increasing levels of AC, whereof three amendments were chosen for the leaching experiments: 0, 5, and 9% of the total ration in the first experiment (Exp. I), and 0, 3, and 9% of the total ration in the second experiment (Exp. II). The second experiment additionally comprised an unfertilized treatment as a control. Dry weight losses from manure ranged between 11 and 42% across both experiments, and declined significantly (Exp. I: $P = 0.012$; Exp. II: $P = 0.015$) with increasing AC enrichment. Carbon and nutrient leaching remained unaffected by AC treatment and ranged between 158 and 203 kg DOC ha^{-1}, 115 and 211 kg NO_3-N ha^{-1}, 1.2 and 1.6 kg PO_4-P ha^{-1}, and 239 and 251 kg K ha^{-1} across both experiments. DON leaching accounted for 6 to 45 % (30 to 125 kg ha^{-1}) of total N leaching, while DOP accounted for 64% (2.1 ± 0.1 kg ha^{-1}) of total P leaching in Exp. II, but was below detection limit in Exp. I. NO_3-N leaching from ion exchange resins ranged between 227 and 238 kg ha^{-1} in Exp. I, and 50 and 104 kg ha^{-1} in Exp. II. Compared with NO_3-N results from suction plates, NO_3-N leaching from ion exchange resins was considerably higher for all treatments in Exp. I (0%AC: P = 0.005; 5% AC: P < 0.001; 9% AC: 0.001).

In Exp. II, the opposite was found: NO_3-N leaching was 76% (control; P = 0.049), 41% (0% AC; P = 0.035), 57% (3% AC; P = 0.012), and 50% (9% AC; P = 0.237) lower from resins than from suction plates. Suction plates and ion exchange resins showed major differences for P and K leaching in Exp. I: Phosphorus leaching from ion exchange resins was significantly (P < 0.001) lower than from suction plates, whereas K leaching from resins was significantly (P < 0.001) higher than from plates. We concluded that AC enrichment had no effects on C and nutrient leaching, and that the significant differences in leaching loads between suction plates and ion exchange resins merit further research.

To date, the effect of AC feeding on manure quality, soil productivity, and plant growth has received little attention. The objectives of the last study were therefore to investigate the effects of (i) AC feeding on manure composition, and (ii) AC-enriched manure on soil productivity and growth of a model crop (*Pennisetum glaucum* L.). To this end two trials were conducted: First, a goat feeding trial where goats were fed increasing levels of AC (3, 5, 7, and 9% of total ration); secondly, a greenhouse pot experiment using the manure derived from the feeding trial as fertilizer for the same sandy soil from Northern Oman as used in the previous two leaching experiments. We measured manure C, N, P, and K concentrations, soil fertility parameters, microbial biomass indices, and plant growth and nutrient concentrations. Manure C concentration increased significantly (P < 0.001) from 45.2% (0% AC) to 60.2 (9% AC) with increasing dietary AC, whereas manure N, P, and K concentrations decreased (P < 0.001) from 0% AC (N: 2.5%, P: 1.5%, K: 0.8%%) to 9% AC (N: 1.7%, P: 0.8%, K: 0.4%). Whereas soil total nitrogen, CN ratio, cation exchange capacity, and microbial biomass C showed no response to AC-manure applications, soil organic C increased (P = 0.040) from 3.7 (0% AC) to 6.2 mg g^{-1} (9% AC), water holding capacity increased (P = 0.044) from 33% (3% AC) to 40% (9% AC), and microbial biomass N increased (P = 0.024) from 6 µg g^{-1} before treatment application to 18-28 µg g^{-1} at the end of the twelve week experimental period. Aboveground biomass of millet (*Pennisetum glaucum* L.) decreased slightly with AC enrichment, whereas K uptake was enhanced with increasing AC. We concluded that the dosage of manure and AC, the properties of AC, the duration of the trial, and the soil type were mainly responsible for our findings.

Zusammenfassung

Versickerung von Kohlenstoff und Nährstoffen auf einem subtropischen sandigen Boden aus dem nördlichen Oman - Ein Vergleich von Methoden und Zusätzen

Es wurde gezeigt, dass Versickerungsverluste von Kohlenstoff und Nährstoffen hoch sind unter heiß-feuchten Bedingungen, die eine rasche mikrobielle Umsetzung von organischer Materie fördern, so wie es der Fall ist auf stark gedüngten, bewässerten, sandigen, subtropischen Böden. Dennoch existieren für Omans intensiv bewirtschaftete Böden nur wenig quantitative Daten aufgrund der Schwierigkeiten der Messung von Versickerungsverlusten unter Feldbedingungen. Desweiteren ist nur wenig bekannt über die Effekte von Filtermaterialien auf die Zusammensetzung von Sickerwasserproben. Eine Studie, durchgeführt auf einem sandigen Modellsubstrat, adressierte daher (i) wie Filtermaterialien (Glas oder Polyethylen, PE) die Konzentrationen von gelöstem organischen Kohlenstoff (DOC), mineralischem Stickstoff (NO_3-N) und Kalium (K) im Sickerwasser beeinflussen, und (ii) ob Ionenaustauscherharze und Saugplatten aus unterschiedlichen Materialien gleichsam geeignet sind gelöste inorganische Nährstoffe (NO_3-N, K) wiederzugeben. Um diese Fragen zu beantworten wurde ein experimenteller Aufbau von uns entwickelt, mit welchem wir zuverlässig von allen initiierten Versickerungsereignissen Proben nehmen konnten. Zwei Düngerbehandlungen wurden verglichen, eine bestehend aus Ziegenmist (ORG), die andere aus mineralischem Dünger (MIN). Die Menge der aufgebrachten Nährstoffe war äquivalent zu 150-65-59 kg N-P-K ha^{-1}. Über einen Zeitraum von sieben Wochen wurde wöchentlich bei -100 hPa Bodenwasser im direkten Anschluss der jeweiligen Bewässerungsereignisse gesammelt, wobei die Ionenaustauscherharzmethode eine kumulative Messung repräsentierte. Die verschiedenen Materialien der Saugplatten hatten keinen Einfluss auf die NO_3-N Versickerungskonzentrationen der ORG Behandlung (Glas: 28 ± 5 kg ha^{-1}; PE: 23 ± 2 kg ha^{-1}), wohingegen von der MIN Behandlung signifikant ($P = 0.012$) weniger NO_3-N Versickerung von den Ionenaustauscherharzen (142 ± 13 kg ha^{-1}) er-

kannt wurde im Vergleich zu den PE Saugplatten (211 ± 17 kg ha^{-1}). DOC Versickerung bei beiden Düngerbehandlungen war signifikant größer (MIN: $P = 0.015$; ORG: $P < 0.001$) von PE Saugplatten (MIN: 25 ± 1.9 kg ha^{-1}; ORG: 24 ± 1.3 kg ha^{-1}) als von Glassaugplatten (MIN: 13 ± 0.2 kg ha^{-1}; ORG: 13 ± 0.8 kg ha^{-1}). Beide Saugplattentypen ergaben ähnliche Ergebnisse für die Versickerung von K: MIN-Glas: 5.5 ± 0.1 kg ha^{-1}, MIN-PE: 4.9 ± 0.6 kg ha^{-1}; ORG-Glas: 3.4 ± 0.4 kg ha^{-1}, ORG-PE: 2.9 ± 0.2 kg ha^{-1}. Im Gegensatz dazu war die K Versickerung von Ionenaustauscherharzen 25-mal höher (131 ± 6 kg ha^{-1}; $P < 0.001$) für MIN und 47-mal höher (147 ± 14 kg ha^{-1}; $P < 0.001$) für ORG als die gemittelte K Versickerung aus beiden Saugplattentypen. Abschließend blieb festzuhalten, dass insbesondere Glassaugplatten und Ionenaustauscherharze für die Bestimmung von NO_3-N im Sickerwasser tauglich sind, wohingegen sich gezeigt hat, dass für DOC Messungen Glassaugplatten die einzig geeignete Wahl sind. Die signifikant höheren K Versickerungsergebnisse verdienen einer weiteren Forschung.

Zugaben von Biokohle (BC) oder Aktivkohle (AC) zu -hauptsächlich tropischen und zu einem geringeren Teil temperierten- Böden sind bekannt dafür die Nährstoff- und Wasserspeicherkapazitäten zu steigern und können dadurch Versickerungsverluste verringern. Obwohl AC weithin Anwendung in der Tierernährung findet, gibt es wenig Daten über die Effekte von AC-angereichertem Mist als Bodenzugabe auf die Kohlenstoff- und Nährstoffversickerung auf subtropischen, sandigen Böden. In zwei Experimenten haben wir daher untersucht (i) wie eine AC-Anreicherung die Mineralisierung von Mist und die Versickerung von gelöstem organischen Kohlenstoff (DOC), gelöstem organischen Stickstoff (DON, NO_3-N), gelöstem organischen und inorganischen Phosphor (DOP, PO_4-P) und gelöstem Kalium (K) beeinflussen, und griffen erneut die Frage auf (ii) ob Ionenaustauscherharze und Saugplatten gleichsam geeignet sind für das Erfassen von gelösten mineralischen Nährstoffen (NO_3-N, PO_4-P, K) auf einem sandigen, subtropischen Boden aus dem nördlichen Oman unter Verwendung des bereits beschriebenen experimentellen Aufbaus. Der AC-angereicherter Mist stammte aus einem Ziegenfütterungsversuch, wo die Ziegen mit ansteigenden Mengen an AC gefüttert wurden, wovon drei Behandlungen für die Versickerungsversuche ausgewählt wurden: 0, 5, and 9% der totalen Ration für das erste Experiment (Exp. I) und 0, 3, and 9% der totalen Ration für das zweite Experiment (Exp. II). Das zweite Experiment verfügte darüber hinaus über eine ungedüngte Kontrollbehandlung. Die Trockenmasseverluste des Mists bewegten sich zwischen 11 und 42% über beide

Experimente hinweg und nahmen signifikant ab (Exp. I: $P = 0.012$; Exp. II: $P = 0.015$) mit steigender AC-Anreicherung. Die Kohlenstoff- und Nährstoffversickerung verblieb unbeeinflusst von der AC-Anreicherung und bewegte sich zwischen 158 und 203 kg DOC ha^{-1}, 115 und 211 kg NO_3-N ha^{-1}, 1.2 und 1.6 kg PO_4-P ha^{-1}, beziehungsweise 239 und 251 kg K ha^{-1} über beide Experimente hinweg. 6 bis 45% (30 bis 125 kg ha^{-1}) der totalen Stickstoffversickerung entfiel auf DON, während sich er Anteil von DOP an der gesamten Phosphorversickerung im Exp. II auf 64% (2.1 ± 0.1 kg ha^{-1}) belief, sich jedoch im Exp. II unterhalb der Nachweisgrenze befand. Die NO_3-N Versickerung gemessen mit Ionenaustauscherharzen schwankte zwischen 227 und 238 kg ha^{-1} im Exp. I, beziehungsweise zwischen 50 und 104 kg ha^{-1} im Exp. II. Verglichen mit den NO_3-N Ergebnissen der Saugplatten war die NO_3-N Versickerung der Ionenaustauscherharze signifikant höher bei allen Behandlungen im Exp. I (0%AC: $P = 0.005$; 5% AC: $P < 0.001$; 9% AC: 0.001). Im Exp. II wurde das Gegenteil festgestellt: Die NO_3-N Versickerung war 76% (Kontrolle; $P = 0.049$), 41% (0% AC; $P = 0.035$), 57% (3% AC; $P = 0.012$) und 50% (9% AC; $P = 0.237$) niedriger von Harzen als von Saugplatten. Saugplatten und Ionenaustauscherharze zeigten bedeutende Unterschiede für die P und K Versickerung im Exp. I: Die P Versickerung von Ionenaustauscherharzen war signifikant ($P < 0.001$) niedriger als von Saugplatten, wohingegen die K Versickerung von Harzen signifikant ($P < 0.001$) höher war als von Saugplatten. Wir schlussfolgerten, dass die AC-Anreicherung keinen Effekt auf die Kohlenstoff- und Nährstoffversickerung hatte, sowie dass die signifikanten Unterschiede der Versickerungsmengen zwischen Saugplatten und Ionenaustauscherharzen weiterer Forschung verdienen.

Bis heute haben die Effekte von AC-Fütterungen auf Mistqualität, Bodenproduktivität und Pflanzenwachstum nur wenig Aufmerksamkeit bekommen. Die Ziele der letzten Studie waren daher die Effekte einer (i) AC-Fütterung auf die Mistzusammensetzung und (ii) AC-Anreicherung des Mists auf Bodenproduktivität und Wachstum einer Modellfrucht (*Pennisetum glaucum* L.) zu ermitteln. Zwei Experimente wurden durchgeführt: Als Erstes ein Ziegenfütterungsversuch, in dem Ziegen steigende Mengen AC (3, 5, 7, and 9% der totalen Ration) gefüttert wurden; Zweitens wurde in einem Gewächshaus ein Gefäßversuch angesetzt unter Verwendung des Mists aus dem Fütterungsversuch auf demselben sandigen Boden aus dem nördlichen Oman wie die vorherigen beiden Versickerungsversuche. Wir ermittelten Mist C, N, P und K Konzentrationen, Bodenfruchtbarkeitsparameter, mikrobielle Biomasse, sowie Pflanzenwachstum und Nährstoffkonzentrationen.

Die Mist C Konzentration stieg signifikant ($P < 0.001$) von 45.2% (0% AC) auf 60.2 (9% AC) an mit zunehmender AC-Fütterung, wohingegen die Mist N, P und K Konzentrationen von 0% AC (N: 2.5%, P: 1.5%, K: 0.8%%) gegen 9% AC (N: 1.7%, P: 0.8%, K: 0.4%) sanken ($P < 0.001$). Während totaler Bodenstickstoff, CN Verhältnis, Kationenaustauschkapazität und mikrobieller Biomasse-Kohlenstoff keine Reaktion gegenüber AC-Mist Applikationen zeigten, erfolgten signifikante Zunahmen des organischen Kohlenstoffgehaltes ($P = 0.040$) von 3.7 (0% AC) auf 6.2 mg g^{-1} (9% AC), der Wasserhaltekapazität ($P = 0.044$) von 33% (3% AC) auf 40% (9% AC) und des mikrobiellen Biomasse-Stickstoffs ($P = 0.024$) von 6 µg g^{-1} vor Applikation der Düngerbehandlungen auf 18 bis 28 µg g^{-1} am Ende der zwölfwöchigen experimentellen Periode. Die überirdische Biomasse der Perlhirse (*Pennisetum glaucum* L.) nahm leicht ab mit AC-Anreicherung, wohingegen die Aufnahme von K mit zunehmendem AC verbessert wurde. Wir schlussfolgerten, dass die Dosierung von Mist und AC, die Eigenschaften der AC, die Dauer des Versuchs und die Bodenart hauptsächlich verantwortlich sind für unsere Ergebnisse.

1 General Introduction

1.1 Carbon and Nitrogen Dynamics in Subtropical Sandy Soils - Challenges for Sustainable Agriculture

About 20% (26,324,770 km^2) of the total ice-free land area on Earth is occupied by soils exposed to an aridic climate (Huang and Summer, 2011). Following the USDA system of soil classification (US Soil Taxonomy), soils of the arid regions belong mostly to the order of Aridisols, which occupy about half (54%) of the mentioned area, followed by Entisols (43%), Vertisols (3%), Oxisols (0.1%), and Andisols (0.005%; Huang and Summer, 2011). Most Aridisols (41%) occur in Asia, stretching eastward from the Middle East to northern China; Africa contains the second largest proportion of Aridisols (21%), followed by Australia (16%), North America (13%), South America (8%), and ≤ 1% in Europe and Central America (Huang and Summer, 2011). While Aridisols are soils of the arid regions, Entisols are not limited to particular climates. Aridisols are distinguished by the presence of horizons or profile accumulations characteristic of soil development in arid regions. In contrast, Entisols have a wide geographical distribution, and are derived from either recently accumulated parent material e.g. on alluvial deposits or on quartz sand; both of which are factors that lead to their distinctive lack of horizon development. Entisols develop into Aridisols outside of floodplains in areas with aridic moisture regimes.

In arid regions, the major factors affecting the chemical properties of soils are climate, topography, and time, with vegetation and parent material playing secondary roles (Dregne, 1976). Located dominantly along the subtropical high pressure belt, the precipitation of these soils is mainly regulated by the movement of the intertropical convergence zone (ITCZ) or monsoon trough. At an average annual precipitation of < 250 mm in hot arid regions, soils generally show neutral to alkaline reactions with a base saturation of 90% or more, less than 2% organic matter, a calcareous horizon within the top 2 m, at least slight salinity, and a clay mineral complex dominated by illite and montmorillonite (Dregne, 1976).

In principle, irradiation, extreme temperature fluctuations, and low moisture conditions slow down the chemical weathering of inherited materials and thus hamper soil formation. The naturally sparse vegetation combined with high soil temperatures lead to low microbial activity and little organic matter accumulation. Hence, the organic carbon content in arid sandy soils is often <1% on a mass basis. Nitrogen (N) occurs mostly in organic matter and is quickly nitrified after the organic matter is decomposed. Consequently, soil N levels are related directly to organic matter content. The main physical constraint of sandy soils is their poor water retention capacity due to their coarse structure and low respective clay and organic matter contents. To overcome the consequences of the low precipitation, soils in arid and semi-arid regions greatly benefit from irrigation for enhanced agricultural production.

Maintaining and increasing soil organic matter contents by application of organic materials such as plant residues or animal manure is a central aim in organic agriculture. In irrigated agriculture of Oman, regular applications of organic matter in form of manure at annual rates often exceeding 30 t ha^{-1} has allowed maintenance of soil carbon levels over millenia (Wichern et al., 2004; Buerkert et al., 2010; Siegfried et al., 2011). However, applied nutrients are subject to loss with the irrigation water, particularly in well draining sandy soils. As they are also inherently low in organic matter, leaching of carbon and nutrients may deplete soil fertility, and thus reduce crop yields (Jalali, 2005; Siegfried et al., 2011). Another off-site effect of concern is the potential contamination of ground- and surface waters due to the accumulation of leached nutrients and organic substances (Spalding and Exner, 1993). Irrigation of crops in hot climates also increases microbial activity, which then accelerates organic matter turnover and consequently the likelihood for leaching of mineral nutrients and carbon (Siegfried et al., 2011).

In the past, leaching studies focused primarily on mineral N. The reason may be that research in nutrient cycling was strongly dominated by European and North American scientists, working in geographical regions where high input agriculture prevails and thus N leaching in form of dissolved mineral nitrate, NO_3, plays the major role in eutrophication of the environment (Neff et al., 2003). Only few researchers have investigated the role of nutrient leaching in dissolved organic forms from agricultural soils. However, as some authors report, the contribution of dissolved organic nutrients to total nutrient leaching can be considerable (Murphy et al., 2000; Siemens and Kaupenjohann, 2002; van Kessel et al., 2009). In organic agriculture, leaching of dissolved organic matter (dissolved organic carbon, DOC; dissolved organic nitrogen, DON; dissolved organic phosphorus, DOP) is of special interest, because large additions of organic amendments may release substantial amounts of dissolved organic nutrients that are prone to be lost in light and weakly structured irrigated soils (Murphy et al., 2000).

The soil for the presented study was classified as a Typic Torrifluvent, a subgroup of the order Entisols (US Soil Taxonomy). It was collected on a private experimental farm in the Al Batinah coastal plain near Sohar (24º20’ N, 56º46’ E; 4 m a.s.l.; Fig. 1), Sultanate of Oman.

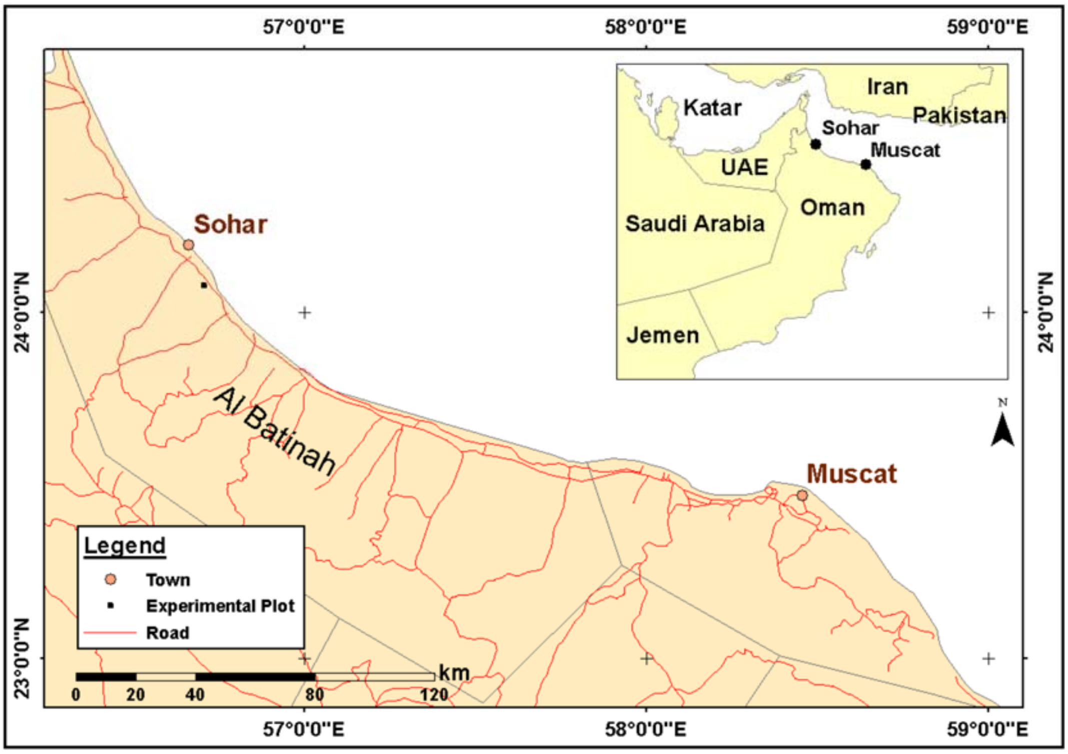

Fig. 1. Geographical location of the soil collection site ('experimental plot') near Sohar, northern Oman (Siegfried, 2011).

The Batinah region consists of extensive alluvial fans incised by ephemeral streams (wadis) and accumulation of fine textured coastal soils (Al-Farsi and Cookson, 2002). It is the principal region for agriculture in Oman, extends for about 270 km southeast as a narrow coastal strip along the Gulf of Oman, and has about 55,000 ha of land under cultivation (Al-Farsi and Cookson, 2002). The climate in this region is characterized by two distinct seasons: a very hot summer with temperatures up to 45°C from May to September and a moderate period from October to April with temperatures declining below 20°C (Rottmann et al., 2011). With an average annual precipitation of 55 mm and a potential evapotranspiration exceeding 2000 mm, agriculture in northern Oman completely depends on irrigation deriving from groundwater aquifers which are fed by winter and rare summer rains in the nearby Hajar mountains (Norman et al., 1998; Siegfried et al., 2011).

Previous research conducted in the Middle East has shown that soil moisture related rapid turnover of organic matter leads to considerable losses of carbon and nutrients via leaching (Jalali, 2005) and gaseous emissions (Buerkert et al., 2010; Siegfried et al., 2011). The rapid agricultural expansion in Oman since 1970 has led to widespread cultivation of alluvial fan soils, a trend that is projected to intensify as the irrigated soils near the coast become increasingly salinized (Al-Farsi and Cookson, 2002). In view of progressive soil degradation and water scarcity, it is critical that the prevailing agricultural practices are modified to minimize the causal impacts on the environment (Tilman, 1999; Tilman et al., 2002). In order to evaluate efficient use of water resources and organic matter in these systems, it is first of all important to accurately measure nutrient losses of which little quantitative data exists for Oman's intensively managed soils (Siegfried et al., 2011).

1.2 Effects of Biochar Additions on Soil Properties and Nutrient Dynamics

An often reported method to increase nutrient retention -and reduce leaching losses- in low fertility soils is the application of biomass-derived black carbon, also referred to as biochar (Glaser et al., 2002; Lehmann et al., 2006; Steiner et al., 2007). The topic received broad interest from the international research community by the relatively recent uncovering of the fertile, anthropogenic dark earths of the central Amazon, called *terra preta* (e.g. Glaser et al., 2001; Lima et al., 2002; Liang et al., 2006; Marris, 2006; Steiner, 2007; Kleiner, 2009; Novotny et al., 2009; Sohi et al., 2010; Barrow, 2012). Evidently, *terra preta* soils were created during the 'pre-Colombian period' (between 500 and 6,000 ybp; Lehmann and Rondon, 2006) by incorporation of partially combusted organic matter (i.e. black carbon, pyrogenic carbon, charcoal) which mainly derived from cooking fires (Glaser et al., 2001; Glaser et al., 2002). Studies using benzenecarboxylic acids (BCA) as molecular markers for the determination of black carbon estimated that *terra preta* soils had average black carbon stocks of 50 Mg ha^{-1} (Glaser et al., 1998; Glaser et al. 2001). The high charcoal content in the patchily distributed *terra preta* led to considerably enhanced soil organic matter levels and nutrient retention compared to the surrounding highly weathered acid soils (Glaser et al., 2002; Sohi et al., 2010). Due to high nutrient retention, nutrient leaching has been shown to be surprisingly low (Lehmann et al., 2003). Such biochar-induced modifications in soil characteristics were recognized to have caused severalfold increases in plant growth several times (Glaser et al., 2002; Lehmann et al., 2003; Major et al., 2010; Steiner et al., 2007; Liu et al., 2012), but negligible or even negative effects on crop performance were also observed (Gaskin et al., 2010; Jones et al., 2012; Güerena et al., 2013; Kloss et al., 2014).

The explanation for the improved fertility lasting for centuries despite heavy tropical rainfalls is found in the biochar quality and its properties. Biochar is produced through burning of organic materials (e.g. wood, plant tissues, bones, manure, etc.) under partial exclusion of oxygen, a process known as pyrolysis (Antal and Gronli, 2003). The result is a highly aromatic organic material, rich in stable carbon, and resistant to biological and chemical decay over hundreds to thousands of years (Lehmann, 2002; Lehmann, 2007). Oxidation during this time produced carboxylic groups on the edges of the aromatic core, which increased the cation exchange capacity and reactivity of black carbon in the soil (Glaser et al., 2001). As surface area, porosity, nutrient content, and charge density are, however, related to feedstock and the temperature reached during charring, biochars differ greatly in their physico-chemical properties, and hence, in their reaction in soils (Okimori et al., 2003; Joseph et al., 2010; Sohi et al., 2010; Alburquerque et al., 2014). Generally, low-temperature pyrolysis (<550°C) produces biochars with a greater recovery of nutrients (N, K, and S) than biochars produced at higher temperatures (Keiluweit et al., 2010). Also, low-temperature biochars are expected to affect soil fertility more than high-temperature ones due to their greater reactivity and cation exchange capacity (Gaskin et al., 2008; Steinbeiss et al., 2009; Mukherjee et al., 2011). High-temperature pyrolysis (>550°C) biochars generally have a high surface area (>400 $m^2 g^{-1}$; Downie et al., 2009), are good absorbents (Mizuta et al., 2004; Lima et al., 2005), and are highly aromatic which makes them very recalcitrant to decomposition (Bruun et al., 2011).

According to Lehmann et al. (2006), the conversion of biomass carbon to biochar carbon via pyrolysis can sequester about 50% of the carbon initially contained within the biomass feedstock. This is a considerably higher retention of carbon compared to burning (3%) or biological decomposition (<10-20% after 5 to 10 years; Lehmann et al., 2006). Therefore biochar applications to soil has not only received attention as a tool for soil fertility management, but also in mitigating climate change by providing a sink for atmospheric carbon dioxide (Lehmann, 2007; Liang et al., 2008; Woolf et al., 2010; Shenbagavalli and Mahimairaja, 2012). Moreover, by-products obtained from pyrolysis such as bio-oil and syngas can be used as a source of energy, replacing conventional fossil fuels (Lehmann, 2007; Laird et al., 2009; Meyer et al., 2011).

In the later presented studies, we used activated carbon, which are carbonized materials (charcoals) that underwent an additional activation procedure using either 1) elevated temperatures (600-900°C) in presence of oxidizing gases, steam, or air (*physical activation*), 2) chemical activating agents such as $ZnCl_2$, KOH, or H_3PO_4 at lower pyrolysis temperatures (*chemical activation*), or 3) a flow of pure steam at moderate temperatures (500-700°C; *steam-pyrolysis*; Ioannidou and Zabaniotou, 2007). Due to activation, surface area and pore size of the charcoals become considerably increased, making activated charcoal a strong nutrient adsorbent which is commonly used for the purification of air and water (Ioannidou and Zabaniotou, 2007), and also as a soil amendment (Berglund et al., 2004; Borchard et al., 2012). Activated charcoal also finds use as gastrointestinal adsorbent in animal diets as it can decrease the bioavailability of phytochemicals and therefore prevent fodder-derived toxicities (Banner et al., 2000; Rogosic et al., 2008). While the effects of charcoal additions to soil on nutrient and water retention, and carbon sequestration are well studied, almost no data exist about the effects of animal-ingested (manure-bound) activated charcoal on soil properties and plant growth.

1.3 *In-Situ* Measurement of Soil Solution - An Overview of Present Systems and their Applicability in Sandy Soils with Emphasis on Suction Plates

Many devices exist for measuring nutrient leaching such as: suction cups, suction plates, resin boxes (= resin cartridges), wick samplers, and lysimeters. All have their advantages and disadvantages in terms of material, installation effort, and operation mode (Weihermüller et al., 2007). Suction cups consist of a cylindrical porous cup sealed to a tube, inside of which a small tube is inserted to collect the extracted water; whereas suction plates have a porous plate inserted into a frame connected to a tube for water extraction. Suction cups and plates as well as lysimeters are available in different porous ceramics, sintered stainless steel or glass, and plastic materials (Dorrance et al., 1991). The tendency of suction cups and plates to sorb organic and inorganic compounds are widely discussed in the literature (Wessel-Bothe et al., 2000; Siemens and Kaupenjohann, 2004). DOM is specifically adsorbed to metal hydroxides via its carboxyl and hydroxyl groups (Weihermüller et al., 2007). Since many ceramic materials therefore sorb considerable quantities of DOM, porous glass or stainless steel seem more suitable (Wessel-Bothe et al., 2000). Adhesives, glues, and elastomers used for the construction of suction cups and plates contain solvents and plasticizers, which can be partly released into the sampled soil solution and may increase the measured DOC concentration (Siemens and Kaupenjohann, 2003). Thus, the sampled solution should not come into contact with such materials. Instead, PTFE tubes seem more appropriate as sampling device material (Weihermüller, 2007). Resin boxes commonly consist of a pipe that is approximately 10 cm in length, which is closed by a mesh at its lower end and filled with a mixture of quarz sand or silt and a synthetic resin (Bischoff et al., 1999). Resin boxes adsorb dissolved nutrients from percolating soil water reversibly on synthetic exchange resins. At the end of the monitoring period, the target compounds are extracted from the exchange resins in the laboratory. Solute fluxes can be estimated through normalizing the retrieved solute mass to the cross-sectional area of the resin box, whereas solute concentrations cannot be monitored with this technique (Weihermüller et al., 2007). Capillary wick samplers sample soil water by the gravitational potential using an inert wick material such as fiberglass (Holder et al., 1991). A wetted fiberglass wick acts as a hanging water column that applies suction to the soil water and intercepts leachate to a sampling bottle (Brandi-Dohrn et al., 1997; Louie et al., 2000). As of yet, little information exists about their performance under field conditions (Siemens and Kaupenjohann, 2004).

Suction cups are by far the most frequently used technique for extracting soil water due to their comparably easy installation (Weihermüller et al., 2007). The installation is typically done from a trench or access chamber into the undisturbed soil profile. Similarly, resin boxes are installed from soil pits into little galleries, which are backfilled after installation. Especially suction plates, lysimeters, and resin boxes require a laborious, complex installation that may cause considerable soil disturbance and the divergence of water flow around the system. Also, the hydraulic properties of the ion exchange resins differ from those of the surrounding soil, which may lead to a deviation of soil water around the box. Due to water divergence, collection efficiencies of less than 10% have been reported for pan lysimeters (Jemison and

Fox, 1992; Zhu et al., 2002). In all cases, a good hydraulic contact between device and surrounding soil is necessary for adequate measurements (Grossmann and Udluft, 1991).

For the operation of suction cups and plates, a negative pressure is required by applying suction to the device using a vacuum system. Optimal height and time of applied suction (continuous or discontinuous operation mode), are still under discussion as they depend on multiple factors such as soil type, soil water content, and the amount of water needed for analysis (Weihermüller et al., 2007; Weihermüller et al., 2005). While a continuous operation may initiate preferential flow paths, it requires high maintenance efforts, and may cause changes in sample composition during storage under field conditions, whereas a discontinous operation may cause only small temporary disturbances of natural soil water flow. The major disadvantage of the latter, however, is that heavy rainfall-induced leaching events or preferential flow-induced changes in solute concentrations are not adequately captured (Jury and Flühler, 1992). The height of the suction to be applied is commonly estimated from independently installed tensiometers. Given the small cross-sectional area of sampling cups and the necessity of soil water flux estimates from independent tensiometers, calculated fluxes may have great uncertainties. What makes the interpretation of results even more difficult is that neither sampling volume around the suction cup nor the imposed changes in matric potential on the natural flow pattern are well known (Hart and Lowery, 1997). Although the larger sampling area and 2D surface of suction plates allow the detection of preferential flow events and a better estimate of the sampling volume (Chiu and Shackelford, 2000; Ciglasch et al., 2005), applying the right amount of suction and securing air-tightness of the vacuum system still remains a major challenges. Particularly on sandy soils, the formation of a saturated zone above the sampling device is often impossible, resulting in complete sampling failures, or underestimations of leaching. Similarly, zero-tension devices such as pan lysimeters, which collect freely percolating soil water, operate reasonably well in soil with large macropores near saturation, but are much less successful once a soil dries out (Zhu et al., 2002).

To overcome these limitations of leaching measurements on sandy soils, we conducted controlled soil column experiments (Fig. 2). Similar setups using freely draining soil columns are described in the literature (Wagai and Sollins, 2002; Jiao et al., 2004; Kay et al., 2005). In our experiments, we attached either glass or polyethylene (PE) suction plates or ion exchange resins, all commonly used in field experiments, to the soil columns in order to directly compare their suitability in capturing dissolved carbon and (in-) organic nutrients, since quantitative data on such comparisons under controlled conditions are scarce.

Fig. 2. Pictures of the experimental setup. Upper left and upper right pictures: Glass cylinders are attached to glass suction plates, glass resin boxes (= resin cartridges), or PE suction plates (from left to right). Suction plates are connected to sampling bottles via PTFE tubes. Lower left picture: Sampling bottles are connected to a vacuum pump, whereas percolate from resin cartridges drains freely into glass collection beaker. Lower right picture: Soil columns are covered with aluminum foil to avoid algae growth.

1.4 Research Objectives

The following experiments aimed at bridging the aforementioned knowledge gaps about the suitability of different filter materials and leaching measurement devices in capturing carbon and nutrient losses, and the effects of charcoal-enriched manure on carbon and nutrient leaching, nutrient mineralization, and plant performance on a sandy subtropical soil collected from a private farm in the Al Batinah plain, Northern Oman, where mineral nutrient leaching is reportedly high (Siegfried et al., 2011).

Against this background, the following research objectives were pursued:

i. Comparison of glass and PE suction plates with ion exchange resins for their suitability in capturing leaching of DOC, NO_3-N, PO_4-P, and K.

ii. Comparison of the effects of AC-enriched manure on nutrient mineralization and leaching of DOC, DON, DOP, NO_3-N, PO_4-P, and K from glass suction plates and ion exchange resins.

iii. Comparison of the effects of AC-enriched manure on soil productivity and plant growth.

The above mentioned research objectives were based on the following hypotheses:

i. Cumulative NO_3-N, PO_4-P, and K leaching loads are comparable between glass suction plates and ion exchange resins, whereas leaching of DOC will vary between glass and PE suction plates.

ii. Nutrient leaching from AC-manure amended soils is lower than in soils treated with unamended manure, whereas DOC leaching is higher in AC-manure treated soils.

iii. Soil productivity and plant growth are increased in soils receiving AC-enriched manure, due to higher microbial activity and thus faster nutrient release.

2 Leaching of Carbon and Nitrogen on a Sandy Soil: A Comparison between Suction Plates and Ion Exchange Resins

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Abstract

To improve our methodological knowledge about how to best measure soil leachates, we investigated (i) how filter materials (glass or polyethylene) affect the concentrations of dissolved organic carbon (DOC), mineral nitrogen (NO_3-N), and potassium (K) in soil percolates and (ii) whether ion exchange resins and suction plates of different materials are equally suited to capture dissolved inorganic nutrients (NO_3-N, K). To achieve these aims, we developed an experimental setup which allowed us to reliably collect samples from seven consecutive leaching events after application of two soil amendments. The first consisted of goat manure, the second of mineral fertilizers adjusted to contain an equivalent of 150-65-59 kg N-P-K ha^{-1}. Over a period of seven weeks, soil water was collected weekly at -100 hPa after irrigation events, whereas the ion exchange resin method yielded a cumulative measurement. DOC leaching from both fertilizer amendments was significantly higher (MIN: $P = 0.015$; ORG: $P < 0.001$) from PE suction plates (MIN: 25 ± 1.9 kg ha^{-1}; ORG: 24 ± 1.3 kg ha^{-1}) than from glass suction plates (MIN: 13 ± 0.2 kg ha^{-1}; ORG: 13 ± 0.8 kg ha^{-1}). The different materials of the suction plates, however, did not affect NO_3-N leachate concentrations. Cumulative NO_3-N leaching was comparable for glass suction plates and ion exchange resins. At both fertilizer treatments, major disparities between suction plates and ion exchange resins were noted for K leachates.

Keywords: Dissolved organic carbon, nitrate leaching, potassium leaching, suction plates, ion exchange resins.

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2.1 Introduction

To this day, measuring nutrient leaching under *in-situ* field conditions remains a challenge. Methods allowing to reliably measure leaching dynamics of carbon (C) and mineral and organic nitrogen (N) or phosphorus (P) beyond firmly installed lysimeters are widely discussed, since nutrient leaching does not only reduce the nutrient use efficiency of sustainable cropping systems, but also leads to groundwater pollution (Spalding et al., 1993; Tilman, 1999; Tilman et al., 2002). One of the approaches to assess plant nutrient availability in soils and to determine leaching of mineral N, P, and potassium (K) are mixed-bed ion exchange resins (Schnabel et al., 1993; Skogley and Dobermann, 1996; Bischoff et al., 1999; Friedel et al., 2000; Qian and Schoenau, 2002). Advantages of this method are its low cost and maintenance requirement, allowing a high number of replicates, which is a prerequisite for adequate accounting of spatial variability in the field (Skogley and Dobermann, 1996). The comparably easy installation does not require expert knowledge or further technical efforts, both of which may be limiting. However, ion exchange resins cannot measure single leaching events and thus fail to ascertain nutrient leaching dynamics (Lehmann et al., 2001). Secondly, they do not capture organically-bound compounds, such as dissolved organic carbon (DOC), nitrogen (DON) or phosphorus (DOP) which may substantially contribute to total losses, especially in organically fertilized systems (Murphy et al., 2000; Qualls et al., 2000; Siemens and Kaupenjohann, 2002; Jiao et al., 2004; van Kessel et al., 2009). One method that allows capturing organically-bound carbon and nutrients is the use of suction plates. However, their installation is cumbersome and costly, which is limiting the number of samplers that can be employed (Siemens and Kaupenjohann, 2002). The different filter materials available for such plates, all have certain advantages and disadvantages which affect their practical use in the field and their ability to deliver uncontaminated samples (Wessel-Bothe et al., 2000; Siemens and Kaupenjohann, 2003). An additional critical aspect in field experiments is that the function of hypotension-controlled devices heavily depends on soil texture and water content, and may thereby either completely fail to deliver samples (Predotova et al., 2011), or lead to substantial misrepresentations of nutrient fluxes by mistakes during installation, handling and measuring.

In view of the aforementioned unsolved problems of leaching measurements in the field, a controlled column study allows to compare measuring systems under controlled conditions such as an air-tied setting that allows consistent sample collection for all treatments across replications. The research objectives of this study therefore were to investigate (i) how filter materials (glass or polyethylene, PE) affect carbon and nutrient (N, P, K) concentrations in the percolates and (ii) whether ion exchange resins and suction plates of different materials yield comparable results in capturing dissolved inorganic N, P, and K.

2.2 Material and Methods

2.2.1 Preparation of the Soil Substrate

The experimental soil was collected near Witzenhausen, Germany (51º20’ N, 9º51’ E), from a breakoff edge under spruce-beech mixed forest vegetation. The soils' properties are described in Mamo et al. (1996). Silica sand used as an admixture was obtained from a gravel plant in Felsberg, Germany (51º8’ N, 9º25’ E), and originated from alluvial deposits of the Eder river. Dry soil and sand were mixed at a gravimetrical ratio of 15:85 and is in the following referred to as 'substrate' (Table 1).

Table 1. Properties of soil-sand-mixture (substrate) and goat manure used in this study. Shown are arithmetic means (n = 4) on a dry weight basis (24 h at 60ºC) for C and N analyses of substrate and manure; and 24 h at 105ºC for pH-H_2O, water holding capacity (WHC), P, and K analyses.

	Substrate	Manure
Texture (% sand-silt-clay)	85-10-5	-
pH-H_2O	8.7	7.7
WHC (%)	25.5	-
Total C (%)	0.26	44
SOC (%)	0.13	-
N (mg g^{-1})	0.07	27.3
P (mg g^{-1})	0.001	11.9
K (mg g^{-1})	0.02	10.7

2.2.2 Description of the Soil Amendments

Based on the nutrient analysis (Table 1), air-dried goat manure (ORG) was applied at 4.32 g dry matter (DM); equivalent to a field application rate of 5.5 t ha^{-1} to each cylinder (see 2.4) in order to reach amounts of 150 kg N ha^{-1}. The manure was weighted into litterbags (nylon, 1 mm mesh) and buried in the glass cylinders at 10 cm depth. In the other half of the experiment, mineral fertilizer (MIN) was loosely buried at 10 cm depth as granules. Nitrogen (13.5% NH_4, 13.5% NO_3) was applied at a rate of 0.55 g, P (46% P_2O_5) at a rate of 0.26 g, and K (30% K_2O) at a rate of 0.19 g per cylinder which corresponded to 150-65-59 kg N-P-K ha^{-1}.

2.2.3 Ion Exchange Resin Cartridges and Suction Plate Types

In previous studies, cumulative leaching losses of mineral N, P, and K were quantified with ion-exchange resin cartridges (Bischoff et al., 1999; Lang and Kaupenjohann, 2004; Predotova et al., 2011). Similarly, glass cartridges (110 mm x 100 mm) were filled with a mixture of cation and anion exchange resins (Amberjet 1200 Na^+ and Amberjet 4200 Cl^-, Rohm & Haas, Philadelphia, USA), and silica sand (< 1 mm) at a volumetric ratio of 1:1:2. As a comparison and to obtain irrigation event-specific leaching values, we used glass suction plates (EcoTech, Bonn, Germany). They had a borosilicate glass filter with a pore width of 1-1.6 µm and a diameter of 100 mm. Additionally used were Polyethylene (PE) suction plates (EcoTech, Bonn, Germany) with a polyamide-membrane filter fitted in a polyethylene frame with a pore width of 0.45 µm and a dimension of 230 mm x 230 mm.

2.2.4 Experimental Design

A total of thirty glass cylinders (400 mm x 100 mm) were placed in a greenhouse at a room temperature of 20 ± 2ºC with natural light. The glass cylinders were fixed either to glass suction plates, PE suction plates, or to resin cartridges and filled with 3.8 kg dry substrate (Figs. 1, 2). At the bottom, all cylinders were closed with nylon gauze (1 mm mesh size) to avoid substrate losses. Uncovered surfaces were sealed with PVC foil and tape or silicone-free nitrile belts. Tubes (0.35 m length and with an inner diameter of 1 mm) connecting the plates with the soil water collection bottles were made of polytetrafluorethylene (PTFE). Weekly gravimetrically controlled flood irrigation events (115% WHC) were simulated by adding de-ionized water with Erlenmeyer flasks. At the onset of each irrigation, -100 hPa vacuum pressure was applied *via* a pump (UMS GmbH, Munich, Germany) and maintained until the water flow stopped after ca. 90 minutes. Soil water was weighted and aliquots were transferred into glass vials, acidified with concentrated HCl, and frozen at -18ºC until analysis. In contrast to these time-resolved measurements, the cartridges were only taken off at the end of the experiment, yielding a cumulative data of leached nutrients.

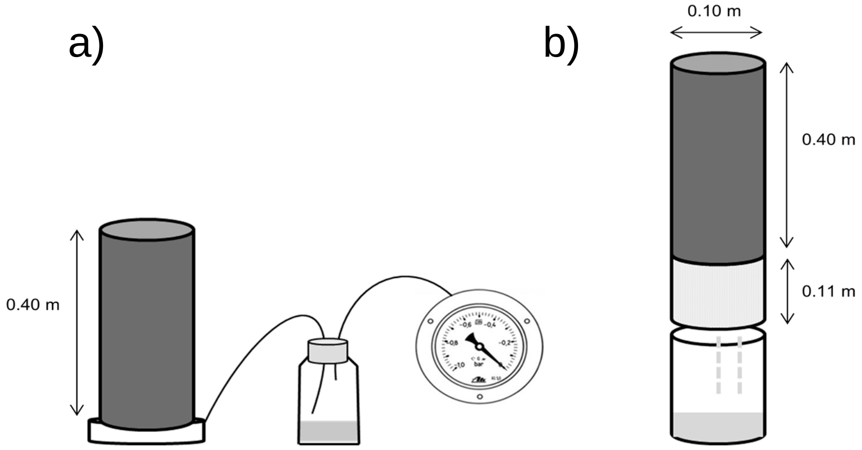


Fig. 1. Principle of sampling with suction plates (a) and ion exchange resins (b).

Fig. 2. Picture of the experimental design. Treatments from left to right: Glass suction plate, ion exchange resin cartridge, glass suction plate, two PE suction plates. PE = Polyethylene.

2.2.5 Analytical Methods

Ion extraction from resins and analysis

After collection of the cartridges from the experimental setup, the resin-sand mixture was separated into five layers (L1 - L5) of about 22 mm each to allow assessment of a nutrient concentration gradient within each cartridge (Bischoff et al., 1999). From each layer, 5 g were taken for dry weight determination (105°C) and another subsample of 30 g was frozen (-18°C) until analysis. For this purpose, the subsamples were extracted six times with an extractant according to the guidelines of TerrAquat Consultants (www.terraquat.com; Stuttgart, Germany), the patent holder of this method. Concentrations of N, P, and K were analyzed following the below described methods. The amounts of leached NO_3-N and K from ion exchange resins were calculated from the concentrations of these elements measured in the extracts, then multiplied by the dry weight of each layer, and summed up per glass cartridge. Cumulative carbon and nutrient leaching losses per hectare were calculated based on the 70.9 cm^2 surface area of the glass cylinders.

Carbon, nitrogen, phosphorus, and potassium in leachate and extracts

Leachate samples were examined simultaneously for concentrations of DOC and for total dissolved N using a CN Analyzer (Multi N/C 2100S, Analytik Jena AG, Jena, Germany). Concentrations of dissolved inorganic N (NO_3, NH_4) of the leachate samples were measured with a segmented flow analyzer (Evolution II, Alliance Instruments, AMS, Frepillon, France). The concentrations of DON were calculated as the difference between total dissolved N and the sum of dissolved inorganic N (NO_3^- + NH_4^+). For P determination, leachates were colored according to the ascorbic acid method (Murphy and Riley, 1962) followed by spectro-photometrical analysis (Hitachi U-2000, Tokyo, Japan). K was measured directly using a flame photometer (Instrumentation Laboratory 543, Bedford, MA, USA). Since $NH_{4,}$ DON, and P concentrations were below the detection limit for all measurements, they are excluded hereafter. The amounts of leached DOC, NO_3-N, and K from suction plates were calculated by multiplying the measured concentrations with the amount of leachate. Cumulative N and K leaching derived from ion exchange resins were compared with the cumulative N and K leaching obtained with suction plates by summing up the calculated leaching loads per irrigation event for all seven irrigation events.

2.2.6 Data Analysis

For each treatment, arithmetic means of five replications per treatment were calculated with their respective standard errors. Treatments were: glass suction plate (glass-SP)-MIN, PE-SP-MIN, resin-MIN, glass-SP-ORG, PE-SP-ORG, resin-ORG. Due to glass suction plate failures for the MIN treatment in the second and third sampling week, only two, and respectively, one replicate(s) remained for this data type and thus data points are displayed without standard errors. The statistical significance of treatment effects was tested by analysis of variance (ANOVA) and post-hoc test statistics (Tukey HSD). Means were compared at $\alpha = 0.05$. All statistical analyses were performed using the statistical software packages Statistica 7.0 (StatSoft GmbH, Hamburg, Germany) and SPSS 17.0 (SPSS Inc., Chicago, IL, USA).

2.3 Results

2.3.1 Leaching Gradients of Nitrogen and Potassium within Cartridges

An average of 101 and 13 mg NO_3-N per cartridge was found for the mineral and organic fertilizer amendments, respectively (Fig. 3a). Across treatments, most NO_3-N was extracted from the top layer (L 1, $P < 0.001$). In the cartridges that were attached to the substrate treated with mineral fertilizer, 99% of the leached NO_3-N was adsorbed by the two upper layers (96% in L 1 and 3% in L 2). Similarly, 94% of the leached NO_3-N from the organic fertilizer treatment was extracted from L 1, while another 5% was adsorbed by L 2. For K, averages of 93 and 104 mg were detected for the mineral and organic fertilizer treatments, but in contrast to NO_3-N (Fig. 3b). All five layers contributed similarly (18-23%) to total adsorbed K.

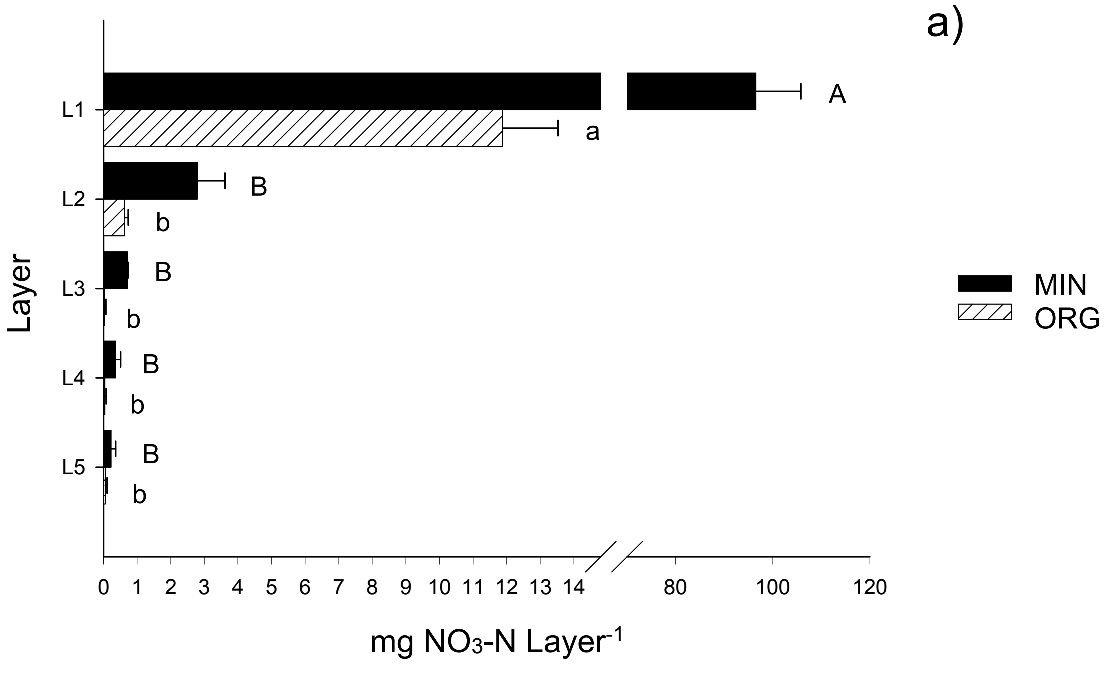


Fig. 3a. Leaching gradients of N adsorbed to ion exchange resins. L 1 to L 5 refer to the separate layers taken from each cartridge starting on top. Horizontal bars denote ± one standard error of the mean (n = 5). Significant differences between layers at $P < 0.05$ are indicated as capital letters for MIN and small letters for ORG. MIN = mineral fertilizer; ORG = goat manure.

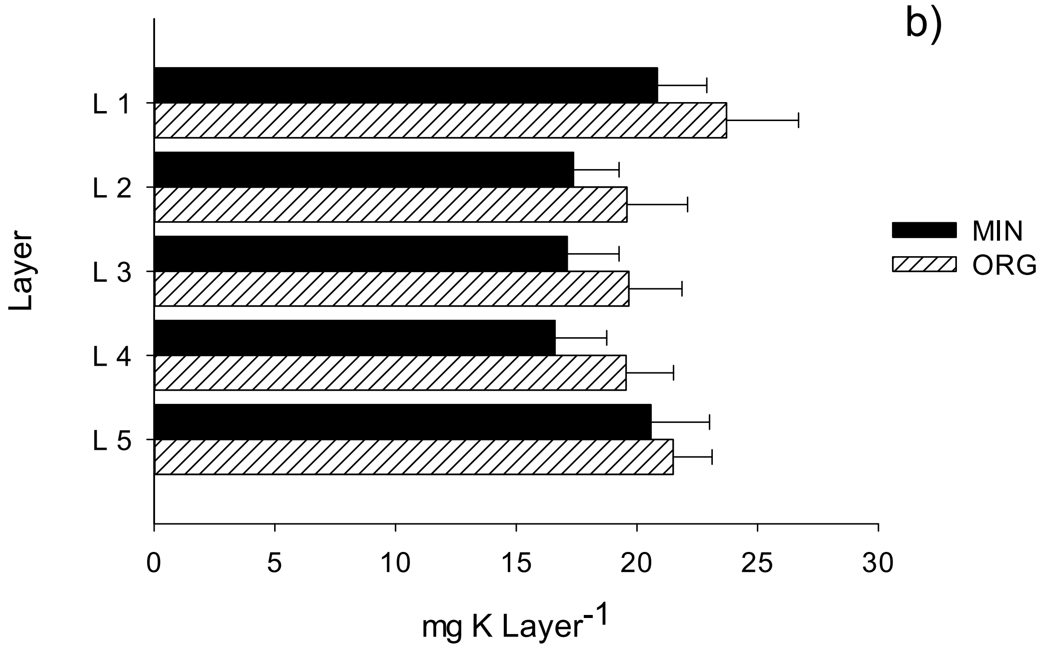


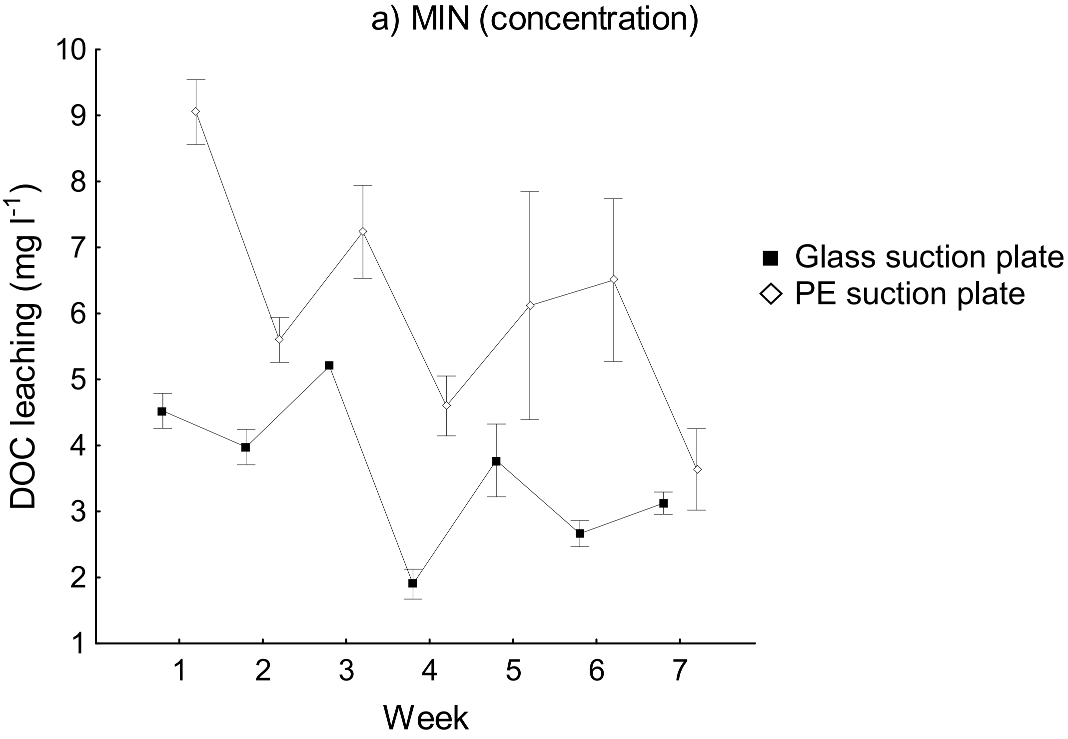
Fig. 3b. Leaching gradients of K adsorbed to ion exchange resins. L 1 to L 5 refer to the separate layers taken from each cartridge starting on top. Horizontal bars denote ± one standard error of the mean (n = 5). Significant differences between layers at $P < 0.05$ are indicated as capital letters for MIN and small letters for ORG. MIN = mineral fertilizer; ORG = goat manure.

2.3.2 Irrigation-specific Leaching Losses of Carbon, Nitrogen, and Potassium on Suction Plates

The concentration of DOC in leaching water of the MIN treatment captured with glass suction plates ranged from 1.9 ± 0.2 to 4.5 ± 0.3 mg C l^{-1}, compared with 3.6 ± 0.6 to 9.1 ± 0.5 mg C l^{-1} from PE suction plates (Fig. 4a-d). Significant differences between the two suction plate types were found in four out of seven samplings: first week ($P < 0.001$), second week ($P = 0.049$), fourth week ($P < 0.001$), and sixth week ($P = 0.019$). The aforementioned DOC concentrations corresponded to a leaching amount ranging from 0.9 ± 0.1 kg ha^{-1} to 1.9 ± 0.2 kg ha^{-1} (glass suction plates) and from 1.7 ± 0.4 kg ha^{-1} to 4.8 ± 0.4 kg DOC ha^{-1} (PE suction plates). The significant effects of suction plate filters detected for irrigation event-specific DOC leaching loads matched with the ones from the concentration readings with: first week ($P < 0.001$), second week ($P = 0.025$), fourth week ($P < 0.001$), and the sixth week ($P = 0.039$). As for the MIN treatment, four out of five glass suction plates failed to deliver samples in the third sampling week. The single data point for that measurement may thereby represent an inflated value (4.4 kg ha^{-1}). Nevertheless, it is comparable with the mean 4.8 ± 0.4 kg ha^{-1} derived from the PE suction plates in the third week. For the ORG treatment, we found between 3.0 ± 0.3 and 4.7 ± 0.6 mg l^{-1} in glass suction plate-derived leaching water, while between 4.5 ± 0.7 and 10.8 ± 1.2 mg DOC l^{-1} were measured in leaching water collected from PE suction plates. Expressed as loads, between 1.3 ± 0.3 and 2.5 ± 0.2 kg DOC ha^{-1} leached from the ORG treatment according to the glass suction plates; between 2.9 ± 0.4 and 3.7 ± 0.3 kg DOC ha^{-1} leached from the same treatment according to the PE suction plates. Similarly to the observed effects for MIN, statistically significant differences between the suction plate types were found for ORG in four out of seven sampling weeks (weeks 1.: $P = 0.001$, 2.: $P = 0.013$, 3.: $P = 0.005$, and 6.: $P = 0.023$) for concentration readings and in five out of seven weeks (weeks 1.: $P = 0.012$, 2.: $P = 0.001$, 3.: $P < 0.001$, 5.: $P = 0.003$, and 6.: $P = 0.031$) for calculated DOC loads.

The NO_3-N concentration in leachates from the MIN treatment ranged between 133 ± 26 and 178 ± 24 mg l^{-1} at the first sampling week, and between 1.2 ± 0.0 and 1.8 ± 0.3 mg l^{-1} in the seventh week of sampling for glass and PE suction plates, respectively (Fig. 4e-h). The corresponding calculated mean loads of leached NO_3-N were 39 ± 12 (glass suction plates) and 82 ± 16 kg ha^{-1} (PE suction plates) at the first week; 0.7 ± 0.0 (glass suction plates) and 0.8 ± 0.2 kg ha^{-1} (PE suction plates) leached from the substrates at the seventh week. In leachates of the ORG treatment, 40 ± 6 mg NO_3-N l^{-1} (14 ± 4 kg ha^{-1}) were found for glass suction plates at the first week, and 2.2 ± 0.4 mg l^{-1} (1.2 ± 0.2 kg ha^{-1}) at the seventh week. For the same treatment, PE suction plates delivered 22 ± 6 mg l^{-1} (7 ± 2 kg ha^{-1}) and 2.1 ± 0.4 mg NO_3-N l^{-1} (1.3 ± 0.3 kg ha^{-1}) for the first and seventh week, respectively. In both fertilizer treatments, NO_3-N leaching showed a second peak between the third and fourth week, but leaching losses were highest at the first irrigation event. Significant differences between glass and PE suction plates were only detected for MIN in both NO_3-N ($P = 0.038$) concentration and load ($P = 0.012$) of the fourth week.

Measurements for K leaching from the MIN treatment revealed that around 0.8 ± 0.2 to 2.5 ± 0.5 mg l^{-1}, and 0.5 ± 0.2 to 2.4 ± 0.3 mg l^{-1} were recorded by glass and PE suction plates, respectively (Fig. 4i-l). These concentrations corresponded to respective 0.5 ± 0.1 to 0.9 ± 0.2 kg ha^{-1} (glass suction plates) and 0.3 ± 0.1 to 1.3 ± 0.1 kg ha^{-1} (PE suction plates). Since the peak K load calculated for the 3. sampling (1.9 kg ha^{-1}; MIN treatment) was based only on one data point, it should be considered as outlier.



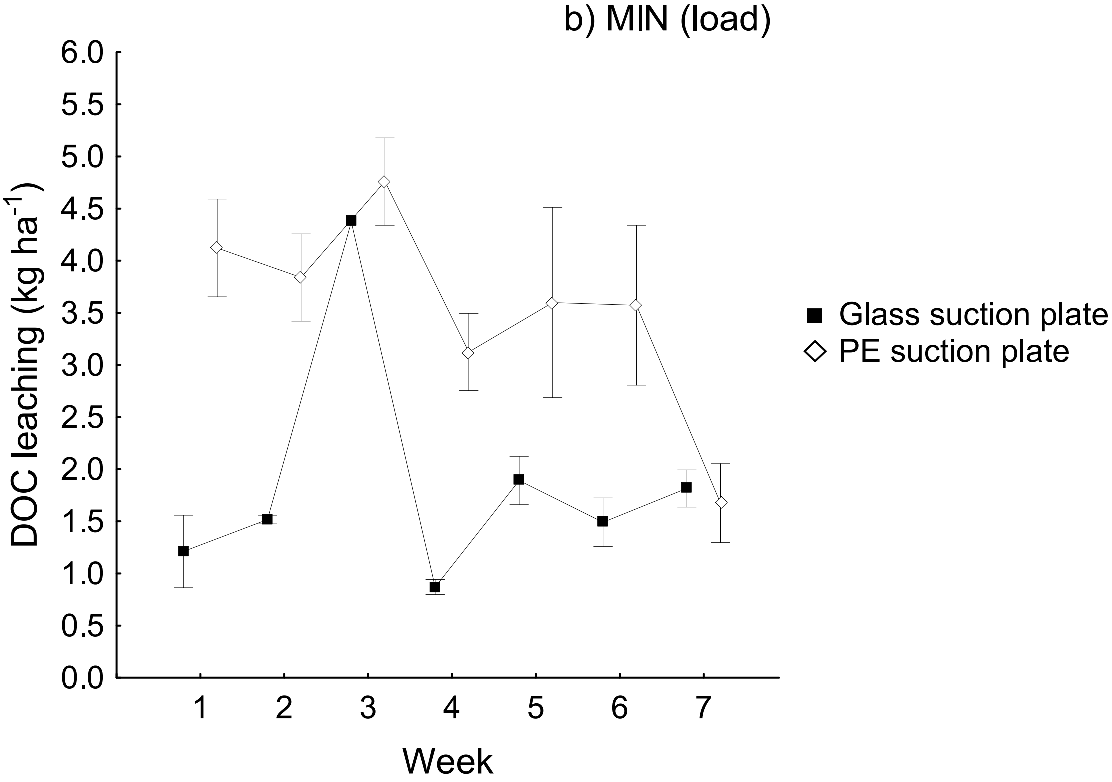
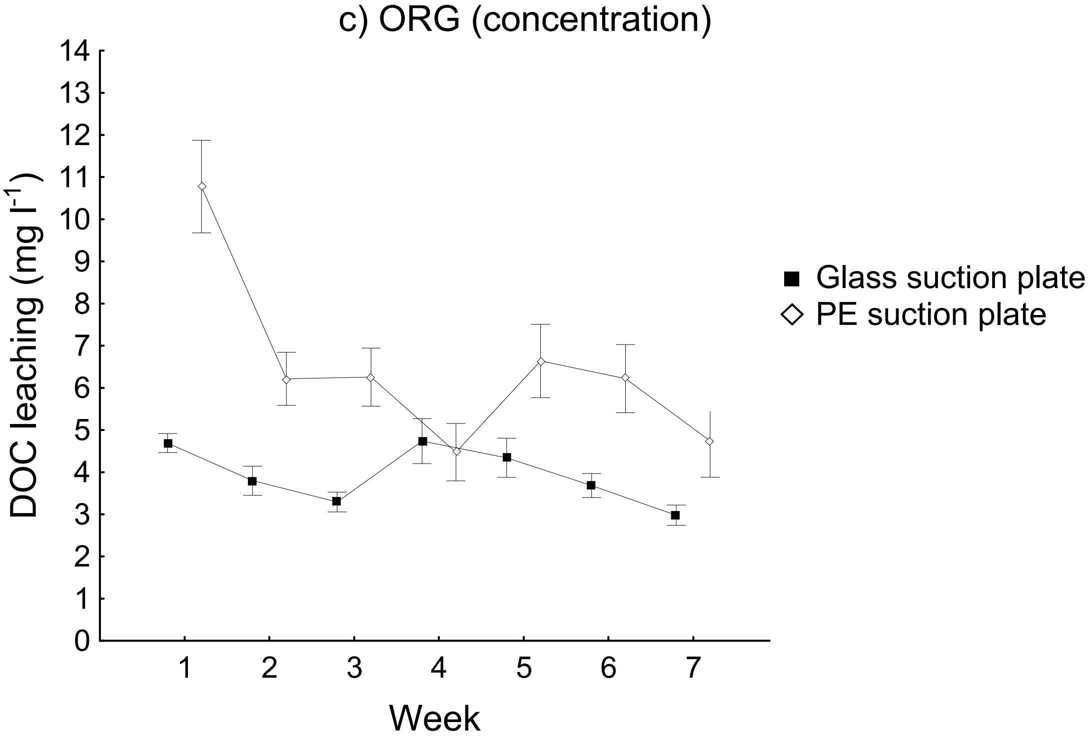


Fig. 4a and b. Leaching of DOC from glass and PE suction plates for the MIN treatment as concentration (a) and load (b). Vertical bars denote ± one standard error of the mean at $P < 0.05$ ($n = 5$ for MIN, except for 2. week, where $n = 2$ and 3. week, where $n = 1$ for glass suction plates; $n = 5$ for ORG). PE = Polyethylene; MIN = mineral fertilizer.



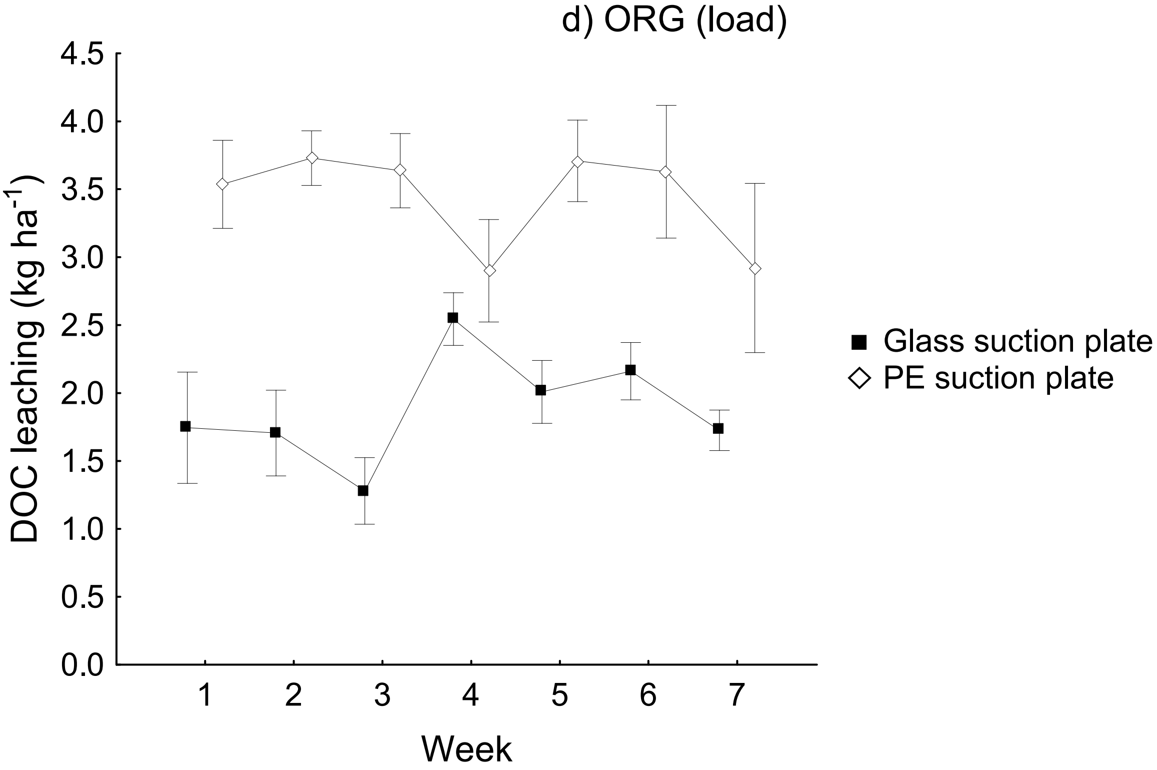
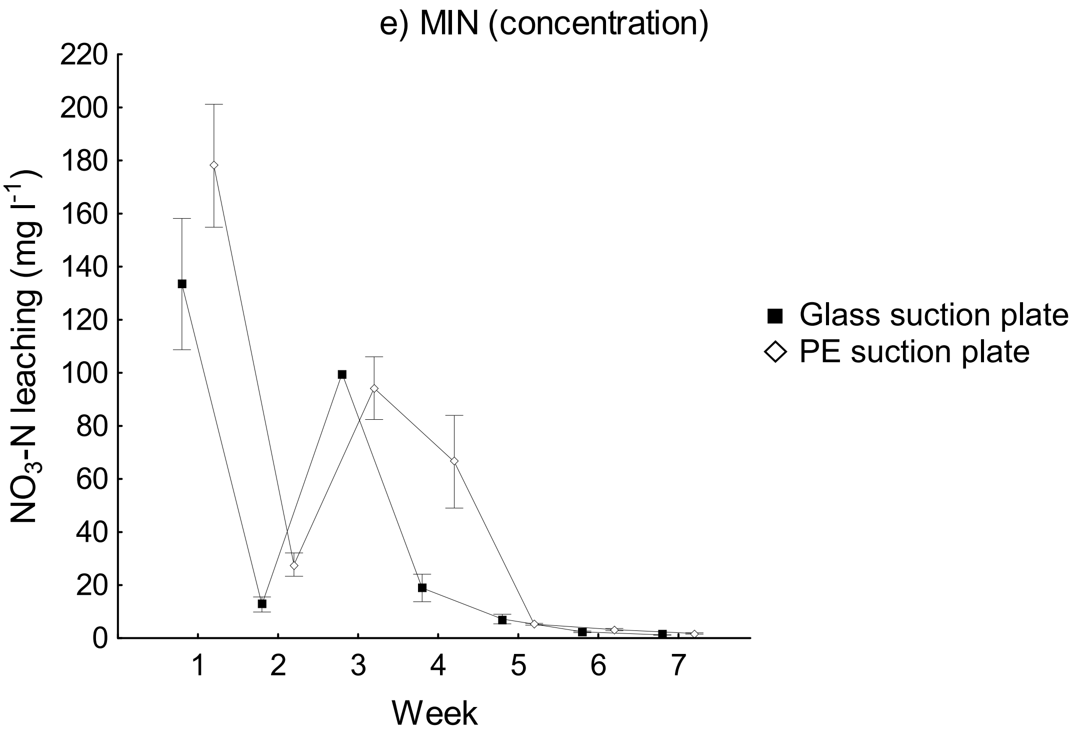


Fig. 4c and d. Leaching of DOC from glass and PE suction plates the ORG treatment as concentration (c) and load (d). Vertical bars denote ± one standard error of the mean at $P < 0.05$ ($n = 5$ for MIN, except for 2. week, where $n = 2$ and 3. week, where $n = 1$ for glass suction plates; $n = 5$ for ORG). PE = Polyethylene; ORG = goat manure.



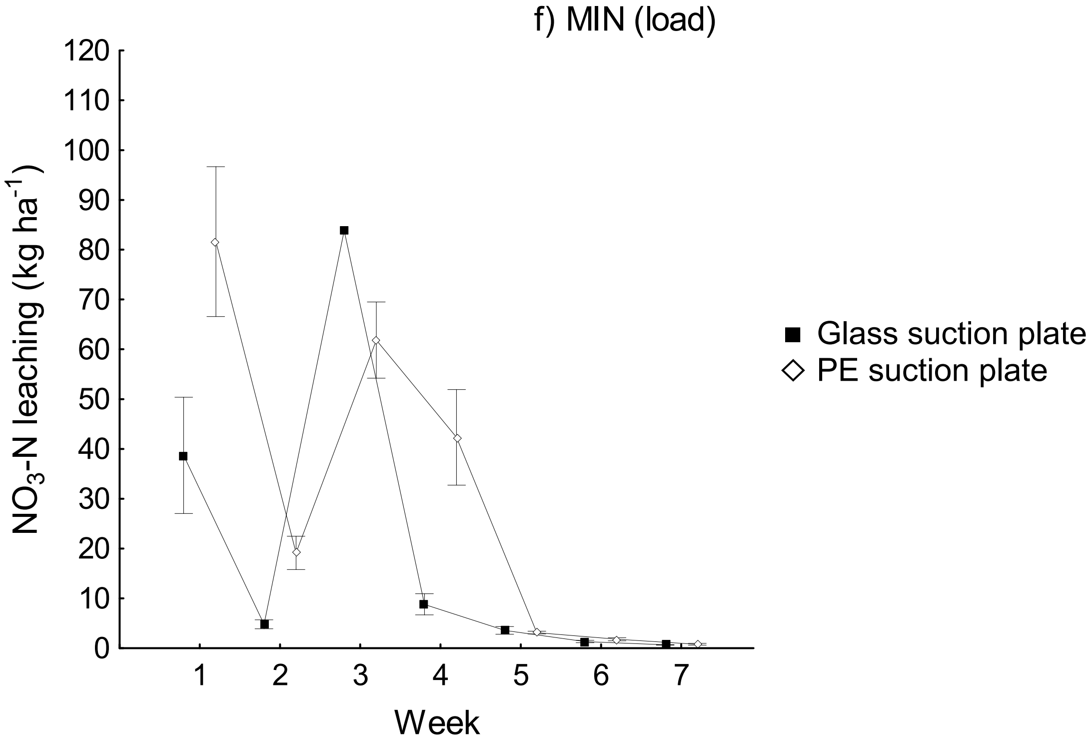
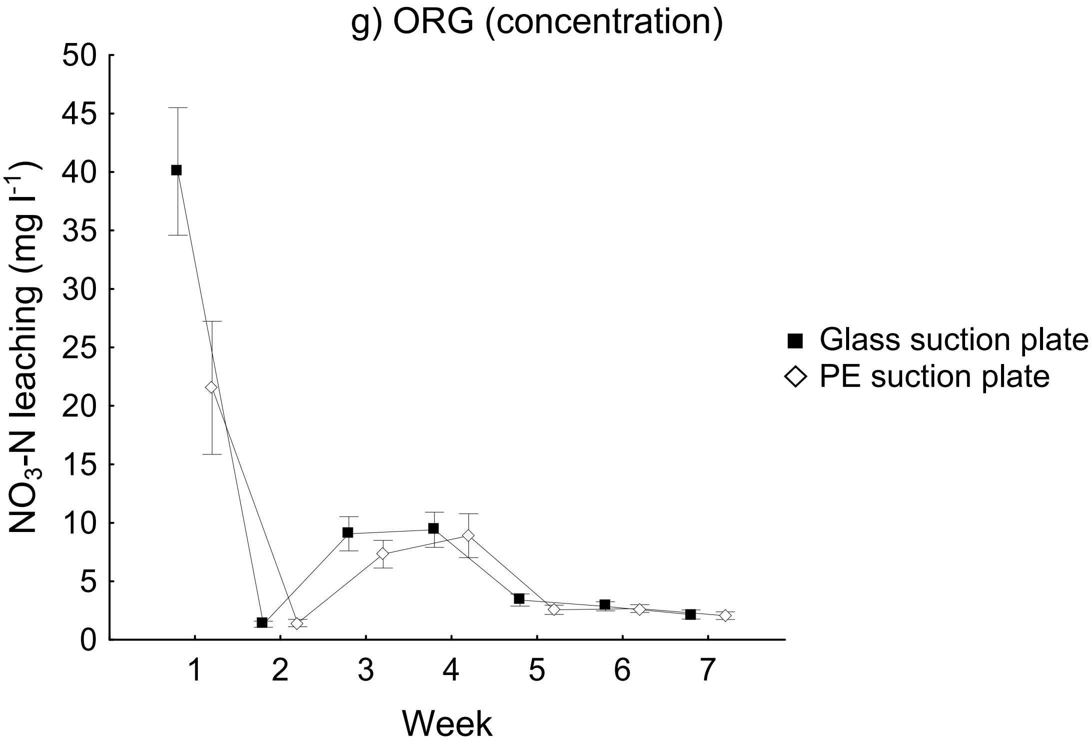


Fig. 4e and f. Leaching of NO_3-N from glass and PE suction plates for the MIN treatment as concentration (e) and load (f). Vertical bars denote ± one standard error of the mean at $P < 0.05$ (n = 5 for MIN, except for 2. week, where n = 2 and 3. week, where n= 1 for glass suction plates; n= 5 for ORG). PE = Polyethylene; MIN = mineral fertilizer.



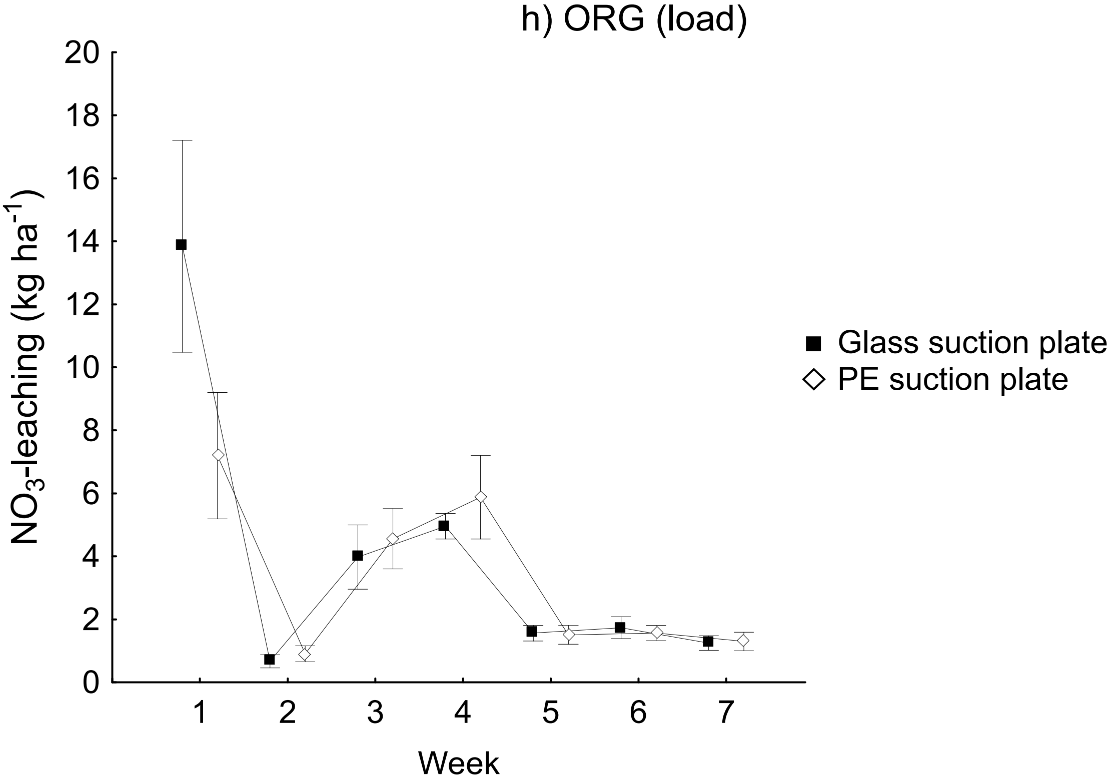
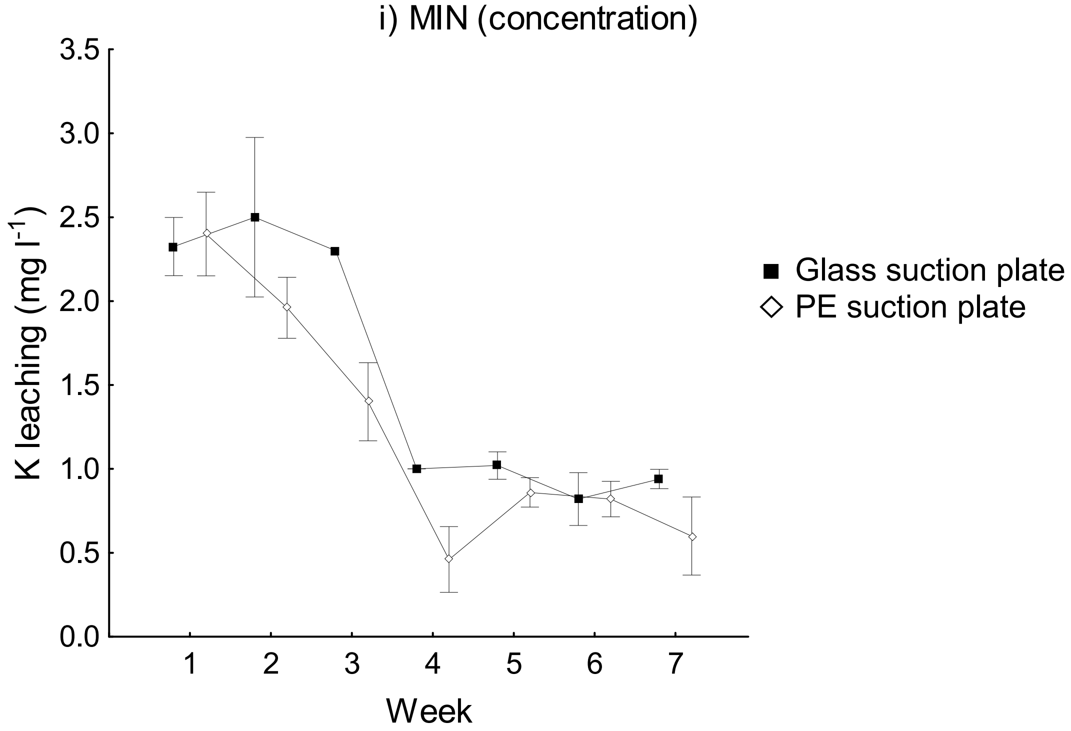
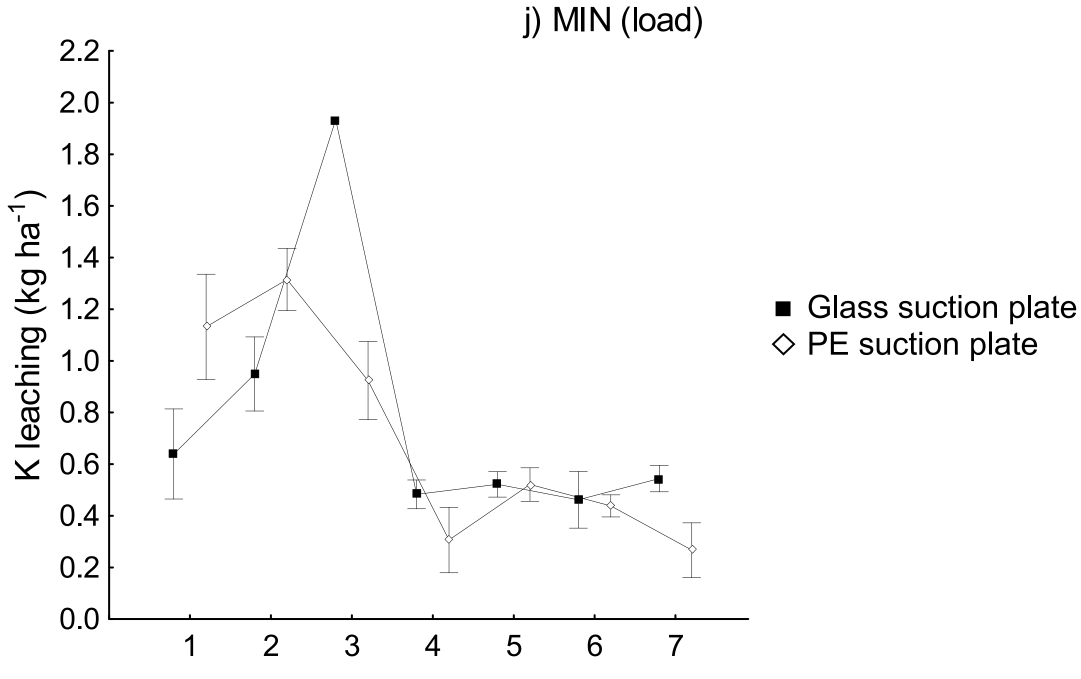


Fig. 4g and h. Leaching of NO_3-N from glass and PE suction plates the ORG treatment as concentration (g) and load (h). Vertical bars denote ± one standard error of the mean at $P < 0.05$ ($n = 5$ for MIN, except for 2. week, where $n = 2$ and 3. week, where $n = 1$ for glass suction plates; $n = 5$ for ORG). PE = Polyethylene; ORG = goat manure.

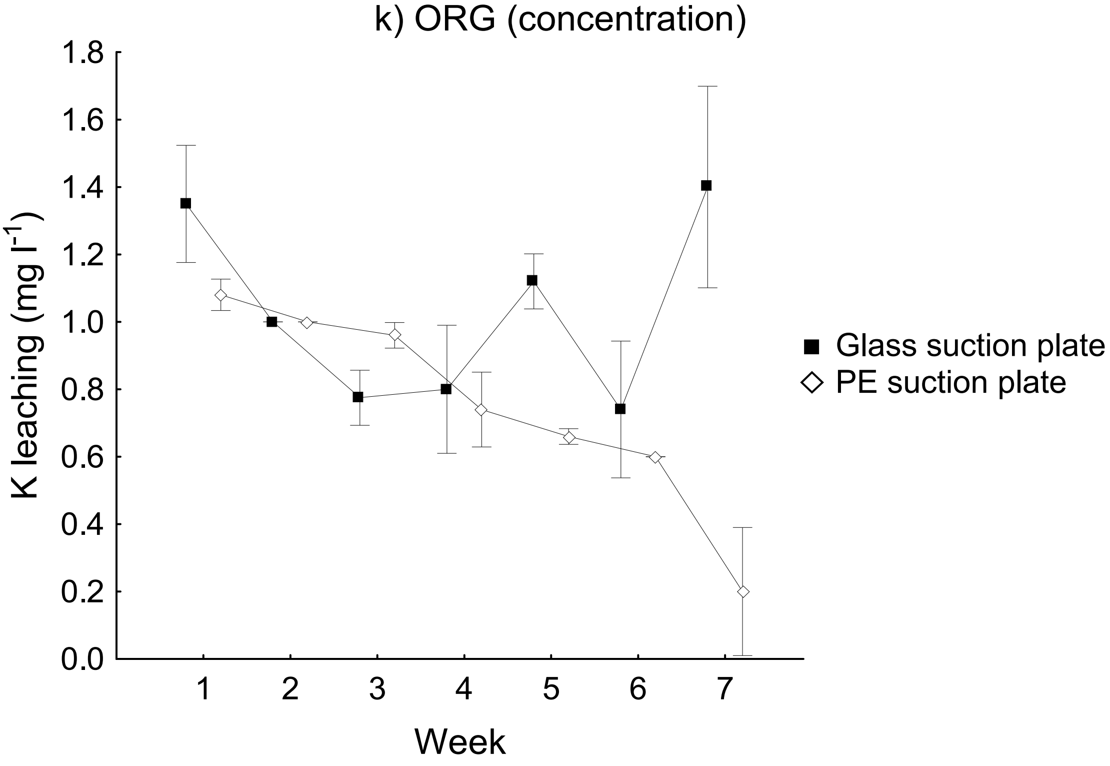


i) MIN (concentration)



j) MIN (load)

Fig. 4i and j. Leaching of K from glass and PE suction plates for the MIN treatment as concentration (i) and load (j). Vertical bars denote ± one standard error of the mean at $P < 0.05$ (n = 5 for MIN, except for 2. week, where n = 2 and 3. week, where n= 1 for glass suction plates; n= 5 for ORG). PE = Polyethylene; MIN = mineral fertilizer.



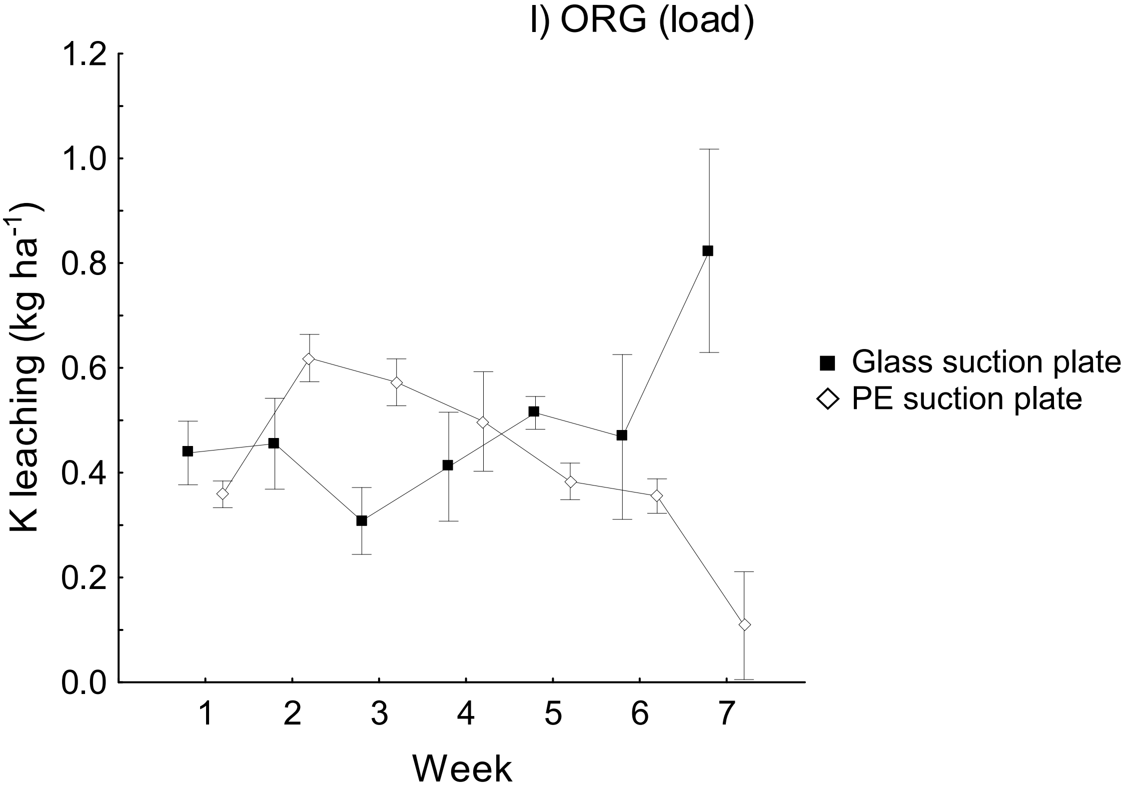


Fig. 4k and l. Leaching of K from glass and PE suction plates for the ORG treatment as concentration (k) and load (l). Vertical bars denote ± one standard error of the mean at $P < 0.05$ ($n = 5$ for MIN, except for 2. week, where $n = 2$ and 3. week, where $n = 1$ for glass suction plates; $n = 5$ for ORG). PE = Polyethylene; ORG = goat manure.

Significant differences between glass suction plates and PE suction plates for K concentrations from the MIN treatment were observed for the 4. sampling ($P = 0.031$). Compared to the MIN treatment, leaching of K from the ORG treatment reached about 0.7 ± 0.2 to 1.4 ± 0.3 mg l^{-1} measured with glass suction plates, and about 0.2 ± 0.2 to 1.1 ± 0.1 mg l^{-1} measured with PE suction plates. Leached K loads from the ORG treatment ranged between 0.3 ± 0.1 to 0.8 ± 0.2 kg ha^{-1} in glass suction plates, and between 0.1 ± 0.1 to 0.6 ± 0.1 kg ha^{-1} in PE suction plates. For K concentrations leached from the ORG treatment, significant differences between suction plate types were documented for the 5. ($P < 0.001$) and 7. sampling ($P = 0.012$); K leaching loads significantly differed between glass and PE suction plates in the 3. ($P = 0.012$), 5. ($P = 0.029$), and 7. week ($P = 0.015$).

2.3.3 Cumulative Leaching Losses from Suction Plates and Ion Exchange Resins

Cumulative DOC leaching was for both amendments significantly lower in glass suction plates than in PE suction plates ($P = 0.015$ for MIN, $P < 0.001$ for ORG): for glass suction plates mean 13 ± 0.2 kg DOC ha^{-1} (MIN) and 13 ± 0.8 kg ha^{-1} (ORG) were recorded, whereas for PE suction plates 25 ± 1.9 and 24 ± 1.3 kg ha^{-1} were found for MIN and ORG, respectively (Fig. 5a).

The magnitude of leached NO_3-N cumulative over seven irrigation events was comparable between glass suction plates (28 ± 5 kg ha^{-1}), PE suction plates (23 ± 2 kg ha^{-1}), and ion exchange resins (18 ± 3 kg ha^{-1}) for the ORG treatment (Fig. 5b). However, for the MIN treatment cumulative NO_3-N leaching was significantly lower in ion exchange resin extracts compared with PE suction plate filtrates ($P = 0.012$; 142 ± 13 and 211 ± 16 kg ha^{-1}, respectively). NO_3-N leaching loads derived from glass suction plates for the MIN treatment (159 ± 17 kg ha^{-1}) were insignificantly lower from mean loads obtained with PE suction plates, and insignificantly higher from mean loads obtained with ion exchange resins.

Both suction plate types indicated similar cumulative K leaching with 5.5 ± 0.1 kg K ha^{-1} for glass suction plates and 4.9 ± 0.6 kg K ha^{-1} for PE suction plates in MIN and 3.4 ± 0.4 and 2.9 ± 0.2 kg K ha^{-1} for ORG (Fig. 5c). Significantly lower K leaching loads in the ORG compared to the MIN treatment were detected by both suction plate types ($P = 0.017$ for glass, $P = 0.013$ for PE), whereas the ion exchange resins failed to reveal such difference. Moreover, when comparing averaged K leaching across both suction plate types with mean K leaching from ion exchange resins, we found that the magnitude of leached K was about 25-times higher (131 ± 6 kg ha^{-1}; $P < 0.001$) in case of MIN, and about 47-times higher (147 ± 14 kg ha^{-1}; $P < 0.001$) in case of ORG.

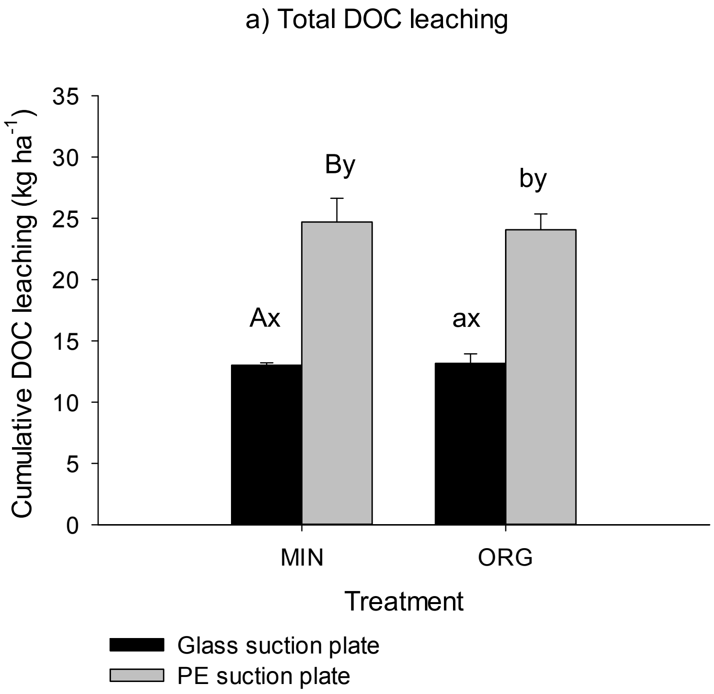
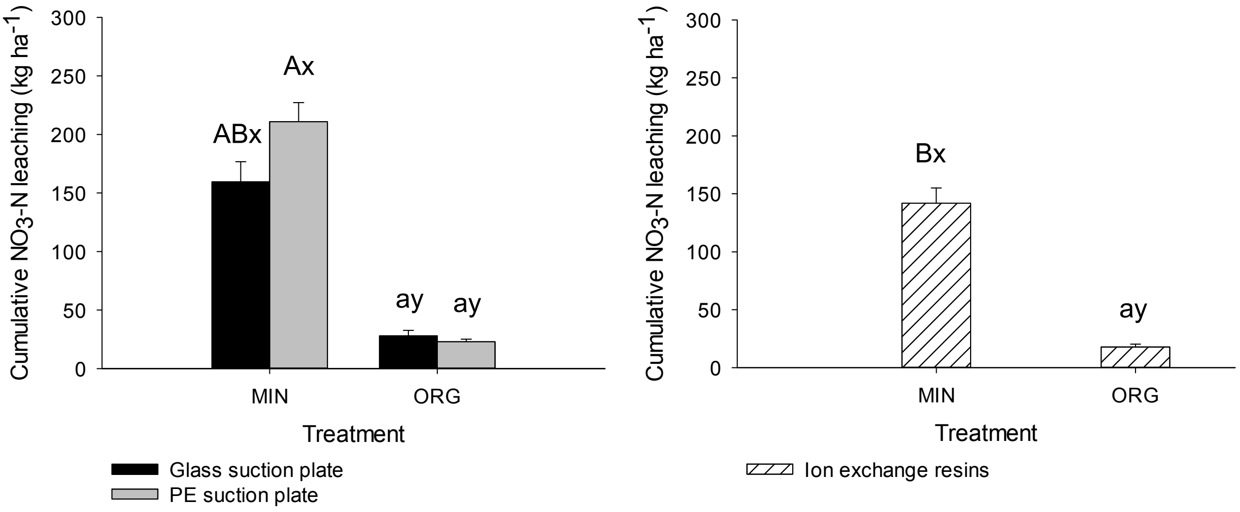
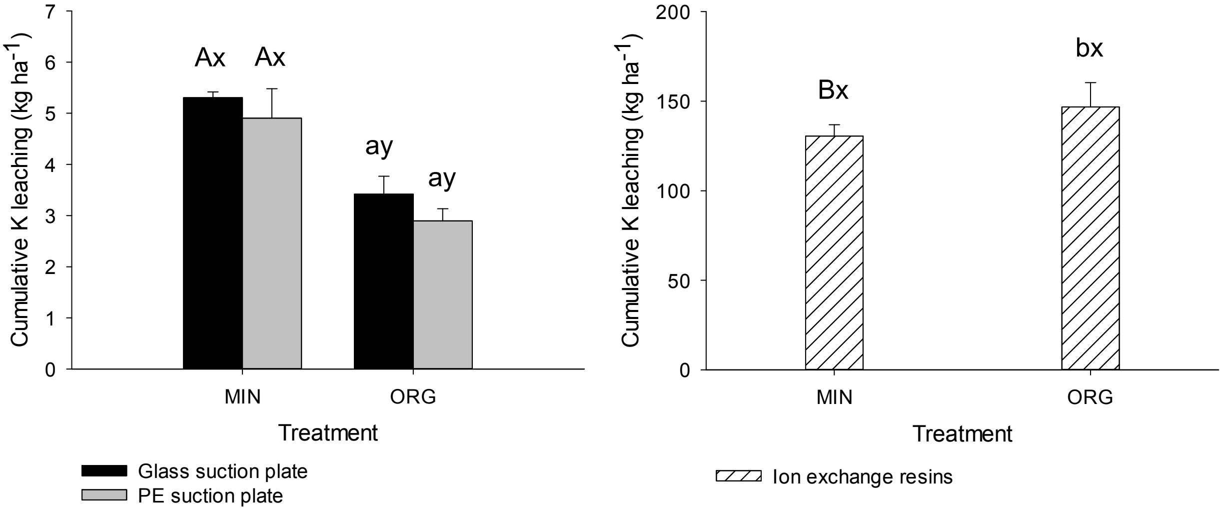


Fig. 5a. Cumulative leaching of DOC from glass and PE suction plates. Vertical bars denote standard error of means at $P < 0.05$ (n = 5 for MIN, except for 2. week, where n = 2 and 3. week, where n= 1 for glass suction plates; n= 5 for ORG). Capital letters (A, B) display significant differences between methods for MIN; small letters (a, b) indicate significant differences between methods for ORG; small letters (x, y) display significant differences between fertilizer treatments for glass suction plates and PE suction plates. PE = Polyethylene; MIN = mineral fertilizer; ORG = goat manure; methods = glass suction plates, PE suction plates.



b) Total NO_3-N leaching



c) Total K leaching

Fig. 5b and c. Cumulative leaching of N (b) and K (c) from glass and PE suction plates, and ion exchange resins. Vertical bars denote standard error of means at $P < 0.05$ (n = 5 for MIN, except for 2. week, where n = 2 and 3. week, where n= 1 for glass suction plates; n= 5 for ORG). Capital letters (A, B) display significant differences between methods for MIN; small letters (a, b) indicate significant differences between methods for ORG; small letters (x, y) display significant differences between fertilizer treatments for glass suction plates, PE suction plates, and ion exchange resins. PE = Polyethylene; MIN = mineral fertilizer; ORG = goat manure; methods = glass suction plates, PE suction plates, ion exchange resins.

2.4 Discussion

Deciding on the most appropriate method for measuring nutrient leaching in the vadose zone is often a choice between representativity and practicability, and it also depends on many factors such as soil type, moisture regime, and research question (Peters et al., 2005; Predotova et al., 2011). Compared with the cumulative data obtained by the use of ion exchange resin cartridges, suction plates allow the assessment of short-term processes, and are therefore preferred to measure nutrient leaching dynamics (Lehmann et al., 2001).

Ion exchange resins were widely used for leaching studies in temperate soils (Lang and Kaupenjohann, 2004; Lehmann et al., 2001) and in subtropical soils (Predotova et al., 2011; Safi et al., 2011; Siegfried et al., 2011). The method was also previously used for studies on plant nutrient availability in tropical soils (Mo et al., 2003; Meason and Idol, 2008). The examination of leaching gradients within the cartridge allows to examine whether installation and adsorption of nutrients (NO_3^-, PO_4^{3-}, K^+) to the exchange sites of the resin surfaces (Bischoff et al., 1999; Predotova et al., 2011) was successful and complete and whether there was any stagnant water that may have distorted the results. In our setup, rise from groundwater or vertical pass flow along the cartridges, and the subsequent infiltration from the bottom of the cartridge can be excluded. Irrespective of fertilizer treatment, we detected highest NO_3^--N in the top layer of the resin cartridge, while from L 3 to L 5 only 1% of total NO_3-N was captured. In contrast, K was found in all layers and at considerably higher rates than what was measured by both suction plate types. Previous research indicated that the ion exchange resins we used may be not suitable for K measurements because they significantly overestimated K fluxes (Siegfried et al., 2012). This certainly merits further investigation.

The similarity of individual NO_3-N leaching estimates between suction plates made from glass and PE, and, once aggregated, to cumulative resin readings, indicates the comparability of methods for the ORG, but not the MIN treatment. In all measurements NH_4, P, and DON leaching was below detection limit. This is not surprising, considering that the major part of the substrate (85%) was pure silica sand and mineralization of the goat manure was negligibly low (data not shown). Phosphorus leaching from the mineral fertilizer treatment could not be measured by any of the used methods.

As demonstrated by Lehmann et al. (2001), resins cannot be used for DOC removal from solution due to their high C contents and limited adsorption. Siemens and Kaupenjohann (2003) showed that the typical elastomer or glue sealings of suction plates may alter leaching water composition by releasing organic C. Therefore, only suction plates that were entirely made of sintered borosilicate glass were reported to be an adequate material to deliver reliable estimates of leached DOC (Siemens and Kaupenjohann, 2003). Our study confirmed these results, since the DOC concentrations from both fertilizer treatments were in all cases higher in the PE suction plate filtrates than in the glass suction plate filtrates. Based on the cited previous work, we conclude that PE suction plates significantly overestimated DOC leaching loads.

Technical problems with the glass suction plates at the onset of the experiment caused a loss of replicates in week 2 and 3. During these measurements, we observed that water bypassed the suction plates, since the suction of -100 hPa was apparently not enough to force the water through the filter. Instead, it accumulated in our nitrile sealings between cylinder and plate, and could not be sampled. This problem was caused by the similar diameters of the soil cores and glass suction plates, hence, water could not be sucked through the plate filter fast enough. This bypass phenomenon is very likely to happen also under field conditions and merits proper attention. We suggest that less dense glass filters (1 mm) should be tested for their reliability combined with stronger tube entry points in the glass plates.

2.5 Conclusions

All of the tested methods were suitable to estimate NO_3 leaching, whereas for DOC measurements, glass suction plates are recommended. Both plate types are appropriate for the assessment of K in leaching water, while the extraction of K from ion exchange resins merits further research. Our experimental setup, regardless of using suction-controlled devices or ion exchange resins, can be easily used to verify field data.

Acknowledgments

We gratefully acknowledge the technical assistance of E. Wiegard, C. Thieme and R. Braukmann. We are also thankful to the German Research Foundation (DFG) for funding this project within the Graduate Research Training Group 1397 'Regulation of Soil Organic Matter and Nutrient Turnover in Organic Agriculture'.

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3 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

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Abstract

Leaching losses of carbon and nutrients are often high in sandy soils that are low in organic matter. Additions of activated charcoal to soil are known to increase nutrient retention capacities and may thereby decrease such losses. We investigated (i) how AC affects manure mineralization and leaching of dissolved organic carbon, dissolved organic and inorganic nitrogen, dissolved organic and inorganic phosphorus, and dissolved K, and (ii) whether ion exchange resins and suction plates are equally suited to capture dissolved nutrients. To this end, greenhouse experiments were conducted with sandy soil from Oman using suction plates or ion exchange resins. Carbon and nutrient leaching remained unaffected by AC treatment and ranged between 158 and 203 kg DOC ha^{-1}, 115 and 211 kg NO_3-N ha^{-1}, 1.2 and 1.6 kg PO_4-P ha^{-1}, and 239 and 251 kg K ha^{-1} across both experiments. Compared with NO_3-N results from suction plates, NO_3-N leaching from ion exchange resins were considerably higher for all treatments in Exp. I (0% AC: $P = 0.005$; 5% AC: $P < 0.001$; 9% AC: 0.001). In Exp. II, the opposite was found: NO_3-N leaching was 76% (control; $P = 0.049$), 41% (0% AC; $P = 0.035$), 57% (3% AC; $P = 0.012$), and 50% (9% AC; $P = 0.237$) lower from resins than from suction plates. Our results indicate that suction plates deliver satisfactory results for mineral and organic nutrient forms, nevertheless require great efforts in handling. The observed differences in leaching loads between suction plates and ion exchange resins merit further research.

Keywords: Biochar, charcoal feeding, dissolved organic carbon, nutrient leaching.

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3.1 Introduction

In flood-irrigated cropping systems of hot subtropical climates such as in the Batinah region of Northern Oman, high microbial activity together with frequent wet-dry cycles lead to a fast turnover of organic amendments. Such conditions have been reported to cause substantial carbon and nutrient losses via gaseous emissions and leaching (Jalali, 2005; Siegfried et al., 2011). Leaching of nutrients from soils may cause environmental problems such as depletion of soil fertility and accelerated soil acidification, as well as economic problems such as increase fertilizer costs for farmers and reduced crop yields (Laird et al., 2010; Yao, et al., 2012). Common practices to replenish soil fertility in this region, which is dominated by sandy soils that are inherently low in soil organic matter (SOM), comprise the regular addition of organic materials such as plant residues, compost, or manure at annual application rates of often > 20 t year^{-1} (Wichern et al., 2004; Buerkert et al., 2010). A consequence of applying such quantities is that given an asymmetry of nutrient availability in the soil and plant nutrient uptake it may lead to large losses of dissolved nitrogen (N), potassium (K), and carbon (C) by stimulating microbial activity (Steiner et al., 2007; Heinze et al., 2010; Rottmann et al., 2011; Siegfried et al., 2011; Sradnick et al., 2013). One approach to maintain or increase the fertility of soils is to add biochar (BC) or activated charcoal (AC) to soil or compost, a procedure which is well known to reduce leaching losses by increasing nutrient and water retention capacities of soils (Glaser et al., 2001; Steiner et al., 2007). Moreover, charcoal may further increase soil microbial biomass compared to additions of organic fertilizer alone because of providing supplementary habitats along with energy and nutrients provided by the organic substrate (Sradnick et al., 2013). Since BC cycles at a much slower rate than non-BC fractions of SOC (Glaser et al., 1998; Glaser et al., 2002), it may also constitute a long-term C sink of atmospheric CO_2 and thus help to mitigate global warming (Lehmann et al., 2006). BC is formed by heat treatment of organic materials under limited oxygen supply (pyrolysis; Mukherjee and Zimmerman, 2013), whereas AC undergoes an additional activation process either by pressurized steam above 850°C or by immersion into a strong acid (Kirubakaran et al., 1991), resulting in a very porous non-soluble powder with a high surface to mass ratio (500-3500 m^2 g^{-1}; Huwig et al., 2001). Since BC or AC are pulverized during processing (Olson, 2010), this fine dust can easily get lost by wind or water erosion if loosely applied to the surface (Verheijen et al., 2009). Ingold et al. (2011) recently demonstrated that ingested or manure-bound AC had a greater recalcitrant capacity than AC mixed with faeces. These results imply that using goats as a vector in nutrient cycling can further improve the efficacy of AC as soil amendment, possibly by increasing the surface area and widening pore size distribution, which could lead to an overall higher adsorption capacity (Martinez et al., 2006). Furthermore, manure-bound AC seems better suited for no-till applications as it is less likely to erode from soil if bound to a sorbent (Quaranta, 2013).

In view of the above, the main purpose of this study was to advance our understanding of microbial biomass and leaching dynamics on a sandy subtropical soil after addition of unamended or AC-enriched manure. Secondly, we aimed at comparing two different approaches of leaching measurement: suction plates and ion exchange resins. Previous studies showed that in contrast to glass suction plates, the use of ion exchange resins may lead to substantial underestimations of N and P leaching since they are unable to reliably capture organic compounds of these elements, which under specific conditions may largely contribute to total N and P losses (Murphy et al., 2000; Siemens and Kaupenjohann, 2002; Langlois et al., 2003; van Kessel et al., 2009). Similarly, ion exchange resins were shown to be unsuitable for dissolved organic carbon (DOC) capture (Lehmann et al., 2001). The importance of dissolved organic nutrients and carbon in agricultural soils is increasingly emphasized by the scientific community for its multiple roles. As such in the maintenance of nutrient stocks in terrestrial ecosystems (Neff et al., 2003), in the formation of soils (Dawson and Smith, 2007), and as an integral component in nutrient cycling and budgeting (Neff et al., 2000; Michalzik et al. 2001; Kalbitz et al., 2000; Cleveland et al., 2004; Ohno and Bro, 2006; Beesley and Dickinson, 2011). However, literature on dissolved organic matter (DOM) dynamics in arable soils, particularly under subtropical conditions are scarce (Chantigny, 2003). A final objective of this study was therefore to quantify the contribution of dissolved organic N (DON) and dissolved organic P (DOP) to total leaching losses as well as to determine the effects of charcoal-enriched manures on DOC leaching. We therefore hypothesized that the application of charcoal-enriched manure to a sandy soil (i) increases soil microbial biomass more than the application of unamended manure and (ii) reduces leaching of dissolved mineral N, P, and K, but may trigger DOC leaching. We also hypothesized that cumulative losses of mineral N, P, and K are comparable between glass suction plates and ion exchange resins.

3.2 Material and Methods

3.2.1 Soil and AC-Enriched Manure Collection and Characterization

Soil (0-40 cm) was collected from a private farm (24º20’ N, 56º46’ E) located at the northeastern Batinah coast of the Sultanate of Oman (Siegfried et al., 2013). The soil was classified as a mixed hyperthermic typic Torrifluvent (US Soil Taxonomy) deriving from recent fluviatile wadi deposits with a gravel-rich subsoil and partial coverage by aeolian sand veneers (Al-Farsi, 2001). The soil has a coarse texture (82% sand, 16% silt, 2% clay), a pH_{H2O} of 8.5, a bulk density of 1.44 g cm^{-3}, a total C content of 12.7 g kg^{-1}, an organic C content (C_{org}) of 4.9 g kg^{-1}, a total N content of 0.6 g kg^{-1}, a $CaCO_3$ content of 6.5%, a CN ratio of 21.2, an Olsen P of 0.04 g kg^{-1}, and $K_{(CAL)}$ of 0.26 g kg^{-1}. Before the experiment started, the soil was air dried, sieved (< 2 mm), and shipped to Germany for experiments under controlled conditions.

Manure was derived from a feeding trial with boer goats (*Capra* L.) at the experimental station of the University of Goettingen, which focused on the performance of goats that were being fed increasing levels of AC over a period of twelve weeks (Quaranta, 2013). Directly after sampling, the manure was oven dried to weight constancy at 40°C for 48 h (Table 1). AC powder was manufactured from coconut shells followed by steam activation (AquaSorb® CP1, Jacobi Carbons Service GmbH, Premnitz, Germany) and contained 92.1% C, 0.1% N, 0.03% P, and 0.8% K. It had a pH of 9.1, a particle size of 44 µm, a surface area of 1050 m^2 g^{-1}, and a total pore volume of 0.62 g cm^{-3}.

Table 1. Properties of manure applied to a typic Torrifluvent collected in Northern Oman (n = 4). AC = activated charcoal fed to goats in % of total ration.

AC in goat feed	C	N	P	K	C/N ratio
%	%				
0	45.2	2.5	1.4	0.8	18.1
3	51.4	2.0	1.2	0.5	25.7
5	56.7	1.9	1.1	0.5	29.8
9	60.2	1.7	0.8	0.4	35.4

3.2.2 Experimental Design

Two experiments were set up in a greenhouse for 12 weeks. In the first experiment (hereafter referred to as Exp. I), the following three fertilizer treatments were used in six replicates: (1) manure with 0% AC in goat feed (control), (2) manure with 5% AC in goat feed, and (3) manure with 9% AC in goat feed. In the second experiment (Exp. II), the following four fertilizer treatments were used in four replicates: (1) no manure (control), (2) manure with 0% AC in goat feed, (3) manure with 3% AC in goat feed, and (4) manure with 9% AC in goat feed. For all treatments, 4.2 kg dry soil was filled into glass cylinders (400 mm x 100 mm), which were taped with nylon gauze (1 mm mesh size) at the bottom to avoid soil losses.

Experiments I and II were fertilized with an equivalent to 160 kg N ha^{-1} and thus received between 6.4 t and 9.4 t of manure per hectare depending on AC treatment. Per cylinder, this accounted for 5.0 g (0% AC), 6.4 g (3% AC), 6.7 g (5% AC), and 7.2 g (9% AC) manure. In both experiments, manure treatments were filled into nylon gauze bags (65 mm ×65 mm) with a mesh size of 1 mm, and buried at 10 cm depth. Prior to the treatment application, soil and manure were analysed separately for microbial and chemical properties. From this analysis, the initial values for soil and all manure treatments were determined.

Table 2. Chemical properties of ion exchange resins used in this study.

Producer	Rohm&Haas	Rohm&Haas	Purolite
Product name	Cation exchanger Amberjet™ 1200 Na	Anion exchanger Amberjet™4200 Cl	Mixed bed resin Purolite® MB3710
Appearance	Amber spherical beads	Yellow translucent spherical beads	Spherical beads
Polymer structure	Styrene divinylbenzene copolymer		Gel polystyrene crosslinked with divinylbenzene
Exchange ions	Na^+	Cl^-	H^+/OH^- (40/60%)
Total exchange capacity	2.0 eq l^{-1}	1.3 eq l^{-1}	1.3-2.0 eq l^{-1}
Water holding capacity	43-47%	49-55%	65% (max)*

*Number given by the producer as water content, used interchangeable with water retention.

The soil cylinders were either connected to suction plates or to resin cartridges. Suction plates were entirely made of glass with filters from porous plates of sintered borosilicate (ROBU, Hattert, Germany, maximum pore width: 10 µm), similar to those of Siemens and Kaupenjohann (2004). Resin cartridges were open glass cylinders (110 mm x 100 mm) closed at the bottom with 400 µm nylon gauze. For the first experiment 0.5 M NaCl pre-treated cation-anion exchange resins (Rohm & Haas, Philadelphia, PA, USA; Siegfried et al., 2011) were mixed with silica sand at a 1:1:2 cation:anion:sand ratio and filled into the glass cartridges, while in the second experiment the treatments (2) and (4) were additionally conducted with Purolite resins (Purolite Co, Bala Cynwyd, PA, USA; 1:1 resin:sand mixture) for a comparison (Table 2). Four days after the installation of the respective experiment and every week thereafter, flood irrigation was simulated by applying demineralized water to 115% WHC (equal to approximately 470-500 ml) with Erlenmeyer flasks. At the onset of each irrigation, -100 hPa vacuum pressure was applied *via* a pump (UMS GmbH, Munich, Germany) and maintained until the water flow stopped. Leaching water was weighted upon collection and approximately 20 ml aliquots transferred to scintillation vials. The samples were immediately acidified with 32% HCl and kept frozen (-18°C) until analysis. Throughout the experiments, climatic conditions in the greenhouse cabin were regulated to 28 ± 1°C during the day and 16 ± 1°C at night with an average relative air humidity of 40%. Soil water content never dropped below 35% WHC between weekly irrigation events.

3.2.3 Analytical Methods

Litterbag analysis

After the respective 12 week duration of each experiment, all manure was removed from the litterbags and dried at 60˚C (24 h). Subsequently, manure was homogenized by grinding in a ball mill. Total C and N concentrations were determined by gas chromatography using a Vario MAX elemental analyzer (Elementar GmbH, Hanau, Germany). The concentrations of P and K were analyzed photometrically (P; U-2000, Hitachi, Tokyo, Japan) and by flame photometry (K; Flame Photometer 543, Instrumentation Laboratory, Bedford, MA, USA) in colored ash solution (32% HCl) after burning the sample in a muffle furnace (24 h, 550˚C). The decline of manure dry matter and nutrient concentrations were calculated as the remaining percentage of initial dry weight element content (Esse et al., 2001).

Soil analysis

Soil samples were collected around the litterbag and then mixed. Total C and total N of soil were determined using a Vario MAX elemental analyzer (Elementar

GmbH, Hanau, Germany). Soil organic carbon (C_{org}) was calculated as the difference between total C and CO_3-C. The latter was measured gas-volumetrically from produced CO_2 following the reaction with 1:2 diluted 32% HCl.

Soil microbial biomass

Microbial biomass C (Vance et al., 1987) and microbial biomass N (Brookes et al., 1985) were measured on fresh soil by chloroform fumigation extraction with 0.5 M K_2SO_4 and subsequent analysis of organic C and total N using a CN Analyzer (Multi N/C 2100S, Analytik Jena, Germany). Microbial biomass C was calculated as E_C/k_{EC}, where E_C is (organic C extracted from fumigated soils)-(organic C extracted from non-fumigated soils), and k_{EC} is 0.45 (Wu et al., 1990). Microbial biomass N was calculated as E_N/k_{EN}, where E_N is (total N extracted from fumigated soils)-(total N extracted from non-fumigated soils), and k_{EN} is 0.54 (Brookes et al., 1985).

Resin extraction and analysis of extracts and leachate

Upon deinstallation, the resin-sand mixture of all cartridges was separated into five layers of about 22 mm each to allow assessment of a nutrient concentration gradient within each cartridge (Bischoff et al., 1999). The layers were weighted and then frozen at -18°C until analysis. Subsequently, 5 g of each layer was taken for dry weight determination (105°C) and a subsample of 20 g was extracted according to the guidelines of TerrAquat Consultants (www.terraquat.com, Stuttgart, Germany), the patent holder of this method. DOC and TN of leaching water were detected using a CN Analyzer (Multi N/C 2100S, Analytik Jena, Germany). For the measurement of NO_3 and NH_4 concentrations, a continuous flow analyzer was used (Evolution II, Alliance Instruments, Frepillon, France). Since NH_4 concentrations were below detection limit for all measurements, it is excluded hereafter. DON was calculated as the difference between TN and NO_3-N. Dissolved P and K were measured colorimetrically by the ascorbic acid method according to Murphy and Riley (1962) on a photo-spectrometer (P; Hitachi U-2000, Hitachi Co Ltd, Tokyo, Japan) and on a flame photometer (K; Flame Photometer 543, Instrumentation Laboratory, Bedford, MA, USA), respectively. For dissolved organic P (DOP), an aliquot of the filtrate was oxidized and digested with $K_2S_2O_8$ and H_2SO_4 in a microwave (µPREP-A, MLS GmbH, Leutkirch, Germany) at 180°C for 15 minutes to receive total dissolved P (Piegholdt et al., 2013). DOP was calculated as the difference in dissolved reactive P between oxidized and un-oxidized samples (Jiao et al., 2004).

The amounts of leached DOC, NO_3-N, DON, P, and K from suction plates were calculated by multiplying the measured concentrations with the amount of leachate. The amounts of leached NO_3-N, P, and K from ion exchange resins were calculated from the concentrations of these elements measured in the extracts, and multiplied by the dry weight of resin-sand mixture per glass cartridge. Cumulative carbon and nutrient leaching losses per hectare were calculated based on the 70.9 cm^2 surface area of the glass cylinders and the glass cartridges, respectively.

3.2.4 Statistical Analysis

The results presented in the tables are arithmetic means on a dry weight basis (24 h at 60ºC) for C and N analyses of manure and soil, and 24 h at 105ºC for DW, P, and K analyses. All graphs display arithmetic means ± one standard error. Homogeneity of variances was tested using Levene’s or Brown-Forsythe tests. Significance of treatment effects was tested by ANOVA and post-hoc test statistics (Tukey HSD), if applicable. Arithmetic means were compared at a level of significance of $\alpha = 0.05$. All statistical analyses were performed using Statistica 7.0 (StatSoft GmbH, Hamburg, Germany) and SPSS 17.0 (SPSS Inc., Chicago, IL, USA). Graphs were drawn using Statistica 7.0 (StatSoft GmbH, Hamburg, Germany) and Sigma Plot (Systat Software GmbH, San Jose, USA).

3.3 Results

3.3.1 Nutrient Decomposition from Litterbags

In both experiments, dry weight losses from manure ranged between 11-30% (Exp. I) and 16-42% (Exp. II), and declined significantly with increasing AC level in goat feed (Table 3). Charcoal-enriched manure showed a decrease of dry weight losses by 16% (low AC) and 27% (high AC) in Exp. I, and by 10% (low AC) and 45% (high AC) in Exp. II as compared to manure without charcoal. In contrast, overall losses of N were minimal during the experimental periods and not affected by AC level fed. Along with the stabilization of C and the minor changes in N, the CN ratio widened significantly with increasing AC level in manure. In comparison with N, a larger percentage of P was mineralized throughout both experiments, although the breakdown of P was not significantly affected by charcoal treatment. As distinguished from the other nutrients, the decomposition of K was highest at the end of both trials with 83-87% and 87-91% of K being lost from the litterbags, respectively. However, charcoal did not affect K losses in either experiment.

Table 3. Manure decomposition from litterbags as mean percentages of initial content and CN ratio of Experiments I and II. Values in parentheses represent ± one standard error of the mean (treatment replicates Experiment I: n = 6; treatment replicates Experiment II: n = 4). Significance of treatment effects at $P < 0.05$ based on contrast tests. CV = mean coefficient of variation between replicates of one experiment. AC = activated charcoal fed to goats in % of total ration. High AC = 9%, low AC = 5% (Exp. I) or 3% (Exp. II). NS = not significant.

	DW	C	N	P	K	CN ratio
	% initial weight					
Experiment I						
Manure (% AC fed)						
0	70 (4.2)	83 (6.8)	95 (8.7)	83 (9.3)	13 (0.9)	17 (3.3)
5	81 (2.4)	98 (3.4)	91 (2.7)	86 (4.4)	17 (3.8)	28 (0.6)
9	89 (1.2)	93 (1.6)	94 (1.5)	83 (3.0)	15 (2.9)	35 (0.4)
Experiment II						
Manure (% AC fed)						
0	58 (1.3)	71 (4.7)	95 (3.7)	85 (3.5)	9 (0.5)	14 (0.5)
3	64 (3.0)	83 (1.3)	96 (3.2)	76 (13.7)	13 (2.4)	22 (0.6)
9	84 (2.0)	90 (2.8)	96 (3.0)	63 (15.2)	11 (2.4)	33 (0.4)
Contrasts						
Experiment I						
Manure -AC vs. +AC	0.012	0.109	NS	NS	NS	0.007
High AC vs. low AC	0.015	NS	NS	NS	NS	<0.001
CV (%)	13	14	13	17	45	33
Experiment II						
Manure -AC vs. +AC	<0.001	0.004	NS	NS	NS	<0.001
High AC vs. low AC	<0.001	NS	NS	NS	NS	<0.001
CV (%)	18	12	6	32	35	37

3.3.2 Soil Organic Carbon and Total Nitrogen

In neither of the two experiments did the application of charcoal-enriched manure change the contents of SOC or TN significantly from initial contents or after manure addition (Table 4). Only in Exp. II there was a 11-15% AC-induced decline in SOC from about 5.4 mg g^{-1} soil (unamended manure) to 4.8 mg g^{-1} soil (9% AC), and 4.6 mg g^{-1} soil (3% AC). Similarly, a 7-9% decline from about 0.58 mg g^{-1} soil (unamended manure) to 0.54 mg g^{-1} soil (9% AC), and 0.53 mg g^{-1} soil (3% AC) occurred in TN contents.

Table 4. Mean concentrations of soil organic carbon and total nitrogen; K_2SO_4-extractable organic carbon and nitrogen; microbial biomass carbon and nitrogen K_2SO_4 of Experiments I and II. Values in parentheses represent ± one standard error of the mean (initial concentrations before treatment application: n = 2, except for SOC and TN where n = 4; treatment replicates Experiment I: n = 6; treatment replicates Experiment II: n = 4). Significance of treatment effects at $P < 0.05$ based on contrast tests. AC = activated charcoal fed to goats in % of total ration. High AC = 9%, low AC = 5% (Exp. I) or 3% (Exp. II). Treatment = all manures. NS = not significant.

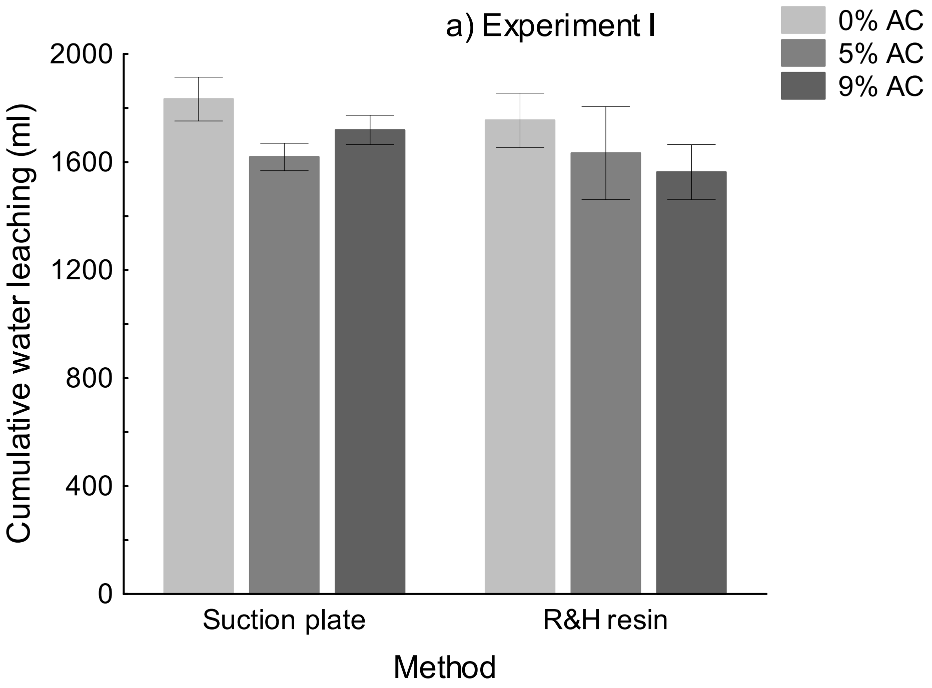
	SOC	TN	K_2SO_4-C	K_2SO_4-N	Microbial biomass C	Microbial biomass C	Microbial biomass N
	mg g^{-1} soil		*µg g^{-1} soil*	*%TN*	*µg g^{-1} soil*	*%SOC*	*µg g^{-1} soil*
Initial concentrations	4.9 (0.6)	0.56 (0.0)	104 (7.1)	4.6 (0.0)	111 (6.4)	2.3 (0.3)	6 (0.2)
Experiment I							
Manure (% AC fed)							
0	4.6 (0.1)	0.54 (0.0)	57 (2.2)	2.2 (0.1)	80 (11.1)	1.7 (0.2)	12 (0.8)
5	5.1 (0.3)	0.57 (0.0)	57 (4.2)	2.4 (0.2)	125 (24.4)	2.5 (0.5)	14 (1.2)
9	4.8 (0.2)	0.55 (0.0)	56 (2.2)	2.8 (0.2)	135 (53.9)	2.9 (1.1)	15 (1.1)
Experiment II							
Manure (% AC fed)							
control	4.5 (0.3)	0.53 (0.0)	48 (4.6)	1.7 (0.1)	98 (16.6)	2.1 (0.3)	10 (1.7)
0	5.4 (0.2)	0.58 (0.0)	51 (7.0)	1.6 (0.1)	112 (10.7)	2.1 (0.2)	13 (1.4)
3	4.6 (0.1)	0.53 (0.0)	42 (5.2)	1.2 (0.2)	144 (27.5)	3.1 (0.5)	17 (3.0)
9	4.8 (0.1)	0.54 (0.0)	44 (9.7)	1.2 (0.3)	126 (6.3)	2.6 (0.2)	15 (1.4)
Contrasts							
Experiment I							
Manure -AC vs. +AC	NS	NS	NS	0.062	NS	NS	0.022
High AC vs. low AC	NS	NS	NS	NS	NS	NS	NS
Initial vs. treatment	NS	NS	<0.001	<0.001	NS	NS	<0.001
CV (%)	11	4	12	20	73	75	20
Experiment II							
Control vs. treatment	0.127	0.086	NS	0.046	NS	NS	0.037
Manure -AC vs. +AC	0.015	0.009	NS	NS	NS	0.069	NS
High AC vs. low AC	NS	NS	NS	NS	NS	NS	NS
Initial vs. treatment	NS	NS	0.023	<0.001	NS	NS	0.008
CV (%)	10	5	28	31	30	30	33

3.3.3 Microbial Biomass Carbon and Nitrogen

Compared with the mean soil microbial biomass C of 111 µg g^{-1} before the onset of the experiments, manure application led to an only minor increase in microbial biomass C of 2% and 8%, respectively (Table 4). In both experiments, microbial biomass C was 62% (Exp. I) and 30% (Exp. II) higher in soils amended with charcoal-enriched manure compared with soils that had received pure manure. However, this numerical rise in microbial biomass C could not be confirmed statistically. Microbial biomass N was significantly higher in soils that received charcoal-enriched manure than in soils that received manure only. Also, all manure-treated soils had higher microbial biomass N contents than the original soil. Given higher levels in microbial biomass C, the microbial biomass to SOC ratio increased from 1.7% and 2.1% after manure application in the first and in the second experiment, to an average of 2.7% and 2.9% following charcoal-enriched manure application. The K_2SO_4-extractable organic C declined to about 45% in Exp. I, and to 56% in Exp. II, and was in both experiments significantly lower than initial contents in all treatments. Similarly, the proportion of K_2SO_4-extractable N to TN diminished during the experimental periods, and was significantly lower for all treatments (mean 2.5% Exp. I, 1.4% Exp. II) than the initial value (mean 4.4%).

3.3.4 Irrigation and Leaching

The experiments received a total of 4.9 l (4.9 mm m^{-2}) and 3.9 l (3.9 mm m^{-2}) irrigation water, respectively. In Exp. I, cumulative mean leaching from both suction plates and Rohm & Haas resins accounted for 1.7 l (34% of irrigation; Fig. 1a); In Exp. II, 1.6 l (41% of irrigation) leached from suction plates, and 1.2 l (31% of irrigation; Fig. 1b) from both Rohm & Haas and Purolite resins. In contrast to our expectations, charcoal-enrichment in manure (or as in the second experiment, manure application compared with the unmanured control) did not lead to differences in leaching losses. As measured in the Rohm & Haas resin percolates from both experiments, leaching tended to decrease with increasing AC level. Among the suction plate leachates in Exp. II, the control treatment had 12% more percolate (mean 1.7 l) than the mean across the fertilized soils (1.5 l).



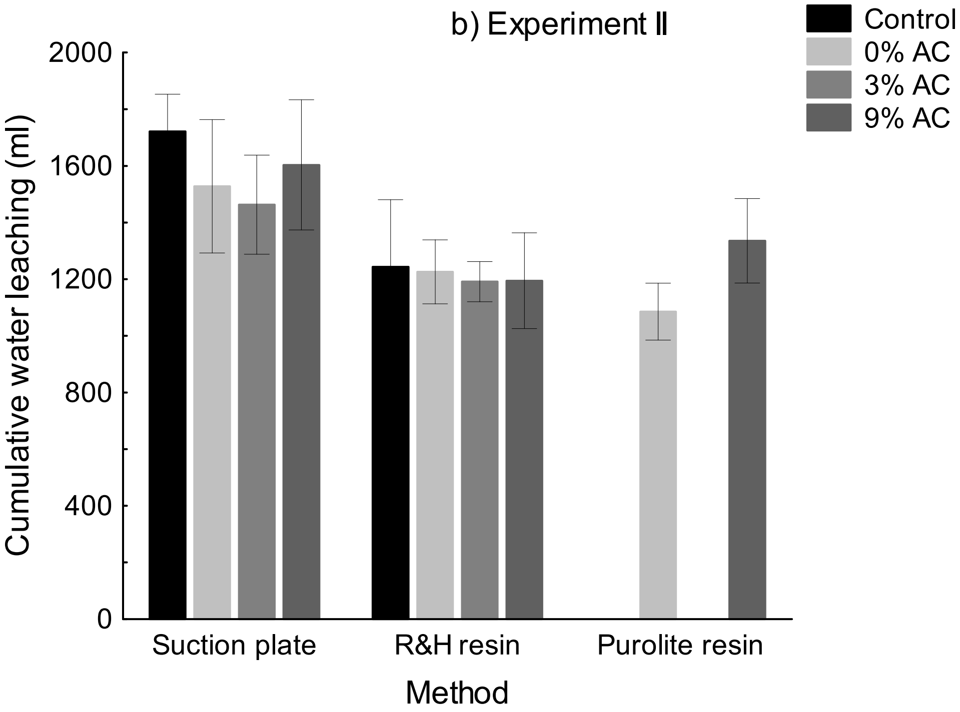


Fig. 1. Irrigation and leaching from suction plates and resins of Experiments I (a) and II (b). Vertical bars denote ± one standard error of the mean at $P < 0.05$ (n = 6 in Exp. I, n = 4 in Exp. II). AC = activated charcoal fed to goats in % of total ration.

3.3.5 Suction Plate-Derived Carbon, Nitrogen, Phosphorus, and Potassium

Leached DOC declined exponentially over 10 (Exp. I) and 12 (Exp. II) leaching events from about 35 kg to 6 kg C ha^{-1} and 28 kg to 12 kg C ha^{-1}, respectively (Fig. 2). Treatment means were not statistically different. Cumulative mean loads of DOC leaching were 203 kg, 166 kg, and 183 kg C ha^{-1} for 0%, 5%, and 9% AC from Exp. I. From Exp. II, 184 kg, 159 kg, 161 kg, and 158 kg C ha^{-1} percolated off the control, 0%, 3%, and 9% AC treatments. Average NO_3-N leaching diminished exponentially in both experiments from 65 kg to 2 kg NO_3-N ha^{-1} (Exp. I), and 84 kg to 2 kg NO_3-N ha^{-1} (Exp. II; Fig. 3). NO_3-N leaching peaked in the first weeks, with 81% (Exp. I) and 78% (Exp. II) of total NO_3-N loads (184 kg NO_3-N ha^{-1} in Exp. I; 144 kg NO_3-N ha^{-1} Exp. II) being leached after three irrigation cycles. Average cumulative mean NO_3-N leaching quantities were 162 kg, 115 kg, and 156 kg NO_3-N ha^{-1} for 0%, 5%, and 9% AC from Exp. I (Fig. 5). From Exp. II, 211 kg, 151 kg, 183 kg, and 191 kg NO_3-N ha^{-1} leached out the control, 0%, 3%, and 9% AC treatments. Similarly, DON leaching was highest in the first week with about 48 kg (Exp. I) and 12 kg DON ha^{-1} (Exp. II) and leveled off exponentially afterwards to 2 kg DON ha^{-1} in the twelfth week of both trials (Fig. 4). Treatment-specific average cumulative DON leaching amounts were 125 kg, 84 kg, and 125 kg DON ha^{-1} for 0%, 5%, and 9% AC from Exp. I, and 59 kg, 64 kg, 31 kg, and 30 kg DON ha^{-1} for the control, 0%, 3%, and 9% AC treatments from Exp. II. It thus appeared that between 42% (5% AC treatment) and 45% (9% AC treatment) of total N losses occurred as DON in Exp. I (Fig. 5a), but only between 6% (9% AC) and 17% (0% AC) of TN percolated as DON in Exp. II (Fig. 5b). For the unfertilized control, DON leaching was below detection limit. In both experiments, differences between fertilizer treatments for NO_3-N and DON records were not statistically significant. Except for the first experiment, in which significantly ($P = 0.049$) less NO_3-N leached from soils amended with the 5% AC compared to the ones with untreated manure. Likewise, no significant differences were detected for PO_4-P and K leaching derived from suction plates (data not shown). Total mean mineral P and K losses across manure treatments after twelve weeks were 1.6 ± 0.1 kg PO_4-P ha^{-1}, and 251 ± 13 kg K ha^{-1} (Exp. I) and in Exp. II, 1.2 ± 0.2 kg PO_4-P ha^{-1}, and 239 ± 28 kg K ha^{-1}. DOP made up for 64% (2.1 ± 0.1 kg DOP ha^{-1}) of TN leaching in Exp. II, whereas no detectable DOP leaching occurred in Exp. I (data not shown).

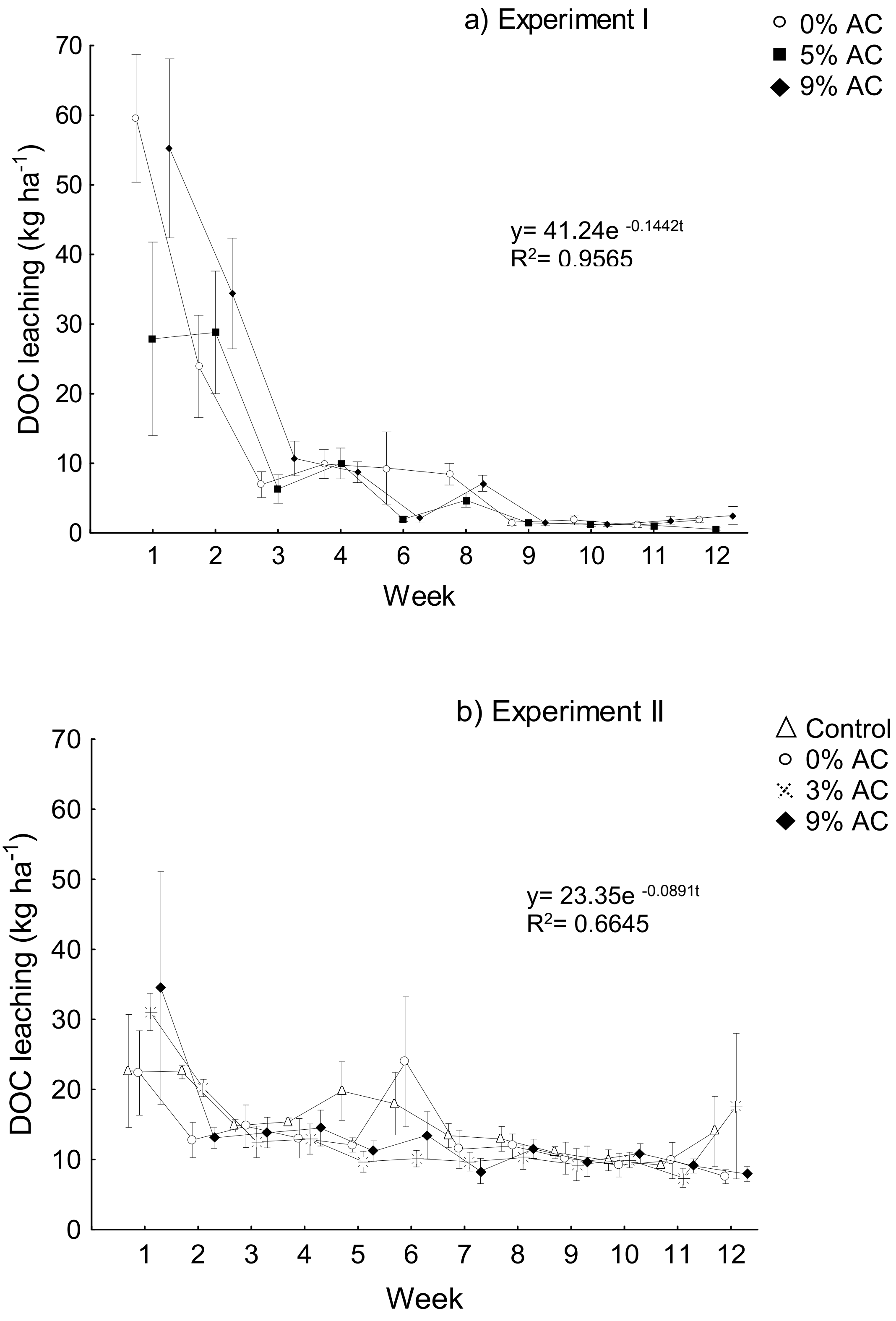


Fig. 2. DOC leaching from suction plates of Experiments **I** (a) and **II** (b). Vertical bars denote ± one standard error of the mean at $P < 0.05$ (n = 6 in Exp. **I**, n = 4 in Exp. **II**). AC = activated charcoal fed to goats in % of total ration.

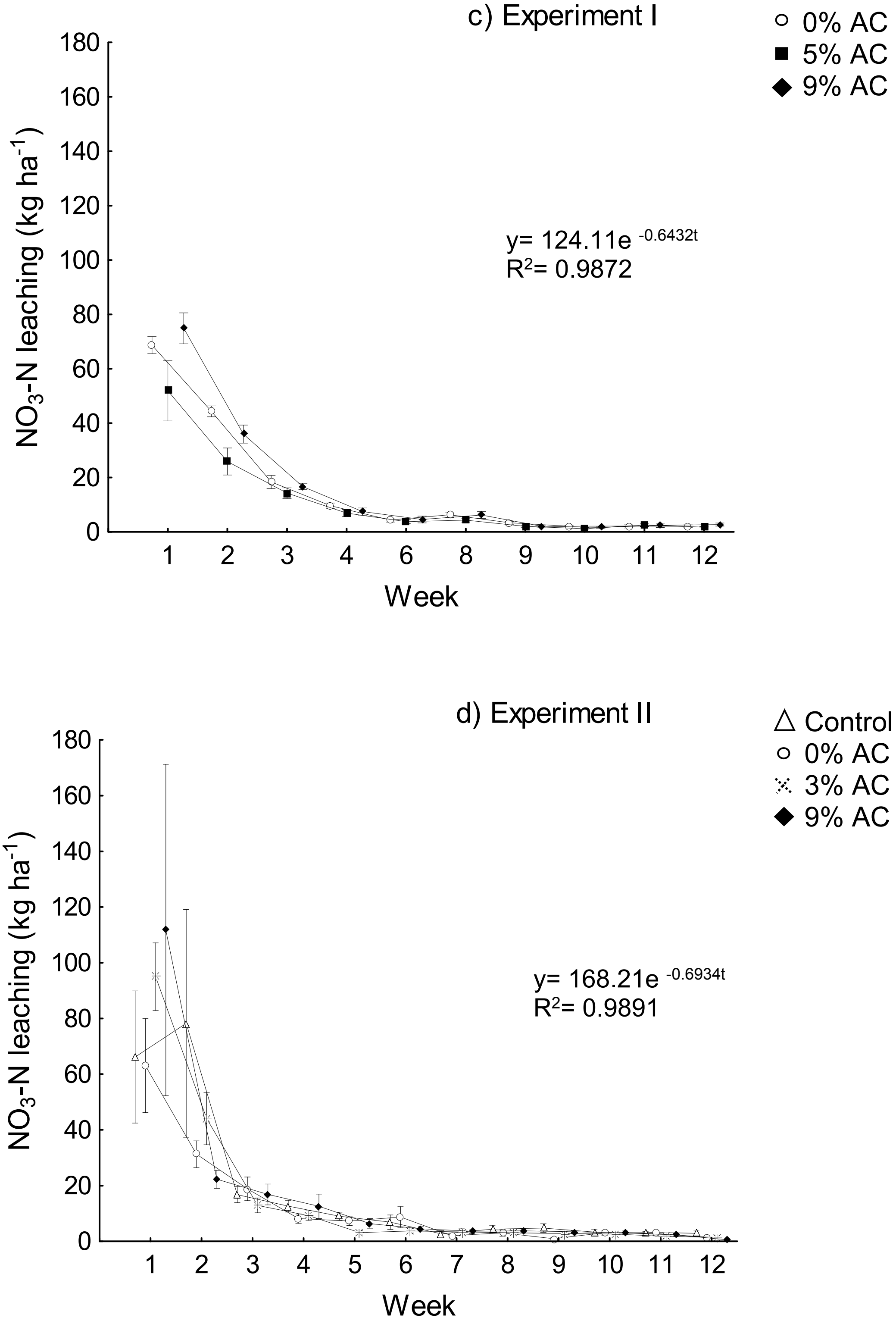
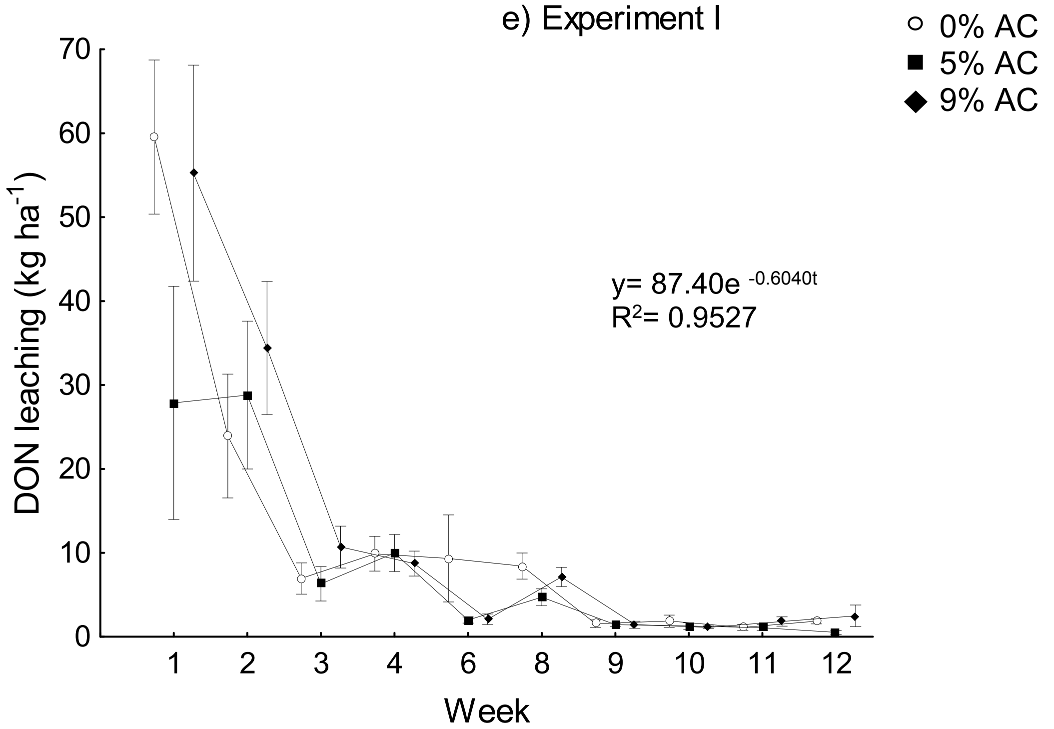


Fig. 3. NO_3-N leaching from suction plates of Experiments I (a) and II (b). Vertical bars denote ± one standard error of the mean at *P* < 0.05 (n = 6 in Exp. I, n = 4 in Exp. II). AC = activated charcoal fed to goats in % of total ration.



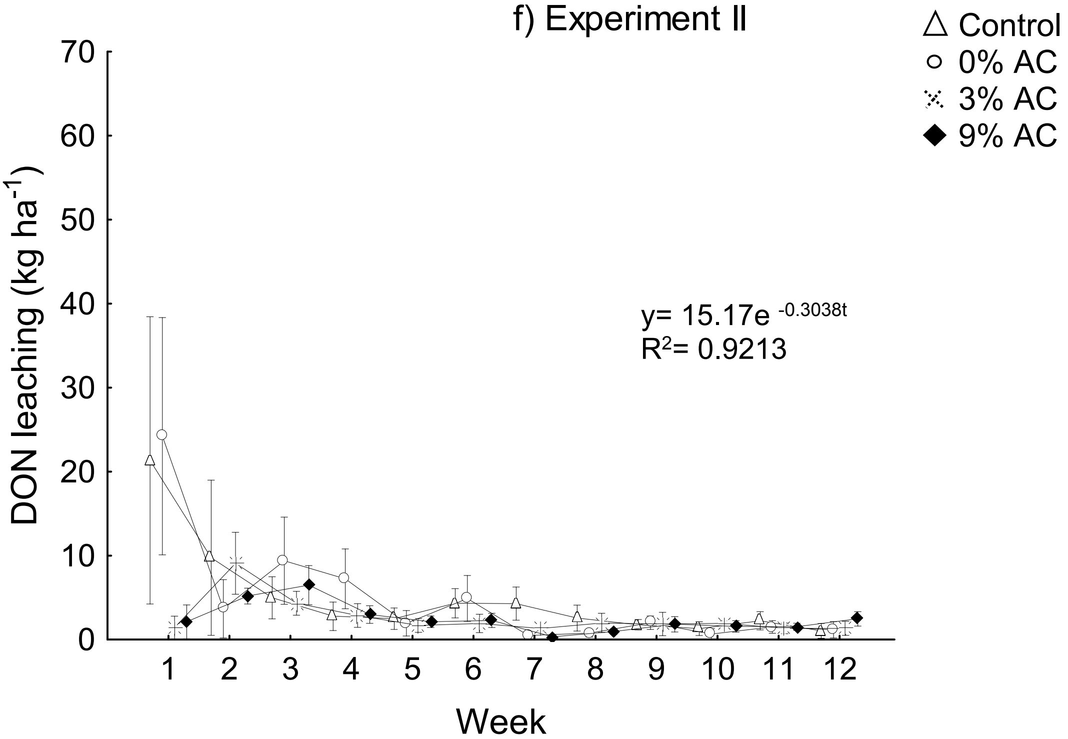


Fig. 4. DON leaching from suction plates of Experiments **I** (a) and **II** (b). Vertical bars denote ± one standard error of the mean at $P < 0.05$ (n = 6 in Exp. **I**, n = 4 in Exp. **II**). AC = activated charcoal fed to goats in % of total ration.

3.3.6 Resin-Extracted Nitrogen, Phosphorus, and Potassium

Between 81% and 100% of all nutrients were found in the first three layers, indicating the absence of preferential flow out of the cartridges (data not shown). Extractions of NO_3-N from Rohm & Haas resins yielded on average 227 kg, 236 kg, and 238 kg NO_3-N ha^{-1} for 0%, 5%, and 9% AC from Exp. I (Fig. 5a).

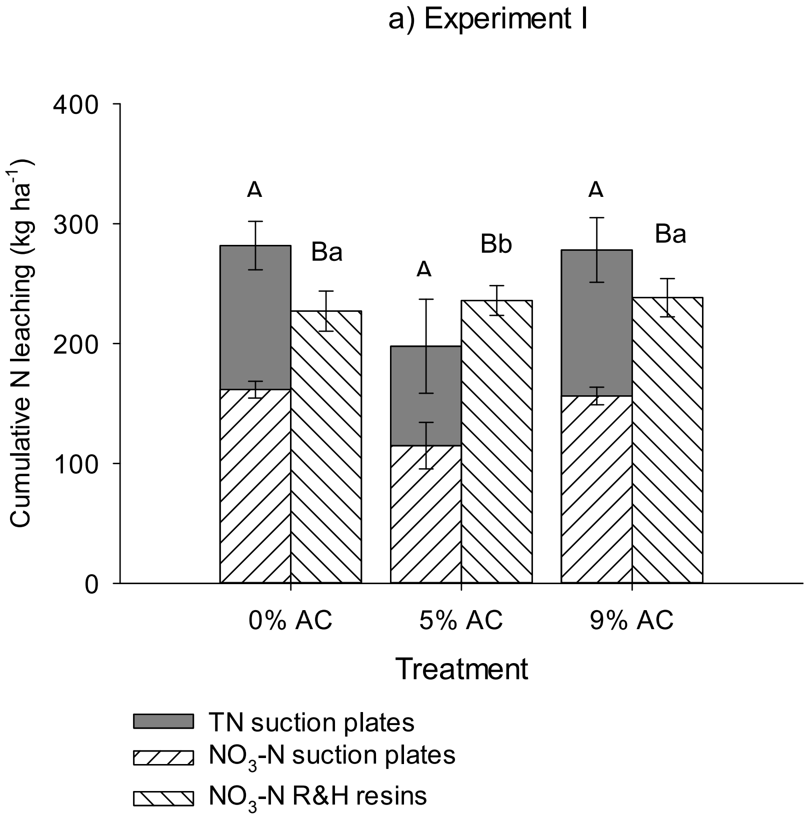
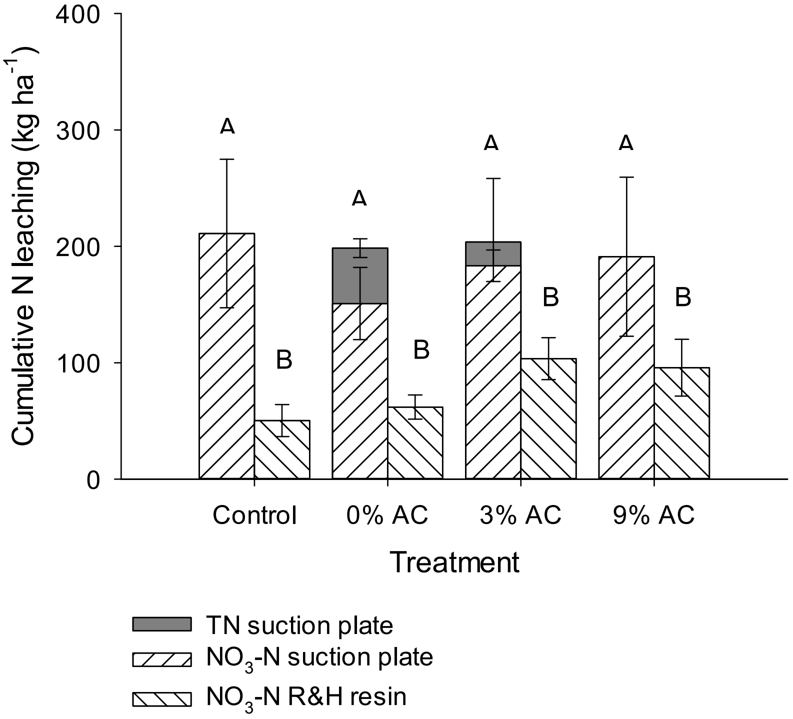


Fig. 5a. Cumulative TN and NO_3-N leaching of Experiment I. Vertical stacked bars denote ± one standard error of the mean at $P < 0.05$ (n = 6). Uppercase letters indicate significant differences between NO_3-N suction plates and NO_3-N R&H resins at $\alpha = 0.05$. Lowercase letters indicate significant differences between treatments measured with R&H resins at $\alpha = 0.05$. AC = activated charcoal fed to goats in % of total ration.

From Exp. II, 50 kg, 62 kg, 104 kg, and 96 kg NO_3-N ha^{-1} seeped through the control, 0%, 3%, and 9% AC treatments (Fig. 5b and c). Compared with NO_3-N results from suction plates, NO_3-N leaching from Rohm & Haas resins were considerably higher for all treatments in Exp. I (0%AC: P = 0.005; 5% AC: P < 0.001; 9% AC: 0.001). In Exp. II, the opposite was found: Leaching of NO_3-N was 76% (control; P = 0.049), 41% (0% AC; P = 0.035), 57% (3% AC; P = 0.012), and 50% (9% AC; P = 0.237) lower from Rohm & Haas resins than from suction plates.

b) Experiment II



c) Experiment II

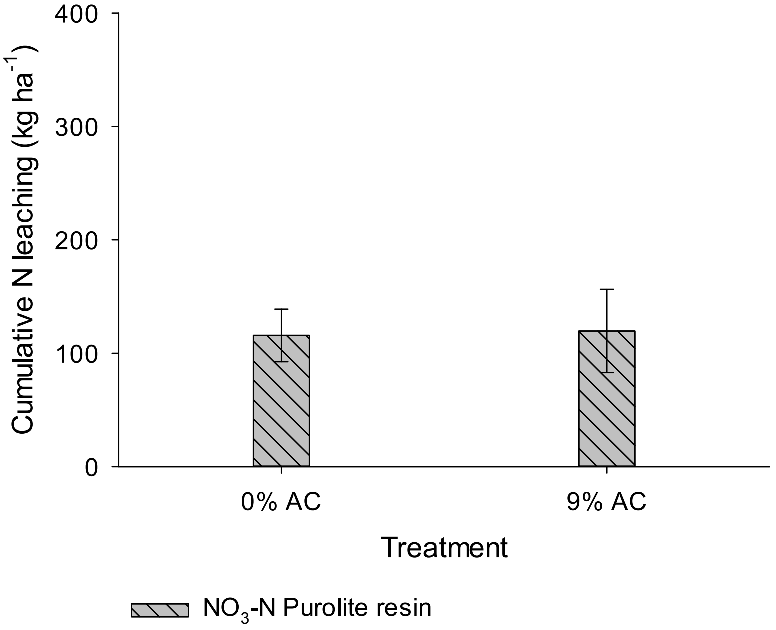


Fig. 5b and c. Cumulative TN and NO_3-N leaching of Experiment II. Vertical stacked bars denote ± one standard error of the mean at $P < 0.05$ (n = 4). Uppercase letters indicate significant differences between NO_3-N suction plates and NO_3-N R&H resins at $\alpha = 0.05$. Lowercase letters indicate significant differences between treatments measured with R&H resins at $\alpha = 0.05$. AC = activated charcoal fed to goats in % of total ration.

In Exp. II, neither of the resin (Rohm & Haas or Purolite) extracts resulted in detectable mineral P leaching. Phosphorus extracted from Rohm & Haas resins in Exp. I were 0.5 ± 0.3 kg PO_4-P ha^{-1}, yet as in Exp. II, without treatment effects. In Exp. I, P leaching from ion exchange resins was significantly lower than the respective measurements from glass suction plates for AC5% and AC 9% ($P < 0.001$), whereas K leaching was for all treatments significantly higher ($P < 0.001$) in resin extracts. In Exp. I, resin-extracted K values were 43% higher ($P < 0.001$) than the calculated K loads from suction plate percolates (mean 251 kg K ha^{-1}). Across all treatments, 54% less K was extracted from Rohm & Haas resins in Exp. II (mean 200 ± 22 kg K ha^{-1}) compared with Exp. I (mean 441 ± 25 kg K ha^{-1}, data not shown). Purolite resins showed 172 ± 7 kg K ha^{-1} and did not differ significantly from the other two methods.

3.4 Discussion

Nutrient mineralization, soil parameters, and microbial biomass

Compared to field research at the same site, the decomposition of C, N, and P was surprisingly low in our greenhouse study. In their litterbag experiment Rottmann et al. (2011) recovered at the end of a 81-day experimental period only 6% of the C, 9% of N, and 9% of P from maize straw, and 31% of the C, 53% of N, and 47% of P from canola straw. Ingold et al. (unpublished data) performed a similar trial using manure of comparable quality with and without additions of charcoal, whereby the latter was either directly mixed in or ingested by goats. After twelve weeks they obtained respective recovery values of 53 and 60% for C, 76 and 69% for N, and 65 and 66% for P. These results indicate a greater recalcitrance of ingested AC compared with the mixed-in addition of AC to manure. The differences to our results may be partly explained by a higher microbial activity in both field trials. Dying plant roots and root exudates may have supplied an additional source of energy for microorganisms. Also, the presence of meso-, and macrofauna such as termites and ants in the field trial may have contributed substantially to the decomposition of organic material and nutrient release from litterbags (Ouedraogo et al., 2004).

The organic C content in our soil was with 0.5% low compared to the 1.3% reported by Siegfried et al. (2011), and considerably lower than those found in Omani mountain oases (Wichern et al., 2004; Al Rawahi, 2012) but it corresponds to the mean SOC content of 0.4% reported for the Batinah region by Cookson and Lepiece

(1996). The total N contents in our study are between the 0.06% of Siegfried et al. (2011) and the 0.04% of Sradnick et al. (2013), and again well below the 0.5% reported by Al Rawahi (2012) from mountain oases. The reason for the differene in soil SOC and TN contents between coastal and mountain oases is likely the many centuries old history of manure application in the latter, as described by Buerkert et al. (2005, 2010). An additional factor affecting C and nutrient leaching in our column system may have been some algae growth (Metting, 1981), which we tried to prevent by covering the glass cylinders with aluminium foil. However, in most of the columns some algae were detected on the soil surface or scattered along the cylinder walls.

Microbial biomass C concentrations assessed by Wichern et al. (2004) in Omani mountain oases were much higher than our values for which we only observed a slight increase after manure addition. However, our values correspond to those of Sradnick et al. (2013) in the coastal Batinah region. In their trial, microbial biomass C and N increased after two years from an initial 106 µg g^{-1} soil to 244 µg g^{-1} after addition of charcoal-enriched manure. Thus, our data did not allow to strongly confirm our first hypothesis, although the application of charcoal-enriched manure led to numerically higher microbial biomass C and N than the application of manure alone. Sradnick et al. (2013), who reported similar findings, argued that the manure effects on the microbial community may have masked any additional charcoal effect.

Carbon and nutrient leaching

Notwithstanding increasing evidence of the importance of DOC in C cycling, only few studies have examined DOC leaching from agricultural soils (Neff et al., 2000; Neff and Asner, 2001; Ghani et al., 2007; Parfitt et al., 2009). DOC can serve as readily available substrate for soil microorganisms, leading to an increase in the mineralization of DON and a subsequent nitrification process. Consequently, the occurrence of DOC and DON is linked to each other, in addition to organic substrates such as plant residues or manure. The heterogeneity of such factors in soils explains the large variation found in DOC leaching. Ghani et al. (2010) reported DOC leaching to range from 280 kg to 1690 kg ha^{-1} based on a lysimeter study conducted in New Zealand. Also, little is known about the effect of BC or AC on leaching of DOC (Major et al., 2010; Mukherjee and Zimmerman, 2013). We hypothesized that AC-enriched manure may trigger DOC leaching as consequence of the additional C, which may get partly dissolved, but our data do not allow to substantiate this.

From the loamy high organic matter garlich (*Allium sativum* L.) planted soils of the Al Jabal Al Akhdar mountain oases, Al Rawahi (2012) reported annual N and P leaching losses of only 0.6 kg NO_3-N ha^{-1} and 0.1 kg PO_4-P ha^{-1} following goat manure applications at annual rates of 37-47 t DM ha^{-1}. These cumulative leaching losses are small compared with those from lowland sandy soils reported by Siegfried et al. (2011). They reported NO_3-N leaching to range from 10 to 56 kg ha^{-1} and PO_4-P from 6 to 10 kg ha^{-1} for a 24 month period after buffalo manure applications of 6 to 12 t DM ha^{-1}. Ion exchange resin-derived leaching data from heavily fertilized sandy urban garden soils in Niamey, Niger, showed respective mineral N and P leaching losses of 7 kg NO_3-N ha^{-1} and 0.7 kg PO_4-P ha^{-1} at a total precipitation of 425 mm and average ambient temperature of 30°C (Predotova et al., 2011). In contrast, Safi et al. (2011) measured leaching losses via ion exchange resins of up to 205 kg NO_3-N ha^{-1} and 10 kg PO_4-P ha^{-1} from sandy soils in Kabul, Afghanistan. In contrast to the field studies, our greenhouse experimental setup did not account for plant nutrient uptake, horizontal water discharge, and preferential flow phenomena along aggregate boundaries or soil cracks. Finally, sieving the soil (<2 mm) may have led to a redistribution of nutrients within the surface soil, as well as to a different water retention capacity as compared to an undisturbed soil, which ultimately resulted in a rapid removal of dissolved nutrients.

The contribution of organic N to total N leaching varies greatly in the literature. In general, DON is formed as part of the decomposition process (van Kessel, 2009) and consists of a complex mixture of compounds of which the mobile, recalcitrant fractions are prone to leaching depending on rainfall amount or irrigation frequency, organic matter content, and soil texture (Neff et al., 2003). Results from field studies indicate that 6 to 21% (6 to 10 kg DON ha^{-1}) of total N may be leached as DON (Siemens and Kaupenjohann, 2002), but up to 28% (13 kg DON ha^{-1}) were reported by van Kessel et al. (2009). In a lysimeter study conducted by Barton et al. (2005) even up to 87% (151 kg N ha^{-1}) of total N were leached as DON on soils irrigated with 2300 mm yr^{-1} of domestic effluents. In particular for DOC, NO_3-N, and DON leaching, we observed a 'priming effect' where the first irrigation events seem to have initiated a boost in microbial activity which led to a fast mineralization of soil organic matter, resulting in highest leaching rates of labile C and N in the first experimental weeks (Kuzyakov et al., 2000). Our results show that DOP is an important form of P leaching, as it is more mobile in soils than inorganic P. The findings of Exp. II are in range with observations of Chardon et al. (1997) who reported a 70 to 90%

contribution of DOP to total P leaching. However, we could not confirm the expected reduction in nutrient leaching with AC-enrichment of manure. Likely, the AC concentrations used in our study were too low to mediate the effects of pure manure additions, or the quality of the AC itself may not be suited to improve nutrient retention sufficiently.

Effects of collection devices on leaching estimates

Both of our experiments yielded contradicting results for NO_3-N, PO_4-P, and K leaching losses from suction plates and ion exchange resins which support the few available results in the literature. Siegfried et al. (2011) compared cumulative NO_3-N leaching with suction plates made of silicon carbide (UMS GmbH, Munich, Germany) and Rohm & Haas resins in a field trial. They found that mineral N leaching derived from suction plates was several-fold larger than from resin extracts. In a tracer study conducted by Siemens and Kaupenjohann (2004), only 6% of the applied Cl^- was recovered by exchange resins (Amberlite MB 20, Rohm & Haas, Philadelphia, USA), which was significantly less than the 107 to 118% recovery with suction plates of sintered borosilicate glass (ROBU, Hattert, Germany). They assumed that fiberglass pads as an additional interface between resin box and soil caused the low recovery rates. This may explain why Bischoff et al. (1999) who installed the resin boxes without fiberglass pads found recovery rates to vary from 60 to 120%. Compared to these results, we detected 162% of N, 31% of P, and 176% of K of the suction plate filtrates in the resin extracts of the first experiment. A total of 42% N and 84% K, and 64% N and 72% K of the suction plate filtrates were recovered from Rohm & Haas resin extracts and Purolite resin extracts, respectively, whereas no P was found in extracts from both resin types in Exp. II. Overall, leaching estimates were similar for the two resin types (Exp. II), indicating that both are suitable for such leaching studies, but such comparisons merit further research.

3.5 Conclusions

Compared to field experiments, mineralization of C and N from manure during our 12 week soil column experiments were surprisingly small. This may largely be the consequence of the absence of the naturally diverse decomposer community, including meso- and macrofauna typically present in field experiments. Also in our study the soil-manure contact was limited by the nylon mesh of the litterbags, which additionally impeded microbial contact with the manure. As a consequence, AC enrichments could not unfold their repeatedly stated potential in reducing leaching losses by improving soil physico-chemical properties. Based on our results, suction plates deliver satisfactory results for mineral and organic nutrient forms, however they require great efforts in handling. The significant differences in leaching loads between suction plates and ion exchange resins merit further research. This may want to focus on overcoming limitations of *in situ* leaching measurements, and investigate dissolved organic matter fluxes in detail as ongoing C and N losses may have detrimental effects on soil moisture and nutrient retention, microbial activity, and aggregate stability, which ultimately leads to a breakdown in soil fertility.

Acknowledgements

The technical assistance of Eva Wiegard and Claudia Thieme is highly appreciated. We are also thankful to Dr. Herbert Dietz and Royal Court Affairs, Sultanate of Oman, for their essential support, and to the German Research Foundation (DFG) for funding this project within the Graduate Research Training Group 1397 'Regulation of Soil Organic Matter and Nutrient Turnover in Organic Agriculture'.

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4 Effects of Charcoal-Enriched Goat Manure on Soil Fertility Parameters and Growth of Millet (*Pennisetum glaucum* L.) in a Sandy Soil from Northern Oman

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Abstract

The effect of charcoal feeding on manure quality and its application to enhance soil productivity has received little attention. The objectives of the present study therefore were to investigate the effects of (i) charcoal feeding on manure composition, and (ii) charcoal-enriched manure application on soil fertility parameters and growth of millet (*Pennisetum glaucum* L.). To this end, two trials were conducted: First, a goat feeding trial where goats were fed increasing levels of AC (3, 5, 7, and 9% of total ration); secondly, a greenhouse pot experiment using the manure from the feeding trial as an amendment for a sandy soil from Northern Oman. We measured manure C, N, P, and K concentrations, soil fertility parameters and microbial biomass indices, and plant yield and nutrient concentrations. Manure C concentration increased significantly ($P < 0.001$) from 45.2% (0% AC) to 60.2 (9% AC) with increasing dietary AC, whereas manure N, P, and K concentrations decreased ($P < 0.001$) from 0% AC (N: 2.5%, P: 1.5%, K: 0.8%%) to 9% AC (N: 1.7%, P: 0.8%, K: 0.4%). SOC, pH, and microbial biomass N showed a response to AC-enriched manure. Yield of millet decreased slightly with AC enrichment, whereas K uptake was improved with increasing AC. We conclude AC effects on manure quality and soil productivity depend on dosage of manure and AC, properties of AC, trial duration, and soil type.

Keywords: Activated charcoal, Goat manure, Microbial biomass C, SOC, Subtropical soils.

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4.1 Introduction

Under the arid subtropical conditions of the Batinah region in Northern Oman, regular additions of organic soil amendments such as manure and compost, and careful irrigation management are determining soil productivity and sustainability of cropping systems. It is well known that microbial activity, and consequently soil organic matter (SOM) turnover, is strongly affected by wet-dry cycles (Lundquist et al., 1999a and b). High microbial turnover is often reflected in rapid decomposition of organic matter (OM) followed by a breakdown of soil fertility (Ghoshal and Singh, 1995; Zech et al., 1997; Wichern et al., 2004). One possibility to counteract soil organic matter decay under year-round conditions of high mineralization is the exploitation of the *terra preta* concept (Glaser et al., 2001 and 2002), adding charred organic material to the soil. Key features of biochar (BC) amended soils are: higher levels of SOM, enhanced nutrient retention capacity, and higher moisture holding capacity than in the surrounding soils (Glaser et al., 2001; Lehmann and Rondon, 2006; Liang et al., 2006). However, in order to substantially affect the aforementioned physico-chemical soil parameters, large quantities of charred material are needed, particularly in view of possible losses through wind and water erosion. Also, there is still little knowledge about the nutrient release dynamics from biochars applications. In many cases it is unclear whether BC is benefiting plants by providing nutrients or inhibiting plant growth by sequestering them (Mukherjee et al., 2013). In contrast to BC, activated carbon or charcoal (AC) is a homogeneous, technically refined type of BC with effects on soil properties similar to those of BC (Lehmann and Rondon, 2006; Braendli et al., 2008). AC is produced from coal, peat, bamboo, coconut shells or other organic materials by incomplete combustion followed by steam activation (Braendli et al., 2008). It is used as a strong sorbent for a wide range of organic compounds in many different applications such as gas and water purification, medicine, sewage treatment, and air filters (Norit Americas Inc., 2006). It is well documented that BC or AC can be used effectively as a gastrointestinal absorbent for treating forage-induced intoxications such as mycotoxins (Buck and Bratich, 1986; Huwig et al., 2001). Positive effects on feed intake and nutrient utilization were also reported for animals feeding on low quality forages containing compounds such as alkaloids, phenols, and terpenes (Banner et al., 2000; Poage et al., 2000; Rogosic et al., 2006). However, so far BC studies primarily addressed effects of BC addition to soils (Glaser et al., 2002; Lehmann and Rondon, 2006), whereas little is known about the effect of AC as feed additive on manure quality, and how ingested, manure-bound AC affects soil properties, C sequestration, and plant growth. Recent results by Ingold et al. (2011) suggest that charcoal-enriched manure has a greater recalcitrant capacity than AC mixed with faeces outside the animal. Moreover, manure-bound AC seems better suited for no-till applications as it is less likely to disintegrate and erode from soil if bound to a carrier.

The objectives of this study consisting of a goat feeding trial followed by a greenhouse pot experiment were (i) to determine if large amounts of AC fed daily to goats have negative effects on animal performance and how ingested AC affects the nutrient composition of the manure, and (ii) to measure AC- manure effects on soil soil microbial biomass, nutrient and water retention capacities, and growth of a test crop.

4.2 Material and Methods

4.2.1 Soil Collection and Characterization

Soil (0-40 cm) was collected from a private experimental farm (24°20’ N, 56°46’ E) located at the northeastern Batinah coast of the Sultanate of Oman (Siegfried et al., 2013). The soil was classified as a mixed hyperthermic typic Torrifluvent (US Soil Taxonomy) deriving from recent fluviatile wadi deposits with a gravel-rich subsoil and partly coverage by aeolian sand veneers (Al-Farsi, 2001). The soil had a coarse texture (82% sand, 16% silt, 2% clay), a pH_{H2O} of 8.5, a bulk density of 1.44 g cm^{-3}, a total C content of 12.7 g kg^{-1}, an organic C content (C_{org}) of 4.9 g kg^{-1}, a total N content of 0.6 g kg^{-1}, a $CaCO_3$ content of 6.5%, a CN ratio of 21.2, an Olsen P of 0.04 g kg^{-1}, and $K_{(CAL)}$ of 0.26 g kg^{-1}. Before the experiment started, the soil was air dried, sieved (< 2 mm), and shipped to Germany.

4.2.2 Experimental Design

Goat feeding and manure collection

Manure was derived from a feeding trial with four male boer goats (*Capra aegragrus hircus* L.; 22.8 ± 3.9 kg) conducted at the Department of Animal Sciences, University of Goettingen. In this trial, increasing levels of AC (0, 1.5, 3, 5, 7, 9% of total diet, dry matter basis) were offered together with concentrate feed, and effects on feeding behavior and goat's health and faecal excretion patterns were observed over six 14-day-periods (Quaranta et al., 2013). To this end, the goats were kept in individual cages and fed twice per day with a mixture of 50% hay (*Lolium perenne* L.) and 50% concentrate, while hay was offered after concentrate was completely taken in. Concentrate was composed of 35% barley, 35% wheat, 15% rapeseed extraction meal, and 15% sugar beet molasse chips. AC powder was mixed with the ground ingredients at 0 (control), 3, 6, 10, 14, and 18% level (corresponding to 0, 1.5, 3, 5, 7, and 9% of total diet, dry matter basis) and pressed into pellets. AC powder was manufactured from coconut shells followed by steam activation (AquaSorb® CP1, Jacobi Carbons Service GmbH, Premnitz, Germany) and contained 92.1% C, 0.1% N, 0.03% P, and 0.8% K. It had a pH of 9.1, a particle size of 44 µm, a surface area of 1050 m^2 g^{-1}, and a total pore volume of 0.62 g cm^{-3}. Feed quantity was administered at 1.5 times energy maintenance requirements and adjusted every two weeks according to goats' weight gain. Feeding behavior (consumption rate, refusals) and manure characteristics (color, odor, consistency) were observed during the first five days of each period. At days 8 to 10 of each 14-day-period, goats were equipped with faecal collection bags, which were attached by harnesses. The complete amount of manure in the collection bags was sampled twice daily before each feeding, weighted and stored immediately at -20°C.

Greenhouse trial

The following five treatments of the feeding trial were carried out in six replicates in a greenhouse for 12 weeks: (i) manure with 0% AC in goat feed (control), (ii) manure with 3% AC in goat feed, (iii) manure with 5% AC in goat feed, (iv) manure with 7% AC in goat feed, and (v) manure with 9% AC in goat feed. In the following, these treatments will be referred to as AC 0 (or control), AC 3, AC 5, AC 7, and AC 9, respectively. For capacity reasons, treatment 1.5% AC was not used in the greenhouse trial.

For all treatments, 4.2 kg dry soil was filled into respective PVC pots (17.5 cm diameter, 22 cm height). The experiment was fertilized equivalent to 160 kg N ha^{-1} and thus received between 6.4 t (AC 0) and 9.4 t (AC 9) of manure per hectare depending on the AC treatment. Per pot, this amounted to 15.3 g (AC 0), 19.5 g (AC 3), 20.6 g (AC 5), 21.0 g (AC 7), and 22.1 g (AC 9) manure. Prior to the treatment application, soil and manure were analysed separately for microbial and chemical properties. From this analysis, the initial values for soil and all manure treatments were determined. Two days before planting, the water content was adjusted to 40% of WHC, which was gravimetrically controlled and adjusted every third to fourth day throughout the experiment, so that the water content remained at > 35% of WHC. One day before planting, the manure treatments were buried at 5 cm soil depth. In each pot, ten seeds of millet (*Pennisetum glaucum* L.) were sown at 2 cm depth, and thinned to four seedlings nine days later. Climatic conditions were regulated to 28 ± 1°C during the day and 16 ± 1°C during the night with a 12/12 h day/night light regime and a light summation per day of at least 120 klx. The pots were re-randomized every fourth day throughout the duration of the trial.

4.2.3 Analytical Methods

Manure nutrient contents and faecal scores

Upon thawing, manure samples were oven dried to constant weight at 60°C for 24 h and ground with a ball mill, then homogenized and analyzed for C and N contents using a Vario MAX elemental analyzer (Elementar GmbH, Hanau, Germany). The concentrations of P and K were analyzed photometrically (P; Hitachi U-2000, Hitachi Co Ltd., Tokyo, Japan) and by flame photometry (K; Instrument Laboratory 543, Bedford, USA) in colored ash solution (32% HCl) after burning the manure in a muffle furnace (550˚C, 24 h; Murphy and Riley, 1962). Organic matter was calculated as difference between dry weight (105˚C, 24 h) and ash content of a sample. Faecal scores for characterizing physical and sensory appearance of AC-enriched manure were obtained by evaluating three factors (Table 1).

Table 1. Faecal scores used to characterize the different manure types.

Consistency		Color		Odor	
1	Diarrhea	1	Light	1	Mild
2	Soft	2	Normal	2	Normal
3	Normal	3	Dark	3	Strong
4	Hard	4	Very dark/black		

Soil organic carbon and total N of soil

Before any soil samples were taken, plant roots were thoroughly removed. Total C and N of soil was determined by gas chromatography after dry combustion to CO_2 and N_2 using a Vario Max CN analyzer (Elementar GmbH, Hanau, Germany). Carbonate (CO_3^-) was measured gas-volumetrically after addition of 1:2 diluted 32% HCl. Soil organic carbon was calculated as difference between total C and CO_3-C.

Microbial biomass indices

Microbial biomass C (Vance et al., 1987) and microbial biomass N (Brookes et al., 1985) were measured on fresh soil by chloroform fumigation extraction with 0.5 M K_2SO_4 and subsequent analysis of organic C and total N using a CN Analyzer (Multi N/C 2100S, Analytik Jena AG, Jena, Germany). Microbial biomass C was calculated as E_C/k_{EC}, where E_C is (organic C extracted from fumigated soils)-(organic C extracted from non-fumigated soils), and k_{EC} is 0.45 (Wu et al., 1990). Microbial biomass N was calculated as E_N/k_{EN}, where E_N is (total N extracted from fumigated soils)-(total N extracted from non-fumigated soils), and k_{EN} is 0.54 (Brookes et al., 1985).

Soil physico-chemical parameters

Soil pH (H_2O) was measured using a glass electrode at a 1:2.5 soil-to-water ratio. WHC of the soil was calculated as gravimetrical difference following complete saturation with deionized water and subsequent drying (105˚C, 24 h). For the determination of cation exchange capacity (CEC), 2.5 g soil were saturated with 30 ml 0.1 M $BaCl_2$ buffered (pH 7) solution and shaken for 2 h. Then, samples were centrifuged (Centrikon T-124, Kontron Instruments, Milan, Italy) at 9000 rpm for 15 minutes, and filtered through a black band filter. K and Na were measured according to Murphy and Riley (1962) on a flame photometer (Flame Photometer 543, Instrumentation Laboratory, Bedford, MA, USA). Concentrations of Ca, Mg, and Al were measured by atomic absorption spectrometry (AAS 906AA, GBC Scientific Equipment, Melbourne, Australia). CEC was calculated as the sum of the exchangeable cations (K, Na, Ca, Mg, Al) and expressed in cmol kg^{-1}.

Plant nutrient uptake and biomass yield

In the fifth, sixth, seventh, ninth, tenth, and twelfth week after planting, shoot height was measured by stretching the longest leaf. Upon harvest, plants were cut above soil surface, dried (60°C, 24 h), and ground with a ball mill. While a subsample was analyzed for total C and N with a Vario MAX elemental analyzer (Elementar, Hanau, Germany). Subsequently, 1.5 g dry matter was ashed in a muffle furnace (550˚C, 24 h) and dissolved in concentrated HCl for colorimetric analysis of P and K using the ascorbic acid method described by (Murphy and Riley, 1962). Shown are mean values per pot (n = 4 plants pot^{-1}) on DW basis (105°C, 24 h) for plant biomass, shoot height, and nutrient concentrations.

4.2.4 Statistical Analysis

Significance of treatment effects was tested by analysis of variance (ANOVA) and post-hoc test statistics (Tukey HSD for manure and soil parameters, LSD for plant parameters). Arithmetic means were compared at a level of significance of α = 0.05. All statistical analyses and graphs were performed using the statistic softwares Statistica 7.0 (StatSoft GmbH, Hamburg, Germany), SPSS 17.0 (SPSS Inc., Chicago, IL, USA) and Sigma Plot (Systat Software Inc., San José, CA, USA).

4.3 Results

4.3.1 Manure Quality and Faecal Scores

Based on feeding behavior observations, intake of concentrate was not affected by AC concentration (Quaranta et al., 2013). Percentage of manure C increased significantly with the amount of AC fed to goats while N and P concentrations steadily decreased (Table 2).

Table 2. Mean carbon and nutrient contents of goat manure from the feeding trial with AC (n = 2). Values in parentheses represent ± one standard error of the mean. Significance of treatment effects at *P* < 0.05 based on contrast tests. CV = mean coefficient of variation between replicates of one column. AC = activated charcoal fed to goats in % of total ration. High AC = 9%, low AC = 3%.

AC in goat feed %	C	N	P	K	CN ratio
	%				
0	45.2 (0.1)	2.5 (0.1)	1.5 (0.0)	0.8 (0.0)	18 (0.3)
3	51.4 (0.0)	2.0 (0.0)	1.2 (0.0)	0.5 (0.1)	26 (0.3)
5	56.7 (0.1)	1.9 (0.0)	1.1 (0.1)	0.5 (0.0)	30 (0.4)
7	57.9 (0.2)	1.8 (0.0)	1.0 (0.1)	0.7 (0.0)	32 (0.0)
9	60.2 (0.5)	1.7 (0.0)	0.8 (0.0)	0.4 (0.0)	35 (0.1)
Contrasts					
Manure -AC vs. +AC	<0.001	<0.001	<0.001	<0.001	<0.001
High AC vs. low AC	<0.001	0.006	0.002	0.175	<0.001
CV (%)	10	15	23	28	22

The increase in C and decline in N resulted in a widened CN ratio with rising AC levels in the goat feed. Manure K concentration was significantly lower in AC-manure compared with the control. AC addition to the feed also affected manure consistency, color, and odor (Table 3).

Table 3. Mode faecal scores of goat manure from the feeding trial with AC (n = 6). AC = activated charcoal fed to goats in % of total ration.

	AC in goat feed (%)				
	0	3	5	7	9
Consistency	3	3	4	4	4
Color	2	3	3	3	4
Odor	2	1	1	1	1

Consistency: 1 Diarrhea, 2 Soft, 3 Normal, 4 Hard.
Color: 1 Light, 2 Normal, 3 Dark, 4 Very dark/black.
Odor: 1 Mild, 2 Normal, 3 Strong.

4.3.2 Soil Physico-Chemical Parameters

Irrespective of AC treatment, manure addition to the soil did not affect SOC concentrations (Table 4).

Table 4. Mean concentrations of soil organic carbon and total nitrogen; CN ratio, water holding capacity (WHC) and cation exchange capacity (CEC). Values in parentheses represent ± one standard error of the mean (initial concentrations before treatment application: n = 4; treatment replicates: n = 4). Significance of treatment effects at *P* < 0.05 based on contrast tests. CV = mean coefficient of variation between replicates of one column. AC = activated charcoal fed to goats in % of total ration. High AC = 9%, low AC = 3%. Treatment = all manures. NS = not significant.

	SOC	TN	CN ratio	WHC	CEC	pH
	mg g^{-1} soil			*%*	*cmol kg^{-1} soil*	
Initial concentrations	4.9 (0.6)	0.6 (0.0)	21 (0.7)	32 (2)	9.7 (0.3)	8.5 (0.0)
Manure (% AC fed)						
0	3.7 (0.8)	0.5 (0.0)	22 (0.8)	33 (3)	10.2 (0.2)	8.5 (0.0)
3	4.3 (0.3)	0.5 (0.0)	22 (0.4)	33 (3)	10.2 (0.1)	8.4 (0.0)
5	4.6 (0.8)	0.5 (0.0)	23 (0.2)	33 (2)	10.2 (0.1)	8.3 (0.0)
7	5.9 (0.8)	0.6 (0.0)	23 (0.1)	35 (2)	9.6 (0.2)	8.4 (0.0)
9	6.2 (0.5)	0.6 (0.0)	23 (0.3)	40 (1)	10.0 (0.2)	8.3 (0.1)
Contrasts						
Initial vs. treatment	NS	NS	NS	NS	0.073	0.001
Manure -AC vs. +AC	0.040	0.062	NS	NS	NS	0.004
High AC vs. low AC	0.050	0.092	NS	0.044	NS	NS
CV (%)	31	12	4	14	4	1

By the end of the trial, however, the SOC concentration in soils treated with AC-enriched manure was significantly higher than in soils which received manure without dietary AC. In contrast, soil TN concentrations remained constant with only marginal increases for the two highest AC treatments. Consequently, the soil CN ratio tended to increase with increasing AC feed. Water holding capacity tended to increase with AC-enriched manure. The increase of the average WHC from the initial soil to the soils amended with the two lower AC treatments (3 and 5) was 1%, and statistically not significant. However, in the soils of the two higher AC treatments (7 and 9) WHC increased by 3 and 8% as compared to the initial soils' WHC; and by 2 and 7% as compared to the soils that received unamended manure. CEC dropped by 2% in soils treated with AC 9 manure, and by 6% in soils treated with AC 9 manure. However, compared to the initial soils' CEC (before treatment application, 9.7 cmol kg^{-1}), average CEC was still slightly higher (10 cmol kg^{-1}) in soils treated with AC 9 manure. There was no difference in pH level between the initial soil and the soil that received unamended manure (both pH 8.5), but pH was significantly lower in soils that were treated with AC-enriched manure than in soils that received manure only.

4.3.3 Soil Microbial Biomass

AC-enriched manure applications did not affect microbial biomass C (Table 5). Compared to the initial value, mean microbial biomass C concentrations were nevertheless higher in all manure amended soils, except for soils that received AC 5 manure, where microbial biomass C was slightly lower than in the initial soil (4%) and considerably lower than in all other fertilized soils (26%). Microbial biomass N was significantly higher in all manure treated soils than before manure application. With increasing manure AC levels, microbial biomass N decreased by 36% from 28 µg g^{-1} (AC 3) to 18 µg g^{-1} (AC 9). The ratio of microbial biomass C to SOC indicated an increase from initially 2% to 3% in the soils of the AC 5 and AC 7 treatments, respectively, and declined in the soils of the AC 9 treatment again to about 2%. The contribution of K_2SO_4-extractable N to total N decreased during the 12 weeks of the experiment from 4.6% to 2.3% and was lowest in the two higher AC treatments (AC 7 and 9).

Table 5. Mean concentrations of K_2SO_4-extractable organic carbon and nitrogen; microbial biomass carbon and nitrogen. Values in parentheses represent ± one standard error of the mean (initial concentrations before treatment application: n = 2; treatment replicates: n = 4). Significance of treatment effects at $P < 0.05$ based on contrast tests. CV = mean coefficient of variation between replicates of one column. AC = activated charcoal fed to goats in % of total ration. High AC = 9%, low AC = 3%. Treatment = all manures. NS = not significant.

	K_2SO_4-C *µg g⁻¹ soil*	K_2SO_4-N *%TN*	Microbial biomass C *µg g⁻¹ soil*	Microbial biomass C *%SOC*	Microbial biomass N *µg g⁻¹ soil*
Initial concentrations	104 (7)	4.6 (0.0)	111 (6)	2.3 (0.3)	6 (0.2)
Manure (% AC fed)*					
3	74 (6)	n.d.	158 (32)	n.d.	28 (4)
5	89 (5)	2.8 (0.6)	107 (19)	3.0 (0.8)	20 (6)
7	99 (5)	2.1 (0.2)	148 (37)	3.2 (1.3)	20 (4)
9	88 (2)	2.1 (0.3)	125 (14)	1.9 (0.1)	18 (1)
Contrasts					
Initial vs. treatment	0.020	0.002	NS	NS	0.024
High AC vs. low AC	0.056	n.d.	NS	n.d.	NS
CV (%)	12	35	39	64	41

*Values for 0% AC are missing. n.d.= not determined. NS = not significant.

4.3.4 Plant Growth and Nutrient Concentrations

The effect of AC-enriched manure on plant growth, measured as shoot height throughout the experiment, is shown in Fig. 1. No significant differences were found for millet after twelve weeks. Nevertheless, towards the end of the experiment plants from the AC-enriched manure treatments showed a slightly smaller growth compared to plants amended with control manure. Plant aboveground biomass yield was on average 8.4 g on dry weight basis and unaffected by AC-manure (Fig. 2). Nitrogen concentrations in plant material ranged between 5.1 (AC 3) and 6.4 mg g DM^{-1} (AC 5) and did not significantly differ between manure treatments (Fig. 3a). Plant P concentration was with 4.3 ± 0.7 mg P g DM^{-1} highest for the AC 3 manure treatment and lowest in plants fertilized with AC 0 manure (3.6 ± 0.2 mg g DM^{-1}) and AC 9 enrichment (3.7 ± 0.1 mg g DM^{-1}), but these differences were not statistically significant (Fig. 3b). Plant K concentrations were insignificantly lower for the control (by 27 %, 27 ± 2.0 mg g DM^{-1}), the AC 3 (by 26 %, 28 ± 2.5 mg g DM^{-1}), and the AC 5 manure treatments (by 27 %, 27 ± 1.7 mg g DM^{-1}) than in the AC 9 manure treatment (35 ± 1.5 mg g DM^{-1}; Fig. 3c).

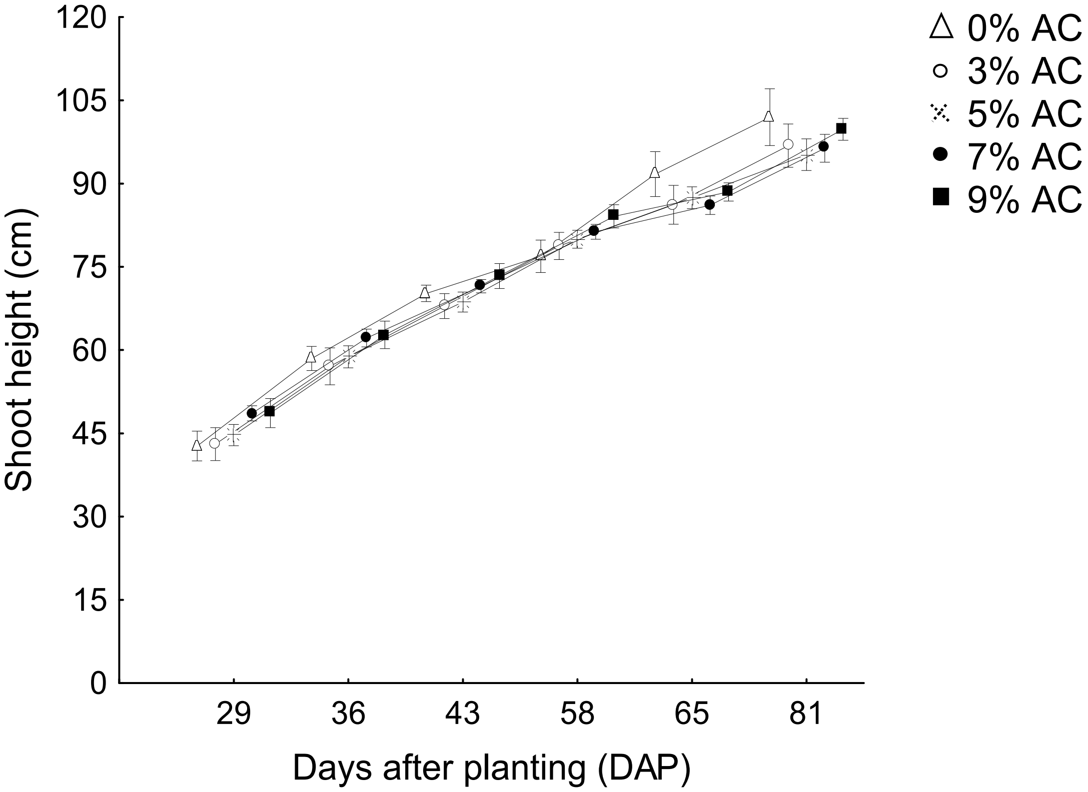

Fig. 1. Mean plant shoot height and one standard error at $P < 0.05$ measured 29, 36, 43, 58, 65, and 81 days after planting (n = 4). AC = activated charcoal fed to goats in % of total ration.

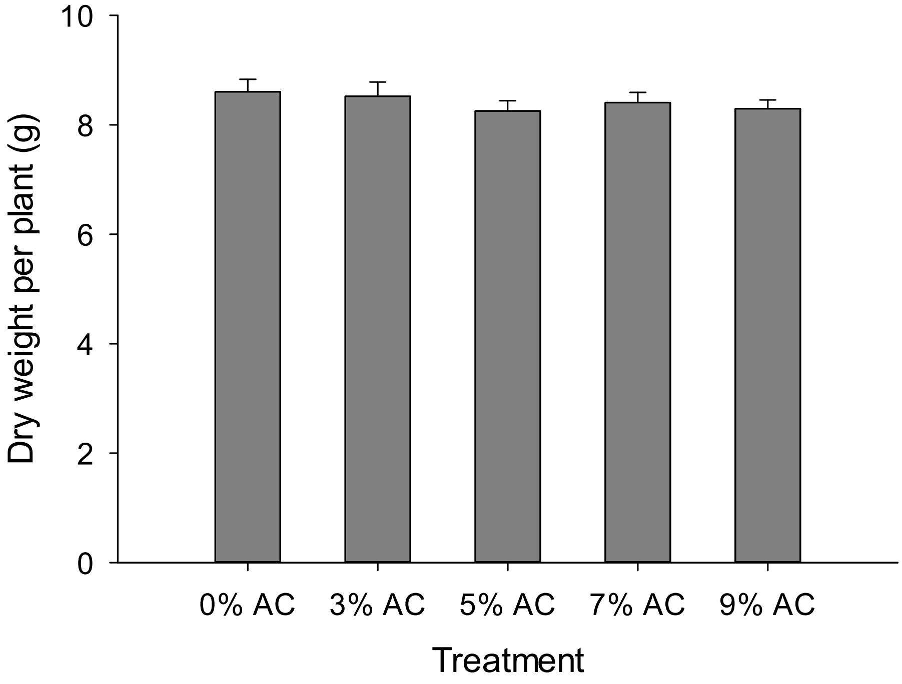

Fig. 2. Mean plant shoot biomass expressed as dry weight and ± one standard error at $P < 0.05$ (n = 4). AC=activated charcoal fed to goats in % of total ration.

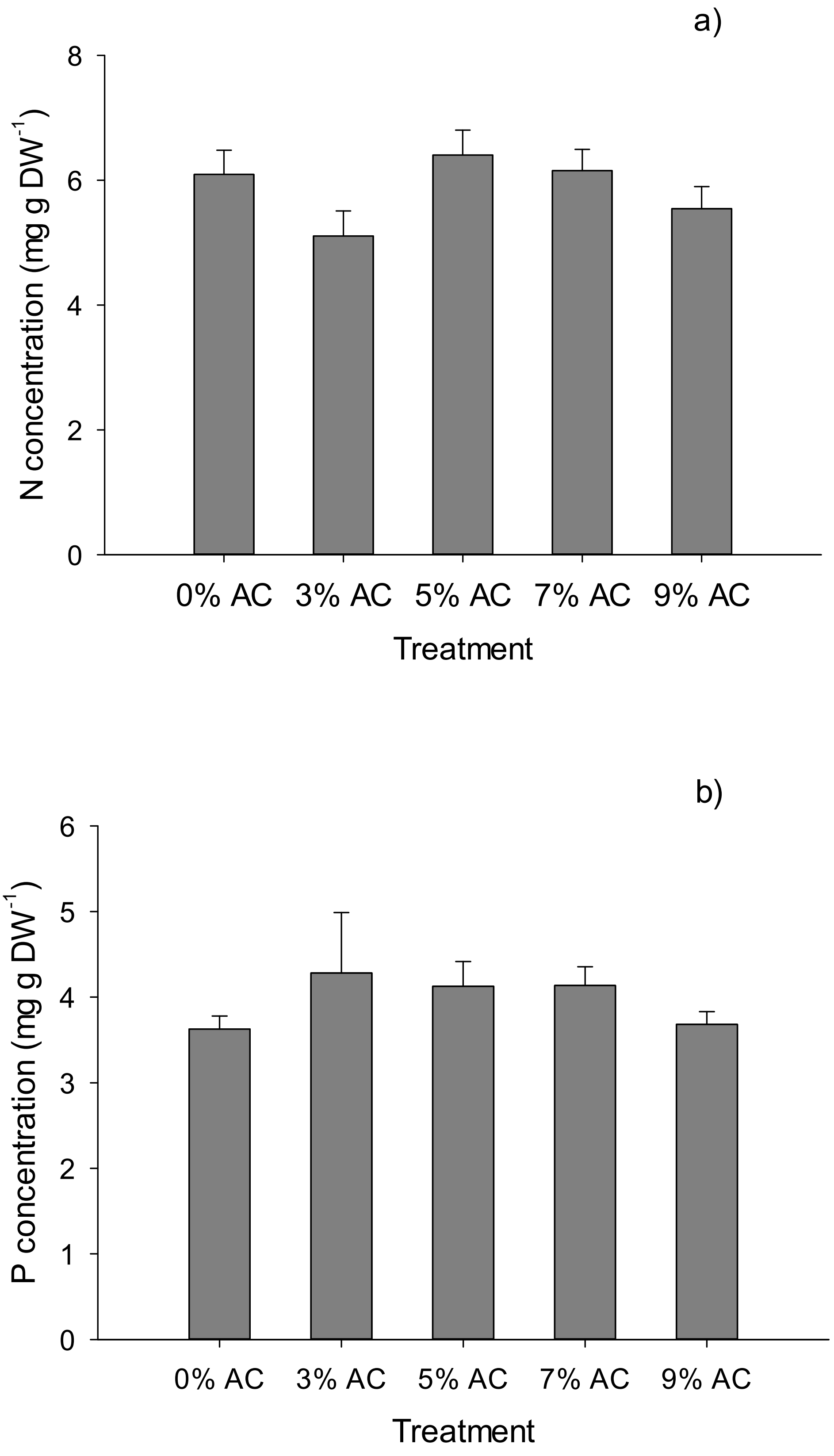

Fig. 3a and b. Mean concentrations and one standard error at $P < 0.05$ of nitrogen (a) and phosphorus (b) in plant aboveground biomass (n = 4). AC = activated charcoal fed to goats in % of total ration.

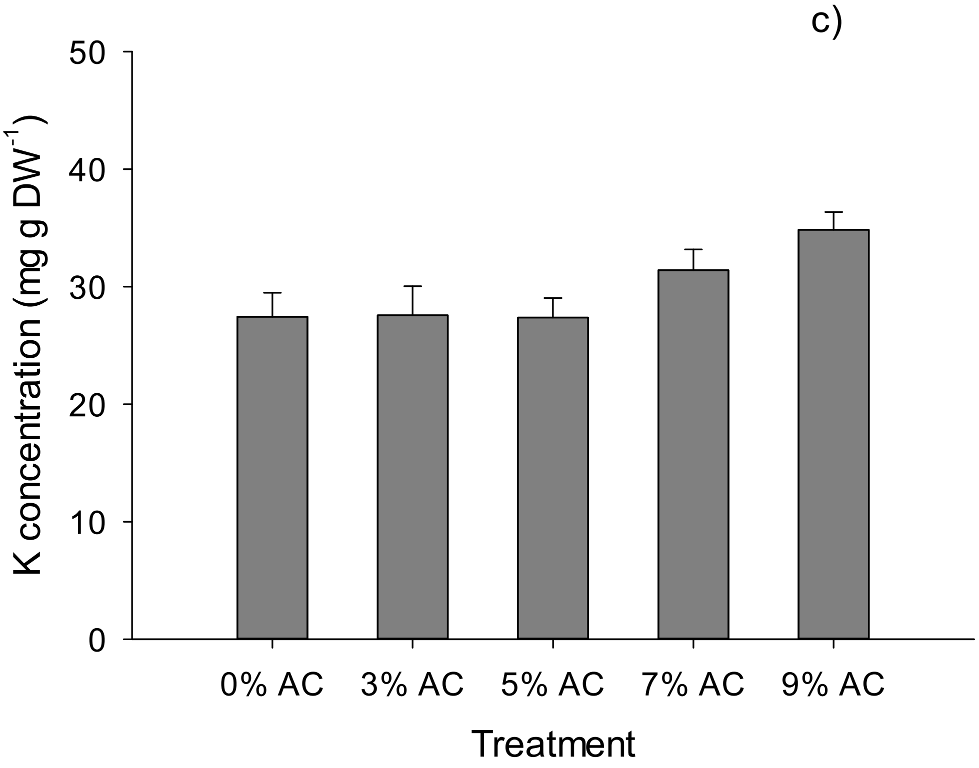

Fig. 3c. Mean concentrations and one standard error at $P < 0.05$ of potassium in plant aboveground biomass (n = 4). AC = activated charcoal fed to goats in % of total ration.

4.4 Discussion

Effects of AC feeding on manure nutrient contents and faecal scores

Feeding AC is widely used in veterinary medicine to treat animals suffering from diarrhoea and intoxication (Buck and Bratich, 1986). The use of AC in the daily diet of ruminants that feed on plants containing secondary compounds like phenolics or terpenes, which can reduce feed intake and decrease nutrient utilization, was examined in several studies (Banner et al., 2000; Villalba et al., 2002). Even at higher AC levels than those of our study effects of AC supplementation on feed intake (Rogosic et al., 2006; Rogosic et al. 2008) and nutrient utilization (Murdiati et al., 1991; Van et al., 2006) were negligible or positive and there is no experimental evidence of negative effects on animal health such as constipation (Villalba et al., 2002). In our study AC intake did not affect feed ingestion by goats. This is in accordance with other studies that did not see differences in feed intake due to AC feeding (Van et al., 2006; Alkindi et al., 2013). As expected with increasing AC rate faeces color changed to dark, odor was reduced, and the consistency turned to hard, without any sign that the goats' digestion or health were negatively affected.

This confirms that daily feeding of goats with significant amounts of AC is physiologically feasible. We assume that AC is inert in the animals' organism, meaning that it is not digested or absorbed by the animal. This assumption is reflected by the results showing a linear increase in faeces C concentration with increasing AC supplementation. The decline in faeces N and P concentrations with increasing AC supplementation reflect a dilution effect due to higher amounts of excreted AC.

Effects of AC-enriched manure on soil fertility parameters and microbial biomass indices

AC-enriched manure increased SOC by up to 68%, while the soil TN pool remained unaffected. The AC effect on SOC was particularly pronounced, because the SOC was lower in the soil treated with control manure than in the initial soil. This is considerable compared to the 20% increase in TOC found by Solaiman et al. (2010) after applying 6 t biochar ha^{-1}. Our applications ranged between 0.4 t AC ha^{-1} (AC 3) and 1.4 t AC ha^{-1} (AC 9), assuming that the difference in manure C concentration between the control manure and the AC-enriched manures derived from the undigestible AC. Sradnick et al. (2013) conducted a field trial on the same soil. They applied 7.5 t dry goat manure ha^{-1} (control) and compared this with (i) goat manure and 2.5% AC (AquaSorb® CP1) as feed additive, which corresponded to 0.85 t ha^{-1}, and (ii) goat manure mixed with AC (AquaSorb® CP1; 0.85 t ha^{-1}) before field application. After the first seven months season, they reported an increase in SOC from 7.6 (initial) to 9.1 (control), 10.6 (i), and 10.5 mg g^{-1} (ii); and an increase in TN from 0.4 (initial) to 0.6 (control), 0.7 (i), and 0.6 mg g^{-1} (ii). In contrast to our measurements, average SOC of manure amended soils were twice as high in the experiment of Sradnick et al. (2013), reflecting a mean increase in SOC of 33% from the initial content after seven months. The positive relationship between AC- enriched manure and soil TN concentrations found by Sradnick et al. (2013) may be caused by the larger input of both manure and AC, as compared to our application rates and microbial biomass indices. AC-manure effects on the soil CN ratio were surprisingly small, most likely because the application doses were too low. It is often discussed that the widening of CN ratios in biochar amended soils can lead to immobilization of N (Lehmann et al., 2003; Ding et al., 2010; Nelson et al., 2011; Kloss et al., 2014). The results of this study show that TN did not differ significantly between treatments, hence we assume that immobilization of N played a negligible role in overall nutrient availability. With SOC the WHC of AC-manure amended soils increased by up to 8%

(AC 9) compared to the manure amended or initial soil. The sensitivity of our soil towards manure-induced changes in WHC supports data of Rawls et al. (2003), who found the highest response of water retention to changes in SOM on sandy soils with low SOC contents. AC-manure application did not increase soil pH, but even decreased it by up to 0.4 units. This is in contrast to other findings that show clear pH increases following BC additions (Kloss et al., 2014). However, most studies on biochar effects on soil quality were conducted on highly weathered acid soils (Glaser et al., 2002; Lehmann et al., 2003; Steiner et al., 2007), where the well known proton buffering capacity of BC was effective. This is consistent with findings of Kloss et al. (2014), where the application of biochar increased the pH of an acid Planosol from 5.3 to 6.9 after seven months, whereas biochar addition at the same rate to an alkalic Chernozem only led to a minor pH increase from 7.4 to 7.6. Similarly, Liu et al. (2012) found on a German Cambisol of pH 6 a significant increase in pH and CEC as response to the addition of compost, but not of BC. Our results are in accordance with data by Ingold et al. (unpublished), who recorded a slight pH decrease of 0.1 units after AC-enriched manure addition to the same soil under field conditions. Similarly, the CEC in their study declined from 10.2 cmol kg^{-1} to 9.4 cmol kg^{-1} after manure addition, and to 9.5 cmol kg^{-1} after the addition of AC-enriched manure. These results are in contrast to numerous reports showing considerable CEC increases after BC amendment, an effect attributed to surface oxidation of BC particles as well as a higher charge density in BC-rich soils (Liang et al., 2006). Recently, Slavich et al. (2013) showed on an Australian acid Ferralsol that the application of BC increased soil pH, but did not affect the pH-dependent CEC.

As a result of its recalcitrance, biochar-C is largely unavailable to soil microbes, but changes in soil physico-chemical properties and biologically available labile C compounds deriving from BC may accelerate microbial biomass and activity (Warnock et al., 2007; Steinbeiss et al., 2009; Anderson et al., 2011). The increase in microbial biomass may lead to a temporal immobilization of mineral N, as shown for instance by Bargmann et al. (2014). Sradnick et al. (2013) reported from the same soil similar microbial biomass C and microbial biomass N.. Their findings for microbial biomass C support our results. We detected a significant increase in microbial biomass N that arose from manure application; microbial biomass N decreased with increasing AC enrichment, possibly due to decreased availability of N with a widening treatment CN ratio.

Effects of AC-enriched manure on plant growth, yield, and nutrient concentrations

Many studies showed an increase in plant nutrient availability and growth after biochar incorporation across a range of soils (Glaser et al., 2002; Lehmann et al., 2003; Steiner et al., 2007; Liu et al., 2012). However, differences in the substrate and pyrolysis conditions greatly affect BC characteristics and its effects on key soil parameters such as CEC and nutrient content (Glaser et al., 2002; Gaskin et al., 2008; Gaskin et al., 2010; Alburquerque et al., 2014). However, charcoal-induced reductions or zero effects on plant growth were also reported (Gaskin et al., 2010; Jones et al., 2012; Güerena et al., 2013; Kloss et al., 2014). Often discussed as main reason for plant yield reductions after charcoal applications is an immobilization of N that leads to N deficiency in plants (Lehmann et al., 2003; Deenik et al., 2011; Kloss et al., 2014). Also, micronutrient deficiencies after pH-induced decreases in micronutrient availability were found (Bolan et al., 2003). In the last two measurements of plant height, we observed a growth retardation for all plants grown on soils amended with AC-manure as compared with the control group. This was also reflected in the final dry matter data.

4.5 Conclusions

The results of this study demonstrate that feeding goats with diets containing up to 9% AC in the ration is possible without negative effects on animal health, while the excretion of C into manure could be increased. Most soil fertility parameters and microbial biomass indices remained unaffected by AC-manure applications, except for SOC, pH, and microbial biomass N. Yield of millet decreased slightly with AC enrichment, whereas K uptake was improved with increasing AC application. Main responsible factors may have been soil type, dosage of manure and AC, properties of AC, and duration of the trial.

Acknowledgments

We gratefully acknowledge the technical assistance of Laura Quaranta, Christian Wagner, Eva Wiegard, and Claudia Thieme. We are also thankful to Dr. Herbert Dietz and Royal Court Affairs (Sultanate of Oman) for their essential support and to the German Research Foundation (DFG) for funding this project within the Graduate Research Training Group 1397 'Regulation of Soil Organic Matter and Nutrient Turnover in Organic Agriculture'.

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5 General Discussion

Effects of filter material and leaching measurement devices on carbon and nutrient leaching

This study showed that DOC leaching was significantly higher using PE suction plates than glass suction plates. This result is in accordance with Wessel-Bothe et al. (2000) and Siemens and Kaupenjohann (2003) who recommended glass as most appropriate material for the determination of DOC, because of the potential contamination of samples by released C from glues and plasticizers used for the production of plastic suction plates such as PE suction plates. However, quantitative data from a direct comparison between those two materials was lacking so far. The DOC leaching values derived from glass suction plates in both experiments using the sandy soil from Northern Oman were within the range of the values reported by Siegfried et al. (2011) from a field trial on the same soil. Their data was derived from silicon carbide suction plates (SiC; UMS GmbH, Munich, Germany), a material which is considered suitable for DOC determination. Results from the first study on a sandy model substrate indicated that NO_3-N leaching was comparable between glass and PE suction plates and Rohm & Haas resins, except for the mineral fertilizer treatment for which significantly less NO_3-N was detected in resin extracts than in leachates of both suction plate types. In both leaching trials using the sandy soil from Northern Oman, the comparison between glass suction plate leachates and Rohm & Haas resin extracts for NO_3-N yielded significantly different results. Whereas 162% of N detected by suction plates were found by Rohm & Haas resins in one experiment, only 42% N were found by Rohm & Haas resins in the other experiment. Although only 64% of suction plate N were detected by Purolite resins, this difference was not significant. These results are not only indicating that differences between ion exchange resin types may affect sample composition, but they also call for further research since they are not in accordance with studies that recommend ion exchange resins for the assessment of mineral nutrients; although Siegfried et al. (2011) also mentioned a several-fold different (lower) mineral N capture by Rohm & Haas resins compared with silicon carbide plates that are known for their low N adhesion. The data from the glass suction plates revealed that between 6 and 45% of total N was leached as DON. These findings are in range with Siegfried et al. (2011) who reported a DON contribution of 36% to total N leaching on the same soil. In the first study using a sandy model substrate with either organic or mineral fertilizer amendments, P leaching was below detection limit for all measurements. While P leaching was captured by glass suction plates in the two trials performed on the sandy soil from Northern Oman, no P was detected by neither of the two resin types in the second trial, and just significantly less (31%) of the P found by glass suction plates was detected by Rohm & Haas resins in the other. Suction plate-derived DOP leaching made up 64% of total P leaching in the second trial, but was below detection limit in the first. Potassium leaching showed similar contradictions to N leaching between glass suction plates and ion exchange resins: Whereas in the first experiment on the Oman soil 176% of K of the suction plate filtrates were recovered in the resin extracts, only 84% and 72% K of the suction plate filtrates were recovered from Rohm & Haas and Purolite resin extracts, respectively. Difficulties in the assessment of K by resins were reported previously (Siegfried et al., 2012). The filter materials of suction plates, however, had no effect on K leaching concentrations. In contrast, K leaching recorded from ion exchange resins was up to 47-times higher than average K leached across both suction plate types in the study with the model substrate.

The presented data was derived from a controlled experimental setup which allowed the reliable sampling of irrigation-specific leaching events as well as the comparison between tension-controlled suction plates with the resin box technique. Compared to field studies, the difficulties arising from air-tightness could be easily managed in our setup. These observations triggered more questions regarding the suitability of the measurement devices under field conditions. In field experiments, low seepage, horizontal water discharge, interruption between the resin-soil or suction plate-soil interface, and changes in hydraulic gradients by the installation of the cartridges may lead to a substantial underestimation of nutrient leaching, if collection of leaching water is at all possible. These problems were among others described by Predotova et al. (2011). However, during the experimental period in standard plot experiments, accessing the suction plates via a soil pit in order to correct their placement is not possible without major disturbances. The installation of the leaching measurement devices itself may considerably bias natural water flow (Close et al., 2004). In order to reduce disturbance effects, some authors incorporate a waiting period of up to several months before first sample collection (Schwendenmann and Veldkamp, 2005). This may oftentimes not be feasible. All of the devices used have their limitations. Both DOC and DON cannot be captured by ion exchange resins. Using the resin method will therefore in principle lead to an underestimation of N leaching, particularly in intensively managed soils with high organic matter inputs and frequent irrigation, factors which are likely to result in substantial leaching of DOC and DON, as pointed out by others (Beesley and Dickinson, 2011; Siegfried et al., 2011). Using suction plates instead is often unsuccessful because of the described difficulties in creating an air-tight capturing system under field conditions. Especially sandy soils are problematic here, because the water content of the vadose zone is mostly too low to have a saturated sampling area. Apart from that, both plate types used in the presented studies have shortcomings, especially when they are operated in the field. The PE suction plates have a thin polyamide filter fixed to the base of the plate. Since this filter is extremely sensitive to mechanical damage and soiling, it is protected by a covering porous shell. However, we observed that the filters nevertheless get polluted with dirt and soil particles, which may drastically shorten their durability. Especially under permanent moist conditions, these filters may disintegrate. Clogging of pores may also occur in borosilicate glass filters under longer exposure to soil. In the present trials, suction plates were therefore cleaned between measurements with deionized water which is not possible under field conditions. Compared with a field experiment, where sudden leaching events or preferential flow may be missed, all irrigated water was forced downwards in our soil cylinders. As for lysimeters, the diameter of the soil column determines how close to natural conditions the leaching results are. The 10 cm diameter are among those of other controlled leaching experiments (Lehmann et al., 2003; Jiao et al., 2004; Yao et al., 2012) and were further chosen to fit onto the glass suction plates that had a similar dimension. Nevertheless, water infiltration and nutrient distribution may be altered in the disturbed soil used in the trials compared with an undisturbed profile under field conditions. Independent of the measuring device attached, we found that some cylinders leached slowly and that water ponded for a few hours on the soil surface before it finally leached and could be sampled. Similar observations were made by Jiao et al. (2004) in microcosm trials using fine-silty, mixed, frigid typic Endoaquents. In some cylinders more than in others fine silt and clay particles may have filled the soil pores and thereby caused a slow water infiltration rate. This, and also some algae growth along the cylinder walls may have affected soil and leaching water sample composition. Future research should focus on the avoidance of potentially biasing factors such as algae growth by using non-transparent glass instead of aluminum covers, or a non-transparent material such as stainless steel for the soil cylinders.

Furthermore, research for resin material that can capture dissolved organic matter should continue to facilitate use of this comparably cheap method.

Effects of AC-enriched manure on carbon and nutrient leaching, soil productivity, and plant growth on a subtropical sandy soil

The data from both leaching trials showed that C and nutrient leaching remained unaffected by AC treatments. Most measured soil fertility parameters did not show a response to manure AC-enrichment. The decomposition of manure decreased with increasing CN ratio due to AC enrichment and was overall small. This may have been influenced by the lack of macrofauna typically present in field experiments (Ouedraogo et al., 2004). The statistically insignificant, but numerical increase in microbial biomass C and the significant increase in microbial biomass N may have been the result of a direct utilization of charcoal in AC-enriched treatments, but might as well have been caused by mineralization of pre-exisitng soil organic matter in which SOC, the main energy source for microorganisms, resides. Overall, soil properties may have not been altered enough to evoke substantial microbial biomass growth (Kolb et al., 2009). The slight decrease in millet seedling growth was not significantly related to AC enrichment, but may have been the result of N and P deficiencies. It is reported that in more alkaline soils, a further increase in pH due to large BC additions may cause an inhibition of nitrifying bacteria (Antoniou, 1990), or immobilization of nutrients such as NH_4^+ and PO_4^{3-} (Vega-Jarquin et al., 2003; Hopkins and Ellsworth 2005). Generally, high quality organic fertilizers with a low CN ratio have a fast turnover in tropical and subtropical agroecosystems (Seneviratne, 2000), which poses a potential risk for nutrient losses via leaching or emanation, but is also a requirement for plant nutrition. AC-enriched manure may slow down the mineralization of manure and may provide slowly releasing nutrients over a longer period of time. Although biochars are resistant to decay, they may contain some proportion of labile organic components (Bird et al., 1999; Hamer et al., 2004), which can serve microorganisms as an energy source during the initial stages of decomposition of N-poor biochars, and hence, could potentially induce short-term soil N immobilization (Lehmann et al., 2006). No comparable data exists thus far concerning the effects of AC-enriched manure within the investigated soil and plant parameters.

However, the results from the conducted studies indicate that -as for applications of BC or AC to soil- effects strongly depend on BC/AC origin and processing temperature, application rate, as well as soil type (Alburquerque et al., 2014; Kloss et al., 2014). Without clear positive effects on plant growth and given the high costs and limited availability of AC-enriched manure, its use in agricultural practice may be limited.

6 General Conclusions

While glass and PE suction plates yielded comparable results for N and K leaching, both plate types significantly differed in the assessment of DOC leaching. The data does not allow a final statement about the suitability of Rohm & Haas resins for the measurement of mineral N, whereas the obtained findings clearly indicate that Rohm & Haas resins are not suitable for K leaching measurements. On the contrary, Purolite resins seem to be a promising alternative to Rohm & Haas resins, as they yielded comparable results to glass suction plates for both mineral N and K. Since not many comparative studies exist and the causes for the partly contradictory results from Rohm & Haas resin extracts are not entirely clear, further research is needed to confirm these findings. The results from this study allows the conclusion that substantial leaching in form of DOC, DON, and DOP takes place on sandy subtropical soils of Northern Oman, and most likely in other soils under similar conditions. Therefore, it is recommended that future research places a stronger focus on dissolved organic matter fluxes in order to counteract the detrimental effects of ongoing C and N losses on soil productivity. AC-enrichment of manure mostly did not result in significant effects on C and nutrient leaching, soil productivity, or plant growth. Although the value of this finding is limited to the presented specific experimental conditions, it sheds light on the use of AC-enriched manure as a soil amendment. The slow mineralization of manure may have been caused by the absence of macrofauna and plant interactions in the greenhouse setup. If this work is to be continued, prior attention should be paid to overcoming such limitations by integrating plants into the leaching trials, which would, however, require leaching columns of greater diameter and the adjustment of leaching measurement devices. Emphasis should also be placed on minimizing the time of irrigation water exposure on the soil surface and the avoidance of algae growth, since those factors may bias sample composition.

7 General References

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Affidavit

"I herewith give assurance that I completed this dissertation independently without prohibited assistance of third parties or aids other than those identified in this dissertation. All passages that are drawn from published or unpublished writings, either words-for-word or in paraphrase have been clearly identified as such. Third parties were not involved in the drafting of the materials contents of this dissertation; most specifically I did not employ the assistance of a dissertation advisor. No part of this thesis has been used in another doctoral or tenure process."

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