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Calibration of a simple method for determining ammonia volatilisation in the field "Experiments in Henan Province, China, and modeling results"

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Calibration of a Simple Method for Determining Ammonia Volatilisation in the Field » Experiments in Henan Province, China, and Modelling Results «

Andreas Siegfried Pacholski

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Kurzfassung

Eine einfache dynamische Kammermethode zur in situ Messung der Ammoniak-Volatilisation (Glockenmethode, DTM; Roelcke 1994, Roelcke et al. 2002 a) wurde durch Vergleich mit mikrometeorologischen Standardmethoden kalibriert. Zwei Varianten der Glockenmethode wurden untersucht. Bei der ersten (Standard)Variante erfolgte der Luftaustausch mit Handpumpe, während bei der zweiten ein erhöhter Luftaustausch mit einer elektrischen Vakuumpumpe erzeugt wurde. Als mikrometeorologische Messverfahren wurden die Methode nach Leuning et al. (1985) (Sherlock et al. 1989) (Space Shuttle Methode, SSM) sowie die Methode nach Schjoerring et al. (1992) (Ammonia Tube Methode, ATM) angewendet, welche beide zur Gruppe der Massenbilanzverfahren (integrated horizontal flux method) mit passiven Ammoniak-Samplern gehören. Wegen ihrer höheren Messfrequenz wurden die SSM Ergebnisse bei der Kalibrierung der DTM mit Handpumpe verwendet. Darüber hinaus wurden die Ergebnisse durch einen indirekten ^{15}N Massenbilanz-Ansatz überprüft.

Die Feldversuche wurden 1998 - 1999 in der Nähe der Agrarökologischen Untersuchungsstation Fengqiu, Provinz Henan, V.R. China durchgeführt. Dieser Untersuchungsstandort wurde ausgewählt, weil die vorwiegende Anwendung Ammonium-basierter N-Dünger in China (Harnstoff, Ammoniumhydrogencarbonat) sowie das semihumide Klima und hohe Boden-pH-Werte in der Region sehr günstige Bedingungen für N-Verluste durch Ammoniak-Volatilisation darstellten. Es wurden fünf Feldexperimente mit einer jeweiligen Dauer von 2 – 3 Wochen, 3 Mais- und 2 Winterweizenexperimente, durchgeführt. Die Ammoniak-Volatilisation nach der Ausbringung von Harnstoff wurde mit den genannten Methoden synchron gemessen. Jedes Experiment beinhaltete zwei Behandlungen mit unterschiedlichen Harnstoff-Ausbringungsverfahren, jeweils eine in der Region gängige Methode mit Düngereinarbeitung (Einmischen, Punktdüngung oder Düngung gefolgt von Bewässerung) sowie die oberflächliche Ausbringung des Düngers. Der Feldaufbau der Versuche bestand aus zwei kreisförmigen Untersuchungsflächen (500 m²) für die Anwendung der mikrometeorologischen Methoden, welche von ungedüngten Feldern gleicher Kultur umgeben waren. Innerhalb jeder Untersuchungsfläche wurden außerdem zwei Mikroplots zur Messung mit der DTM angelegt, sowie eine Messapparatur zur *in situ* Bestimmung meteorologischer Variablen (Windgeschwindigkeiten, Temperaturen) installiert. Darüber hinaus wurden N_{min}-Gehalte, Bodenwassergehalte und pH(H_2O)-Werte in Bodenprofilen (1 – 1.2 m) und oberflächlichen Bodenproben (0 – 3 mm) untersucht.

Die Glockenmethode (DTM) mit Handpumpe und SSM ermittelten sehr ähnliche zeitliche Verläufe der Ammoniak-Volatilisation für alle Experimente und Behandlungen. Die qualitativen Unterschiede

zwischen Ammoniakverlusten unter Berücksichtigung von Harnstoff-Ausbringungsverfahren, Düngermenge und Vegetationsperiode wurden durch beide Methoden in gleicher Weise erfasst. Dies wurde auch durch den Vergleich der Anpassung einer sigmoidalen logistischen Gleichung an die gemessenen kumulierten Ammoniakverluste bestätigt. Allerdings unterschätzte die DTM mit Handpumpe die mit der SSM bestimmten kumulativen Ammoniakverluste um ungefähr eine Größenordnung. Die Diskrepanz zwischen den mit DTM (Handpumpe) und SSM gemessenen Ammoniak-Flüssen hing vom saisonalen Einfluss der Temperatur (Maisexperimente) bzw. der Temperatur und der Windgeschwindigkeiten (Weizenexperimente) ab. Zur Kalibrierung der DTM mit Handpumpe wurde ein indirekter Ansatz verwendet. Eine Kalibrationsgleichung wurde auf der Grundlage von zeitlich gewichteten mittleren DTM Ammoniak-Flüssen, Temperaturen und Windgeschwindigkeiten in Abhängigkeit von SSM Probenahme-Intervallen berechnet. Ein Ansatz mit der getrennten Behandlung von Mais- und Weizenexperimenten ergab ein zufriedenstellendes Ergebnis für die Bestimmung der Kalibrationsgleichung (modelling efficiency c^2 0.86). Nach Berechnung kumulativer NH_3-Verluste mit den korrigierten DTM Flüssen ergab sich ein durchschnittlicher absoluter Schätzfehler von 6.5 kg N ha^{-1} bzw. ein relativer Fehler von 17 % der geschätzten NH_3-Verluste. Ein ähnlich gutes Ergebnis wurde unter der Verwendung eines zweiten Kalibrationsansatzes erreicht (r^2 0.95). Dieser basierte auf den kumulierten NH_3-Verlusten am Ende der Experimente, welche durch die beiden Methoden gemessen wurden, sowie auf für die gesamten Versuchszeiträume gemittelten meteorologischen Variablen. Da aber die Schätzung dieser Gleichung auf nur 9 Datensätzen basiert, ist die Verwendung der ersten Kalibrationsgleichung, welche auf einer Vielzahl von Ammoniak-Flussmessungen beruhte, für die zukünftige Berechnung von korrigierten DTM Ammoniak-Verlusten zu empfehlen.

In den verschiedenen Experimenten wurde sowohl gute Übereinstimmung als auch größere Abweichungen der Ergebnisse der mikrometeorologischen Methoden festgestellt. Dies deutete darauf hin, dass sowohl SSM als auch ATM ebenfalls einen nicht unbeträchtlichen Messfehler aufwiesen, welcher nach Harper et al. (1998) für mikrometeorologische Messungen ± 15% oder bis zu 50% beträgt. Die Messwiederholungen der Glockenmethode wiesen bei der Messung auf vegetationsfreien Kleinparzellen einen Messfehler von 20% des mittleren Messwerts auf. Der Messfehler der Messmethoden erhöht zusätzlich die Unsicherheit der Kalibrations-Ergebnisse.

Die Kalibrierungs-Ansätze wurden durch den Vergleich der mit SSM und DTM (Handpumpe) bestimmten Ammoniak-Flüsse mit berechneten Ammoniak-Partialdrücken an der Bodenoberfläche bestätigt. Ammoniakpartialdrücke wurden mit Gleichungen in Denmead et al. (1982) berechnet, welche die Gesamtgehalte an ammoniakalischem N, pH-Werte und Bodenwassergehalte an der

Bodenoberfläche (0 – 3 mm) sowie in situ Bodentemperaturen als Eingangsgrößen benötigten. Während NH_3-Flüsse, welche mit der DTM gemessen wurden, gute Übereinstimmung mit den berechneten Partialdrücken aufwiesen, lagen größere Diskrepanzen zwischen SSM-Flüssen und den Partialdrücken vor. Die Beziehung zwischen den mit der SSM gemessenen NH_3-Flüssen und den Partialdrücken konnte durch die Multiplikation der Partialdrücke mit den vorherrschenden Windgeschwindigkeiten erheblich verbessert werden. Diese Ergebnisse zeigten, dass die DTM mit Handpumpe den Einfluß der Windverhältnisse auf Ammoniak-Verluste nicht hinreichend berücksichtigt, während die SSM das Produkt aus Windgeschwindigkeit und atmosphärischer NH_3-Konzentration bestimmt und damit den gesamten NH_3-Massenfluss erfasst. Die Windgeschwindigkeiten und Luftaustauschraten in den Kammern hatten vor allem einen wesentlichen Einfluss auf die Ausprägung der Diskrepanzen zwischen den beiden Methoden. Der Vergleich von gemessenen und simulierten NH_3-Volatiliationsverläufen stellte heraus, dass die Verläufe der NH_3-Verluste durch Windgeschwindigkeiten nicht so ausgeprägt beeinflusst werden wie etwa durch die Temperaturverhältnisse.

Der große Einfluss der niedrigen Luftaustauschraten in den Messglocken (1 Vol. $Minute^{-1}$) auf die Unterschätzung der Ammoniakverluste durch die DTM mit Handpumpe wurde durch die Anwendung der DTM mit erhöhten Luftaustauschraten, welche mit einer elektrischer Vakuumpumpe erzeugt wurden, bestätigt. In Mikroplot-Experimenten wurde ermittelt, dass die Luftaustauschrate in den Kammern und nicht die Zahl oder das Volumen bzw. Fläche der Messglocken die entscheidende Größe für die Höhe der bestimmten NH_3-Verluste durch die DTM ist. Durch kontinuierliche Steigerung der Luftaustauschraten in den Kammern wurde ein Schwellenwert von 40 Vol. $Min.^{-1}$ ermittelt, oberhalb dessen keine signifikante Erhöhung der gemessenen NH_3-Verluste zu erwarten ist. Die Anwendung von Luftaustauschraten von ca. 20 Vol. $Min.^{-1}$ in den Feldexperimenten ergab Ammoniak-Verluste von der Größenordnung der mit der SSM ermittelten Verluste. Allerdings zeigte der Vergleich der Ergebnisse für verschiedene Behandlungen eine sehr gute Übereinstimmung während zugleich auch große Diskrepanzen auftraten. Diese Ergebnisse unterstützen den indirekten Kalibrierungsansatz, welcher auf konstant niedrigen Laufaustauschraten und synchron gemessenen meteorologischen Variablen beruht. Es ist einfacher meteorologische Variablen zuverlässig und mit hinreichend hoher Genauigkeit in situ zu messen, als den Messaufbau der DTM an die verschiedensten Umweltbedingungen anzupassen.

Die Einarbeitung von Harnstoff führte zu einer deutlichen Senkung der Ammoniak-Verluste im Vergleich zur oberflächlichen Düngung. Dieser Zusammenhang war im Winterhalbjahr besonders ausgeprägt. Es wurden Ammoniakverluste zwischen 47.9 und 0.6 % des ausgebrachten Harnstoff-N ermittelt. Die höchsten Verluste wurden nach oberflächlichen Düngung von 200 kg Harnstoff-N ha^{-1} im Mais gemessen, die niedrigsten im Winterweizen nach Einwaschung des Harnstoffs (100 kg N ha^{-1}) in

den Boden. Hohe Bodenwassergehalte und Evaporationsraten (nach Bewässerung) sowie heiße Temperaturen bedingten hohe NH_3-Verluste im Sommerhalbjahr auch von Varianten mit eingearbeitetem Harnstoff (10.8 – 19.9 % des ausgebrachten Harnstoffs). Die mit den mikrometeorologischen Methoden ermittelten NH_3-Verluste stimmten mit den Ergebnissen der ^{15}N Massenbilanz-Analyse gut überein. Der Vergleich der Ergebnisse zeigte das Ammoniak-Volatilisation einer der wichtigsten Verlustpfade für ausgebrachtes Dünger-N ist. In der Wurzelzone lagen während des gesamten Jahresverlaufes sehr hohe N_{min}-Gehalte vor (100 kg N ha^{-1}). Die ^{15}N- und N_{min}-Messungen zeigten, dass in der Region Harnstoff im Überschuss appliziert wird, und somit ein hohes Potential zur Einsparung von Dünger-N und damit auch von N-Verlusten besteht. Neben den Verlusten durch Ammoniak-Volatilisation können jedoch auch hohe N-Verluste durch Nitratauswaschung in Folge unsachgemäßer und uneffektiver Bewässerung angenommen werden.

Volatilisationsverluste und damit verbundene Bodenprozesse in Fengqiu wurden unter Verwendung des deterministischen Simulationsmodells von Rachhpal-Singh un Nye (1986a) berechnet. Zur besseren Berücksichtigung der Feldbedingungen wurde das Modell modifiziert, indem neue Gleichungen zur Berechnung der Temperatur- und Wassergehaltsabhängigkeit von Urease-Aktivität, Ammonium-Dissoziationskonstante, Henry Konstante sowie der Tortuositätsfaktoren für die Diffusion in wässriger Phase und Gasphase in das Modell eingefügt wurden. In situ gemessene Temperaturen, Windgeschwindigkeiten und Wassergehalte wurden durch eine neue Routine in zehnminütigen Zeitintervallen eingelesen und als Datengrundlage der Simulationsrechungen verwendet. Die Modellparameter für Ammoniumadsorption, pH-Pufferkapazität und Urease-Aktivität wurden in Labor-Batchexperimenten bestimmt.

Die Simulation der in situ gemessenen NH_3-Voltilisationsverluste unter Verwendung des modifizierten Modells von Rachhpal-Singh und Nye stieß auf Probleme. Die simulierte Kinetik der NH_3-Verflüchtigung in den Weizenexperimenten und im dritten Maisexperiment (ohne Bewässerung) entsprach zwar den gemessenen Verläufen, doch die Kinetik in den ersten beiden Maisexperimenten wurde verfehlt. Dies konnte darauf zurückgeführt werden, dass NH_3-Volatilisation in diesen Versuchen auf Grund hoher Evaporationsraten nach Bodenbewässerung und zeitgleich vorherrschenden hohen Temperaturen vom NH_3-Massenfluss in wässriger Lösung dominiert war. Das Modell berechnet dem entgegen Ammoniak-Entgasung auf der Basis von Diffusionsprozessen in wässriger Phase und Gasphase und beinhaltet keine Berechnung konvektiven Wasserflusses. Dessen ungeachtet entsprachen die Höhen der berechneten kumulierten NH_3-Verlustmengen in etwa den gemessenen Verlusten. Vor allem die unterschiedlichen Ammoniak-Verluste in Folge der verschiedenen N-Düngungsmethoden konnten gut abgebildet werden. Dabei wurden in der Regel die Ammoniak-Verluste deutlich überschätzt, da das Modell die Verringerung der NH_4^+-Konzentration im Boden durch Nitrifikation und

Pflanzenaufnahme nicht berücksichtigt. Die Ansätze zur Berechnung der Urease-Aktivität und der pH-Dynamik wurden im Allgemeinen durch Vergleich von Simulations- und Messergebnissen bestätigt. Abgesehen von den Diskrepanzen in den beiden ersten Maisexperimenten zeigten die Simulationen, dass Diffusionsprozesse die wichtigsten Transportprozesse mineralischer N-Spezies im Boden in Bezug auf NH_3-Volatilisationsverluste waren. Auf Grund dieser erfolgreichen Simulationsergebnisse wäre es eine vielversprechende Aufgabe, das Modell für zukünftige Simulationen durch die zusätzliche Berücksichtigung von NH_4^+-Massenfluss in wässriger Phase sowie von Nitrifikation und Pflanzenaufnahme von NH_4^+ in den Berechnungen zu verbessern.

1. Introduction

During the last decade P.R. China had one of the fastest growing economies in the world. In the early 1990s the annual growth rates were two-digit declining to about 7 percent in the last few years. These economical developments entailed structural changes in Chinese society. The industrial and services sectors gained more and more importance for the national income while agriculture could not keep pace (growth rate 3.5 % in 1996, Chinese Embassy Germany, 2001). The percentage of agricultural production of the combined agricultural-industrial output value decreased from 56.9 in 1952 to 18.1 in 1995 (Li et al. 1998). Although the percentage of rural population has been decreasing steadily, the total Chinese agricultural population (i.e. total population whose livelihood depends on agriculture) is assumed to stay stable on a level of about 850 million people (FAOstat, 2001). Therefore, the pressure on this part of the population will increase to produce more intensively and efficiently in order to catch up with city dwellers with regard to family income. Another consequence is an increasing population movement from the countryside to the prosperous cities close to the coast in the east of the country. Although the great dynamics of economic growth has started only about 20 years ago, after Deng Xiao Ping's open policy, the environmental effects of unsustainable industrial development are already quite severe. Smil (1997) estimated annual economic losses due to environmental deterioration in the mid 1990s amounting to 6 – 8 percent of the Chinese GDP (gross domestic product). This was not much less than the economic growth rate at that time and did not include the qualitative effects as decreasing living quality due to air and water pollution, traffic noise and degraded landscapes. The most pressing environmental problems include air and water pollution as well as soil degradation due to changes in land use and deforestation. On the one hand the agricultural sector is heavily affected by environmental pollution, while on the other hand it is itself one of the driving forces leading to the degradation of the environment. The investigation of processes related to environmental deterioration by agriculture is thus one of the key issues on the road to a sustainable economic system in P.R. China.

The research presented in this thesis focuses on gaseous losses of nitrogen by NH_3-volatilisation as well as excess mineral nitrogen in soil due to heavy mineral N application in Chinese agriculture, which is in line with the above mentioned general issue. However, Chinese policy will cause further ecological degradation as it aims at continuing its current economic development at least until the year 2020 (Chinese Embassy Germany, 2001). But this unsustainable policy is not viable for creating a sound basis of economic prosperity all over China.

1.1. Natural setting and developments in agriculture of China

Agriculture is one of the key sectors which have to be considered when trying to find solutions for China's 'environmental crisis' (Smil 1993). China has one of the longest traditions in soil cultivation in the world. However, the general conditions in the most parts of China for agriculture are not very favourable. The prevailing monsoon climate with precipitation mainly in summer (May – September) leads to declining annual precipitation from the south-eastern coast (Fujian, 2000 mm) to the north-western interior parts of the country (e.g. Ürümqi, less then 300 mm) and to irregularity of the precipitation pattern. As a consequence historical reports about droughts and floods in China are likewise abundant. About 58 percent of China are covered by mountains or high plains and plateaus of more than 1000 m above sea level, 33 % of its land surface is situated higher than 2000 m (Smil 1984). Only about 10 - 15 % (100 – 150 Mio. ha) of its total surface area (959.8 Mio ha) can be used as arable land. These figures are based on current estimates of the arable land in China which can be assumed to correspond the potential arable land (Ash and Edmonds 1998, Smil 1999). Until the late (1800) Qing Dynasty (1644 - 1911) arable land in China summed up to about 50 million ha without much increase in the preceding centuries. The dramatic increase of the Chinese population since the early 18th century has entailed a policy of continuous land conversion and reclamation. However, the trend of declining available cultivated land per capita from 0.9 in the Ming Dynasty (1368 – 1644) to 0.08 ha/capita today could not be reversed (Smil 1999). Against this background of scarcity of arable land in China, King (1984) stressed that some regions of China have a *continuous* agricultural history of even longer than 5000 years. The common use of organic fertilisers dates back to 2000 aBP (Qin Dynasty 2221 – 2206 aBP (years before present) and Warring States period)(Jin et al. 1999, Mo 2000), in some regions even much earlier (e.g. Taihu region). On the field scale and village level in some parts of China (e.g. Taihu Region, Pearl River (Zhu Jiang) Delta) traditional agricultural systems developed cultivation methods which achieved an almost complete recycling of nutrients and record yields if compared with other historical traditional agricultural systems all over the world (King 1984, Ellis and Wang 1997). This perfection was reached at about 1000 aBP in the Song Dynasty and sustained stable rice yields until the rise of yields by introducing mineral fertilisers in the 1950s. Since 1000 aBP animal manure, nightsoil (human manure), cooking ash, canal sludge (sediments scooped from canals), oilcakes (residues from oil pressing) and compost were commonly used as fertilisers in the Taihu-region (Ellis and Wang 1997). These landuse systems combined careful recycling of all plant nutrients, irrigation and agroforestry (mulberries for silk production). In many parts of the country they also included agricultural and hydraulic engineering as building and maintenance of terraced fields.

However, these systems were mainly found in the relatively humid and warm alluvial plains close to the cost in the east of China as the Taihu-region or the Pearl River Delta (Zhujiang) or some parts of the loess plateau. In spite of using harvest residues as main heating and cooking fuel, with respect to wood provision even those regions were not self-supporting but depended on imports from the more western or mountainous regions. The regions close to the mouths of the large rivers as Yellow-, Yangtze- or Pearl River also profited to some extent from continuous deposition of sediments rich in nutrients by periodic flooding (King 1984, Jin et al. 1999). At 5000 aBP the climatic conditions with regard to agriculture at the Yellow (Huang) River – the cradle of the Chinese culture - started to worsen towards a more cool and dry climate, with naturally accelerated sedimentation in the rivers. So, the importance of the more eastern and southern regions increased considerably. Since about 1400 aBP anthropogenically accelerated soil erosion rates (Tang Dynasty) due to large scale destruction of natural vegetation (Xu 1998) in the upper reaches of the Yellow and Yangtze River provided more fertile original material to be deposited in the deltas and flatlands close to the coast. Nevertheless, in these granaries of China the soil was managed in a way which can be described as highly sustainable with respect to soil fertility and high yield levels. On the other hand, agricultural work was extremely hard (3700 h ha^{-1} a^{-1}), and the farmers' diet almost merely consisted of rice (64%), legumes and vegetables (Ellis and Wang 1997).

To sum up, China has been living for quite a long period of its history on the margin of sufficient food supply in the most of its regions. This was not only because of an ever growing population and limited land resources but also because of a strongly militarised society with long periods of warfare (Elvin 1998). Moreover, the Chinese feudal system lead to an impoverished agricultural population and urged the peasants to advance more and more southwards to what is present-day China.

The problems of increasing flooding in the fertile plains of the Yangtze and particularly of the Yellow river was met by intensified damming. However, in spite of medium-term reduction of river bank sedimentation in the middle reaches of the rivers and increased sedimentation in the river mouths, after a period of time the tailback by the rising river bed levels lead to catastrophic flood events. Thus, the combination of environmental deterioration in the western parts of the country causing high sediment contents of the rivers and damming of the rivers led to increasing environmental and agricultural problems. The Chinese reacted by fortifying the dams, refining agricultural systems and enlargement of the cultivated land area. Thus, the highly productive and sustainable agricultural systems close to the river banks were accompanied by land conversion and deforestation in the more western parts of the country. Although or just because China can be characterized as the most forest dependent civilisation in the world, it has been mostly deforested for several centuries. Today’s per capita forest resources equal one-eighth of the global average (Harkness 1998).

The above mentioned degradation pattern can still be found in present-day China when taking a closer look at the causes of the Yangtze flood in 1998 (deforestation at the headwaters of the river)(Liu and Xu 1999) and dust storms which increasingly affect the North of China (conversion of grassland to arable land and overgrazing)(Brown 2001).

After a last expansion of the traditional Chinese economy in the 18th century, scarcity of arable land because of population growths was one of the reasons which led to a crisis followed by a period of about 100 years of warfare and civil war. Since 1850, about the time of the Taiping-Revolution (1850-64), dramatically increased rates of land degradation can be proven by rising sedimentation rates in the Yellow River (Xu 1998). In the year 1949 the communist government of Mao Zedong came into power. This further worsened the described trends of land and forest degradation by conversion of unsuitable grassland and slopes to arable land, and over-cutting of forests. In general, forests were treated as free goods which lead to an tremendous over-exploitation of this slowly renewable resource (Harkness 1998). In particular the revolutionary episodes of the Great Leap Forward and the Cultural Revolution as well as the changing land policy under Deng Xiao Ping are referred to as the 'Three Big Cuttings'. There have been several campaigns for afforestation, but as they were organised as short-run mass-mobilisations, they were rather ineffective with low survival rates of the tree seedlings (Smil 1984).

1.2. Problems related to agriculture in present-day China

1.2.1 Environmental problems

The most important innovation with regard to agriculture following the communist revolution or 'liberation' in the year 1949 was the introduction of synthetic mineral fertilisers throughout the country. The 2.5 and 5 fold increase in per ha yields from 1952 to 1995 for rice and wheat, respectively, is mainly attributed to this factor (Wang et al. 1996, Jin et al. 1999). During this period the application of mineral N-fertilisers increased 290 fold. Mineral P and K were not applied before 1949 (Ash and Edmonds 1998, Jin et al. 1999) and application of these nutrients rose considerably by 1995. These improvements in crop production could only be achieved in combination with the introduction of high-yield wheat and rice varieties and increased irrigation. In addition, institutional reforms, in particular the agricultural reforms carried out immediately following the opening policy initiated in 1978, contributed substantially to growing grain production in the years 1978-1984 (Li et al. 1998). The average annual increase in rice yield by 84 kg ha^{-1} from 1952 - 1995 was unprecedented in Chinese history, compared to an average increase of 40 kg ha^{-1} every 50 years in the 1200 years before (Jin et al. 1999).

Nevertheless, per capita growth of grain production in the late eighties and nineties could not keep pace with population growth. Moreover, as the overall living standard in China has been increasing since 1978, food consumption patterns have changed towards a more meat and (vegetable) fat oriented diet (Sheng 1999, Veeck and Veeck 2000). As a consequence, more and more agricultural production is diverted to meat (feed) and oilseed production. There is a lot of debate whether China will be able to self-support its population with grain in the 21st century (Brown 1995, Li et al. 1998, Heilig 1999). If China had to basically rely on grain imports, this would substantially affect prices on the global grain market.

There are different reasons for reduced growth rates of grain yields in China. Firstly considerably large areas of the most fertile arable land are directly swallowed in the course of further industrialisation activities, as building of roads, factories etc., in the prospering coastal provinces. More than one million of hectars were lost in China due to industrial construction in the 1990s (Li et al. 1998). These land losses were to be compensated by conversion of grassland (grassland cover in China 1998 400 million ha (FAOstat 2001)) in the more northern and western provinces (Gansu, Quinghai, Shaanxi or Inner Mongolia) (Brown 2001). As the grassland converted is not suitable for cultivation, this policy, apart from overgrazing, is the major reason for soil deterioration, the current expansion of deserts and intensification of spring dust storms. The latter even affect Korea and Japan, or – as in March 2001- the western coast of North America. Since 1999 a new policy has been adopted by the Chinese government ("tui geng huan lin") which promotes the conversion of arable land to its original grassland or forest vegetation. For 1991, 17 percent of the Chinese cultivated area was estimated to be harmed by moderate or heavy erosion. Ash and Edmonds (1998) conclude that the major proportion of land loss can be attributed to structural changes in Chinese agriculture in contrast to the encroachment of industrial facilities. Total arable land and arable land quality are also reduced by salinisation of fields and through irrigation of greenhouses. Ash and Edmonds (1998) show that about 7% (> 6 mio. ha) of the degraded arable land in China have been affected due to salinisation-alkalisation and water-logging.

An additional reason for declining growth rates of grain production in China is shortage of labour because of better income opportunities in the industrial sector. Moreover, as 45% of China's arable land have to be watered regularly, the increasing overall water scarcity in the northern parts of the country and its over-consumption in combination with the aggravating competition with the industrial sector for water resources, has led to reduced agricultural production. Although the overall Chinese multi-cropping index increased in the years 1979-1996 the production restraints due to land loss could not be compensated by increasing the multi-cropping index (Ash and Edmonds 1998), in particular as there is a decreasing trend in recent years (e.g. Guangzhou province (Li et al. 1998)). In the high productivity regions agricultural production does also stagnate as the potential yield levels of the currently used rice

and wheat varieties might have been reached by now. Thus, some hope rests on the introduction of new high-yield varieties.

Furthermore, in spite of ever increasing rates or mineral fertilizer application, the application rates of N, P and K are rather unbalanced. In particular, K has been in deficit. This has had negative impacts on N-uptake efficiency and caused gaseous N-losses and N-losses by leaching (Jin et al. 1999). Although sufficient as well as environmentally and economically sustainable agricultural production is one of the vital interests of Chinese policy, a large proportion of the capital accumulated by improving agricultural productivity has been diverted to industrial development in the last decades. This way, the 'original accumulation' of capital by the farmers helped to develop the industrial sector but was lacking for investment in the agricultural sector. Thus, the present-day agricultural technologies and constructions are out of date and an obstacle to a sustainable agricultural production (Li et al. 1998).

The paragraphs above show that the situation of Chinese agriculture is rather complicated. The high economic and environmental constraints on China's agriculture result in ecological problems caused by current changes in the agricultural practice. Apart of large scale conversion of the different land use types (grassland, urban construction, arable land, forests), the excessive and unbalanced use of mineral fertilisers is a major environmental concern related to agriculture. Until the 1950s of the last century only organic fertilisers (compost, green manure etc.) were used for fertilization. In particular in the regions with highest agricultural productivity the use of organic manure has become insignificant due to high labour costs. At present China is the country with the highest consumption of N-fertilisers in the world, accounting for one-fourth of the world total (Xing and Zhu 2000). Aside from the unbalanced application of N-, P- and K-fertilisers mentioned above, the application rates of mineral N are geographically quite unevenly distributed between the richer coastal and the poorer interior provinces. In 1994, annual application rates to cereals ranged from 838.5 kg N ha^{-1} (3 crops a^{-1}) in Fujian province to 150 kg N ha^{-1} (1 crop a^{-1}) in Heilongjiang and Gansu (Jin et al. 1999). In North China alluvial plain (Huang-Huai-Hai-plain) or the coastal flatlands (Yangtze-/Pearl River Delta) N is applied in great excess. One reason for this is the high proportion of gaseous N-losses, in particular as ammonia, due to the use of predominantly unstable ammonia based N-fertiliser formulations (ammonium bicarbonate, urea). Ammonia losses range from a few percent in winter wheat to more than 50 percent of fertilizer N applied in flooded rice fields in summer (Cai 1997). Xing and Zhu (2000) estimate that on a national average 11 percent of synthetic fertilizer N applied are lost as NH_3. The volatilisation of ammonia is one of the main sources of anthropogenic N in the atmosphere contributing to the eutrophication of natural ecosystems, soil acidification and as second source of N_2O and NO. Galloway et al. (1996) estimate that NH_3-volatilization is the main pathway for N mobilisation in China, with increasing tendency. China accounts for about 15 percent of the world total of anthropogenic N mobilised. Eighty percent of the anthropogenic N in China stem from chemical fertilisers.

In addition to gaseous losses excess fertilizer-N is transferred to surface and ground water bodies by leaching and surface-runoff. Worrisome levels of nitrate concentrations were found in more than 50% of farmers' drinking water wells and 93.3% of the rivers in the Taihu region in 1987(Ma 1997). Recent investigations in china gave similar findings (Zhang et al. 1996, Emteryd et al. 1998). Up to 250 mg nitrate per litre and 100 mg nitrate-N per litre (WHO health threshold value 11,3 mg Nitrate-N l^{-1}) were found in farmers' wells in the North China plain and Shaanxi province (Loess Plateau), respectively. However, apart from these case studies only little knowledge exists about leaching and surface-runoff loss amounts in China (Xing and Zhu 2000). Estimated total surface run-off and leaching losses range in between 25% (Li and Zhang 1999) and <10% (Xing and Zhu 2000) of fertilizer N applied. The nitrogen contamination of Chinese surface waters is quite severe and has increased substantially during the last two decades, particularly because of mineral N-fertiliser application (Chen et al. 2000) and increasing amounts of industrial and household wastewater discharged (Sun and Chen 2000). In addition to the pollution of water bodies, excess N-fertilization has lead to the contamination of vegetables by nitrate and nitrite, and the incidence of cancer in the digestive system is high for people in China (Zhou et al. 2000 a). According to the current knowledge a high proportion of fertiliser N applied, up to 73.6 %, is lost from Chinese agro-ecosystems (Li and Zhang 1999).

Besides the contamination of agricultural produce with nitrate, pesticides and other anthropogenic pollutants harass consumers' health in China. At present pesticide application rates in southern and eastern China are among the highest in the world (Thiers 1997). Although the application of DDT, HCH and other high risk pesticides was prohibited in the 1980s, rather high concentrations can still be found in agricultural produce and drinking water wells (Li and Zhang 1999). This is even true for easily decomposable modern pesticides as *Metamidophos* etc. (Wang et al. 1999). Non-occupational pesticide poisoning has stayed on a high level since the early 1980s (Xue et al. 1998).

Another factor influencing the quality of food and agricultural produce in China is the contamination with heavy metals. The discharge of heavy metals into the environment has increased during the last decades. Heavy metal concentrations in vegetables often exceed Chinese limits for heavy metals in foods (Zhou et al. 2000 b). As a rule heavy metal loading of vegetables in the northern parts of China is higher than in southern China. The main reason for this circumstance is the use of waste water for irrigation purposes in the northern and western parts because of the general water scarcity. As outdated industrial plants are widely used and the separation of waste with regard to batteries, tins etc. is not practised, heavy metal concentrations in waste waters are presumably much higher than in western developed countries. Apart from contamination of agricultural produce, industrial pollution of irrigation water and air also entails the pollution of arable land and thus reduced yields. About 10% of land degradation could be imputed to industrial pollution in 1996 (Ash and Edmonds 1998).

1.2.2 Related scientific problems

Although the environmental and economic problems of agriculture in China are quite severe, only limited knowledge exists with regard to the causes of the adverse environmental effects and their respective importance. As has been already mentioned above, the lack of capital invested in agriculture and agricultural research might be one reason for this circumstance (Li, et al. 1998). In recent years China has had one of the fastest growing economies, being the world's 6th largest economy with regard to total GDP in 2001 (Worldbank 2002). But the per capita GDP is rather small, China still being a developing country, particularly in the countryside. In general China is lacking the scientific and financial resources for a thorough investigation of its entire agricultural sector. Furthermore, agricultural production systems, natural settings and climatic situations in China – rather a continent than a country - are extremely diverse. Beyond that, all these diverse systems have been changing as described above, particularly since the year 1978. On this account only limited numbers of case studies for the most environmental problems exist. The calculations of balances, critical loads, emission factors etc. on a national level are therefore quite uncertain. There is at least some monitoring work done by the national and province governments. However, despite great improvements, the results are frequently subject to manipulations or are not made publicly available due to political constraints on a national or local level. Therefore, this raises doubts whether official data are reliable.

Investigation of ammonia losses in China

As an example, ammonia volatilisation following mineral N-fertilizer application has only been systematically studied in three Chinese agro-ecosystems (Cai et al. 1992, 1995, Cai 1998). These three agricultural situations should represent three major regions of agricultural production in China (Red Soil Region, Yangtze Delta, North China Plain). However, these studies were carried out on merely one study site in each region, respectively. Although the three regions could be characterized as distinct landscapes with respective specific features, the investigations could not cover even a small proportion of (agricultural, soil, climatic) variability within the areas, each having an extension of a medium-sized European country. Apart from the reasons given above, there are also technical problems to carry out the experiments. Ammonia volatilisation is usually measured by micrometeorological methods (see Chapter 2.4). The most refined micrometeorological methods require in-field current supply, adjacent laboratories and comparatively large homogeneous fields. All these preconditions could not be fulfilled by almost all Chinese countryside situations. For this reasons ammonia-volatilisation measurements could only be carried out close to agricultural experimental stations or agricultural universities. This explanation also applies to many other environmental studies as nutrient leaching, surface-runoff or immission of pollutants.

1.3. Objectives of the thesis

The investigations presented in this thesis are focussing on the measurement of ammonia volatilisation by a simple *in-situ* measurement method, in the following called 'Draeger-Tube method', a special type of dynamic chamber methods. This method has been developed for the measurement of CO_2-evolution from soils by Richter (1972) (see also Anderson 1982). Roelcke (1994) and Roelcke et al. (2002) used the method for the measurement of ammonia volatilisation following fertilization of urea and ammonium bicarbonate in the Loess Plateau in China. Comparisons with laboratory measurements and ^{15}N field studies showed that the Draeger-Tube method underestimated actual volatilisation losses by about one order of magnitude. Thus the main purpose of this thesis is the calibration of the 'Draeger-Tube method' for the estimation of ammonia volatilisation by comparison with the results of standard micrometeorological methods.

The modification of the Draeger-Tube method for the measurement of gaseous ammonia has mainly been done for agronomic purposes, i.e. the measurement of ammonia volatilisation following (mineral) fertilizer application. The measurement of (quasi-natural) ammonia emissions of low concentration cannot be covered by this method. Because of the way of ammonia enrichment involved and the limited sensitivity of the Draeger ammonia indicator tubes employed (> 0.025 Vol. NH_3 ppm), only higher fluxes of gaseous ammonia close to the soil surface can be detected.

The low air exchange rate in the chambers was considered as the main hypothesis for the explanation of the underestimation of ammonia losses by the Draeger-Tube method. The air exchange rate in the chambers is much lower than the air exchange rates at the soil surface induced by commonly prevailing ambient wind speeds. Maximum ammonia fluxes measured by dynamic chamber methods were determined at air exchange rates of 15 – 20 Vol. $min.^{-1}$ (Kissel et al. 1977, Roelcke 1994) but the air exchange rate in the cups used in the Draeger-Tube method is only about 1 Vol. $min.^{-1}$. On the other hand the time courses of ammonia fluxes as well as significant differences in ammonia losses of different fertilizers applied and application methods detected by Draeger-Tube method measurements agreed well with literature data and theoretical considerations (Roelcke 1994, Roelcke et al. 2002 a).

The scientific strategy adopted in this thesis for the calibration of the Draeger- tube method consists in the comparative measurement of ammonia volatilisation following urea fertilization with the Draeger-Tube method and a micrometeorological standard method. A calibration formula sufficient for agronomic purposes shall be developed by relating the Draeger-Tube measurement results to the fluxes approximated by micrometeorological measurements. As climatic conditions are decisive factors for the effective realization of ammonia volatilisation, meteorological measurements and measurement of ammonia fluxes were carried out in parallel.

Since the correlation between the results of the two measurement methods shall be compared with respect to different crops, fertilizer application methods and seasons, 5 field experiments (3 maize, 2 wheat) altogether were carried out in the years 1998 - 99. Additionally, ^{15}N balancing experiments and mineral N-measurements were included. The objectives of this study can be summarized as follows:

- Analysis of the dependency of ammonia fluxes measured by the different methods on the intensities of the meteorological variables.
- Determination of the differences between the ammonia losses detected by the methods applied with respect to different field experiments and fertilizer application methods.
- Comparison of ammonia losses determined by direct measurements (Draeger tube method, micrometeorological method) with respective results from the ^{15}N-measurements.
- Calibration of the Draeger tube method by relating the ammonia fluxes measured to those determined with a micrometeorological standard method with simultaneous consideration of the relevant environmental variables.
- Assessment of the importance of ammonia volatilisation as pathway of N-loss with regard to crops and climatic conditions.
- Simulation of the measurement results by means of a mathematical computer simulation model in order to integrate and comprehend the measurement results.

2. Present knowledge of processes and measurement techniques of ammonia volatilisation

2.1. Reaction kinetics and basic equilibria

Ammonia is a gas at normal atmospheric temperatures and pressures, so it might be expected that any NH_3 present in soils, waters, fertilisers and manure would quickly volatilise to the atmosphere. However, it is a basic gas which reacts readily with protons, metals, and acidic compounds to form ions, compounds or complexes of varying stability and is thereby protected in solution or solid forms. Ammonia also has a very strong affinity for water and its reactions in water are fundamental determinants of the rate of volatilisation (Freney 1983).

The driving force for NH_3 volatilisation from a moist soil or a solution is normally considered to be the difference in NH_3 partial pressure between that in equilibrium with the liquid phase and that in the ambient atmosphere (Denmead et al. 1982). The equilibrium vapour pressure of NH_3 is controlled by the NH_3-concentration in the adjacent solution which in absence of other ionic species is affected by the ammonium ion concentration, pH and temperature. Furthermore, in case of urea fertilisation urea hydrolysis is an additional process included in the chain of reactions.

Ammonia volatilisation following urea fertilisation is therefore a relatively complex process relying on several chemical sub-reactions which are depicted in Fig. 1. The process can be subdivided in 4 steps:

1. urea hydrolysis,
2. sorption of ammonium and dissociation of ammonium to ammonia and proton,
3. transfer of ammonia from the aqueous phase into the gas phase of the soil,
4. NH_3-volatilisation depending on the difference between ammonia partial pressure at the immediate soil surface and in the ambient atmosphere.

As can be inferred from point 4, in this study ammonia volatilisation is defined as transfer of gaseous ammonia from the surface soil layer (surface boundary layer) to the ambient atmosphere close to the soil surface (Rachhpal-Singh and Nye 1986a). According to a more agronomic understanding ammonia volatilisation could also be defined as the emission of ammonia passing through and emitted by the plant canopy (Schjoerring 1995). So, the difference between the definitions lies mainly in the positioning of the respective system boundary. The latter approach focuses on balancing the ammonia fluxes at the upper boundary of the plant canopy corresponding to the net ammonia fluxes from the

field. In order to differentiate between the two definitions, in the following the first definition will be used in order to refer to ammonia *volatilisation* while the second definition will be applied to refer to ammonia *losses* from the field.

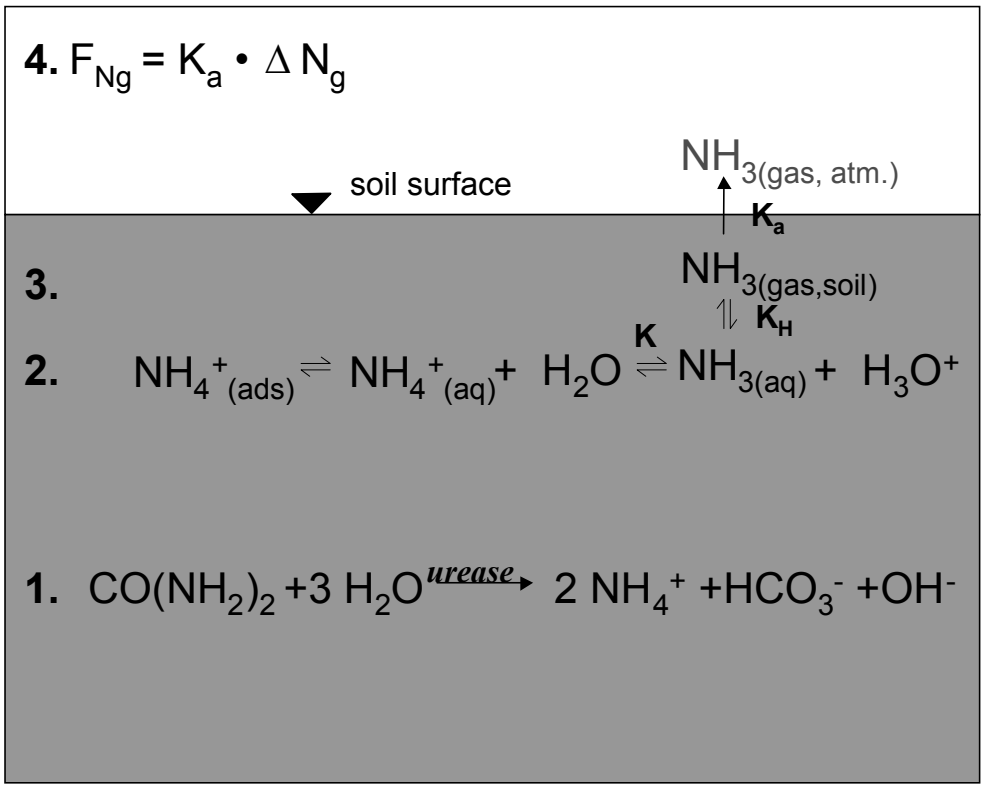


Fig.1: Ammonia volatilisation following urea fertilisation and related soil processes

1. Urea is fertilised to the field by surface broadcasting or incorporation of the fertiliser. In the soil urea gets into contact to the (exo-)enzyme urease which catalyses the hydrolysis of urea to ammonium, bicarbonate and hydroxide anions. The rate of the process is referred to as urease activity. As the formula shows, the process depends on soil water content. In addition, soil temperature and urea concentration have a major effect on urease activity (Rachhpal-Singh and Nye 1984). So, the hydrolysis of urea is better described not just by one rate parameter but by a function which calculates the rate constant depending on the above mentioned factors. One mole of ammonium and one mole of bases (HCO_3^- and OH^-) are released per mole urea-N, thereby increasing soil pH and thus improving conditions for ammonia volatilisation (see 3.) Laboratory measurements and modelling results by Rachhpal-Singh and Nye (1986 a-c) showed that the CO_2-evolution in the course of urea hydrolysis had only a minor impact on the CO_2 distribution in soil

which was mainly dominated by soil respiration. A modelling study by Roelcke et al. (1996) using Chinese calcareous soils also yielded a limited influence of CO_2 evolved during urea hydrolysis on ammonia volatilisation losses (see also 2.2).

2. Ammonium released from urea hydrolysis exists either in soil solution or adsorbed by clay minerals and organic soil material, participating in the cation exchange processes, or can be specifically adsorbed in clay particles. The adsorption of ammonium in soil is usually described by ammonium adsorption isotherms, Freundlich and Langmuir isotherms are the most common approaches. In both cases the adsorption of ammonium to soil particle surfaces depends on the concentration of ammonium in the soil solution (at a specific temperature) (Rachhpal-Singh and Nye 1986a). A proportion of ammonium released after urea hydrolysis can also be removed from soil solution by fixation in the lattice structure of clay minerals. The removal of ammonium from the aqueous solution can be very fast, thus directly influencing the ammonia volatilisation process while the release of fixed ammonium from clay minerals can be considered as a relatively slow process (Nieder et al. 1995, Nieder et al. 1996).

   An equilibrium between ammonium and ammonia in solution exists which mainly depends on soil pH and indirectly on temperature. Temperature has effects on the dissociation constants for water ($H_2O \leftrightarrow H^+ + OH^-$) and aqueous ammonia ($NH_3 + H_2O \leftrightarrow NH4^+ + OH^-$; *K* in Fig. 1). Starting from a pH of 7.5 considerable concentrations of dissociated ammonium (i.e. NH_3) can be found. The proportion of NH_3 of total ammoniacal nitrogen (NH_3 and NH_4^+) in the solution increases exponentially with pH (Freney 1983). So, major ammonia volatilisation can be expected from soils and solutions with a pH higher than 7.5. Thus, the pH markedly effects the equilibrium of the dissociation of ammonium to ammonia and proton. However, urease hydrolysis additionally increases the pH by release of OH^- and HCO_3^-. But as can be seen from the equilibrium equation, ammonium dissociation results in the release of 1 mole protons per mole ammonium dissociated counteracting the rise in pH caused by urea hydrolysis. As a result, the alkalinity produced during urea hydrolysis is balanced by H^+ remaining in soil after ammonium dissociation and subsequent ammonia volatilisation. However these processes do not occur fully synchronically: first hydrolysis of urea, a relatively fast process, raises soil pH which thereafter is continually decreased in the course of the ammonia volatilisation process. A typical pH pattern of soil pH during ammonia volatilisation after urea application would thus result in an increase in soil pH (urea hydrolysis) in the beginning followed by decreasing values as a consequence of continued ammonia volatilisation. The pattern, the length and the intensity of each phase, depends on soil moisture, initial soil pH, pH buffer capacity, temperature etc., i.e. all factors influencing the ammonia volatilisation process.

3. The transfer of ammonia from the aqueous phase to the gas phase of the soil depends on the equilibrium between ammonia concentrations in those two phases. According to Henry's law a constant relation between a concentration of a substance (NH_3) in the liquid phase and the gaseous phase depending on temperature exists. The temperature dependent Henry constant K_H (atm m^3 mol^{-1} ln K_H = -4200/T (°K) + 3.133) characterises the equilibrium between molar NH_3-concentration in the liquid phase and its partial pressure in the surrounding atmosphere. The dimensionless Henry constant K'_H can be derived from K_H (K'_H = H/RT) in order to calculate the equilibrium in terms of NH_3 concentration in the liquid phase and in the gas phase. Both parameters are positively related to temperature.

4. Gaseous ammonia diffuses in soil or is transported convectively with water vapour to the soil surface. From there NH_3 diffuses to the ambient atmosphere depending on the difference in NH_3-concentration between the air at the soil surface and ambient air (Fig. 1; ΔN_g), but is mainly transferred by other turbulent transport processes. The transfer coefficient K_a for the transfer of ammonia in the soil gaseous phase to the ambient atmosphere (F_{Ng}) mainly depends on wind speed (Freney 1983). Wind speed itself is modulated by plant cover, length of the fetch and surface roughness. As K_a also includes the diffusive fraction of the transport process, it reflects the influence of temperature and solar radiation on the ammonia volatilisation rate, too (Kirk and Nye 1991).

In the beginning of this chapter it was mentioned that the difference between ammonia partial pressure at the soil surface and the ambient atmosphere is the driving force of ammonia volatilisation. Up to now only the evolution of ammonia from soil following fertiliser application was described. In most cases atmospheric ammonia concentration is very low compared to the concentration at the soil surface after fertiliser application and can be neglected. So, in most calculations of ammonia volatilisation from fertilised soils atmospheric ammonia concentration is regarded as zero (Rachhpal-Singh and Nye 1986a, Roelcke 1994). The importance of atmospheric ammonia concentration is, however, much different with regard to the immission of ammonia.

2.2. Factors affecting ammonia volatilisation

As can be inferred from the above mentioned physical and chemical relationships, soil moisture, soil temperature and soil pH are essential factors for the ammonia volatilisation process. In addition urease activity and urea concentration affect ammonia emissions. In the following the importance of these

factors and the influence of other variables on ammonia losses are discussed on the basis of empirical studies carried out under several environmental and geographical conditions.

It was confirmed by many studies that temperature was one of the major factors influencing the ammonia volatilisation process (Freney 1983 (review), Tian et al. 1998, He et al. 1999). Apart of diurnal variations in ammonia flux pattern caused by temperature oscillation, e.g. Hargrove et al. (1977), seasonal differences in the magnitude of ammonia losses observed between summer and winter crops can be attributed to the effect of temperature (Hargrove et al. 1977, Zhang et al. 1992, Cai 1998). The effect of temperature could be superimposed by the more direct influence of solar radiation which is closely related to the heating of surfaces. In particular in case of surface applied ammonium based fertilisers the influence of solar radiation can be very strong (Sommer and Olesen 2000). Furthermore, high soil temperatures (> 40 °C) could lead to increased ammonia losses by reducing the nitrification rate of ammonium (He et al. 1999).

Soil moisture is important for both, urea hydrolysis and the transport of ammonia to the soil surface. As ammonia is affected by co-transfer in the course of soil water evaporation, its loss is also related to atmospheric relative humidity (Hargrove et al. 1977) and moisture loss of the soil (Stevens et al. 1989). Sufficient water supply was observed to be a major precondition of high ammonia losses (Black et al. 1986, Cai 1997, Tian et al. 1998, Sommer and Olesen 2000). When soil moisture was too low, urea was not hydrolysed and ammonia volatilisation was slow. However, in case of re-wetting of the soil ammonia loss may take a longer period of time but still exhibits the same cumulative amount of ammonia lost (Black et al. 1986). There are conflicting effects of rain on ammonia losses: in case of high rainfall (> 16 mm/event) ammonia losses even from dry soil are reduced, on the other hand, in case of low amounts, rainfall may lead in new bursts of ammonia losses (Black et al. 1986). The effect of rainfall does also depend on the cumulative rainfall provided by several subsequent rainfall events (Sommer and Olesen 2000). However, the soil moisture status modifies the effect of rainfall on ammonia losses. In soils with field capacity moisture status even small amounts of rainfall can lead to a reduction of ammonia volatilisation by washing down urea and ammonium into the soil (Freney 1983; Black et al. 1986). This effect is made use of by several fertilisation methods for the reduction of ammonia loss, e.g. surface application of urea followed by irrigation (Katyal 1987, Kumar et al. 1995, Cai 1998).

As was described above soil pH has a decisive impact on ammonia volatilisation. This was also observed in several field and laboratory studies (Stevens et al. 1989, Fan and Mackenzie 1993, Sommer and Ersboell 1996, He et al. 1999, Duan and Xiao 2000, Sommer and Olesen 2000). However, in many cases the influence of the dynamics of soil pH, characterised by soil pH buffer capacity, titratable acidity or exchangeable H^+, is more important than the absolute (equilibrium) soil pH. In case of low

initial soil pH a thorough buffering of pH-changes can reduce ammonia losses due to a limited increase of soil pH in the course of urea hydrolysis (Reynolds and Wolf 1987, Stevens et al. 1989, Sommer and Ersboell 1996). On the other hand, buffering of the pH drop due to intensive ongoing ammonia volatilisation can help to sustain high ammonia losses in case of high initial soil pH. If the soil pH can rise high enough, considerable ammonia losses were observed even from acidic soils with low pH buffering (Stevens et al. 1989). Fan and Mackenzie (1993) reported that high soil pH (pH 7 – 9) may also promote ammonia volatilisation by providing optimum conditions for urease activity. The $CaCO_3$ content has an indirect promoting effect on ammonia volatilisation by forming precipitation products with H^+ released in the course of the volatilisation process and, thus maintaining high soil pH (Freney 1983, Rachhpal-Singh and Nye 1986a, Roelcke et al. 1996, Duan and Xiao 2000). In order to reduce the pH rise in the course of urea hydrolysis the addition of acidic components (e.g. phosphates) was successful in lowering ammonia losses (Fan and Mackenzie 1993).

The effect of CEC on ammonia losses is related to the influence of $CaCO_3$. Alkaline salts adsorbed to the surface of clay particles, in particular Ca^{2+}, could precipitate H^+ and thus sustain high soil pH (Freney 1983). On the other hand, high CEC reduces ammonia volatilisation by adsorbing ammonium and lowering the ammonia concentration in the soil solution (Reynolds and Wolf 1987, Duan and Xiao 2000). However, if CEC is low, no effect of CEC on ammonia volatilisation was observed (Sommer and Ersboell 1996). Freney (1983) reported that there is a CEC threshold value of 25 [meq g^{-1} soil] for the reduction of ammonia losses. Both, clay particle and organic matter content, were significantly negatively correlated to ammonia fluxes (Reynolds and Wolf 1987). The effect of CEC can also be related to the fast fixation of ammonium in soil solution in the lattice structure of clay minerals (Nieder et al. 1995).

High wind speeds were shown to have a positive effect on ammonia losses (Sommer and Olesen 2000). Laboratory chamber experiments using different air exchange rates also proved the importance of wind speed and air exchange on volatilisation losses (Kissel et al. 1977, Roelcke 1994). Freney (1983) estimated that pH, temperature and wind speed have the same effect on ammonia volatilisation. However, there is no simple linear effect of wind speed on ammonia losses as the influence of wind speed does also depend on landscape surface characteristics and surface roughness (plant canopy) of the measurement site (Freney 1983, Van der Molen et al. 1990).

Agronomic factors also influence ammonia losses: the two main parameters are fertilizer application rate and method of placement as well as fertilizer type (Sommer and Ersboell 1996, He et al. 1999). In general, ammonium based (mineral and organic) fertilisers show the highest ammonia losses. This shall not be discussed in detail at this place, but urea application is connected to comparatively high NH_3-losses (E.C.E.T.O.C. 1994, Gezgin and Bayarakli 1995, Freney 1997, Harrison and Webb 2001).

Increasing relative ammonia losses as percent of N applied were observed with increasing fertilisation rates (Roelcke 1994, He et al. 1999, Roelcke et al. 2002 a), though not in all cases (Hargrove et al. 1977).

2.3. Ecological relevance of the process

Asman et al. (1998) estimated that about 54 Mt a^{-1} of ammonia is emitted globally, of which 60% is anthropogenic. The main natural ammonia sources are animal urine, microbial decomposition of organic material on the earth's surface and metabolic processes in terrestrial plants (Galbally and Roy 1983), while animal husbandry (including slurry/manure storage and application) and mineral fertilizer production and application (including NH_3 emission from crops) were identified as main anthropogenic sources. In western Europe livestock is the main source while in China the production and usage of ammonium based fertilisers is most important. Other considerable sources of anthropogenic N emission (NO_x) are traffic and stationary combustion sources (Ferm 1998). Between 1950 and 1980, ammonia emissions increased by about 50% in Western European countries. NH_3 concentrations over oceans and at high remote mountains are mostly below 1 µg NH_3-N m^{-3}. In urban areas concentrations of about 16 µg NH_3-N m^{-3} are common. Rural areas have lower concentrations within the range from 1 – 14 µg NH_3-N m^{-3}, with about 1 – 6 µg NH_3-N m^{-3} being typical (E.C.E.T.O.C. 1994). However, after the application of fertiliser or slurry ammonia concentrations of the dimension [mg NH_3-N m^{-3}] were observed (Fangmeier et al. 1994).

Galloway et al. (1996) estimated that nowadays altogether 140 Mt of reactive N are mobilised by human activities (fossil-fuel combustion, use and production of commercial fertilisers, legume and rice cultivation). A large proportion of the reactive nitrogen is emitted to the atmosphere as NH_3 and NO/N_2O. On the global level in 1990 the P.R. China and the United States were the largest emitters of gaseous reactive N with 9 Mt a^{-1}, respectively. Emissions of the U.S. were dominated by NO_x (6 Mt a^{-1}) while NH_3 was the main form of gaseous reactive N emitted in China (7 Mt a^{-1}). The authors projected that China's total gaseous reactive N emissions would have overtaken those of the U.S. by far in the year 2020, mainly because of raised NH_3 emissions (12 Mt a^{-1}) due to increasing fertiliser use. Although steps have already been taken for the reduction of ammonia losses, mainly from animal husbandry (Kirchmann 1998, Sutton 1998), NH_3 emissions will remain an important environmental issue for the first decades of the 21st century, particularly in China.

In the atmosphere ammoniacal nitrogen exists as NH_3 and NH_4^+. Ammonia is highly water soluble. When NH_3 is dissolved in water NH_4^+ and the alkaline OH^- ions are formed. The reaction is reversible

and the solubility increases if acidic species are also dissolved in the water. NH_3 is the dominating basic compound in the atmosphere. Therefore, NH_3 will react with acidic gases and particles forming fine hygroscopic salt particles containing $(NH_4)_2SO_4$ and NH_4NO_3 (Ferm 1998). The reaction between atmospheric ammonium and the acidic gases is fast and almost complete. Galbally and Roy (1983) reported results that 95% of all sulfuric acid particles formed in a plume were ammoniated at 15 or more hours after the release of SO_2 from a smelter.

Atmospheric ammonia is mainly deposited in two forms: wet deposition (as NH_4^+-salts) and dry deposition (as NH_3). Dry deposition does mainly account for short distance immissions while acidic ammonium salts can be transported over longer distances. It was calculated that 19% of emitted ammonia were deposited inside a grid of 150 x 150 km², other model results showed that 40% of emitted ammonia were dryly deposited inside a radius of 50 km (6 % wet deposition). However, when gaseous ammonia has reached the mixing height, it can be transported as ammonium over long distances. It was calculated that the annual average deposition originating from the Netherlands is halved every 400 km at distances exceeding 300 km (Ferm 1998). For European countries it was estimated that typically 40 – 60 % of the NH_3 emission emitted by a country is exported to other countries, which illustrates that NH_x is not only a local problem (Asman et al. 1998). The transport distance of $(NH4)_2SO_4$ and NH_4NO_3 may be as far as 2500 km (Fangmeier et al. 1994). High SO_2-contents in Chinese coal, which is the main fossil fuel used in the country, promote thus long transport distances of NH_3 emitted from agricultural areas in China.

In case of dry deposition gaseous ammonia is adsorbed at plant surfaces, or is taken up by plants through the stomata. The adsorption/desorption of ammonia is fairly variable due to different plant surface characteristics and growth patterns (e.g. forest / moorland). Furthermore, the uptake and release of ammonia through stomata depends on the ammonia 'compensation point' of the respective plant. A key feature of the exchange of NH_3 between the biosphere and the atmosphere is its bi-directional nature. The NH_3 flux will depend on the difference between the leaf mesophyll concentration and the concentration in the air overlying that surface (Fangmeier et al. 1994). For the plant leaf surfaces a compensation point at which there is no NH_3 uptake exists (Farquhar et al. 1980). At atmospheric concentrations below the compensation point NH_3 is emitted from the leaves. In general, the compensation point is larger for agricultural than for semi-natural plant covers, and varies with plant growth stage (Asman et al. 1998, Ferm 1998). However, 15-20% of ammonia emissions are estimated to be directly emitted by crops (Asman et al. 1998). As a result, it is very hard to give good estimates for small range dry ammonia deposition. Altogether, the uncertainty of ammonia emissions ranges in between 30 – 50 % (E.C.E.T.O.C. 1994).

According to E.C.E.T.O.C. (1994) the (anthropogenic) emission of ammonia entails several negative effects on the environment:

1. NH_3 concentrations in the air in the vicinity of point sources (e.g. large animal husbandry units) can damage vegetation.

2. Increased aerial deposition of NH_3 and ammonium contributes to water and soil acidification and may be part of the complex factors causing forest damage. Along with sulphur dioxide and nitrogen oxides atmospheric ammonia is one of the three main primary pollutants leading to acidifying depositions (Fangmeier et al. 1994, Sutton 1998). In particular nitrification of NH_4^+ in soil leads to a net release of protons (Pitcairn 1994, Ferm 1998). High NH_4^+ supply also entails K^+ and Mg^{2+} deficiencies, tree root growth could be reduced (Asman et al. 1998). As a consequence, ammonia/ammonium deposition is one of the major factors accountable for novel forest damages ('Waldsterben').

3. NH_3 emissions are one of the principal sources for increased nitrogen (N) supply to natural areas; increased N supply to such areas can change the flora, contribute to eutrophication of oligitrophic terrestrial (moorland or poor pastures and forest floors) and aquatic ecosystems (e.g. North Sea) (Ferm 1998, Sutton 1998). Consequently, deposition of ammoniacal N results in threatening of plant species which do not tolerate high nitrogen loads and, thus, in a reduction of biodiversity. It can yet lead to an endangerment of ecosystems e.g., highmoor ecosystems in Germany.

4. Ammonia deposition on natural areas also increase the fluxes of climate relevant gases (mainly N_2O) to the atmosphere from those sites. NH_3 is also oxidised in the atmosphere by OH radicals, mainly in the tropics. A fraction of the oxidised NH_3 is transformed to N_2O and this can constitute 5% of the global N_2O emission (Ferm 1998).

2.4. Methods for the measurement of ammonia volatilisation

The methods for the measurement of ammonia volatilisation can be distinguished according to the level of scale on which ammonia losses are determined (Fowler and Duyzer 1989, Denmead 1995). One can differentiate between methods for three different levels of scale:

- microscale - ≤ 1 m (chamber methods, Standard Comparison Method)
  - isotopic methods (^{15}N)
- field scale - tens of meters (mass balance methods)
  - hundreds of meters ('conventional' micrometeorological methods)
- regional scale - 100 – 1000 km² (Convective Boundary Layer Budget Methods, aircraft based measurements)

Before deciding on the methods, the important question has to be answered which temporal and spatial accuracy the measurement results are to provide. However, there is a converse relation between those two requirements. Chamber methods are quite suitable for measurements with high temporal resolution but it is comparatively hard to extrapolate these results to larger surface areas, i.e. hundreds of square meters or hectares. On the other hand, large scale or regional methods often lack resolution in time as, for example, to cover diurnal variations in ammonia fluxes.

2.4.1 Chamber methods

A large variety of chamber methods is available for the measurement of ammonia volatilisation. The general characteristic of all chamber methods is that chambers only cover a quite limited surface area. The principle is to restrict exchange of air with the atmosphere so that changes in the concentration of the emitted (or absorbed) gas in the head space can be detected readily (Denmead and Raupach 1993). Thus, the enrichment of the gas in the headspace of the chambers provides that sensors for gas measurements do not have to be as sensitive as for the other methods. As additional advantage, chamber methods are portable and versatile. They allow for process studies and treatment comparisons that cannot be realised with micrometeorological methods due to their high spatial requirements. Chamber methods can be divided into closed and open systems (Hutchinson and Livingston 1993).

Closed chambers

In closed systems there is no replacement of air in the headspace and the gas concentration increases continuously (Marshall and Debell 1980, Lara Cabezas et al. 1999). This kind of system was used more commonly in the past because larger concentrations occur, and the system is mechanically simpler. The rate of concentration change is used to calculate the gas flux to or from the soil system for closed chambers.

$$F_g = (V / A) \cdot d\rho_g / dt \quad (1)$$

F_g flux density of the gas
V volume of the headspace
A surface area of land enclosed
ρ_g gas density within the chamber
t time

A main problem of this approach is that the increasing gas concentration within the chamber may influence the fluxes from the soil. This is true for ammonia measurements at least. Therefore open systems are more widely applied than closed chambers nowadays. Gas concentrations may be determined by absorption of the gas produced (acid traps) or by syringe sampling.

Open chambers (dynamic chambers, forced-draught systems)

In difference to the closed chambers the headspace is continuously exchanged in open chamber set-ups. A continuous flow of air through the head space is maintained and the gas concentration attains a steady difference from the background concentration in the ambient air. In open systems the flux is calculated from

$$F_g = \frac{\nu \cdot (\rho_g - \rho_b)}{A} \quad (2)$$

F_g flux density of the gas
ν gas flow rate [e.g. Vol. s^{-1}]
A surface area of land enclosed
ρ_g gas density within the chamber
ρ_b background gas concentration

In open systems where air is pumped through the headspace , the pressure differential in the chamber induced by pumping should be monitored so as to keep it negligibly small. Even small pressure differentials in the chamber can induce a mass flow of air into or out of the chamber through the soil. As a consequence the soil-atmosphere gas exchange conditions and the land area covered may be

modified to a high degree resulting both in non-reliable ammonia loss estimates. Open systems can be divided into small chambers through which the air is drawn by hand or electrical pumps covering several hundred square centimetres (Kissel et al. 1977, Gezgin and Bayarakli 1995, Singh et al. 1995, Tian et al. 1998, Sommer et al. 2001) and taller constructions which could be described as wind tunnels set up in the field, measuring losses from 1 to several square meters surfaces (Braschkat et al. 1993, Sommer and Jensen 1994, Mannheim et al. 1995). A special case of the former approach is the method by Svensson (1997) which is a mixture of a forced-draught open system and micrometeorological method. A third kind of open systems consists in chambers in which the headspace is exchanged passively by the wind passing through or over the chamber (Lara Cabezas et al. 1999). In these semi-open systems the air exchange in the head space of the chambers is mainly based on diffusion or strongly reduced wind speed inside the chambers. If no measures are taken to correct the fluxes measured, ammonia losses determined in closed chambers are usually lower than measured with other chamber methods (Marshall and Debell 1980) because the occurrence of ammonia losses depends to a high degree on wind speeds above the soil.

The major problem in applying the open chamber methods lies in the adjustment of the air exchange rates to natural conditions effectuated by ambient wind. Many open chamber methods with forced-draught systems determine ammonia losses at air exchange rates which correspond to maximum ammonia volatilisation rates (e.g. Tian et al. 1998), i.e. potential ammonia losses at given temperatures. The level of potential ammonia volatilisation is reached at air exchange rates of about 15 – 20 Vol. (volume of head space) min^{-1} (Kissel et al. 1977, Roelcke 1994, Roelcke et al. 2002 a) depending on design and geometry of the chambers. Thus, in most instances ammonia losses are overestimated by dynamic chamber methods due to excess air exchange rates in the chambers. In addition, these methods cannot account for the influence of rainfall decreasing ammonia volatilisation losses because soil and plants are protected from rain by the chambers.

The major drawback of chamber methods lies in the severe physical and biological disturbances (temperature, pressure, concentration effects and site disturbances) of natural conditions inside and outside the chambers (Hutchinson and Livingston 1993), i.e. soil temperature, soil moisture, air exchange rates above the soil surface etc.. These effects can differ considerably between closed and open chambers. For long term measurement of ammonia fluxes it is, thus preferable to use several short enclosure periods than to measure continuously on the same site. Given the temperature dependencies of many trace gas emissions and the diurnal temperature variation as well as the time needed for the gas to diffuse from the different production zones in the soil to the soil surface, the minimum period for flux measurement would seem to be 24 h (continuously or at regular intervals) (Denmead and Raupach 1993). However, even if it is possible to take account of longterm volatilisation losses by the use of chamber methods, it still requires careful consideration to infer area-average volatilisation rates from

microscale point measurements due to high spatial variability of gaseous emission processes in soil. Another problematic feature of chamber methods, in particular of closed chambers, is the model estimation bias. If concentration measurements are made at distinct points of time a flux model is needed to determine the mean flux rates. In many instances a linear model is chosen while a non-linear model would be the appropriate choice, and fluxes could therefore be miscalculated. Thus, a great deal of consideration has to be given to the choice of the correct calculation model.

To sum up, the main problematic features of chamber methods are their lack of field scale reliability due to soil variability, possible disturbances of natural atmospheric and soil conditions at the measurement site and the difficult adjustment of air exchange rates in the chambers to ambient wind speeds. According to Denmead (1983), it must be conceded that a good deal of uncertainty can attach to enclosure measurements of NH_3 flux.

Nevertheless, keeping the possible shortcomings of chamber methods in mind, chamber approaches for the measurement of NH_3 volatilisation have been developed which give reliable in situ estimates of ammonia losses. These methods are based on dynamic open chamber approaches. Since the 80s of the last century wind tunnel approaches have been adapted to environmental conditions (e.g. Lockyer 1984, Ryden and Lockyer 1985, Mannheim et al. 1995) mainly by coupling of the air exchange rates to simultaneously measured ambient wind speeds. In recent years novel dynamic open chamber methods (Svensson 1997, Sommer et al. 2001) which have a smaller design and are thus more versatile have been adapted to ambient conditions in the same manner. However, although ambient wind speeds can be accounted for by these adaptations, the influence of the chambers on precipitation and temperatures on the covered soil surface could not be circumvented. These systems are problematic when no wind and rain occur, particularly if sampling takes a longer period of time (several hours or longer). In addition, air temperatures inside the chambers may deviate considerably if chambers are kept for a long time on the soil.

The calibration of the method in the focus of this study (Draeger Tube Method, see chapter 3.2.1) can be seen in line with the approaches given above. The main advantage of the Draeger Tube Method compared to the other in situ chamber methods consists in its high simplicity (no current supply, no laboratory equipment). Moreover, this method reduces the disturbance of the study site and of environmental conditions to a minimum.

2.4.2 Standard Comparison Method

This novel method developed by Vandré and Kaupenjohann (1998) allows the in situ measurement of ammonia fluxes on the micro scale level by avoiding the problems of chamber methods regarding the adaptation of the sampling to ambient environmental (temperature, wind, precipitation) conditions.

The method is based on the comparison between the unknown NH_3-release from manured experimental plots and standard NH_3 sources of known strength. In this open indirect measurement technique sampling is done by means of small passive flux samplers (40 mm x 40 mm x 65 mm) placed 0.15 m above the experimental area. Fluxes from treatment sites are corrected for atmospheric background values by subtraction of measured values determined at some distance from the plots. Standard plots with known NH_3 release rate emitted from a gas cylinder via perforated plastic tubing spread over the soil surface are used to determine the transfer factor (f) of NH_3 from the source to the sampler. This factor is thereupon used for the calculation of background-corrected NH_3-flux estimates from the treatment plots. No absolute measurement of NH_3 concentration in the air is needed for the estimation as it is based exclusively on the proportionality between NH_3 release and sampler measurements.

As the passive flux samplers are positioned above the soil surface this measurement method has no effect on wind speed or precipitation at the soil/atmosphere interface and, thus does not affect the ammonia volatilisation process at the soil surface. This measurement approach proved to be particularly valid for the in situ determination of ammonia fluxes from treatment sites with bare soil or limited density of vegetation. However, the accuracy of the Standard Comparison Method compared favourably to micrometeorological methods and wind tunnel systems given in the literature.

2.4.3 Micrometeorological methods

These methods overcome several of the above mentioned problems of chamber methods (Ferguson et al. 1988, Fowler and Duyzer 1989). Firstly, micrometeorological methods are used for experiments on a field scale basis and help, therefore, to avoid the problems of microscale soil variability. Secondly, they do not disturb environmental and soil processes which influence gas exchange. Micrometeorological methods are based on atmospheric turbulence as medium for the gas exchange between terrestrial (or water) surfaces and the atmosphere.

2.4.3.1 'Conventional' methods

The two most common – conventional – micrometeorological methods for measuring trace gas fluxes, eddy correlation and gradient diffusion methods, are both limited to situations in which the air moves

over a homogeneous exchange surface for a long distance so that gas concentration profiles in the air are in equilibrium with the local rate of exchange and *horizontal* concentration gradients are negligible. In such circumstances, the vertical flux density of the gas will be constant with height in the air layers close to the ground, and a one-dimensional (vertical) analysis can be made (Denmead 1983). The vertical mass flux of gas emissions measured at one point can be considered as the ammonia volatilisation rate from the whole site. The upper boundary of the layer in which the flux is constant with height depends mainly on the fetch, i.e. the distance the wind travels over the plain, homogeneous experimental fields. Fetch/height ratios are vary between 200:1 to 100:1 (Denmead 1983, Moncrieff et al. 1997). For a fetch of 100 m, these ratios would give maximum working heights of 0.5 to 1 m. The size of the eddies, the micro-scale turbulent flow in form of coherent patches of swirling air, depends on landscape and canopy structure. The dimension of the eddies determines at which height gas sampling and wind speed measurement have to be carried out: the rougher the surface the higher the placement of the measurement devices. Moreover, for measurement's sake sampling must be carried out in several metres height for both Eddy Correlation and Gradient Diffusion Method. As a result, fetches of several 100 metres, i.e. uniform areas of several hectares, are required for the successful application of these methods. In addition to the problem of finding homogeneous locations, in particular in densely structured Chinese agricultural regions, the methodological obstacle of properly applying the treatments emerges as it takes considerable time to apply mineral fertilizer or slurry to an area of several hectares. But ammonia volatilisation from e.g. slurry or ammonium bicarbonate starts immediately after broadcasting.

The main difference between the two conventional approaches is that eddy correlation methods directly measure gaseous fluxes by sampling the air as it flows past a sampling point for vertical wind speed and direction as well as gas concentration, while gradient diffusion methods measure indirectly by quantifying the rate of diffusion down a concentration gradient (Moncrieff et al. 1997).

Eddy Correlation Method (Eddy Covariance, (Relaxed) Eddy Accumulation)

This method is a straightforward implementation of the measurement approach common to all micrometeorological methods. Small eddies, the micro-scale turbulent flow in form of coherent patches of swirling air, in the atmosphere close to the soil surface are considered as the medium of transport for gases emitted from soil. Instantaneous concentrations of the gas of interest are measured at one height within the air layer which is influenced by its emission and correlated with the instantaneous vertical wind speed at the same point. In the natural environment the eddies important for these vertical transport processes have a frequency of 5 to 10 Hz. Concentration and wind speed measurements have to be carried out with the same frequency. For some gases appropriate measurement devices (e.g. CO_2,

CH_4 and N_2O laser trace gas analysis (Wagner-Riddle et al. 1996)) already exist. As ammonia is adsorbed at surfaces to a high degree and is readily soluble in water films on objects, no proper instruments for high frequency measurement of ammonia exist yet.

However, the eddy correlation approach has been modified to the eddy accumulation technique and has even been more simplified to the relaxed eddy accumulation method (REA) (Fowler et al. 1995, Moncrieff et al. 1997) which can be used for ammonia volatilisation measurements (Neftel et al. 1999, Zhu et al. 2000). The eddy accumulation method disentangles high frequency sampling and accurate measurement. According to vertical up or downward wind speed signals air samples are sucked into two different sampling reservoirs or denuder tubes. Thus, the air content in the two up- and downward wind reservoirs is weighted by the high frequency air sampling into one of the tubes induced by high precision wind speed measurements. This corresponds to the integration of the fluxes over specific time periods. Precise analysis of gas concentrations (or the amount of gas sampled) is carried out later on in the laboratory.

In contrast to the eddy accumulation method, high frequency air sampling is relaxed when applying the relaxed eddy accumulation technique as the sampling rates do not have to be proportional to the vertical wind fluctuation. Air sampling is carried out at the same rate throughout the whole experiment but the valves are directing the samples to one of the two different reservoirs with regard to up and down vertical wind signals. Not the rate of the sampling but its direction to the respective reservoir is controlled by the vertical wind direction is up or down. However, according to Neftel et al. (1999) even for REA the problem of ammonia adsorbed in the system exists, thus causing memory effects leading to different offsets in the two channels.

Gradient Diffusion Method (aerodynamic, Bowen ratio methods)

As mentioned before gradient diffusion methods are also based on the principle of gas transport by the eddying motion of the atmosphere close to the surface. In contrast to the eddy correlation method, gas concentration measurements and vertical wind speeds are not correlated directly at one height but indirectly by measuring gas concentrations at several heights and the transport parameters in between those heights (Eq.3).

$$F_\chi = -K_\chi \frac{d_\chi}{d_z} \qquad (3)$$

F_χ Flux of the gas with the concentration χ
K_χ Exchange coefficient (eddy diffusivity)
χ concentration of the trace gas
z height

Gas concentrations are measured at several heights (at least two) by denuder tubes or other adsorption devices. The exchange coefficient (K_χ) is obtained by invoking a principle of similarity which says that all scalars (heat, mass) are transported equally effectively, and, once the exchange coefficient for one is found, the rest are equal (Moncrieff et al. 1997). Typical scalar variables measured for the determination of the eddy diffusivity parameter are heat, water vapour or momentum; they are kind of tracer entities behaving similar as the gas of interest in turbulent air. The eddy diffusivity depends on wind speed, surface roughness and atmospheric stability. One problem of gradient diffusion approaches is that the concentration differences between the measurements at two heights have to be large enough in order to properly calculate gaseous fluxes. For that purpose the height differences have to be sufficiently large, i.e. 2 or 3 m (Denmead and Raupach 1993). But this requirement increases the need for a sufficiently large measurement field entailing above mentioned problems. In addition, measurements in sites with rather tall, rough vegetation, close to vegetation surfaces or within plant canopies are difficult because of small concentration gradients. The major advantage of the conventional gradient diffusion approach is its use of simple instrumentation.

The *Bowen ratio*-energy balance approach (Denmead 1983, Fowler et al. 1995, Moncrieff et al. 1997) for the derivation of the diffusivity parameter can be used to make the gradient diffusion method applicable in above mentioned critical situations. The Bowen ratio, the ratio between sensible and latent heat flux (in energetic dimension), can be applied in the roughness sublayer above low vegetation (grass, agricultural crops etc.) as it only assumes a similarity of the exchange coefficient between scalars (Fowler and Duyzer 1989). The Bowen ratio can be used for the determination of sensible and latent heat flux. The latter themselves can be used for the derivation of transfer coefficient of trace gases. The assumption is that the transfer characteristics for humidity, temperature and the trace gas species are identical. As in applying the Bowen ratio method the transfer coefficient is derived from latent and sensible heat fluxes no wind velocity profile measurements are required.

Gradient diffusion methods are applicable to NH_3-measurement (Denmead 1983, Harper 1995, Génermont et al. 1996, Herrmann et al. 2001), but some corrections have to be made e.g. because of the temperature dependence of gas concentrations in the air sampled (Denmead 1983).

2.4.3.2 Mass Balance Methods (IHF Methods)

Mass balance methods (Integrated Horizontal Flux Methods, IHF-Methods) are based on the calculation of vertical trace gas fluxes from horizontal fluxes measured. This calculation also requires the precise knowledge of the fetch distance. Mass balance methods are meeting the requirement of a non-disturbing technique that integrates over larger space and time scales than is possible with chambers while not being based on the micrometeorological preconditions which call for large fetches as needed for

gradient and eddy-correlation approaches (2.4.3.1). Plot dimensions are typically tens of meters instead of the hundreds of meters required for the latter methods. Moreover, instrumentation requirements are quite simple when trapping techniques can be used to concentrate the gas (Denmead and Raupach 1993). Short fetches are sufficient as mass balance methods measure trace gas concentration profiles right through the boundary layer developed over the plot rather than just in the much smaller, equilibrium layer close to the surface. As a result, these methods are most successful when the fetch is small so that the height of the boundary layer (Z) is also conveniently small. When the fetch (x) is 10 to 20 m, z is around 1 to 2 m, its actual height depending on fetch surface roughness and atmospheric stability.

IHF-methods determine the downwind *vertical* gas flux (e.g. ammonia volatilisation) from a horizontal plain of a specific breadth by measuring the upwind *horizontal* fluxes through a vertical plain of the same breadth (Denmead 1983). Samplers are mounted in several heights quantitatively absorbing the ammonia of the air passing through them horizontally. Thus, the vertical ammonia flux from the fertilised field is calculated from the measurement of the cumulative vertical concentration profiles of ammonia which was established after the wind had passed over the field. Mass balance methods can be based on active and passive air sampling. If active sampling is chosen the ammonia fluxes measured have to be corrected for the influence of wind speed by simultaneous wind speed measurements. In case of the measurement poles not being placed in the centre of a *circular* plot corrections for wind direction are necessary, too. Denmead et al. (1977), McInnes et al. (1985), Denmead 1995; Mannheim et al. (1995) and Denmead et al. (1998) show the application of active flux mass balance approaches. Passive flux IHF-methods directly determine the product of ammonia concentration in the air and wind speed, i.e. the mass flux of ammonia. Therefore no wind speed and –direction have to be measured when this variety of the IHF-method is applied. Examples for passive flux methods used in the experiments are given in Chapter 3.2.2 and 3.2.3. Total ammonia losses are calculated by integration of the flux densities measured over the sampled measurement height intervals (e.g. 0 – 0.5 m, 0.5 – 1 m etc.). For all Mass Balance Methods the vertical flux density from the soil surface is calculated using the following equation:

$$F = \frac{1}{x}\int_0^z \overline{u\rho_g}\,dz \qquad (4)$$

F vertical flux density
x travelling distance of the wind over the sampling site (fetch)
$\bar{u}$ average horizontal wind speed
$\overline{\rho_g}$ average concentration (density) of the gas minus background concentration
$\overline{u\rho_g}$ time based mean horizontal flux densities in each sampled air layer above the vertical plain
z height above ground

The horizontal flux consists of a mass flux out of the experimental area and the turbulent diffusive flux in the opposite direction. The measurement of the latter would require the same fast-response instrumentation as for eddy-correlation measurements but accounts for about 10 percent (Denmead 1983, Denmead and Raupach 1993) of the measured mass fluxes only. Therefore, most mass balance methods determine only the convective fraction $\bar{u}\,\overline{\rho_g}$ of $\overline{u\rho_g}$, which is the product of average horizontal wind speed and mean ammonia concentration. The results can be corrected by a subtraction of 10% of the mass fluxes measured. As a consequence, mass balance methods require only comparatively simple and no fast-response instrumentation.

One of the disadvantages of mass balance methods is that background trace gas concentration profiles have to be measured as well. So, they include the subtraction of experimentally determined data, which can be an error-prone procedure. It is thus advisable to use these methods when the fluxes from the treatments are high in comparison to the background fluxes.

There is another special application of mass balance method. Theory and experiment indicate that in certain situations, it is possible to infer the surface flux from a measurement of the horizontal flux at just one height above the plot centre. There are two requirements: Although the treated plots should be small, the area in which they are located should be large and uniform so that the wind profiles are equilibrium profiles. Second, the treated area should have no vegetation cover, or at least a very short one, so that virtually all of the horizontal flux occurs in the unobstructed air layer above the surface. If the surface roughness and the plot geometry are known and atmospheric stability is given, it is possible to predict the existence of a particular height within the plot boundary layer, at which the normalised horizontal flux has almost the same value in all stability regimes. This measurement height is called ZINST (Denmead 1983). Measurements at that particular height with the passive flux samplers as mentioned below are sufficient to determine the vertical flux density (Denmead and Raupach 1993).

In some instances it is necessary to measure trace gas emissions from rather small point sources (e.g. ammonia volatilisation from urine patches or faeces). Although it is possible to measure such emissions with chamber methods, spatial integration remains still problematic. As a consequence, modified mass balance methods provide a remedy, e.g. Denmead et al. (1998).

A specific approach for the application of the mass balance method within plant canopies is the Inverse Lagrangian Method by Raupach (Denmead and Raupach 1993, Denmead 1995). It shall not be described in detail here. As with chamber methods, advantage is taken of the restricted air movement in the canopy, which makes for larger and more easily measurable concentration changes than in the unobstructed atmosphere. Within the canopy, the source or sink strength of the gas is determined. The method's main advantage is that it does not rely on rigid preconditions of atmospheric stability. However, there are still some theoretical meteorological problems connected with this approach.

Nevertheless, it can be particularly useful for the measurement of gases with sources and sinks in the foliage.

2.4.4 Approaches for the regional scale

Although accurate measurement methods for trace gas emissions on the field scale level exist it is hard to infer trace gas emissions on the landscape scale from these measurements. Landscapes consist of several ecosystems with differing soil and land cover properties. In some ecosystems (e.g. forests) it is particularly difficult to carry out reliable trace gas measurements. As a result, it may be preferable to have measurement approaches which are able to integrate trace gas fluxes over larger areas and landscape mosaics.

The Convective Boundary Layer Budget Method by Raupach (Denmead and Raupach 1993, Lloyd et al. 2001) uses atmospheric turbulence much larger in scale than eddies, the convective turbulence often more than 1 km deep by evening. There are diurnal gas exchange processes via this convective boundary layer (CBL) between the surface layer close to the ground and the stable overlying air. In the course of a day budgets of CO_2 or other scalar trace gases can be calculated. These measurements can be used to infer trace gas fluxes at the surface of the earth on a regional scale (100 – 1000 km²). This budget method for flux measurements amounts to using the CBL as a large "natural chamber". Its bulk properties are independent of small-scale surface heterogeneities, so it acts as a natural integrator of surface fluxes over heterogeneous terrain. The distance over which the CBL carries some "memory" of conditions upwind, its "footprint", is typically 5 – 30 km. This method has been applied for the measurement of N_2O-fluxes(Denmead and Raupach 1993) but not yet for NH_3-fluxes. Samples are taken by aircraft sampling at different heights in and above the CBL. For the development of a well mixed CBL and of reliable average trace gas concentrations the surface area sampled should not be too heterogeneous in vegetation and topography (preferably flat). The area should also be larger than the dimension of a CBL turbulence cell. Otherwise boundary effects would bias the results(Lloyd et al. 2001).

A second approach also based on airborne determination of trace fluxes by aircraft measurements, e.g. (Desjardins et al. 1993; Luke et al. 1998), is the application of the eddy correlation method on the regional scale. A Twin Otter aircraft was supplied with fast-response detectors for trace gases (CO_2, O_3 and NO) and for meteorological parameters (H_2O, heat, momentum). Sampling was carried out in the planetary boundary layer (heights 30, 90, 150 and 300 m above ground level). Comparison with dynamic chamber method and conventional micrometeorological measurements in two surface flux stations showed good agreement. However, due to the requirement of fast response detectors this approach has not yet been used for the measurement of NH_3-fluxes on the regional scale. Desjardins et

al. (1993) showed that also the eddy accumulation method can be adapted to aircraft-based measurement approaches.

2.4.5 Indirect methods

The most common approach for an indirect estimation of N-losses by ammonia volatilisation is the ^{15}N-balance method (isotopic method) (Reynolds and Wolf 1988, Sharpe and Harper 1995, Vlek et al. 1995, Génermont et al. 1996, Rees et al. 1997, Pilbeam and Hutchinson 1998, Lara Cabezas et al. 1999). It also belongs to the methods which determine ammonia volatilisation on the microscale level. This approach is described in more detail in Chapter (3.4.1). In most instances the ^{15}N balance method is used in combination with other measurement methods, in particular chamber and micrometeorological methods.

3. Material and Methods

3.1. Experimental site description

3.1.1 Location

The experiments were carried out on farmers' fields (Tunli village) adjacent to Fengqiu Agro-ecological Experimental Station (Chinese Academy of Sciences), Pandian town, Fengqiu County, Henan Province (35°1'N, 114°4'O, Fig. 2).

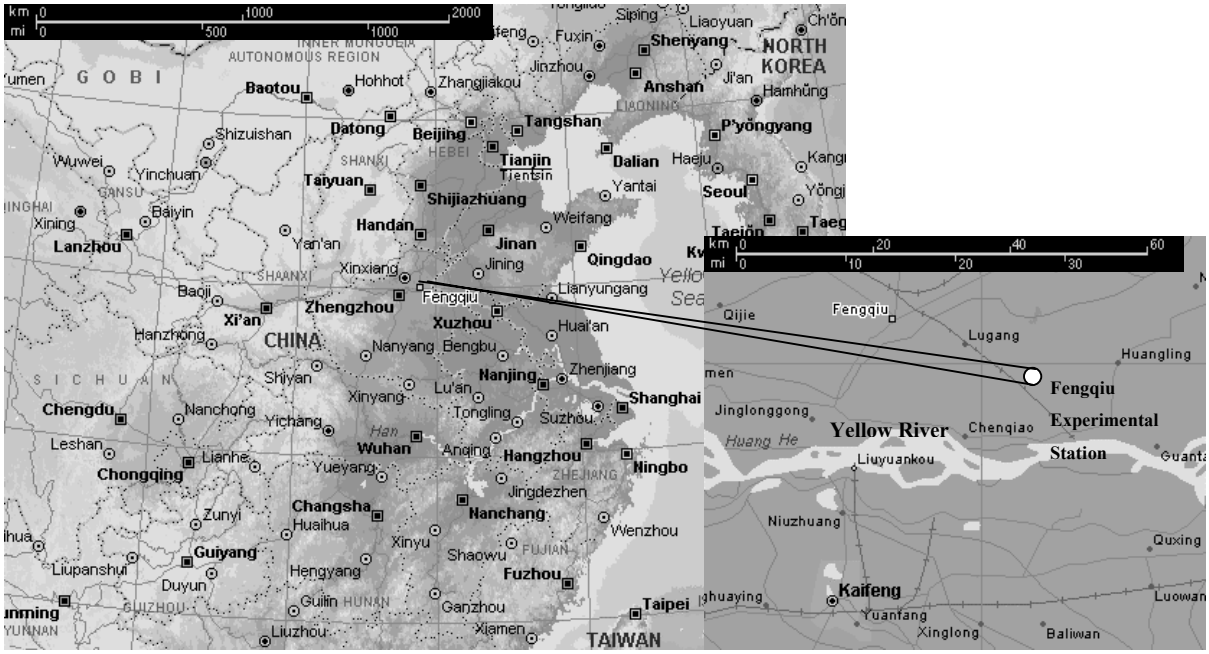


Fig. 2: Location of Fengqiu Agroecological Station in Henan Province, north of the Yellow River

Fengqiu County is located in the North China Alluvial Plain (Huang-Huai-Hai-Plain) which was formed by sedimentation (flooding) processes of three major rivers, Huang-, Huai- and Hai-river. Due to the long lasting flooding and sedimentation history, a rather complicated vertical and horizontal pattern of soil textures can be found in the plain with high regional and local variations. However, in the area of former sedimentation fans, e.g. of the Huang He (Yellow River), typical regional sequences of soil texture and soil types can be found. The Huang-Huai-Hai-Plain (300.000 km²) is China's largest agricultural area, accounting for about 40% of China's grain production (Brown 2000). Fengqiu County borders on the Yellow River (Huang He) to the South, the Experimental Station is located about 10 km north of the river. Fengqiu County can be considered as representative for the Huang-Huai-Hai-Plain with respect to land use pattern and yield levels (Xu and Zhao 1999).

3.1.2 Climate

The North China Alluvial Plain has a semi-humid climate (Li et al. 1990) with a mean annual temperature of 14 °C and a mean annual precipitation of 615 mm. The warmest month is July with an average temperature of 27 °C, the coldest January with -1 °C. In general main rainfall occurs during midsummer (June – August), while in many years spring is markedly dry. The average annual potential evaporation amounts to 1713 mm. Annually, Fengqiu has 2310 hours of sunshine and 220 frost-free days. The ground water table ranges between 2 and 4 meters depth. Because of periodical droughts and deficient irrigation technologies secondary salinisation also occurs in this region.

3.1.3. Soil characteristics

Soil characteristics of Fengqiu soil were determined at the Institute of Geoecology, Braunschweig, and the Institute of Soil Science, Nanjing. Laboratory methods used are shown in Tables 1 and 2.

Table 1: Soil analyses carried out at the Institute of Geoecology, Braunschweig

soil property	Measurement Method
soil texture	Sedimentation method (Moschrefi 1983)
C_{org}	Sample pretreatment with 10% HCl, coulometric measurement (dry combustion), (Ströhlein Coulomat 701, Germany)
$CaCO_3$	Ströhlein-measurement (see above) without HCl pretreatment. Calculation of difference to C_{org}-contents.
cations in soil solution	Soil samples (air dried) and deionized H_2O (ratio 1:2), atom absorption spectrometry (AAS 4001, Perkin Elmer, USA)

Table 2: Soil analyses carried out at the Institute of Soil Science, Nanjing

soil property	Measurement Method
CEC_{pot}	Ammoniumacetate-EDTA-method (1 mol l^{-1} NH_4-acetate, 0.005mol l^{-1} EDTA at pH 8.5)
N_{tot}	Kjeldahl-method
K (exchangable)	Ammoniumacetate-method
P (available)	Olsen ($NaHCO_3$)-method

The complicated sedimentation processes in the Huang-Huai-Hai-plain condition that soil properties at the study site show a high degree of variation, even on the field scale level. Table 3 gives the textures of soil profiles in the two winter wheat study sites. Three mixed soil cores were taken from each study site sampled with a soil auger and bulked for each layer. The depth increments correspond to N_{min} -sampling depths and not to natural soil horizons with exception of the top layer which corresponds to the plough layer. The plough layers (Ap) both have a sandy loam texture. But in the deeper layers of the two profiles differ considerably in soil texture. Due to this circumstance it is hard to give a general description of the characteristics of the soil profiles in the study area. Moreover, the differences found in the soil profiles shown in Table 3 do not reflect the high variability in soil texture as they only take into account the simplified N_{min} sampling depths. In fact all soil profiles consisted of a multitude of clay and silt layers, of between some millimetres and several centimetres thickness (see Fig. 3), in particular below a 0.1 – 0.2 m thick clay layer at a depth around 0.2 – 0.5 m. However, in general the region's dominating soil type can be classified as ochric aquic cambisol (US Soil Taxonomy) or calcaric fluvisol (FAO).

Table 4 shows the soil properties of the plough layers of several study sites. The top soils have only low C_{org} contents, and CEC_{pot} is also comparatively low. In comparison to German soils of similar texture the soils' supply with potassium and phosphorus can be considered as low. The mean pH (H_2O) in the soils is 8.5.

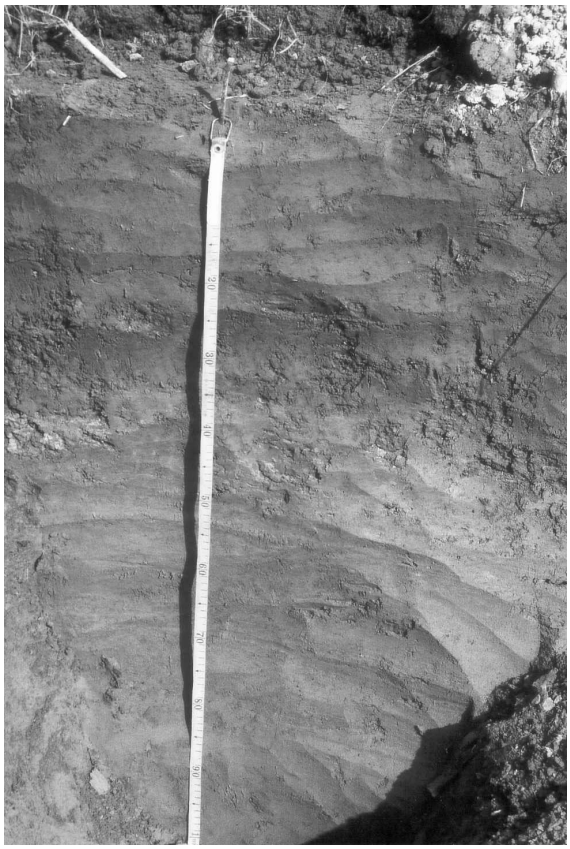


Fig. 3: Soil profile at Fengqiu Agroecological Experimental Station

Table 3: Soil texture in soil profiles taken in winter wheat study sites (autumn 1998 and spring 1999)

study site [No.]	depths [m]	clay (<0.002 mm) [%]	silt (0.002–0.063 mm) [%]	sand (0.063-2.0 mm) [%]	texture (FAO classification)
wheat, surface broadcast fertilization	0-0.2	11	25	64	sandy loam
	0.2-0.6	30	45	25	clay loam
	0.6-0.9	20	75	5	silt loam
	0.9-1.2	10	82	8	silt loam
wheat, mixed fertilization	0-0.2	10	27	63	sandy loam
	0.2-0.6	16	36	48	loam
	0.6-0.9	41	51	8	silty clay
	0.9-1.2	12	80	8	silt loam

Table 4: Soil properties in Fengqiu (surface soil 0-0.2 m)

experimental site	pH (H_2O)	C_{org} (%)	P available (mg kg^{-1})	K available (mg kg^{-1})	N total (%)	CEC_{pot} ($mmol_c$ kg^{-1})
maize, site 3 (surface broadcast)	8.36	0.56	3.00	66.3	0.0601	73.3
maize, site 4 (deep point placement)	8.79	0.64	4.29	72.5	0.0659	80.3
wheat, site 5 (surface broadcast)	8.47	0.47	26.01	75.0	0.0520	80.9
wheat, site 6 (mixed incorporation)	8.69	0.48	3.29	62.5	0.0576	72.0

3.1.4 Agricultural practice

A large portion of Fengqiu County's arable land has been improved by leaching of salts accumulated in the top soil by intensive irrigation measures in the 1950s and 1960s. In the years immediately following 1949 the water used for irrigation was mainly derived from the Yellow River and was pumped through a system of canals into the neighbouring agricultural areas. In recent years on average of 210 mm of river water has been applied. In the 1970s and 1980s of the last century the numbers of irrigation wells was raised considerably. Present-day, about 140 mm a^{-1} of ground water are used for irrigation purposes. Overall, 347 mm of irrigation water altogether has been a applied annually to Fengqiu fields in recent years.

In the 1970s Fengqiu county still depended on external grain subsidies, because the grain yields in the area were too low to support the local population. Since the mid seventies wheat- and maize yields have been quadruplicated due to continually increased mineral fertilizer application, improved irrigation and better wheat and maize varieties. Present-day Fengqiu County is a net grain exporter and the railway-tracks which had been built to transport grain to the county were given up (Xu 1998). Nevertheless, agriculture in Fengqiu county is still challenged by several problems. In particular, the inefficient use of ground water for irrigation purposes leads to the depletion of this valuable resource. But also the increasing diversion of water upstream the Yellow River has diminished the water resource base of the

county (Xu and Zhao 1999). Since the last decade groundwater tables in the North China Plain and likewise in Fengqiu county have been dropping dramatically (Brown 2000).

The agricultural management in the region is characterized by a double-cropping system of winter wheat (*Triticum aestivum* L.) – maize (*Zea mays* L.). In the winter half year almost all fields are planted with winter wheat, while in summer in parallel to maize soy beans (*Glycine max*), peanuts (*Arachis hypogaea*), sweet potatoes (*Ipomoea batatas*) and cotton (*Gossipium depuratum*) are also grown. Both main crops are irrigated. The fields are cultivated independently by farmers' families (on average 5 persons). Each family is cultivating an average area of 1.4 mu (0.093 ha). Close to the Yellow River rice (*Oryza sativa L. var. japonica*) is grown instead of maize in summer.

In recent years on average 180 – 220 kg of mineral fertilizer N ha^{-1} were applied to winter wheat and maize, respectively. Urea is the predominant N-fertilizer used in the county, besides NH_4HCO_3. For wheat mineral N fertilizer is applied in two rates: the first (100 – 120 kg N ha^{-1}) is applied as basal dressing at sowing in October, about 5 months later, the second rate (ca. 100 kg N ha^{-1}) (top-dressing) in early spring. The fertilizer application method for basal dressing is uniformly mixing of the fertilizer with the soil (at ploughing), for top-dressing fertilization immediately followed by irrigation (40 – 60 mm).

Maize is sown without ploughing into the stubble remaining on the field after wheat harvest. For maize N-fertilizer is applied in one *or* two doses. In case of only one fertilization, urea is applied 5 weeks (height of plants ca. 0.8 m) after sowing at a rate of about 200 kg N ha^{-1}. In this case the predominant application method is the so-called 'deep point placement': about one spoonful of urea is placed in a whole of ca. 5 cm depth to every second maize plant in the row and covered with soil. If fertilizer is applied twice, the first dose (80 kg N ha^{-1}) is given 4 weeks after sowing (height of plants ca. 0.4 m), the second (120 kg N ha^{-1}) in the 7th to 8th week (height 1.2 m). In case of split fertilizer application the first rate is applied as fertilization followed by irrigation, the second as deep point placement or fertilization followed by irrigation. Surface broadcasting of urea can be considered as an exception.

A traditional Chinese form of organic manure is sporadically applied: soil material (up to 90% of the manure total) is put into the stable and thereby mixed with livestock dung. In Fengqiu County K is usually provided by the application of above mentioned organic manure ('soil manure') or as straw and ash. Maize and wheat are fertilised with ~120 kg P_2O_5 ha^{-1} and ~150 kg P_2O_5 ha^{-1}, respectively (Cai, pers. comm.). Present-day average yields at Fengqiu are 5.55 t ha^{-1} and 5.48 t ha^{-1}, for wheat and maize respectively.

3.2 Methods for the measurement of ammonia volatilisation

Eddy-correlation- and Gradient Diffusion Methods are the most accurate methods for determining gaseous losses in the field (see Chapter 2.4.3.1). However, they have several disadvantages with regard to their applicability under field conditions in China. Firstly, they depend on on-site current supply and neighbouring or easily available laboratory facilities which under many circumstances are not at hand during field experiments in China. Secondly, both methods require sufficient field sizes in order to provide micrometeorological conditions for a proper application of those methods. The average Chinese field is quite small with about one tenth of a hectare. Fields are also very often close to channels and rows of trees which both obstruct an even land surface. In order to circumvent those problems two mass balance methods (IHF-methods, see Chapter 2.4.3.2) were chosen for the calibration of the dynamic chamber method (DTM) by simultaneous ammonia loss measurements during field experiments in Fengqiu.

3.2.1 Draeger-Tube Method

3.2.1.1 Draeger Tube Method with hand pump

The Draeger Tube Method was developed by Richter (1972) for the measurement of CO_2 evolution from soil. Roelcke (Roelcke 1994, Roelcke et al. 2002 a) adapted the method for the measurement of ammonia volatilisation in arable soils following the application of mineral N fertilisers. It can be described as a special variant of the dynamic chamber methods (see Chapter 2.4.1). Four conical cups (chambers) covering a soil surface of 415 cm² altogether (~ 104 cm² each) are gently pressed into the soil. Ambient air is sucked through the chambers via an air inlet consisting of a copper pipe with 4 lateral perforations (1 – 2 mm in diameter) close to the soil surface by means of a hand pump. On its passage through the chamber the air is enriched with NH_3 volatilising from the soil surface. The pump rate is about 1 l min^{-1}, corresponding to an air exchange rate of less approximately 1 vol. min^{-1}. The air sucked through the chambers is led through teflon tubing to a NH_3-sensitive Draeger indicator tube (Drägerwerk AG, Lübeck) which immediately displays the NH_3 concentration (in volume ppm) by the displacement of a calibrated reaction front in the tube. Figure 4 shows a transverse section of a measurement cup and a sketch of the setup of the Draeger-Tube measurements in the field. Ammonia fluxes are calculated from the ammonia concentration measured, the covered soil surface [cm^2] and the pump rate [l $min.^{-1}$] (Eq.5). The pump rate is determined by the volume of pump strokes [100 ml $stroke^{-1}$] and the time period used for pumping measured with a stop watch. For the calculation of ammonia concentration in the air passed through the cups from the NH_3 volume concentration displayed on the Draeger Tubes, the latter values have to be corrected by a factor for the barometric air pressure and air

temperature. Thus, for each measurement air pressure and air temperature have to be determined simultaneously. Concentration values have to be corrected by subtraction of background NH_3-concentrations.

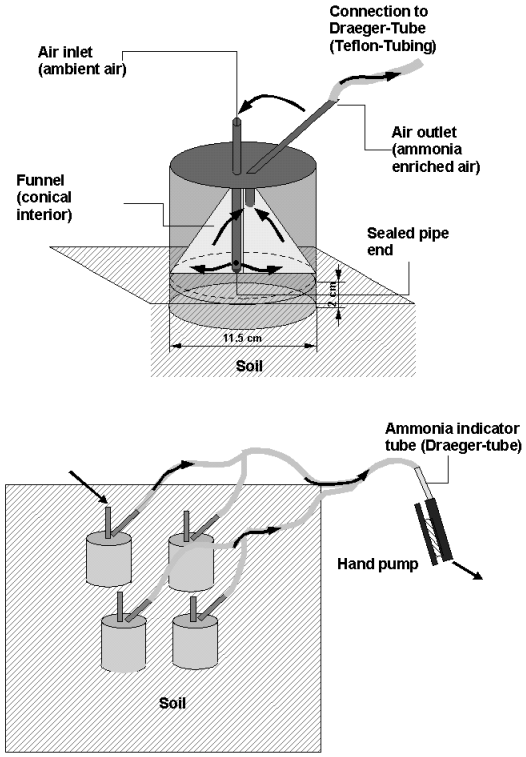


Fig. 4: Experimental set-up of the Draeger-tube method applied with a hand pump

$$\mathbf{F_{Ng} = volume \cdot |conc| \cdot 10^{-6} \cdot \rho_{NH3} \cdot U_N \cdot U_F \cdot U_Z} \quad (5)$$

F_{Ng} :	ammonia flux [mg N m^{-2} h^{-1}]
volume:	air volume sucked through the chambers [l]
| conc | :	value of NH_3-Vol.-concentration (ppm)
ρ_{NH3} :	temperature dependent density of NH_3 [mg l^{-1}]
U_N:	molecular weight conversion factor of NH_3 to N
U_F :	surface area conversion factor [m^{-2}]
U_Z :	time conversion factor [h^{-1}]

Subject to the intensity of the ammonia volatilisation process, 2-5 measurements are carried out per day with 2 – 3 replicates (Fig. 5). Each single measurement takes about 3 minutes. The timing of measurement was chosen taking into consideration the diurnal variation in ammonia emission, i.e. low ammonia fluxes at night time and high fluxes at about noon. Measurement events should cover time

periods of both comparatively high and low ammonia fluxes. By linear interpolation between the ammonia fluxes measured at two subsequent sampling events these punctiform measurements are used for the calculation of the whole time course of fluxes and cumulative ammonia losses (g N m^{-2}, kg N ha^{-1}; Eq.5) from the soils.

Fig. 5: Draeger-Tube measurement (hand pump) in Fengqiu; in the background: micrometeorological measurement pole

In case of deep point placement of urea (see chapter 3.1.4) ammonia fluxes were determined by a modified calculation. It was assumed that the whole soil surface through which ammonia is volatilised above a fertilizer amended point was covered by one measurement cup. Four fertilizer points were included in each measurement and one fourth of the measured flux value was considered as the ammonia flux from one fertilizer point. The extrapolation from the measurement results of a single point to the ammonia losses from an area of 1 ha was carried out by multiplying the results with the number of fertilizer amended points per ha.

It has already been mentioned in Chapter 1.3 that application of the Draeger-Tube method with hand pump led to an underestimation of the 'true' ammonia losses of almost one order of magnitude in earlier

experiments. The comparatively low air exchange rate in the cups due to the application of the hand pump was considered as the main explanation for this circumstance. An air exchange rate of about 1 Vol. min^{-1} in the cups applied with the hand pump is too low to correspond to field conditions of ammonia volatilisation and, thus, leads to the underestimation of ammonia losses in most probable instances.

3.2.1.2 Draeger Tube Method with electric pump

As the major calibration approach, the Draeger-tube method with hand pump was calibrated by correlating the measurement results with ammonia measurements by a micrometeorological standard method and meteorological variables. In addition, the Draeger-tube method was modified with regard to higher air exchange rates in the cups. For that purpose the teflon tubes leading the gas sucked through the cups to the indicator tube were connected to an electric vacuum pump (FÜRGUT, DC 12/90S2, Aichstetten, Germany) driven by a portable battery (Fig. 7). Air exchange rates in the system were determined by means of an air flow metre installed between the electric pump and air outlet of the cups. In contrast to the set-up with the hand pump the Draeger Tubes were not directly connected to the air-flow passing through the cups. The indicator tubes are calibrated to a particular air stream moving through the substrate matrix contained in the tubes and the particular suction characteristics of the hand pump. Inserting the indicator tubes between electric pump and cups would had entailed an exceedingly high air stream through the tubes and thus inaccurate measurements. As a remedy, a part of air stream through the teflon tubing was deviated for taking gas samples by means of the hand pump and indicator tubes. A check-valve was used as a safeguard to prevent ambient air to be sucked via the by-pass into the system.

Preliminary measurements with the new system revealed that the diameter of the air inlet pipe of the ordinary measurement cups was too small to prevent air to be sucked out of the soil when applying higher pump rates with the electric pump. The Draeger-Tube method relies solely on ambient atmospheric air passing over the soil surface in the chambers. Thus, the design of the chambers was to be modified, as well. The air inlet consisting of one copper pipe with lateral holes for the cups applied with the hand pump was replaced by three copper pipes of a diameter of 15 mm (Fig. 6). Laboratory checks showed that no air was sucked out of the soil into the system.

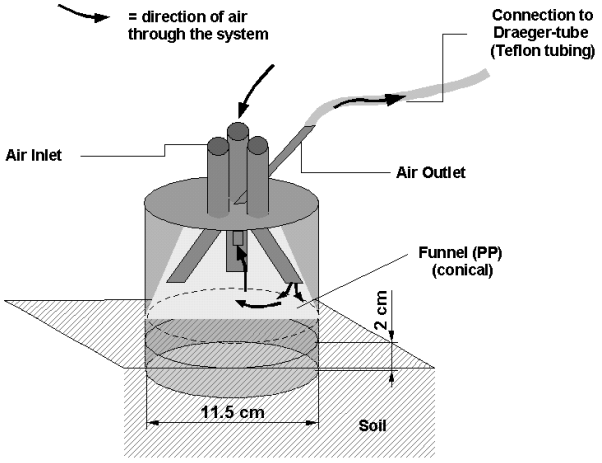


Fig. 6: Design of the chamber combined with the electric vacuum pump

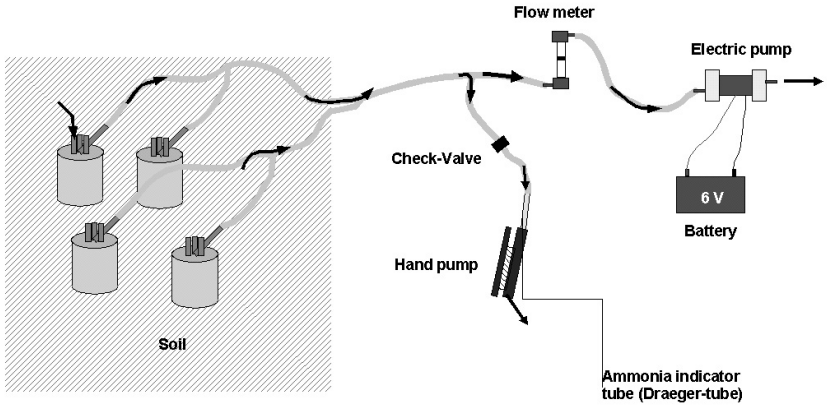


Fig. 7: Set-up of Draeger-tube measurements combined with an electric vacuum pump

The equation for calculating ammonia fluxes was adapted to the new set-up of the modified method (Eq. 6). Cumulative ammonia losses [kg N ha^{-1}] were calculated in the same way as for the unmodified original Draeger-tube method.

$$\mathbf{F_{Ng} = |conc| \cdot 10^{-6} \cdot \rho_{NH3} \cdot U_N \cdot U_F \cdot pump\ rate} \quad (6)$$

F_{Ng} : ammonia flux [mg N m^{-2} h^{-1}]
$|conc|$: value of NH_3-Vol.-concentration (ppm)
ρ_{NH3} : temperature dependent density of NH_3 [mg l^{-1}]
U_N: molecular weight conversion factor
U_F : surface area conversion factor [m^{-2}]
pump rate: [l h^{-1}]

In the field experiments an air exchange rate of about 20 Vol min^{-1} was chosen. To that end only two cups were connected in order to achieve the appropriate air exchange rate at a pump rate of 1250 l h^{-1}, which was the maximum pump rate of the vacuum pump. The effect of the reduction of cup numbers on ammonia fluxes measured was tested in separate experiments and proved not to be significant (see chapter 4.1.1). When applying the Draeger-Tube method with electric pump each measurement comprised three replicates. The quite effective vacuum pump was comparatively light (1 kg) and the current supply consisted in a 6 V motorcycle battery. This way a high applicability was still provided when applying the modified Draeger-tube method.

3.2.3 Mass Balance Method by Leuning et al. (1985) and Sherlock (1989)

(Space Shuttle Method SSM)

The mass balance method (see Chapter 2.4.3.2) by Leuning et al. (1985), further modified by Sherlock et al. (1989), was the main micrometeorological method used for the comparison with and calibration of the Draeger-tube method. Due to the characteristic shape of the passive flux samplers this method will further be referred to as Space Shuttle Method (SSM, Fig. 8). This method was also applied by Wood et al. (2000) for the calibration of an improved method for field-scale measurement of ammonia volatilisation.

The pivoted passive flux samplers are attached at a measurement pole by means of metal frames in different heights. The internal absorbing surfaces consist of a spiral of thin stainless steel sheet wound on two wire formers attached to a sealed, central tube. Oxalic acid coating is used as absorber of ammonia in the air passing the sampler. In general the samplers were mounted at heights 0.4 m, 0.8 m, 1.2 m, 1.6 m and 2 m above ground. Fins at the rear end keep the samplers aligned with the wind whenever the wind changed its course. The measurement pole is put into the centre of a fertilised circular experimental plot surrounded by a large unfertilised area. As a consequence, the distance the wind travels over the fertilised area (fetch) is always identical. Background ammonia concentrations are accounted for by measuring ammonia flux profiles with an identical device in unfertilised fields upwind of the fertilised plots.

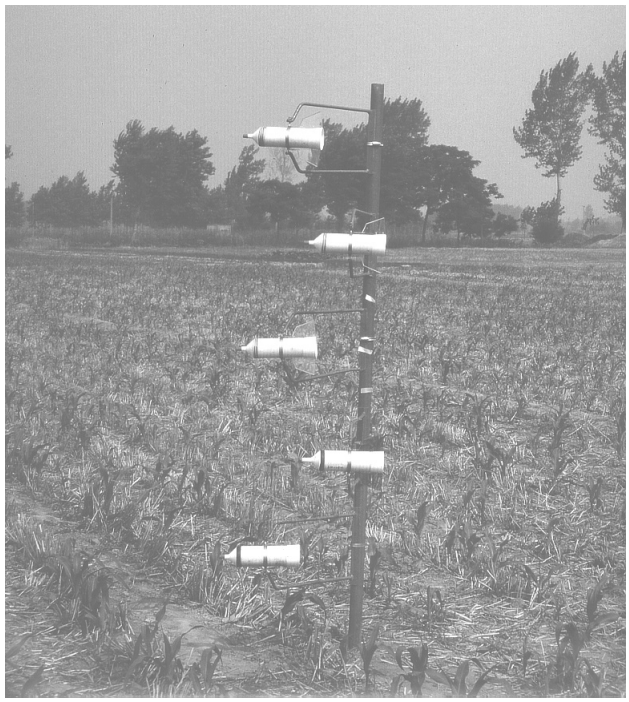


Fig. 8: Measurement pole equipped with SSM samplers (Leuning et al. 1985) in Fengqiu (maize crop)

The calculation of the horizontal flux densities through one sampler is calculated by following equation (Eq.7, Sherlock et al. 1989):

$$\overline{\overline{u\rho}}_A = \frac{M}{A_e t} \tag{7}$$

$\overline{\overline{u\rho}}_A$	mean horizontal flux density of ammonia [mg NH_3-N m^{-2} h^{-1}]
M	measured mass of ammonia collected in the sampler [mg]
t	measurement time interval [h]
A_e	effective cross-sectional area of the sampler determined in wind tunnel experiments [$2.42 \cdot 10^{-5}$ m²]

The *vertical* flux density of ammonia as measured with the passive flux samplers (F_S) is calculated from equation (8).

$$F_S = \frac{1}{X}\int_0^z (\overline{\overline{u\rho}}_{AC} - \overline{\overline{u\rho}}_{AB})dz \tag{8}$$

F_S	vertical ammonia flux from the fertilised area [mg NH_3-N m^{-2} h^{-1}]
X	radius of the circular area (fetch) [m]

$\overline{\overline{u\rho}}_{AC}$ mean horizontal flux density of ammonia [mg NH_3-N m^{-2} h^{-1}] from the fertilised area

$\overline{\overline{u\rho}}_{AB}$ background mean horizontal flux densities [mg NH_3-N m^{-2} h^{-1}] measured in the unfertilised area

z height of the plume of ammonia over the circular area [m]

For each height increment the average horizontal ammonia flux density is calculated from the measurements of the two samplers delimiting the increment. If 5 measurement heights were applied, the vertical ammonia flux densities were calculated as derived from Eq. 7 and Eq. 8 (Eq. 9):

$$F_S = \frac{1}{X}\sum_{1}^{5}\frac{(\overline{\overline{u_{i-1}\rho_{i-1}}} + \overline{\overline{u_i\rho_i}})}{2}\cdot\Delta h_i \qquad (9)$$

$\overline{\overline{u_i\rho_i}}$ horizontal ammonia flux density at sampler (height) i [mg N m^{-2} h^{-1}] corrected by subtraction of ammonia background fluxes

Δh_i height increment between sampler i and sampler i-1 [m]

A horizontal flux density of 0 [mg N m^{-2} h^{-1}] was assumed for i=0, i.e. at the soil surface.

The duration of each sampling period, i.e. the time interval in which one set of samplers was installed on the experimental site, depended on the ammonia concentration in the atmosphere close to the soil surface. In case of high ammonia concentration the samplers were exchanged 2 - 3 times a day during the Fengqiu experiments. In line with decreasing ammonia concentrations in the atmosphere sampling periods were extended to 1 –2 days.

3.2.4 Mass Balance Method by Schjoerring et al. (1992)

(Ammonia Tube Method ATM)

Because of its glass tube passive flux samplers this method developed by (Schjoerring et al. 1992) is referred to in the following as Ammonia tube method (ATM). The sampler consisted of two pairs of glass tubes (7 x 10 mm, 100 mm length) coated with oxalic acid on the inside which are mounted close to each other (1 cm distance) in parallel (Fig. 9).

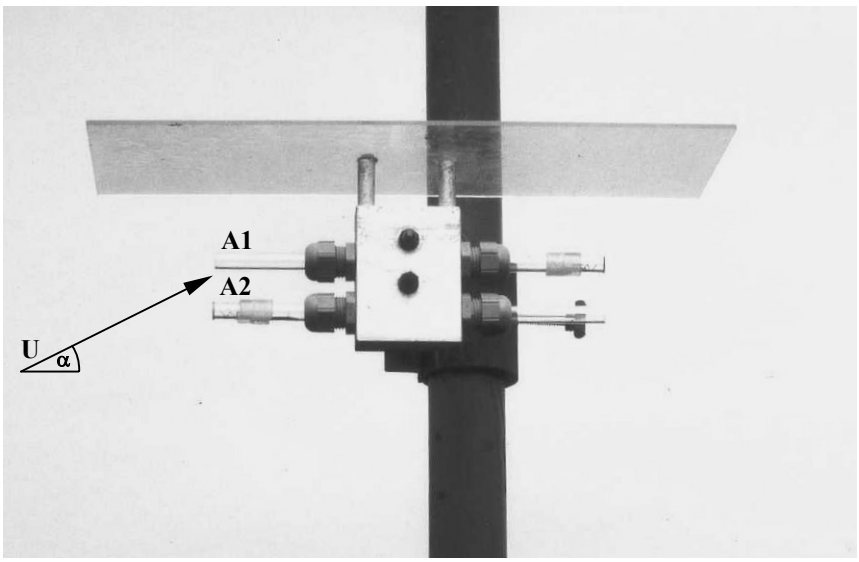


Fig. 9: ATM sampler as applied in Fengqiu (wind vector U)

Fig. 10: ATM measurement pole during winter wheat experiment in Fengqiu

Two tubes were connected by means of a metal frame to another pair of tubes with the openings pointing in opposite directions (Fig 9). A stainless steel disc with a hole (1 mm) (A2) was connected to one tube of each pair. The two types of orifice were used to keep a balanced absorption of NH_3 in the tubes in spite of different impact angles of the wind (α, U). The horizontal ammonia flux from the opposite direction of the tube orifice could thus be calculated from the ammonia absorbed in both tubes calibrated in wind tunnel experiments (Eq. 10). In contrast to the original method by (Schjoerring et al. 1992), a plexiglas roof was put above the samplers as a shelter from rain.

$$\overline{\overline{u\rho}}_A dt = \int_{t_1}^{t_2} U \cdot \cos\alpha \cdot [NH_3] \cdot dt \approx \frac{(A_1 + A_2)}{2 \cdot \pi \cdot r_T^{\,2} \cdot K_c \cdot \Delta t} \qquad (10)$$

U	wind speed [m s^{-1}]
$[NH_3]$	ammonia concentration [µg l^{-1}]
α	angle of wind
A_1	NH_3 collected in tube A1 [µg]
A_2	NH_3 collected in tube A2 (with stainless steel disc) [µg]
r_T	radius of the tube [0.5 mm]
K_c	dimensionless correction factor [0.77]
Δt	sampling time interval [s]

As for all mass balance methods the whole profile was sampled at several heights for the calculation of gaseous emissions from the measurement sites (Fig. 10). The effective ammonia absorption by the ammonia samplers had only a limited tolerance with regard to the wind impact angle. As the samplers are in a fixed position to the measurement pole and cannot be turned into the wind direction, four poles had to be installed at the border of the circular experimental site. The measurement poles were posted perpendicularly to each other. In case of the wind direction not directly pointing to the orifices, the length of the fetch and the amount of ammonia absorbed by the tubes changed inversely to each other. As the effect ammonia losses could be calculated form an effective fetch $X = 2\ r_C$.

One pair of orifices (see Fig. 9, A1 and A2) pointed towards the experimental site, the other pair to the opposite direction for taking up background ammonia fluxes from the unfertilised surrounding fields. Thus, ammonia fluxes to and from the fertilised experimental site were measured simultaneously. For the calculation of ammonia losses the horizontal ammonia flux measured in direction of the unfertilised areas was subtracted from the ammonia fluxes from the fertilised site (Eq.11). As a result, background ammonia concentrations had not to be measured separately in the surrounding fields.

In case of 4 measurement poles and 5 sampling heights vertical ammonia losses were calculated as follows (Eq.11):

$$F_S = \frac{1}{2r_C} \sum_{h=1}^{h=5} \sum_{m=1}^{m=4} (\overline{u\rho_{AC}} - \overline{u\rho_{AB}}) \Delta h \qquad (11)$$

h	height of measurement [m]
m	measurement pole
r_C	radius of the circular plot (fetch x = 2 r_C) [m]
$\overline{u\rho_{AC}}$	horizontal ammonia flux from the circular area fertilised [µg m^{-2} s^{-1}]
$\overline{u\rho_{AB}}$	horizontal flux from background area surrounding the plot [µg m^{-2} s^{-1}]
Δh	incremental height between two samplers [m]

For both mass balance methods applied, after thoroughly washing the samplers with distilled water, ammonia concentrations in the extracts were measured with an ORION ammonia electrode (USA) and a millivolt meter.

3.3 Experimental setup

3.3.1 Field experiments for measuring ammonia volatilisation

All field experiments were carried out in co-operation with the Chinese partners of the Institute of Soil Science, Nanjing, namely Prof. Dr. Guixin Cai and Dr. Xiaohui Fan, which were particularly responsible for the mass balance- and ^{15}N measurements.

Table 5: Field experiments carried out at Fengqiu Agroecological Experimental Station 1998 – 1999

No.	Date (beginning and end of NH_3-measurements)	Crop/growth stage	Application rate [kg urea-N ha^{-1}]	Application method	Irrigation [mm]
1	29 June – 07 July 1998	maize (seedling stage, 0.4 m)	75	**a.** surface broadcast (SB) **b.** fertilization followed by irrigation (BI)	40-60
2	19 – 30 July 1998	maize (10-leaf-stage, 1.2 m)	200	**a.** surface broadcast (SB) **b.** deep point placement (DP)	40-60
3	11. – 23 Oct. 1998	winter wheat (fertilisation at sowing)	120	**a.** surface broadcast (SB) **b.** mixed fertilisation (MF)	——
4	09 – 24 March 1999	winter wheat (spring treatment)	100	**a.** surface broadcast (SB) **b.** fertilisation followed by irrigation (BI)	40 - 60
5	12 - 24 July 1999	maize (6-leaf-stage, 0.8 m)	150	**a.** surface broadcast (SB) **b.** deep point placement (DP)	——

Table 5 summarises the field experiments. Five field experiments with urea application followed by the measurement of ammonia volatilisation were undertaken altogether. Fertilisation rates and fertiliser application techniques were carried out in accordance with common practice in Fengqiu County as described in chapter 3.1.4. In addition to these application methods each experiment also comprised a urea surface broadcast application as a second treatment, using the same amounts of fertiliser as in the first treatment. It has been shown in many field experiments that ammonia volatilisation losses from

urea are higher following surface broadcast application than after other application methods. Thus a wider range of ammonia fluxes would be available for the calibration of the 'Draeger Tube Method'.

The experimental sites were irrigated by simple flood irrigation according to the local practice. Small earth ridges (ca. 0.2 m height) were built surrounding the fields. Irrigation water was pumped by Diesel pumps from irrigation wells to the fields. In case of 50 mm of irrigation water applied, it took about 1-2 hours until the water infiltrated into the soil. The experimental sites were irrigated immediately following fertiliser application. In case of surface broadcast application of urea irrigation water was applied 1 day before start of the experiment as the soil surface would have been still too wet to apply fertiliser immediately after irrigation. Fertilizer was applied by hand.

According to the requirements of the measurement methods used field experiments were designed as shown in Fig. 11 and 12.

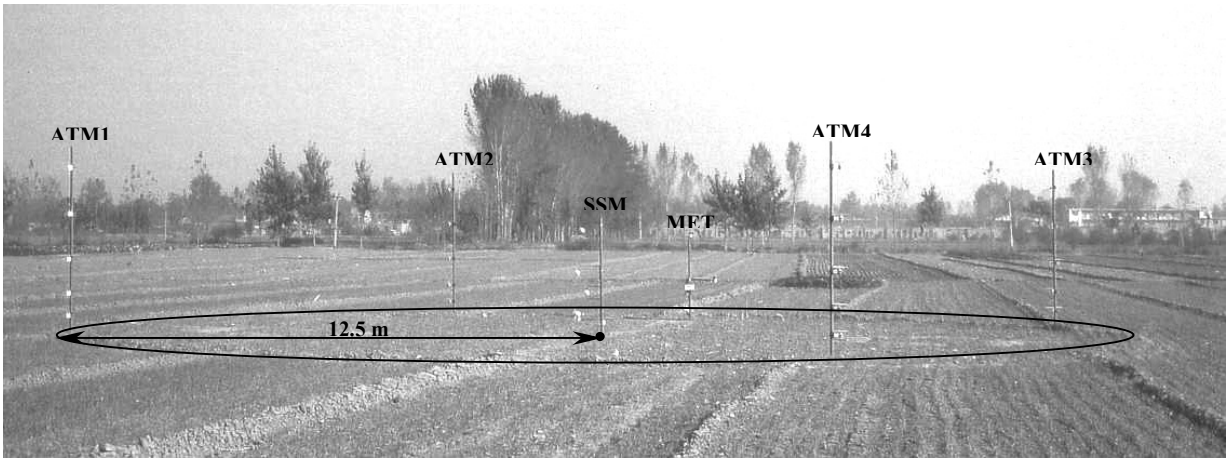


Fig. 11: Experimental set-up of ammonia measurements during 1998 winter wheat season in Fengqiu (SSM = SSM measurement pole, MET = on-site meteorological station, ATM = ATM measurement pole)

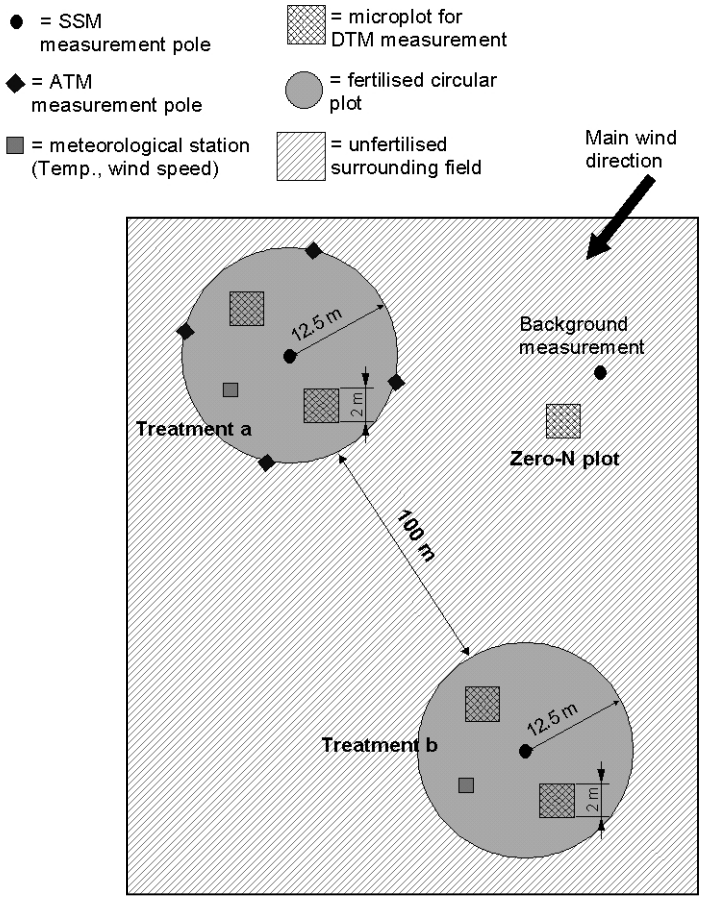


Fig. 12: Set-up of field trials in Fengqiu 1998 -1999

For each treatment one circular measurement area was set up (radius of 12.5 m, area 491 sqm). Each experiment included two circular sample areas about 100 m apart from each other. Every sample area also contained 2 microplots of 4 m² (2 m x 2m), for the measurements with the Draeger-Tube method. Another microplot and a measurement pole with SSM samplers were set up in the surrounding unfertilised fields for the measurement of background ammonia concentrations. A measurement pole with SSM passive flux samplers was put up in the centre of each of the circular plots. The meteorological stations were put downwind of the SSM measurement poles - according to the main wind direction - in order to avoid perturbance of ammonia measurement (see Chapter 3.4.4.1). The axis connecting the centres of both sampling areas was orthogonal to the main wind direction. In this way the influence of the ammonia emitted from one sampling area on the other was minimised.

3.3.2 Methodological experiments with Draeger Tube Method

In addition to the field experiments the DTM was also tested systematically in separate microplot experiments. The experiments focused on the investigation of the importance of air exchange rates in the cups, cup sizes and number of cups on the measurement results. Two different approaches were chosen: First, four DTM-cups of three different sizes, respectively, were employed and measurements were carried out with a hand pump using the same pumping rates, the three different cup volumes resulting in three different air exchange rates inside the cups. Second, the DTM-cups constructed for the measurement with electric vacuum pump were tested with regard to different cup numbers and flux rates. One of the aims of the experiments was the determination of a pumping rate threshold value corresponding to the air exchange rate above which no further increase in ammonia losses would occur, i.e. the pumping rate at which the maximum volatilisation rate is reached corresponding to the potential ammonia volatilisation rate at given soil moisture and temperature conditions.

a.) Experiments using the first approach were carried out in July 1998. Three sets, each consisting of 4 cups, of different sizes of DTM-cups were tested. The largest cup was the above described DTM-standard cup (1 *large* cup: 104 cm² surface area, 352 cm³ volume). The other two smaller cup types consisted in the *medium* cup (1 cup : 77 cm², 173 cm³) and the *small* cup (1 cup: 42 cm², 65 cm³). The corresponding air exchange rates inside the cups are listed in Table 6 a. In comparison to the large cups air exchange rates inside the small cups were 5 times higher, in the medium cups twice as high.

Four adjacent fallow microplots (4 sqm each) were irrigated with 40 mm and fertilised with urea (surface broadcast) corresponding to a fertilization rate of 200 kg N ha^{-1}. Ammonia volatilisation was measured synchronically on all 4 plots with the large cups. As for the field measurements each sampling included 2-3 replicate measurements. Measurements with small and medium cups were carried out in two separate pairs of plots respectively. As ammonia losses are dependent on temperature and temperature changed during each round of sampling (about 1 h altogether) the order of measurement with the systems and the order of the microplots was rotated throughout the experiment which lasted for 6 days.

b.) The following two experiments using the second approach were carried out in analogue (Tab.6 b-c). In contrast to the first experiment, measurements were carried out on one plot only. In March 1999 urea fertilizer corresponding to 200 kg N ha^{-1} was surface broadcast. Ammonia loss was measured using the modified DTM-cups with four different air exchange rates which were provided by an electric vacuum pump. In order to investigate the influence of the number of cups on the measurement results, 2 of the 4 air exchange rates were applied using two different sets of DTM-cups consisting of different numbers of cups (Tab.6 b). As for the first experiment the order of the measurements with the different systems was rotated in order to avoid systamatic temperature effects.

As the air exchange rates chosen for the second experiment were not high enough to reach the level of potential ammonia volatilisation, a third experiment was carried out in July 1999. Air exchange rates in the cups were increased considerably in comparison to the second experiment Table. 6 c).

Table 6 (a-c): Plot experiments carried in Fengqiu for the investigation of the influence of air exchange rates in DTM-cups on NH_3-fluxes measured

a: July 1998, measurements using three different cup sizes and hand pump and corresponding three air exchange rates inside the cups

ferilization rate [kg N ha^{-1}]	duration [days]	number of plots	cup size	air exchange rate [Vol min^{-1}]
200 (surface braodcast)	6	2	small	3.8
		2	medium	1.45
		4	large	0.8

b: March 1999, measurements with modified DTM-cup with vacuum pump in one measurement plot.

application rate [kg N ha^{-1}]	duration [days]	number of cups	air exchange rate [Vol min^{-1}]
200 (surface broadcast)	6	1	33.3
		1	16.7
		2	16.7
		2	8.3
		4	8.3
		4	4.2

c: July 1999, measurements with modified DTM-cup with vacuum pump on one measurement plot.

application rate [kg N ha^{-1}]	duration [days]	number of cups	air exchange rate [Vol min^{-1}]
150 (surface broadcast)	4	1	50.0
		1	40.0
		2	23.3
		4	12.5

3.4 Field measurements

3.4.1 ^{15}N balance studies

^{15}N balance method results can be used as indirect estimate for N-losses following mineral N-fertilisation. ^{15}N-enriched fertiliser was applied to small microplots consisting of metal frames which were pressed into the soil. These microplots were located outside the circular plots in the surrounding unfertilised fields. ^{15}N enrichment of fertilisers applied was 7 atom percent for the 1998 maize and wheat experiments and 6 atom percent for the 1999 wheat and maize experiments. Fertilisation rates, timing and application method corresponded to those in the circular experimental plots. Each treatment was carried out in 4 replicates. Metal frames (0.5 m x 0.5 m, 0.6 m height) were used for fencing off the microplots in order to avoid lateral diffusion of ^{15}N in the soil profile. The metal frames were inserted up to a depth of 0.55 m. 0.05 m of metal frame above the soil surface served for the retention of surface soil material and of ^{15}N at the soil surface.

Three experiments were carried out altogether. The first experiment corresponded to the second maize experiment in July 1998, the second to the two farmers' methods treatments (mixed fertilisation / fertilisation followed by irrigation) during the 1998/99winter wheat experiments and the third to the summer 1999 maize experiment.

The soil was taken out of the frames in layers of 0–0.2 m, 0.2–0.5 m and 0.5–0.8 m at harvest time. Roots were removed from the soil and ^{15}N contents were determined separately. ^{15}N contents were also measured separately in plant stems and leaves as well as cobs and grain harvested. Soil sampling for the determination of soil ^{15}N contents was not carried out the same way in the three experiments. In the maize 1998 experiment the whole 0 – 0.2 m layer was sampled as bulk soil, mixed thoroughly and subsamples were taken. The two layers underneath were sampled by 5 soil cores (4 cm of diameter), respectively. In case of the wheat experiment the 0.2 – 0.4 m layer was also sampled as bulk soil. Layers underneath were sampled by soil coring. In the maize 1999 experiment 0 – 0.6 m samples were taken in 0.1 m layers as bulk soil, the deepest layer (0.6 – 0.9 m) was sampled with an auger.

^{15}N contents in plants and soil were determined using a Finnigan mass spectrometer at the Institute of Soil Science in Nanjing. With the ^{15}N mass balance method one can only distinguish between fertiliser-N distribution in soil, plant parts and unaccounted-for N. In case of unaccounted for N there are several pathways to account for N-losses: ammonia volatilisation, denitrification (N_2, N_2O) losses or N-transfer to the subsoil by nitrate leaching.

3.4.2 Ammonia volatilisation

Table 7 gives the treatments and the measurement methods employed for the measurement of ammonia volatilisation near the Fengqiu Experimental Station. Ammonia losses were determined directly by DTM, SSM and ATM measurements (see paragraphs 3.2.1, 3.2.2 and 3.2.3). The ATM was only used for measuring ammonia losses in one of the two respective treatments, usually the farmers' method (see Tab.7). ATM samplers were mounted at 0.4 m, 0.8 m, 1.4 m, 2.2 m and 3 m height in 1998 and at 0.6 m, 1.2 m, 2 m, 3 m and 4 m in 1999. As an indirect measure for ammonia losses, ^{15}N mass-balance experiments corresponding to the second and third maize experiments and to the winter wheat mixed incorporation treatments were carried out in the unfertilised area.

Table 7: Methods employed for the measurement of ammonia volatilisation during the Fengqiu field experiments 1998 – 1999 (DTM = Draeger Tube method, ATM = Ammonia Tube method, SSM = Space Shuttle method)

No.	Date	Application rate [kg N ha^{-1}]	Application method	DTM		SSM	ATM	^{15}N
				hand pump	vacuum pump			
1	29 June – 07 Jul. 1998 (maize)	75	**a.** SB[1]	X		X	X	
			b. BI[2]	X		X		
2	19 – 30 July 1998 (maize)	200	**a.** SB	X		X		X
			b. DP[3]	X		X	X	X
3	11 –23 Oct. 1998 (wheat)	120	**a.** SB	X		X	X	
			b. MF[4]	X		X		X
4	09 – 24 March 1999 (wheat)	100	**a.** SB	X	X	X		
			b. BI	X	X	X		X
5	12 – 24 July 1999 (maize)	150	**a.** SB	X	X	X		X
			b. DP	X	X	X	X	X

[1] Surface broadcast; [2] Broadcast followed by irrigation; [3] Deep point placement; [4] fertilizer mixed into topsoil

In deviation from the general design of the experiments, an additional maize experiment was carried out on a 1 ha square experimental site in summer 1999. This was done for applying the Gradient Diffusion Method (Bowen ratio approach) for the measurement of ammonia losses (see chapter 2.4.3.1). As the experiment failed, no further account of this experiment shall be given. However, as a control a SSM sampler was put at ZINST height (0.8 m) above the crop surface in that experimental site.

3.4.3 Soil sampling

3.4.3.1 Mineral nitrogen

Soil cores were taken with a four-piece N_{min} soil auger (diameter 40/35/30/25 mm, 0.3 m length each, STITZ GmbH, Gehrden, Germany) at the beginning and the end of each measuring period. In each study site (491 m^2) 3 samples were taken (≅ 60 samples ha^{-1}). The soil profiles were subdivided into following layers: 0 – 0.2 m (plough layer), 0.2 – 0.6 m, 0.6 – 0.9 m and 0.9 – 1.2 m. Soil cores of 0.2 m or 0.6 m depth were also taken during the experiments depending on rainfall pattern. Soil cores were also sampled at the beginning and the end of each vegetation period, i.e. before sowing and harvesting of winter wheat and maize. In the fifth experiment (summer 1999) the number of soil cores taken was increased to 10 samples for the enlarged field where the Bowen ratio method for measurement of ammonia losses was applied. Five samples were taken from the circular plots in that experiment. All mineral N values were determined from bulked samples (for each layer) duplicate. In the field and during transport samples were stored in cooling boxes. At the experimental station samples were kept in a refrigerator. Extraction with 1 M KCl (soil solution ratio 0.25 kg l^{-1}) was carried out a few days after sampling in duplicate by shaking for 1 h. The extracts were frozen and later analysed for NH_4^+ and NO_3^- -contents at the Institute of Soil Science Nanjing using a Skalar continuous flow auto-analyzer (Breda, The Netherlands).

3.4.3.2 Surface soil sampling

Surface soil samples (0 – 3 mm, diameter 10 mm) were taken with a small soil auger (Fig. 13) developed at the Institute or Food and Land Resources, University of Melbourne. This was done for the determination of mineral N contents, urea content, pH values and water contents at the soil surface. These data were used for additional information on ammonia losses, in particular for the comparison of the results of the Draeger-Tube- and the micrometeorological methods (see Chapter 4.1.2). Ammonium contents, pH-values and water contents at the soil surface were also used for the calculation of the ammonia partial pressure in the soil atmosphere close to the soil surface (see Chapter 5.1). This variable

is crucial for the ammonia volatilisation process at the soil/atmosphere interface. During each experiment, usually once a day before noon, mixed surface soil samples were taken randomly inside the circular plots consisting of hundreds of individual samples due to the low volume (0.25 cm^3) of each single sample.

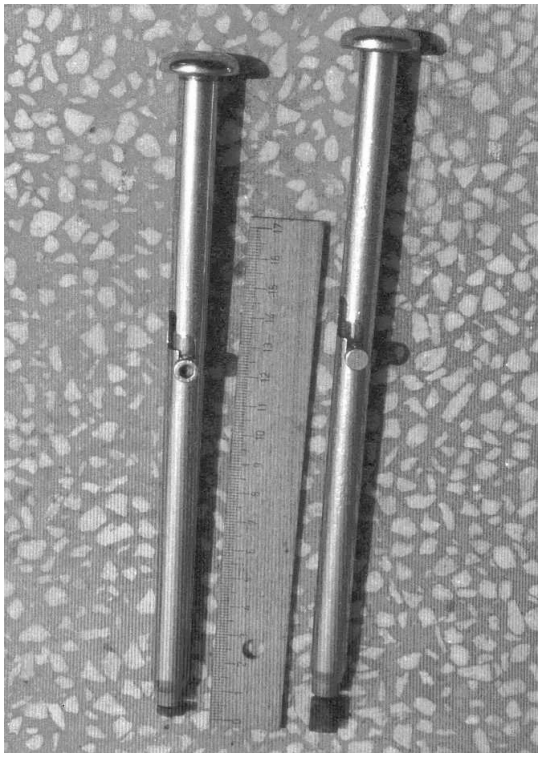


Fig. 13: Small soil auger for surface soil sampling

In order to determine urea contents in the soil, extraction was carried out with 1 M KCl solution containing 10 mg l^{-1} Phenyl Mercuric Acid (PMA) as urease inhibitor. Urea contents were measured by the procedure of Malvaney and Bremner (1979) at the Institute of Soil Science in Nanjing. In addition to mineral N contents, gravimetric water content (24 h at 105 °C) and pH(H_2O)-values (soil:solution ratio 100 g 250 ml^{-1}, for surface soil samples with high mineral N content the ratio was extended to 10g 100 ml^{-1}) were determined in the samples.

Soil bulk densities were determined in several depths in an exemplary soil profile in the Experimental Station. For the determination of soil bulk density in the plough layer 8 samples were also taken in the experimental fields.

3.4.4 Other important field and soil parameters

3.4.4.1 Measurement of meteorological variables

In every study site a measurement pole was put up equipped with several meteorological sensors (Fig. 14). The instrumentation consisted of two cup anemometers (THIES optoelectronic (aluminium), THIES compact (synthetic material)) and two resistance temperature sensors (PT 1000 soil temperature sensor, PT 100 radiation protected temperature sensor). For the duration of the whole experiment the sensors were connected to a data logger (WILOG306, Wilmers Messtechnik Hamburg) which recorded the data at 10-second intervals and calculated 10 minute average values as output data.

Wind speed was measured in two heights, 0.2 m and 2 m. The more sensitive optoelectronic cup anemometer (measurement range 0.3 ... 15 m s^{-1} ± 0.3 m s^{-1}) was installed at 0.2 m height, the plastic cup anemometer (measurement range 0.5 ... 15 m s^{-1} ± 0.5 m s^{-1}) at 2 m. The radiation protected temperature sensor (accuracy or measurement 0 °C ± 0.3 °C ... 50 °C ± 0.6 °C) was mounted at a height of 1 metre while the soil temperature sensor (accuracy of measurement ± 1 °C) was deployed in a soil depth of 0.05 m. In addition to these variables measured *in situ*, weather data were obtained from the meteorological station at Fengqiu Station including air pressure, humidity (hourly averages), duration of sunshine etc..

Fig. 14: On-site meteorological station in Fengqiu

3.4.4.2 Determination of soil parameters in laboratory studies

Further important soil characteristics were analysed in laboratory studies. Urease activity, ammonia-adsorption characteristics and pH-buffering capacity in the upper (plough) layer are of particular importance for the ammonia volatilisation process.

Urease activity

Urease activity was measured using the method by Kandeler (1996) with non-buffered soil-pH at the Institute of Soil Science in Nanjing. The non-buffered method was chosen because this is the appropriate way to characterise urease activity under field conditions (Bremner and Mulvaney 1978). 5 g of field-moist soil was weighed into an Erlenmeyer-flask, 2.5 ml of urea solution were added and the flask was closed with a rubber stopper. The samples were incubated for 2 hours. The experiments were designed in analogue to the measurements by Rachhpal-Singh and Nye (1984 b): four sets of samples were incubated on 4 levels of temperature (10, 20, 30 and 37 °C), each set consisting of samples supplied with solutions of 8 different urea concentrations (0.1, 0.2, 0.3, 1, 2, 4, 6, and 10 M urea-N). For each concentration level 2 replicates and one check were determined. After incubation 2.5 ml of distilled water and 50 ml of 1 M KCl-solution were added. Samples were shaken for 0.5 hours, and the solution was extracted.

Ammonium adsorption isotherm

The experiments were carried out at the Institute of Geoecology using field-moist soil (gravimetric water content: 18.7 %) samples from the Fengqiu experimental sites. The soil was sieved to 2 mm. 5 g of soil were weighed into a synthetics centrifuge and 25 ml of 0.01 M $CaCl_2$-solution containing NH_4Cl in 12 graded concentrations (0.1, 0.2, 0.5, 1, 2, 5, 10, 20, 40, 60, 100, 200 mmol NH_4^+-N l^{-1}) were added. Subsequently the tubes were shaken for 1 hour at 20 °C, centrifuged and filtered. Ammonium concentrations in the supernatant solutions were measured using a Skalar continuous flow analyzer (Breda, The Netherlands). Each concentration level was measured in 4 replicates. Adsorption behaviour was characterised by fitting adsorption isotherms to the data measured (e.g. Freundlich-isotherm, Evangelou et al. (1986), Thompson and Blackmer (1992)).

pH buffer capacity

The pH buffer capacity in soil determines to what degree soil pH is changing in relation to one unit of protons or OH^- -ions added to the soil. Changes of soil pH after adding several unit volumes of acid and base solution were measured for the determination of the pH buffer capacity (Kretzschmar 1989) at the Institute of Soil Science, Nanjing. 10 g of air dried soil were weighed into an Erlenmeyer flask and stepwise supplied with 0.025 M $Ca(OH_2)$-solution (1 ml corresponding 0.005 Mol OH^- kg $soil^{-1}$) or 0.05 M HCl-solution (1 ml corresponding 0.005 Mol H^+ kg $soil^{-1}$). The flasks were stoppered and kept in the dark for 72 hours. Subsequently $pH(H_2O)$-values were measured using a pH-electrode.

3.5 Statistics

The measured data were statistically analysed with SPSS (10.0.7) statistics software for statistical testing, regression and correlation analysis. Fitting analyses were carried out using the Origin 6.1. software package. The numerical solution of the non-linear ammonium adsorption-isotherm equation for the calculation of ammonium contents in the aqueous solution from total ammonium contents in soil (chapter 5.1.) was obtained from the Solver-routine included in the EXCEL-software-package.

Fitting ammonia volatilisation with a logistic equation

Logistic equations were fitted to cumulative ammonia flux curves over time for comparison of the cumulative ammonia losses measured with the different methods. This approach was chosen by several authors e.g. Stevens et al. (1989), Demeyer et al. (1995), Sommer and Ersboell (1996). For this study the approach by Demeyer et al. (1995) was selected. As, generally, the cumulative flux pattern of ammonia loss can be characterised by a slow initial (lag) phase, a fast second phase and a third phase with decreasing fluxes, this process can be best described with a sigmoidal logistic equation.

$$Y = a\,(1 - e^{(-ct)})^{\,i} \qquad (12)$$

Y cumulative ammonia loss [kg Nha^{-1}]
a asymptotic maximum ammonia loss [kg N ha^{-1}]
c rate constant (process velocity)
t time [days]
i parameter of sigmodiality

Y, a, c, t and i must have positive values. If i > 1 the process can be described by a sigmoidal curve, otherwise (i≤1) the curve has no turning point and thus no sigmoidal shape. The maximum flux rate (i.e. slope at $F_{Ng\ max}$) and its point of time t_{max} (days after fertilizer application) can be derived from this model by forming the first and second derivation. As the fluxes determined with the DTM were always lower than those of the SSM, the parameters c, i and t_{max} were mainly used for the comparison of the measurement results between the two methods. t_{max} can be calculated from:

$$t_{max} = \ln i / c \qquad (13)$$

tmax [days]

As the fitted curve corresponds to a smoothing of the measured data points the parameters allow a more distinct comparison of the curves of the cumulative ammonia fluxes measured.

4. Results and Discussion

4.1. Ammonia loss measurements

Ammonia measurements with the DTM comprised field trials in parallel with micrometeorological methods and systematic measurements with different sets of cups and cup types in combination with different pumping rates (air exchange rates). First, the results of the comparative measurements with the different cup sets are presented in order to give an insight into the general features of the measurement process when applying the DTM.

4.1.1. Methodological experiments with different cup sizes and air exchange rates inside the cups

The first plot experiment included the investigation of the influence of different cup sizes with hand pump on measured ammonia losses (July 98, see Chapter 3.3.2). Fig. 15 shows the cumulative ammonia losses determined by the three cup systems (small, medium and large/standard cups) after 6 days. Ammonia losses measured increased with increasing air exchange rates in the cups.

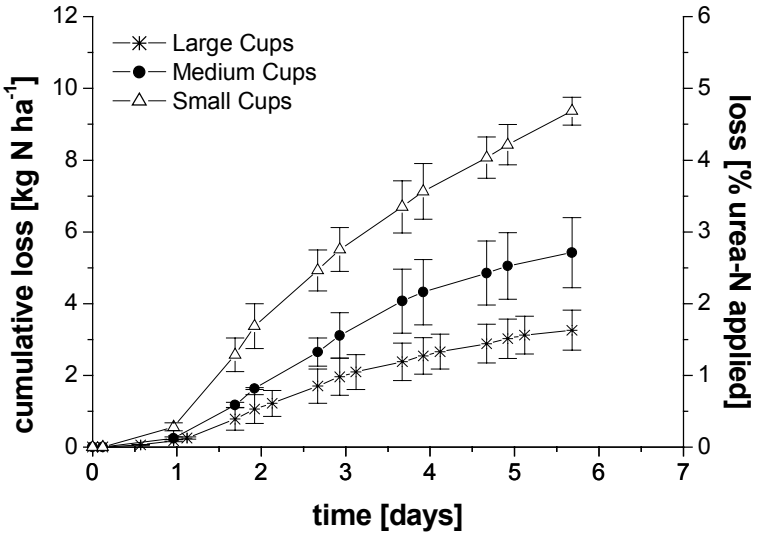


Fig. 15: Cumulative ammonia loss rates after 6 days (mean ± range) measured by 3 different types of cup sets (hand pump) corresponding to 3 air exchange, Fengqiu, July 1998, 200 kg urea- N ha^{-1} (large cups: 4 replicates, small and medium cups: 2 replicates)

After 6 days cumulative losses determined with the small cups were about three times, those determined with the medium cups 1.7 times higher than those determined with the large cups. This confirms the air exchange rate in the cups as being one of the decisive factors of the measurement of ammonia losses

with the DTM (see Chapters 2.4.1 and 3.2.1). Although the application of the DTM always entails some variability, e.g. different depth of the cups in the soil or variations in the pumping rate with the hand pump, the scattering of the measurement results was low for the three cup sets. Disregarding the variability induced by soil heterogeneity and taking the measurements as 'true' replications, the DTM exhibited a mean measurement error of 22 %, 16 % and 11 % for large, medium and small cups, respectively. Thus, the DTM with hand pump allows for reproducibility of measurements on a small measurement site without vegetation.

The cumulative losses determined with the small cups (9.4 kg ha^{-1}) were already considerably higher than those determined with the large cups (3.46 kg N ha^{-1}). However, they were still quite lower than those measured with the SSM on fields close to the systematic microplots with the same fertilizer application rate (95.8 kg N ha^{-1}) about one week later (see 4.1.2). Although there was a considerable difference between the two experimental set-ups and the environmental conditions (wind speed), the factor of 10 between the results using DTM with small cups and the SSM results shows that the air exchange rates had not yet been high enough to represent ambient air exchange processes. As a result, ammonia losses were underestimated by about one order of magnitude even when applying the small cups.

Methodological experiments with DTM and electric pump

In the experiment following the second approach (i.e. increasing the air exchange rate by an electric pump using the modified cups) in March 1999, the number of cups was varied, and the air exchange rates were increased considerably. Although the order of magnitude of ammonia losses concomitantly measured with the SSM at the same time was reached, a maximum air exchange rate in the cups of 33 Vol. $min.^{-1}$ was still not high enough to determine the air exchange rate within the cups corresponding to the potential ammonia loss. The curve of ammonia losses with increasing air exchange rate had not yet reached its assymptotic part corresponding the maximum ammonia volatilisation. However, the combination of the same air exchange rates in different cup systems with varied number of cups showed that the number of cups had no significant effect on the measurement results as long as the same air exchange rates in the cups were applied. The statistical testing of the mean ammonia flux rates of 6 different set-ups revealed only significant differences between different air exchange rates but not between different surface area covered by the cups (Fig. 16, t-test, $n=16$, $p < 0.01$). In line with the results of the first systematic experiment, the air exchange rates in the cups and not the surface area covered were decisive for the measurement results at sites without vegetation, and the DTM proved to provide reproducible measurements using hand and electric pumps.

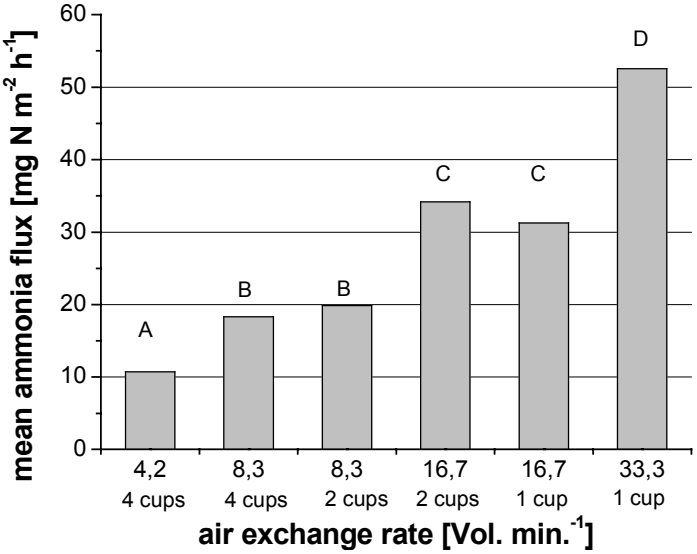


Fig. 16: Comparative determination of mean ammonia flux rates with 4 different air exchange rates and varied number of cups. Significant differences are marked by different letters (t-test, $p < 0.01$), Fengqiu, March 1999, 200 kg urea-N ha^{-1} (surface broadcast)

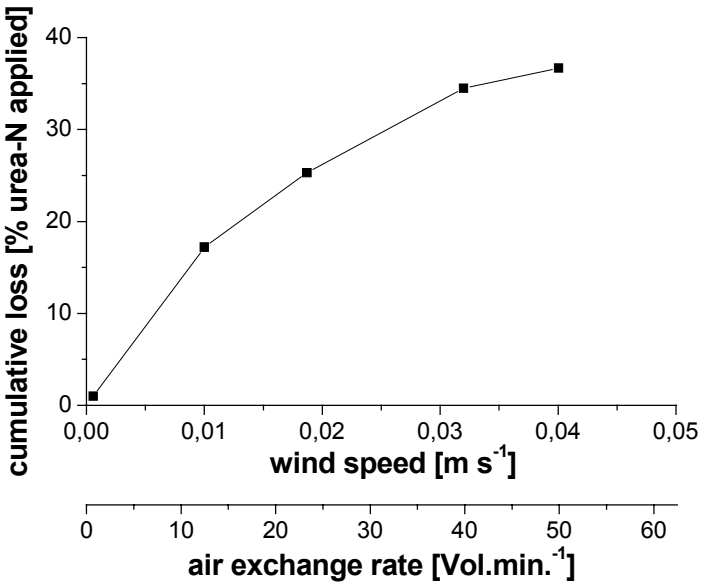


Fig. 17: Influence of different air exchange rates inside the cups on cumulative ammonia loss after 4 days, using modified DTM-cups with electric vacuum pump and DTM-cups with hand pump (lowest value), Fengqiu July 1999, 150 kg urea-N ha^{-1}, surface broadcast.

Because of the good reproducibility of the DTM measurements in the preceding two systematic experiments replicate measurements in different plots (not in each sampling!) were omitted in the third

experiment In this experiment air exchange rates in the cups were increased to the threshold value at which the maximum (potential) ammonia volatilisation rate is almost reached (Fig. 17). A logistic model similar to that presented in Chapter 3.5 but depending on air exchange rate in place of time was successfully fitted to the data:

$$Y = a\,(1 - e^{(-c\,\nu)}) \qquad (14)$$

Y	cumulative ammonia loss [% urea N applied]
a	maximum (potential) ammonia loss [% urea N applied]
c	rate constant [min. Vol.$^{-1}$]
ν	air exchange rate [Vol. min.$^{-1}$]

An *a* of 42,65 and a *c* of 0,04 was the result of the fitting analysis of the data set (r^2 0.999). If *a* and *c* are known, the corresponding air exchange rate for each cumulative ammonia loss value can be calculated by:

$$\nu = \frac{\ln\left(\frac{(Y-a)}{a}\right)}{-c} \qquad (15)$$

Above an air exchange rate of 40 vol. min.$^{-1}$, which corresponds to a cumulative ammonia loss of 80 percent of N_{max}, only a slight further increase of ammonia losses occurs (e.g. 60 Vol. min.$^{-1}$ $\rightarrow$ 90,7% of N_{max}). As a result, 40 Vol. min.$^{-1}$ can be roughly considered as the air exchange rate producing the maximum potential ammonia loss because even a much higher increase in the air exchange rate would only result in slightly raised ammonia losses. This air exchange rate value is about double of the threshold value of 15-20 vol. min.$^{-1}$ which was determined for chamber methods by other authors (e.g. Hargrove et al. (1977), Roelcke et al. (2002 a)). The DTM chamber geometry differs considerably from those used in the above cited literature. While conventional chambers were designed to approximately provide a laminar air flow through the chambers, a turbulent flow can be assumed for the DTM. This may account for the large difference between the threshold values given in the literature and that determined for the DTM.

4.1.2. Comparison of DTM results with two micrometeorological methods

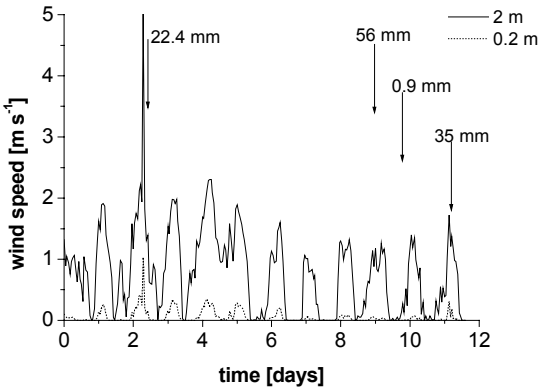
One principal difference between the DTM and the SSM (ATM) is their approach towards sampling ammonia: while the DTM is based on direct point measurements which are linearly interpolated for the calculation of time averaged ammonia fluxes, the SSM (ATM) samples the air for a longer period of time (integrating methods), and the ammonia flux at a specific point of time can only be referred to by calculating average fluxes for the time period sampled. This is also reflected in the graphs which show the ammonia fluxes by the respective method. On the one hand diurnal variations of the ammonia fluxes measured by the DTM are presented as a (regularly) fluctuating time series, on the other hand SSM results are given as horizontal average values resembling histograms. As the sampling frequency of the ATM was comparatively low with 2 – 3 samplings during each experiment, no graphs were included to show the outcome of these experiments. However, cumulative ammonia losses measured with the ATM will be compared with the results of the other methods at the end of this chapter.

In the following, as a first step, the comparison of DTM- and SSM-results is carried out by presenting and discussing graphs for ammonia fluxes, cumulative ammonia losses and the prevailing environmental conditions for a set of example experiments. Results of the second 1998 maize experiment (surface broadcast urea), the autumn 1998 wheat measurements, and the 1999 maize experiment are presented in detail. The data are also compared by giving the parameters of the fitted sigmoidal function presented in Chapter 3.5. Results of the other experiments are summarised in a table at the end of this chapter, details are given in the appendix of the thesis. The SSM results are also compared to the DTM results with electric pump for the Wheat 99 and Maize 99 experiments (Chapter 4.1.3).

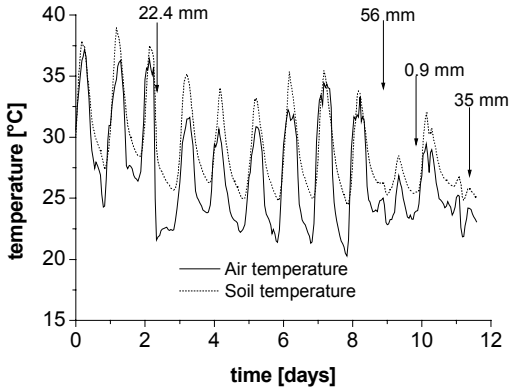
4.1.2.1 Second maize experiment (19 – 30 July 1998)

Surface broadcast treatment

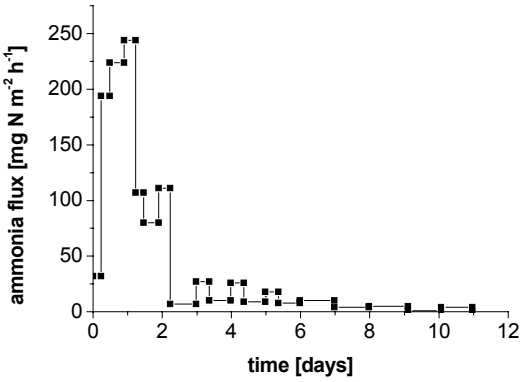
Figure 18 a – f shows the results for the surface broadcast treatment of the second maize experiment. The two graphs at the top depict the environmental conditions (a: wind speeds and rainfall; b: temperatures and rainfall). Underneath, on the left hand side, the ammonia fluxes measured by SSM (c) and DTM (e) are given. On the right hand side cumulative ammonia losses (SSM (d); DTM (f)) are presented.



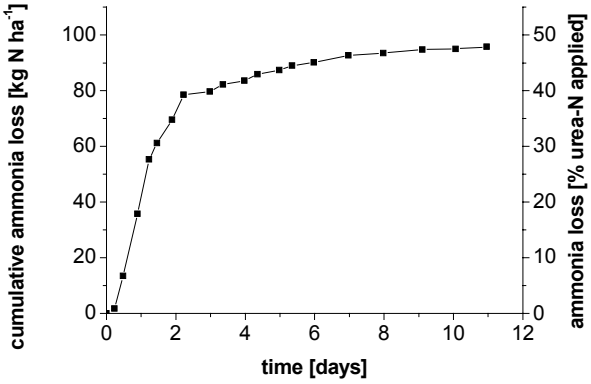
a. wind speed (2 m and 0.2 m) and reainfall events



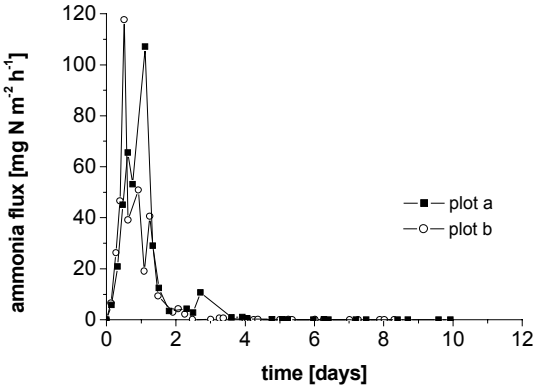
b. temperatures (1 m and –0.05 m) and rainfall events



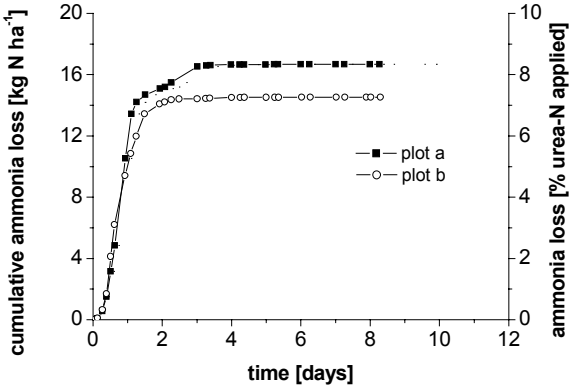
c. SSM ammonia fluxes



d. SSM cumulative ammonia losses



e. DTM ammonia fluxes



f. DTM cumulative ammonia losses

Fig. 18 a – f: Comparison of DTM (hand pump) and SSM ammonia flux measurements, second maize experiment (19 – 30 July 1998), surface broadcast treatment (200 kg N ha^{-1})

Since ammonia fluxes measured with the DTM were about one order of magnitude lower than those determined by the SSM, the curves of the two methods are shown in separate graphs.

With temperatures up to 40 °C, very high temperatures prevailed during this experiment. The wind situation can be characterized as a night / day system, convective wind mostly driven by solar radiation energy. There was one period with increased wind speeds between days 4 – 6. Wind speeds at the height of 0.2 m were decreasing continuously. This can be interpreted as a 'footprint' of the growing maize plants which grew from 0.8 m to a height of more than 2 m during the course of the experiment. At the third day of the experiment a thunderstorm occurred with rainfall of 22.4 mm. At the end of the measurements a total of 92 mm of rainfall were recorded in a period of 2 days.

In general, the ammonia flux patterns determined by DTM and SSM method agreed very well. The replicate DTM measurements in the two micro plots yielded good agreement. Ammonia volatilisation started almost immediately after urea fertilization. Soil and weather conditions were very favourable for ammonia volatilisation: high soil pH, high water content throughout the experiment (Fig. 19) and high temperatures (Fig. 18 b). Urea hydrolysis occurred almost instantaneously (Fig. 20). As a consequence, the highest ammonia fluxes during the whole experiment were determined on the first day. For both methods the largest portion of ammonia losses was measured in the first two days, followed by a period of very low fluxes till the end of the measurements.

The effect of the thunderstorm with 22.4 mm of rainfall on the third day of the experiment on cumulative ammonia losses measured by the two methods is worth discussing (Fig. 18 d+f). The DTM curve shows that the asymptotic part of the sigmoid ammonia loss curve had already been reached before the thunderstorm. The thunderstorm occurred in a SSM sampling period of 18 hours. It is therefore difficult to determine when precisely the asymptotic part of the curve was reached. The preceding sampling still yielded relatively high fluxes, while the DTM fluxes had already decreased strongly. This discrepancy could be explained by the high wind speeds prevailing in the hours before the thunderstorm. The ammonia partial pressure at the soil surface was already comparatively low, but the high wind speeds led to considerable volatilisation rates measured by the SSM as the SSM determines the product of ammonia concentration in the atmosphere and wind speed. The DTM, however, mainly reflects the ammonia concentration in the air close to the soil surface (see Chapter 5.1). As a consequence, the rainfall event presumably decreased ammonia losses to some degree. This interpretation of the ammonia fluxes is corroborated by the results from the surface soil samples (Fig. 20). Ammonium concentrations at the soil surface were already considerably lower on the third day, prior to the thunderstorm. There was still some ammonium in the surface soil on the following day but the heavy rainfall had washed some ammonium deeper into the plough layer. Ammonium was nitrified and nitrate diffused to the soil surface during the warm, dry days after the thunderstorm. The decrease

in nitrate concentration at the soil surface after day 7 can be attributed to both, plant uptake and heavy rain washing nitrate into the soil at the end of the experiment.

The good agreement of the flux patterns determined by the two methods is confirmed by comparison of the parameters of the fitted sigmoid curves (Table 8). In order to illustrate the fitting, two graphs are given with the sigmoid curves fitted to the SSM and average DTM cumulative ammonia loss curves (Fig.21 and 22). In the following, for the other experiments presented only the parameters of the fitted curves will be shown. The parameter *a* was about six times lower for the DTM curve than for the SSM curve. So, the parameters *c*, *i*, and t_{max} are much more important for the comparison of the curves.

For both methods the point of time t_{max} with the highest ammonia fluxes was estimated as 0.6 days. The rate constants *c* and the parameters of sigmoidality *i* were very similar, as well. Both, *i* and *c* were higher for the DTM curve. The higher sigmoidality *i* compensates the higher *c* value resulting in a similar t_{max} as that determined for the SSM curve. On the one hand this can be explained by the different effect of wind speed on both measurement methods, on the other hand by the higher frequency of DTM measurements resulting in a more pronounced lag phase at the beginning of the ammonia volatilisation process.

The main difference between the results of the two methods lay in the amounts of cumulative ammonia losses. Cumulative ammonia loss determined by the SSM was about sixfold higher than that determined by the DTM (Table 8). This is also shown by the estimated cumulative loss *a* of the fitted curves. The cumulative ammonia loss of 96 kg N ha^{-1} (45 % of urea N applied) determined by the SSM was exorbitantly high. The very favourable soil and temperature conditions caused an almost 'exploding' ammonia volatilisation process and limited the relative impact of other meteorological factors, i.e. wind speed, on the volatilisation process. Thus, the discrepancy between DTM and SSM results, which can be mainly explained by the low air exchange rate of the DTM not sufficiently reflecting ambient air exchange conditions, was comparatively small for this treatment (see Chapter 4.4.1).

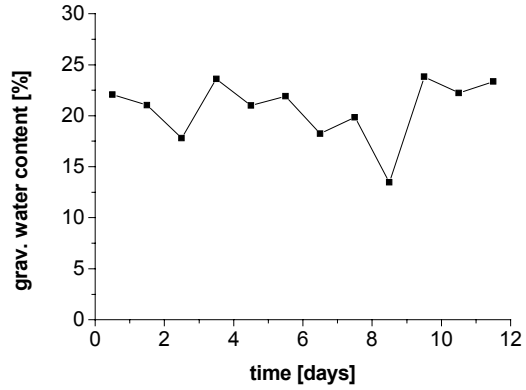


Fig. 19: Surface soil (0-3 mm) water content

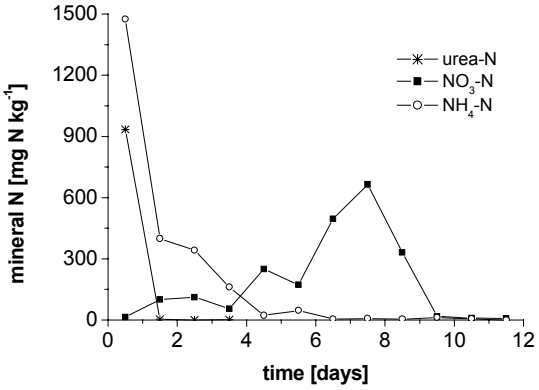


Fig. 20: Surface soil mineral N content

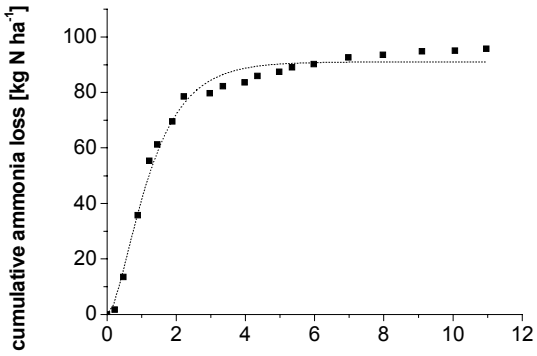


Fig. 21: Log. equation fitted to cum. SSM losses

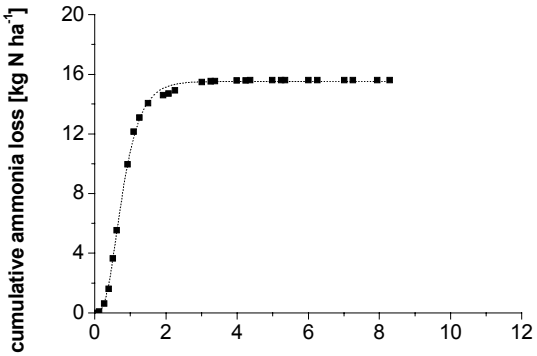


Fig. 22: Log. equation fitted to cum. DTM losses

Table 8: Parameters of logistic equation fitted to cumulative DTM (mean) and SSM losses, (in brackets: standard error), second maize experiment (19 – 30 July 1998), surface broadcast treatment

Parameter	DTM	SSM
a	91.00 (±1.17)	15.52 (±0.04)
c	1.09 (±0.12)	2.65 (±0.07)
i	1.91 (±0.31)	4.88 (±0.28)
t_{max}	0.59	0.60

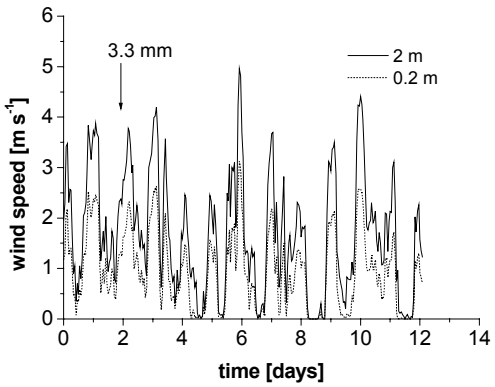
4.1.2.2 First wheat experiment (11 – 23 October 1998)

Surface broadcast treatment

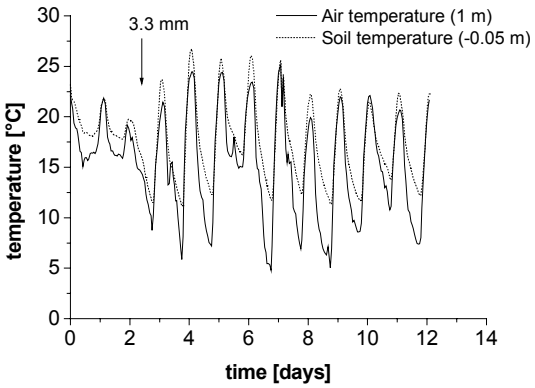
The results of the first wheat experiment in autumn 1998 are given in Figure 23 a-f. The fluxes measured with the DTM (Fig. 23 e) were about one order of magnitude lower than those determined with the SSM (c). The factor of about ten between the results of the two methods confirms a similar factor for the underestimation of ammonia fluxes by the DTM derived by Roelcke (Roelcke 1994) from comparison of DTM measurements with chamber measurements in the laboratory and in situ ^{15}N-studies. In general the DTM-measurements on the two microplots yielded quite similar ammonia fluxes (23 e), the fluxes in plot b) being slightly lower than those in plot a). Discrepancies can most probably be accounted for by lightly varying soil properties (texture, soil moisture) in the two plots.

The course of the curves of the ammonia fluxes measured by DTM and SSM was generally quite similar in this experiment. Both methods determined ammonia flux maxima at the same points of time but not with the same rate at the respective point in time. For example, both DTM and SSM detected maximum fluxes after about 3 days and on the fifth day, but the highest flux occurred on the third day for the SSM, while the highest DTM flux was determined on the fifth day.

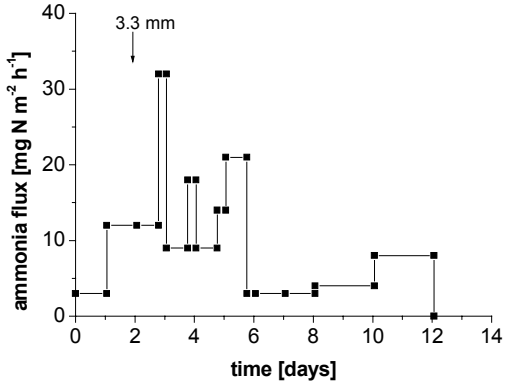
Soil and air temperatures (23 b) were fluctuating periodically during the experiment and had most probably only little influence on the occurrence of absolute minima and maxima of the ammonia fluxes. Nevertheless, diurnal changes in temperature were the driving force of the daily curve of wind speeds (23 a) and ammonia fluxes. The diurnal ammonia flux variations were well reflected by the DTM (23 e) measurements while the SSM (23 c) only showed daily average values. Wind speeds, however, were more strongly fluctuating in the course of the experiment than the temperatures. Both maximum flux peaks measured by the SSM occurred at time periods when wind speeds were highest within the first half of the experiment. A detailed comparison of ammonia fluxes measured by the DTM and wind speeds reveals that the DTM flux maxima were determined slightly prior to the wind speed maxima. At these times ammonia released from the soil surface was removed comparatively slowly due to lower wind speeds. As the SSM measures the product of ammonia concentration and wind speed (i.e. the mass flux), the differences between DTM and SSM results were comparatively lower at times of low wind speeds. The DTM measurements more strongly reflected the situation of ammonia volatilisation at the soil surface (i.e. ammonia partial pressure at the soil surface, see chapter 5.1). They did not sufficiently take into account the influence of changing wind speeds on the removal of ammonia from the soil surface which is one of the decisive parameters for the process of ammonia volatilisation.



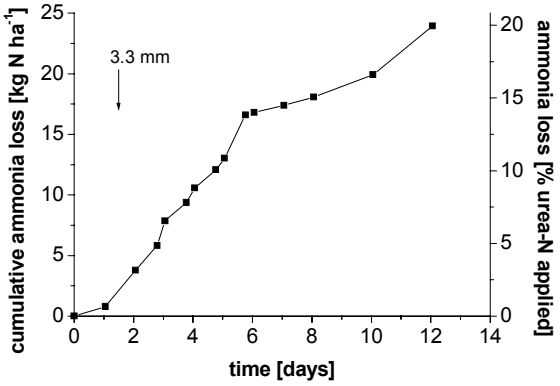
a. wind speed (2 m and 0.2 m) and rainfall events



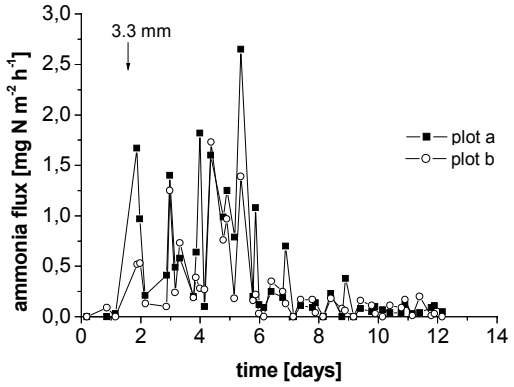
b. temperatures (1 m and –0.05 m) and rainfall events



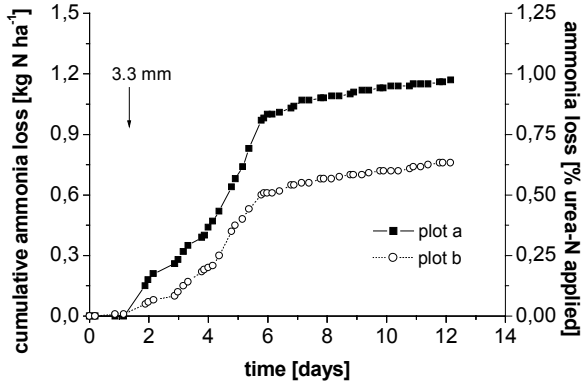
c. SSM ammonia fluxes



d. SSM cumulative ammonia losses



e. DTM ammonia fluxes



f. DTM cumulative ammonia losses

Fig. 23 a – f: Comparison of DTM (hand pump) and SSM ammonia flux measurements, first wheat experiment (11 – 23 Oct. 1998), surface broadcast treatment (120 kg N ha^{-1})

Before the winter wheat experiment the fields had not been irrigated. The surface soil (0- 3 mm) moisture content was very low (about 5 %, Fig. 24). As a consequence, the hydrolysis of urea was slow compared to other experiments. At the beginning of the second day almost all urea applied was still present at the soil surface, unhydrolysed, and had not yet diffused to deeper soil layers. Both measurement methods reflect the low ammonia fluxes caused by retarded urea hydrolysis. At the second day 3.3 mm of rain fell which raised the water content at the soil surface and accelerated urea hydrolysis. The DTM results show very well how ammonia fluxes increased a few hours after the rainfall. It followed a phase of high ammonia fluxes which decreased at the 6th day of the experiment. At that time there was still a considerable amount of ammonium at the soil surface (Fig. 25). Thus, not the depletion of ammonium at the soil surface but very low soil moisture was the cause for the reduction in ammonia losses in autumn 1998. Ammonium in the surface soil layer and from greater depth could not diffuse to the surface and volatilise there. The convective transport of ammonia to the atmosphere by way of evaporative soil water flux was strongly limited, as well. A similar effect of limited soil moisture contents on urea hydrolysis and ammonia volatilisation was also encountered by Roelcke et al. (2002 a) during in situ ammonia volatilisation experiments in China.

The curves of cumulative ammonia fluxes (23 d and f) determined by the DTM and the SSM show that both methods in principle recorded the ammonia volatilisation process in the same way save the total amount of ammonia loss. Besides this systematic difference, the most striking discrepancy between the two curves can be found during the last tow days (days 10 –12) of the experiment. The SSM curve shows a further increase in ammonia losses after several days of small fluxes while the losses determined by the DTM were already very small. In the course of the whole experiment relatively high wind speeds prevailed (Fig. 23 a) which led to the above mentioned differences between the methods with regard to the determination of ammonia flux peaks.

The logistic model was satisfactorily fitted to the cumulative ammonia loss time courses of the SSM and mean DTM values. The parameters of the fitted curves are given in Table 9. The rate constant *c* was twice as high and the shape parameter *i* four times greater for the DTM curve compared to the SSM results. This means that the DTM measurements showed a longer or more pronounced lag phase than the SSM followed by a comparatively faster volatilisation process resulting in a higher sigmoidality of the DTM curve. On the one hand, this discrepancy in sigmoidality could be explained by a higher measurement frequency of the DTM measurements which recorded the course of volatilisation more precisely than the SSM. On the other hand DTM measurement can be considered as less sensitive than the SSM which could lead to a delayed increase in the values at the beginning of the volatilisation process and an accelerated decline of the values at its end. Both hypotheses could explain a higher sigmoidality of the DTM curve. The lower rate constant *c* of the SSM curve could had been caused by

an increase in ammonia losses measured at the end of the experiment and by the lower sigmoidality of the curve.

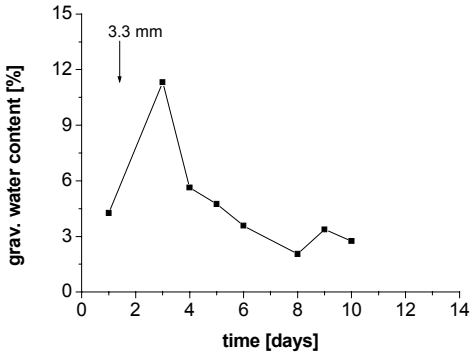


Fig. 24: Surface soil (0-3 mm) water content

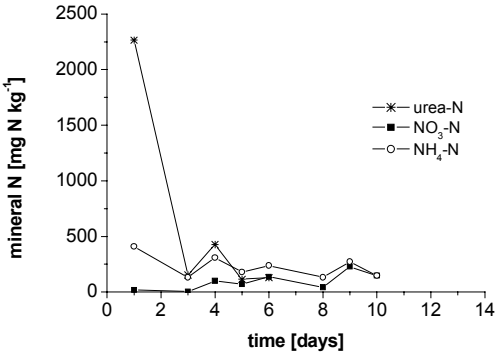


Fig. 25: Surface soil (0–3 mm) min. N content

Table 9: Parameters of log. equation fitted to cumulative DTM (mean) and SSM losses (in brackets: standard error), first wheat experiment (11 – 23 Oct. 1998), surface broadcast treatment (120 kg N ha^{-1})

Parameter	DTM	SSM
a	0.96 (±0.01)	24.10 (±1.40)
c	0.60 (±0.04)	0.30 (±0.05)
i	9.30 (±1.46)	2.33 (±0.45)
t_{max}	3.72	2.82

However, since the parameters *i* and *c* were of the same order of magnitude for both methods, the point of time of maximum ammonia flux (t_{max}) was also similar. Altogether, except for the order of magnitude of losses determined (*a*), measurements of ammonia loss with the DTM from micro-plots and with SSM from circular macro-plots yielded similar results.

ATM measurements had a comparatively low measurement frequency. As a consequence, it is hard to compare the time courses of the ATM and the other methods in detail. However, a comparison of the cumulative losses determined by the other methods during ATM sampling periods is possible, in particular as a check for the SSM measurements. For this experiment the ATM determined a total cumulative ammonia loss of 21 kg N ha^{-1} (Table 10) which matched the SSM results of 24 kg N ha^{-1}. The results of the two methods also show a good agreement for the two single ATM sampling periods.

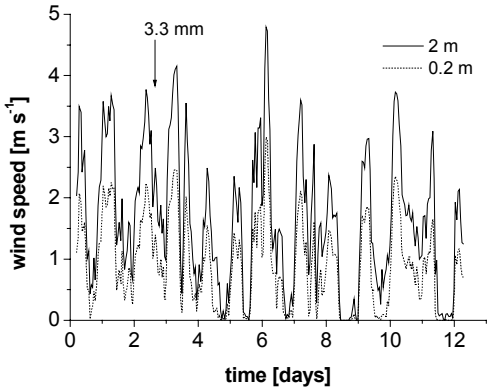
For this experiment these outcomes validate the SSM as a reference method for the calibration of the DTM.

Table 10: Cumulative ammonia losses determined by ATM and SSM, first wheat experiment (11. - 23. Oct. 1998), surface broadcast treatment (120 kg N ha^{-1})

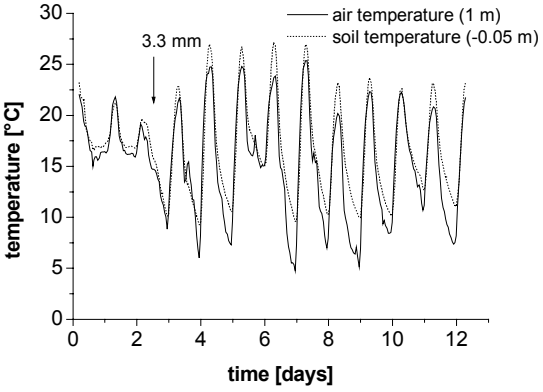
time [days]	ammonia-N volatilised [kg N ha^{-1}]	
	ATM	**SSM**
0 - 3.74	7.8	9.4
3.74-12.02	13.2	14.6
total	21	24

Mixed fertilization treatment

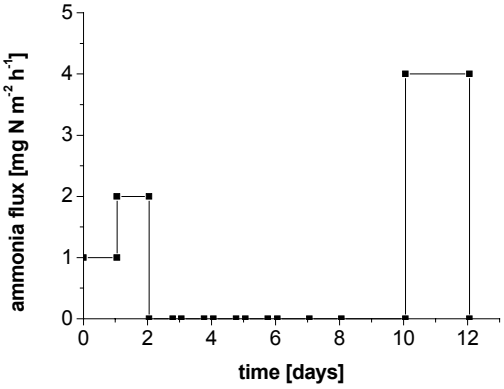
Fig. 26 a – f presents the results of the mixed fertilization treatment. There were major differences between the DTM and the SSM measurements. While the DTM determined continuous ammonia fluxes from the microplots (18 e), the fluxes measured by the SSM (18 c) appeared more like discrete volatilisation 'events'. However, in general both methods agreed in the determination of very low fluxes. The discrepancy between the cumulative losses measured was also about one order of magnitude (DTM 0.17 kg N ha^{-1};SSM 2.78 kg N ha^{-1}), as in the surface broadcast treatment.



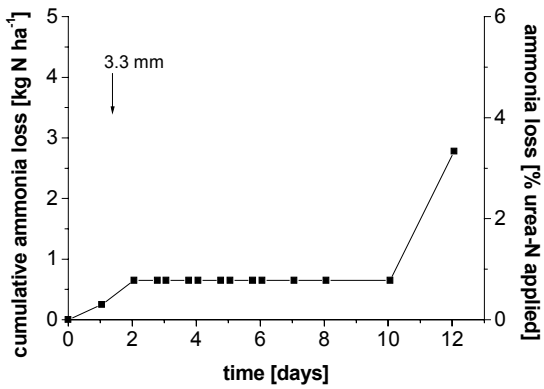
a. wind speed (2 m and 0.2 m)



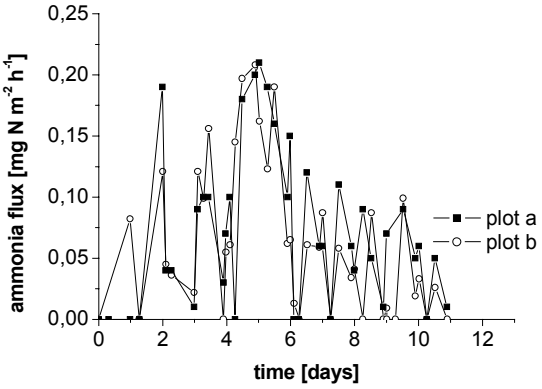
b. temperatures (1 m and –0.05 m)



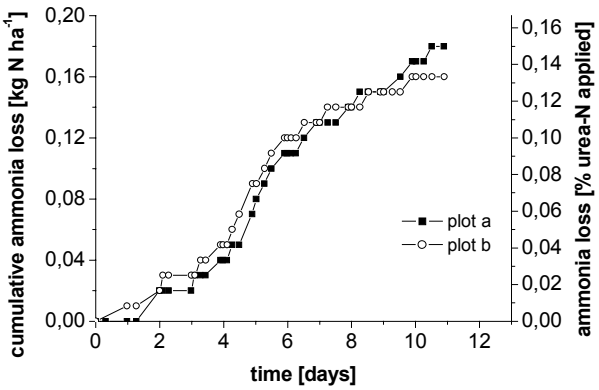
c. SSM ammonia fluxes



d. SSM cumulative ammonia losses



e. DTM ammonia fluxes



f. DTM cumulative ammonia losses

Fig. 26 a – f: Comparison of DTM (hand pump) and SSM ammonia flux measurements, first wheat experiment (11 – 23 Oct 1998), mixed fertilization (120 kg N ha^{-1})

Nevertheless, the time courses determined by the two methods were completely different. The SSM determined ammonia fluxes only at the beginning and – the maximum flux - at the very end of the measurements, detecting no ammonia losses between days 2 and 10, whereas the DTM measurements gave continuous ammonia fluxes throughout the experiment, maximum fluxes occurring at days 4 – 6.

Soil conditions for urea hydrolysis were quite different in this treatment in comparison to the surface broadcast treatment. The fertilizer was mixed with the soil using a hand-held hoe by incorporating it in the plough layer (0 – 0.2 m). The soil moisture conditions were therefore not as limiting as for the other treatment. The water content in the plough layer was 14 % at the beginning and 12 % at the end of the measurements. There was always at least some moisture available for the hydrolysis of urea. This could explain the continuous volatilisation of ammonia till the end of the measurements. Ammonia and urea concentrations at the soil surface were very low throughout the experiment (Fig. 27). This agrees with the small changes of surface soil pH in the mixed fertilisation treatment compared to the surface broadcast treatment (Fig.28) and with the low continuous ammonia fluxes determined by the DTM. Soil cores (0 – 0.2 m) taken after finishing the ammonia measurements (23 Oct. 98) contained no detectable ammonium. The remaining soil moisture in the plough layer also provided favourable conditions for nitrification of ammonium. Nitrate contents in the plough layer increased from 20 N kg ha^{-1} (08 Oct.) to 60 kg N ha^{-1} at the end of the measurements (23 Oct). As a result, there occurred most probably no major ammonia losses later on.

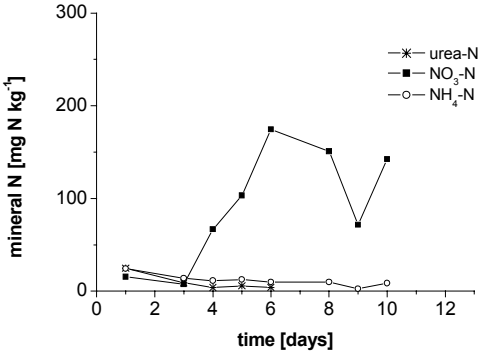


Fig. 27: Surface soil (0–3 mm) mineral N content

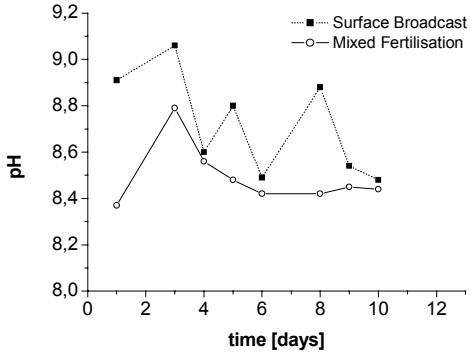


Fig.28: Surface soil (0–3 mm) pH

Considering these results of the soil sample analysis, the results of the DTM seem to be more plausible than the SSM results. During the first 10 days of the experiment the ammonia concentration at the soil surface remained almost at the same level. As soil moisture was not that limiting for ammonia volatilisation as for the surface broadcast treatment, continuous ammonia losses throughout the

experiment seem to be plausible. Probably the main cause affecting the SSM-measurement were comparatively high ammonia background concentrations which blurred the measurements of the SSM in the circular plots (Cai, 2002; pers.comm.). DTM background values were also regularly subtracted from the DTM results but the fluxes measured were still higher than the background concentrations. As ammonia fluxes were quite low, no major impact of specific meteorological events on the ammonia flux pattern could be observed in the mixed incorporation treatment.

4.1.2.3 Third maize experiment (12 – 24 July 1999)

Surface broadcast treatment

The results of this experiment are presented in Fig. 31 a-f. This experiment corresponded to the second maize experiment 1998, with a slightly lower fertilization rate of 150 kg N ha^{-1}. But the soil and meteorological conditions were quite different for this experiment. As rainfall was very high before starting the experiment, the fields had not been irrigated. The rainfall (4.6 mm) at the first day of the experiment increased the surface water content which then continuously decreased until the end of the experiment (Fig. 29).

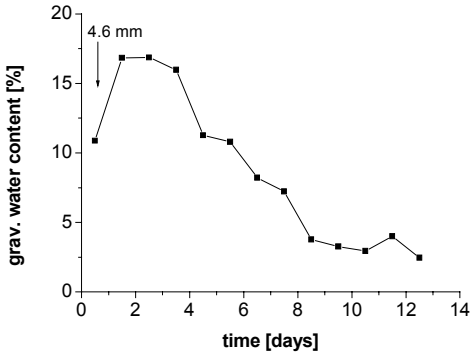


Fig. 29: Surface soil (0–3 mm) grav. water content

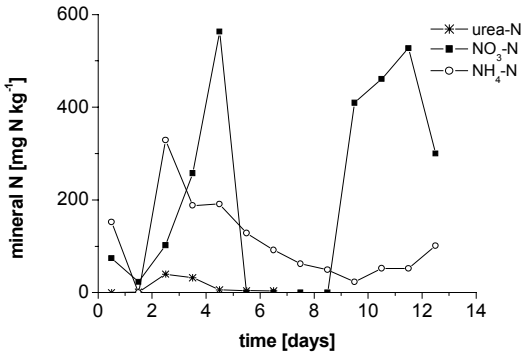
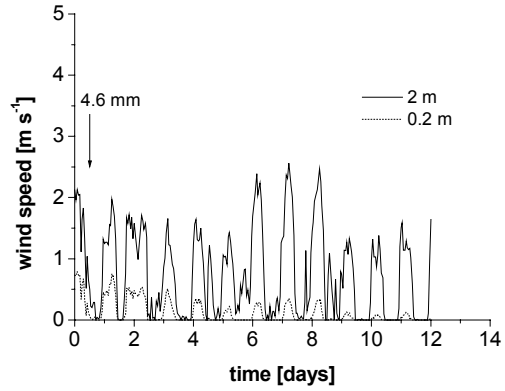
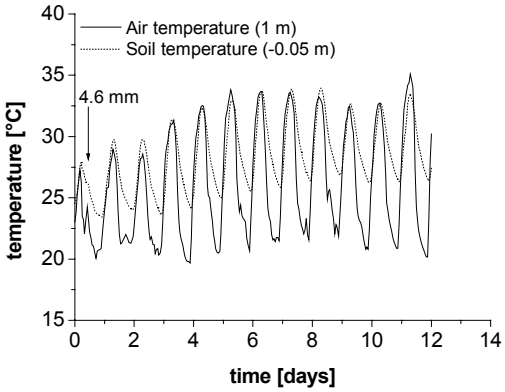


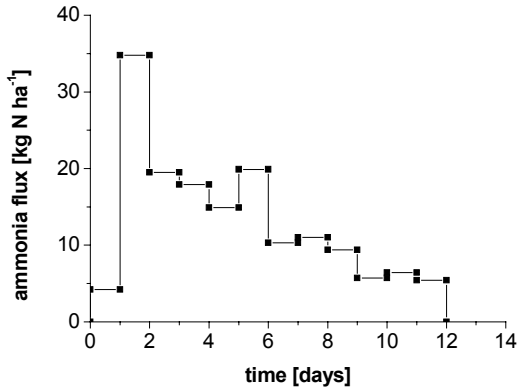
Fig. 30: Surface soil (0–3 mm) min. N-content



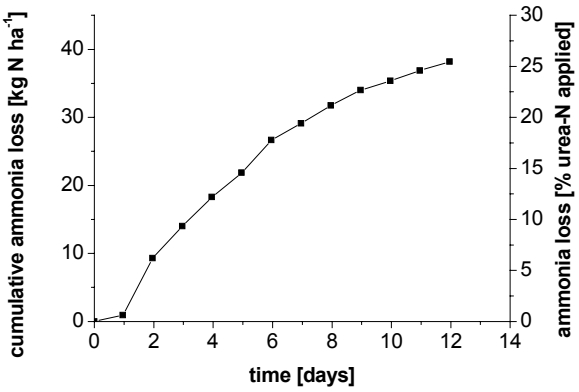
a. wind speed (2 m and 0.2 m)



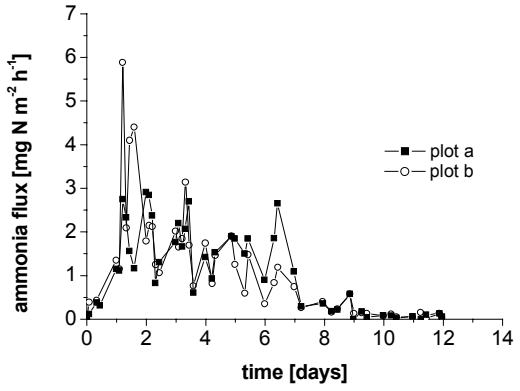
b. temperatures (1 m and –0.05 m)



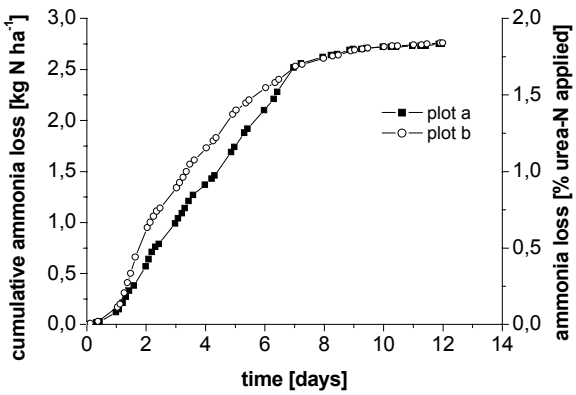
c. SSM ammonia fluxes



d. SSM cumulative ammonia losses



e. DTM ammonia fluxes



f. DTM cumulative ammonia losses

Fig. 31 a – f: Comparison of DTM (hand pump) and SSM ammonia flux measurements, third maize experiment (12 – 24 July 1999), surface broadcast treatment (150 kg N ha^{-1})

The mean soil and air temperatures in July 1999 were similar to the temperatures measured in the second maize experiment 1998. However, in the beginning of the 1999 experiment temperatures were considerably lower than in 1998. Therefore, environmental conditions with regard to ammonia volatilisation were not as favourable in July 1999 as in July 1998. As a consequence, the percentage ammonia loss in July 1999 was considerably lower than in July 1998. This difference was determined by both methods. While in 1998 the SSM determined a total cumulative ammonia loss of 48 [% urea-N applied] and the DTM 7.8 [% urea-N applied] in 1999 the methods determined losses of 25 [% urea-N applied] and 1.8 [% urea-N applied], respectively.

DTM and SSM ammonia flux measurements show that the start of ammonia volatilisation was slightly retarded due to rainfall of 4.6 mm on the first day of the experiment. But this most probably did not have an impact on the overall volatilisation losses. On the contrary, the raised water content improved the conditions of ammonia volatilisation in the following period. The flux patterns determined by both methods agreed very well (Fig. 31 c. and e.). The fluxes measured differed in a factor of about ten, with total cumulative ammonia loss determined by the SSM amounting to 38.2 while the DTM measured a total cumulative loss of 2.8 (kg N ha^{-1}). The highest fluxes were measured on the second day of the experiment and were continuously decreasing till the end of the measurements. The replicate DTM measurements also showed a very good agreement (Fig. 23 f).

In the surface broadcast treatment the influence of meteorological factors did not lead to major differences between the flux patterns determined by the two methods. The only striking difference lies in the stronger decrease of DTM ammonia fluxes during the last days of the measurements compared to the SSM results (Fig. 31 d + f). This could be explained by the perturbation of the surface soil structure by repeated DTM measurements, and its influence on water transport to the soil surface. Fig. 31 shows that from the second day on water content in the surface soil decreased throughout the experiment. However, there was still some ammonium remaining in the surface soil at the end of the measurements (Fig. 30). Thus, soil surface water content was the limiting factor for ammonia volatilisation in the later stages causing a relatively slow volatilisation rate compared to the Maize July experiment 1998. The surface soil structure in the micro plots was disturbed by the repeated DTM measurements and probably restricted the water supply from the deeper soil layers than the surface soil in the surrounding field. As a result, the decrease of ammonia fluxes after the eighth day of the experiment was more pronounced for the DTM results than for the SSM measurements.

The sigmoidal curve was fitted to both data sets with the same satisfactory coefficient of determination (Table 11, R^2 0.997). Like in the other experiments the main discrepancy between the two curves lay in the different estimates for the parameter *a* (DTM 2.89; SSM 42,05 [kg N ha^{-1}]). Both fits yielded the same point of time of maximum ammonia flux t_{max} (2.18 days). Similar to the curves fitted for the

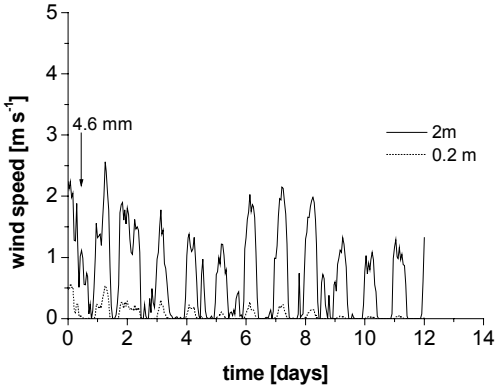
previous treatments, there was a minor discrepancy between the two curves for the parameters *c* and *i*. Again the DTM curve was characterized by a higher sigmoidality than the SSM curve compensated by a slightly higher rate constant *c* resulting in the same t_{max} for both curves. The higher sigmoidality of the DTM curve can be explained by the higher measurement frequency of the DTM and the stronger flattening out of the values described above. In general the flux patterns determined by the two methods agreed very well.

Table 11: Parameters of log. equation fitted to cumulative DTM (mean) and SSM losses of the 3rd maize experiment (in brackets: standard error), surface broadcast treatment

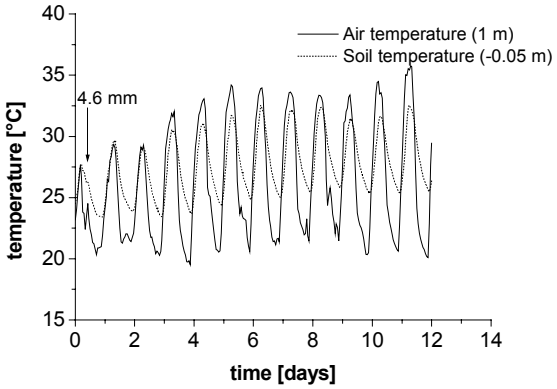
Parameter	DTM	SSM
a	2.89 (0.03)	42.05 (1.62)
c	0.36 (0.01)	0.23 (0.03)
i	2.19 (0.10)	1.65 (0.18)
t_{max}	2.18	2.18

Deep point placement treatment

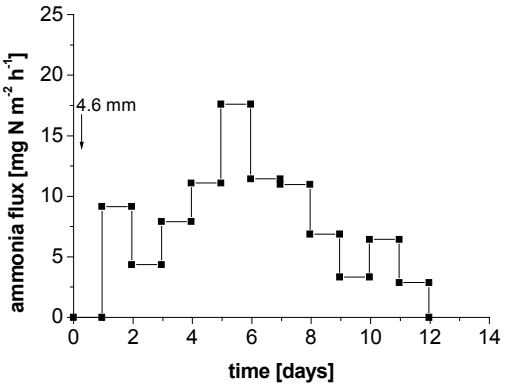
Results of this experiment are presented in Figure 32 a – f. As in the surface broadcast treatment the meteorological conditions had no specific effect on the ammonia flux pattern save the diurnal oscillation of the fluxes caused by the regular temperature (day / night) fluctuations (Fig. 32 a – f). In general the ammonia flux patterns determined by SSM and DTM were quite similar. As in the other experiments the factor between the cumulative ammonia losses measured by DTM and SSM was about 10 (DTM (mean) 1.95; SSM 18.2 [kg N ha^{-1}]). The influence of the surface soil water content on the fluxes at the end of the measurements was not very high because the fertilizer was placed at a depth of about 5 cm below the soil surface. Therefore, the differences between the flux patterns by the DTM and the SSM in the final phase of this treatment were quite small compared to the surface broadcast treatment.



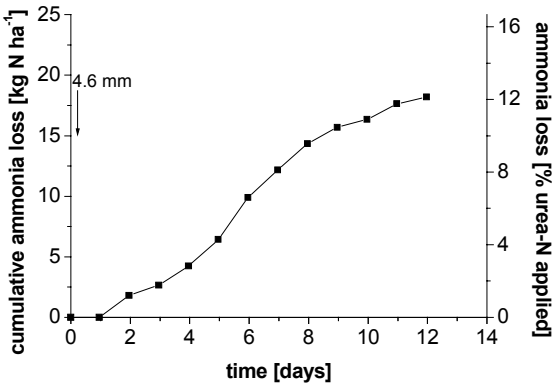
a. wind speed (2 m and 0.2 m)



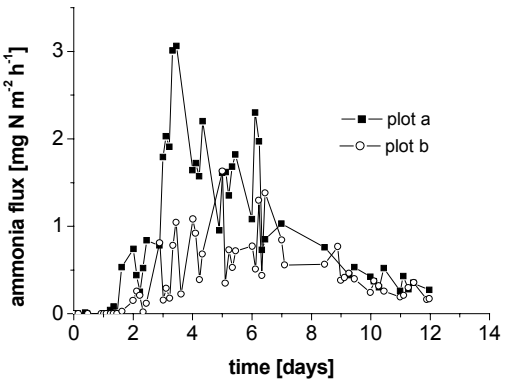
b. temperatures (1 m and –0.05 m)



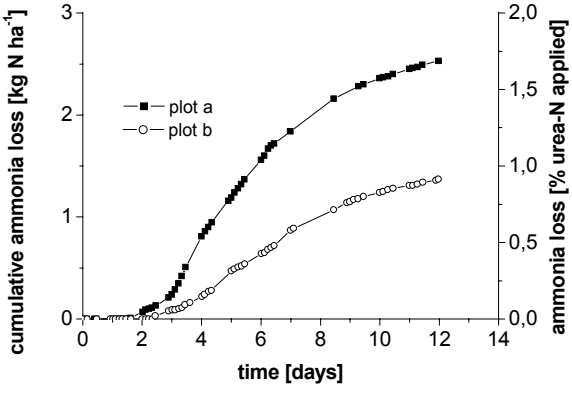
c. SSM ammonia fluxes



d. SSM cumulative ammonia losses



e. DTM ammonia fluxes



f. DTM cumulative ammonia losses

Fig. 32 a – f: Comparison of DTM (hand pump) and SSM ammonia flux measurements, third maize experiment (12 – 24 July 1999), deep point placement (150 kg N ha^{-1})

In this experiment the replications of the DTM measurements did not agree well. Much lower fluxes were determined on plot b as compared to plot a. The flux patterns determined on the two plots were also different. On plot a the highest fluxes were measured on the 4th day while in plot b the highest fluxes occurred on days 5 – 7. The general shape of the ammonia flux curve determined in plot b matched the SSM flux pattern better than that of plot a. However, the highest ammonia flux determined by the SSM occurred on the fifth day with no corresponding maximum of the fluxes in plot b. These discrepancies could be explained by the variations in the placement of the fertilizer. The manual deep point placement of urea is necessarily connected to a considerable variability with regard to the depth of placement, and thickness of soil cover. This variability is reflected in the different curves of ammonia fluxes determined by the DTM. Each DTM micro plot contained 9 fertiliser amended spots. In addition, the DTM measurements themselves might had influenced the fluxes from the points. It was already mentioned that DTM measurements disturb the surface soil structure to some degree. This could lead to a soil cover on the fertilised points with an increased air permeability and thus to an enhanced situation for ammonia diffusing to the soil surface. Most probably both hypotheses hold for the explanation of the discrepancies of the fluxes from the two microplots.

Table 12: Parameters of log. equation fitted to cumulative DTM (mean) and SSM losses of the 3rd maize experiment, deep point placement (in brackets: standard error of the estimate)

Parameter	DTM	SSM
a	2.02 (±0.01)	20.61 (±1.01)
c	0.41 (±0.01)	0.30 (±0.04)
i	6.79 (±0.25)	4.08 (±0.74)
t_{max}	4.67	4.69

The comparison given above is validated by the similarity of the parameters of the sigmoid function fitted to the SSM (r^2 0.999) and the mean DTM (r^2 0.996) data set (Table 12). Both fits yielded the same t_{max} of day 4.7. The parameters *a* differed in one order of magnitude. As in the other experiments the DTM was characterized by slightly higher sigmoidality *i* and rate constant *c*. This can mainly be attributed to the higher measurement frequency of the DTM. As a result, the mean NH_3-fluxes measured on the plots a and b determined by the DTM agree with the pattern measured by the SSM.

Table 13: Cumulative ammonia losses determined by ATM and SSM, third maize experiment (12 – 24 July 1999), deep point placement (150 kg N ha^{-1})

time [days]	ammonia-N volatilised [kg N ha^{-1}]	
	ATM	**SSM**
0 – 4.95	2.5	6.4
4.95-11.95	6.0	11.8
total	8.5	18.2

Table 13 compares the amounts of ammonia loss [kg N ha^{-1}] measured by SSM and ATM. In contrast to the results presented for wheat 1998 surface broadcast treatment the agreement between the outcomes of the SSM and ATM measurements was not good in this experiment. Total ammonia loss determined by the SSM were more than twice as high as the ATM measurements. It is difficult to determine why this discrepancy between the two methods occurred. One possible explanation could lie in the different influence of ambient wind speeds on the ammonia measurements. While in October 1998 an average wind speed (2 m) of 1.68 m s^{-1}prevailed, a mean wind speed of 0.76 m s^{-1} was measured in July 1999. In addition, maize plants growing during the experiment from a height of about 0.5 m to almost 2 m could have had a different effect on the two measurement methods as well. As a consequence, it can be stated that the simplified micrometeorological methods applied were also subject to a certain degree of measurement error which, unfortunately, cannot be specifically quantified for the single experiments.

4.1.3 Ammonia measurements with DTM and electric pump

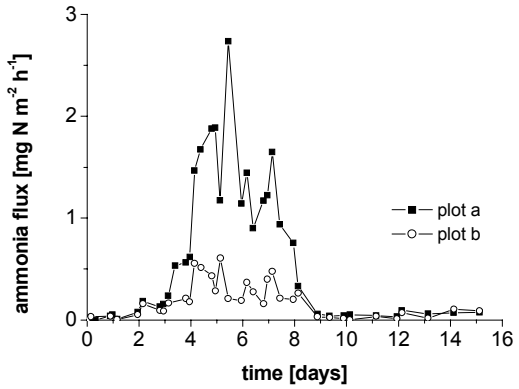
In the wheat and maize experiments 1999 was also applied DTM with electric pump. Several pumping rates were tested and compared with the results of SSM and DTM with hand pump. The presentation of the results shall focus on the comparison of the fluxes and total ammonia losses determined by the different methods. The effect of environmental conditions on the measurement results will not be discussed in detail. Two treatments (wheat 1999 surface broadcast, maize 1999 deep point placement) are presented in this chapter. Chapter 4.4 will give an overview about all ammonia loss results.

4.1.3.1 Second wheat experiment (09 – 24 March 1999)

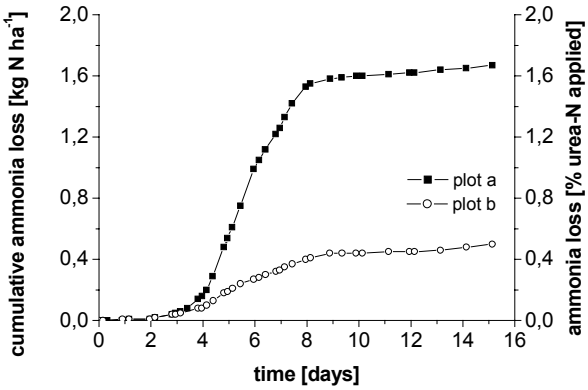
Fig. 33 shows ammonia fluxes (left column) and cumulative ammonia loss (right column) curves determined by DTM, DTM (electric pump) and SSM. Fig 33 (a) shows the repeated DTM measurements in plots a and b, Fig 33 (e) depicts the results of DTM (electric pump) with two different exchange rates inside the cups (16 + 33 Vol. min^{-1}) just in plot a. This also applies to the presentation of cumulative ammonia losses in Fig. 33 b + f.

The general shapes of the ammonia flux curves are quite similar. The replicate DTM (hand pump) measurements on plot a and b did not agree well. The much higher fluxes measured in plot a compared to plot b can most probably be attributed to different soil properties in the plots as the replications were satisfactory in the other experiments. As the DTM with electric pump was only applied on plot a, only the DTM curve in this plot shall be used for the comparison. The maxima of the ammonia fluxes measured with DTM (hand pump) and DTM (16 Vol. $min.^{-1}$) occurred about one day before the maxima determined by SSM and DTM (33 Vol. $min.^{-1}$). The discrepancy between DTM (hand pump) and SSM curve can be explained by the influence of wind speed (see appendix) on the measurement methods like in the other experiments.

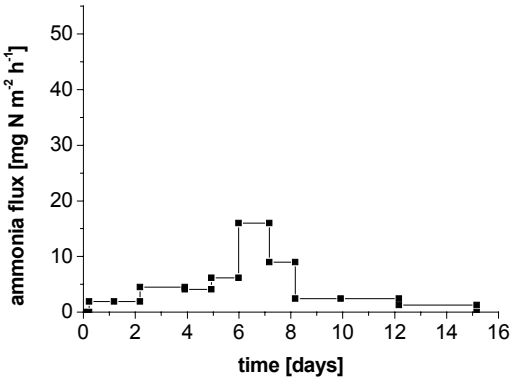
Particularly striking is the difference between the fluxes determined with electric pump using two different pumping rates. The measurement set-up of DTM with electric pump consisted of two cups connected with teflon tubing which was intersected by a gas tap. Each set of measurements comprised measurements with one and two cups (i.e. 33 / 16 Vol min^{-1}) on the same spot. Therefore, due to the same local conditions, the fluxes determined should mainly depend on the air exchange rate provided by the pump. As a consequence, sampling with one and two cups followed immediately after each other and were, thus supposed to yield at least the same flux pattern. However, the flux maximum determined at an air exchange rate of 33 Vol. min^{-1} occurred on the seventh day while the maximum for 16 Vol. min^{-1} was detected on the fifth day. In contrast to the systematic microplot experiments (4.1.1), an effect of the number of cups on the ammonia fluxes measured with the DTM seemed to exist. As the plot was sown with wheat there might had been an uneven distribution of soil properties and urea in the microplots. The measurement with one cup did not always yield higher fluxes than with two cups, e.g. on days 5 – 6. This implies that the discrepancies between the two samplings were not systematic, but also depended on the different properties of the two small spots of soil under the cups. However, as this experiment was mainly considered as a testing of the DTM with electric pump under field conditions, sampling was not very frequent, and the



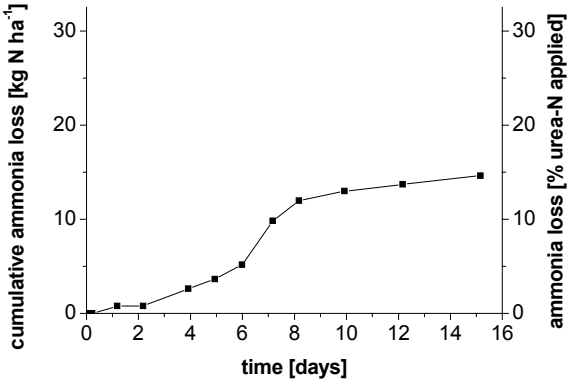
a. DTM (hand pump) ammonia fluxes



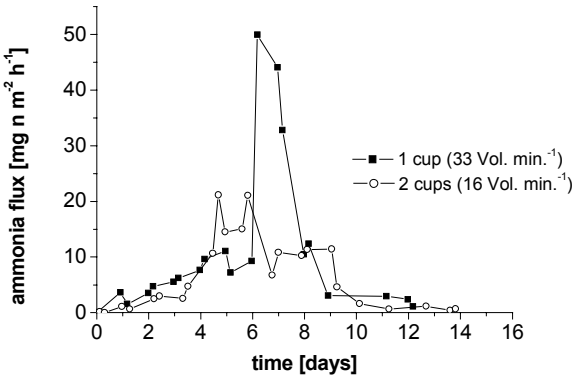
b. DTM (hand pump) cumulative ammonia loss



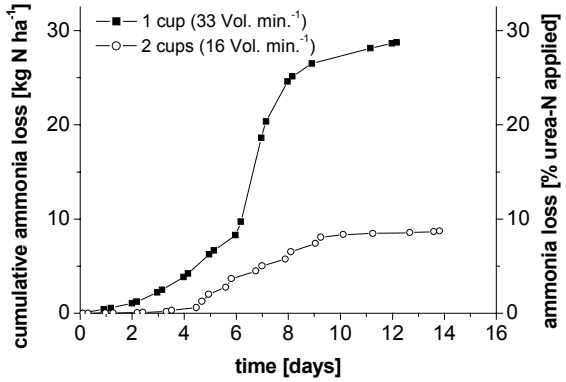
c. SSM ammonia fluxes



d. SSM cumulative ammonia loss



e. DTM (electric pump)ammonia fluxes



f. DTM cumulative ammonia losses

Fig. 33 a – f: Comparison of DTM (hand pump), SSM and DTM (electric pump) ammonia flux measurements, sec. wheat experiment (09.03. – 21.03.1999), surface broadcast treatment (100 kg N ha^{-1})

measurements were connected with some degree of unreliability. Another explanation for the observed discrepancies could lie in the depletion of ammonia at the soil surface by the first ammonia loss measurement.

The cumulative ammonia flux curves (Fig. 33 b, d, f) show a quite similar shape. The parameters of the fitted sigmoid curves are given in Tab.14.

Table 14 Parameters of logistic equation fitted to cumulative DTM (mean, hand and vacuum pump) and SSM losses of the 2nd wheat experiment, surface broadcast treatment (in brackets: standard error)

	parameter				
	a	***c***	***i***	t_{max}	r^2
DTM 33 Vol. min^{-1}	30.25 (±15.96)	0.59 (±0.09)	30.25 (±1.41)	5.78	0.96
DTM 16 Vol. min^{-1}	9.98 (±0.65)	0.49 (±0.06)	13.85 (±3.65)	5.36	0.99
DTM (hand pump)	1.06 (±0.01)	0.69 (±0.02)	31.33 (±3.02)	4.99	0.99
SSM	14.79 (±0.69)	0.46 (±0.08)	12.38 (±5.72)	5.47	0.99

Cumulative ammonia losses (*a*) determined with DTM (electric pump) had the same order of magnitude as the SSM result. While the outcome of the measurement at an air exchange rate of 16 Vol. min^{-1} almost matched the SSM value, the air exchange rate of 33 Vol. min^{-1} led to a twofold overestimation of ammonia loss. The value for DTM (hand pump) was about one order of magnitude lower, as in the other experiments. However, the estimate of the curve parameters for DTM (33 Vol min^{-1}) - in particular of *a* (30.25 kg N ha^{-1}, estimation error 15.96) - was not very good, thus reducing their comparability.

The t_{max} for DTM (electric pump) and SSM were almost the same while the value for DTM (hand pump) was 0.5 days smaller. The DTM (electric pump) was much less affected by the influence of ambient wind speed than DTM (hand pump). The curve for DTM (16 Vol. min^{-1}) shows the best agreement with the SSM curve for all parameters. Therefore, for that specific experiment an air exchange rate of 16 Vol min^{-1} in the cups almost corresponded to the mean ambient natural air exchange resulting in similar ammonia losses to those determined by the SSM.

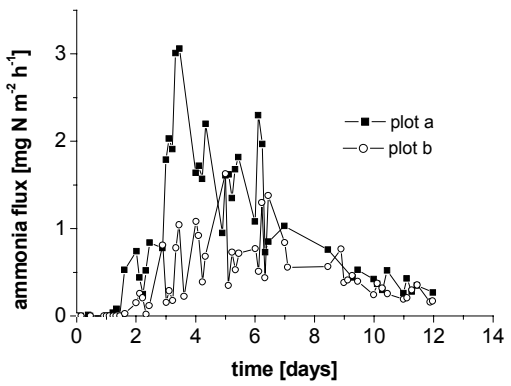
4.1.3.2 Third maize experiment, deep point placement (12 – 24 July 1999)

The set-up of the DTM (electric pump) measurements was changed in this experiment. Only one air exchange rate was applied (20.5 Vol. min^{-1}) using two cups. The air exchange rate was slightly increased compared to the preceding wheat experiment as the air exchange rate of 16 Vol. min^{-1} had resulted in a minor underestimation of ammonia losses in that experiment. Sampling with DTM (electric pump) was carried out on both plots. So, the two curves in Fig. 34 e + f depict ammonia fluxes and cumulative ammonia losses from the same plots as in a + b for DTM (hand pump).

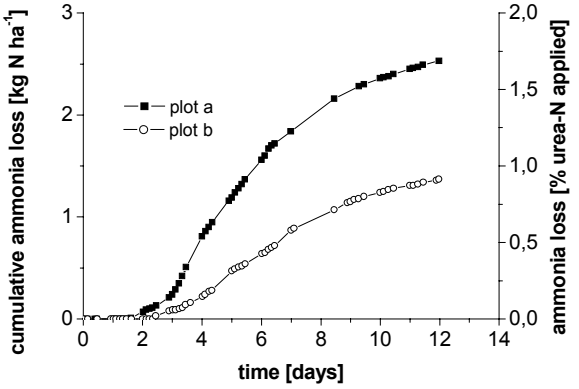
The ammonia flux patterns determined by the methods agreed very well in this treatment. The discrepancy between the measurements of the DTM (hand pump) on plots a and b has already been discussed above (Chapter 4.1.2.3). The measurements with DTM (electric pump) on the plots also showed the discrepancy between the two plots. Both variants of the DTM method determined higher ammonia losses on plot a than on plot b (Fig. 34 b and f). The differences between the ammonia fluxes measured could be related to the specific problem of determining ammonia loss following deep point placement of urea. As was mentioned above, ammonia volatilisation from the different spots was quite variable.

Table 15: **Parameters of logistic equation fitted to cumulative DTM (mean, hand and vacuum pump) and SSM losses of the third maize experiment, deep point placement treatment (in brackets: standard error)**

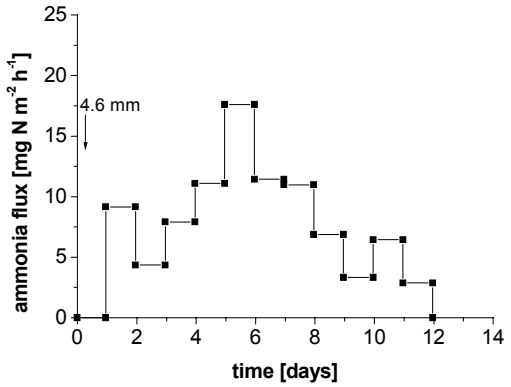
	parameter				
	a	**c**	**i**	**t_{max}**	**r^2**
DTM 20.5 Vol. min^{-1}	23.52 (±0.65)	0.25 (±0.01)	3.42 (±0.10)	4.92	0.99
DTM (hand pump)	2.02 (±0.01)	0.41 (±0.01)	6.79 (±0.25)	4.67	0.99
SSM	20.61 (±1.01)	0.30 (±0.04)	4.08 (±0.74)	4.67	0.99



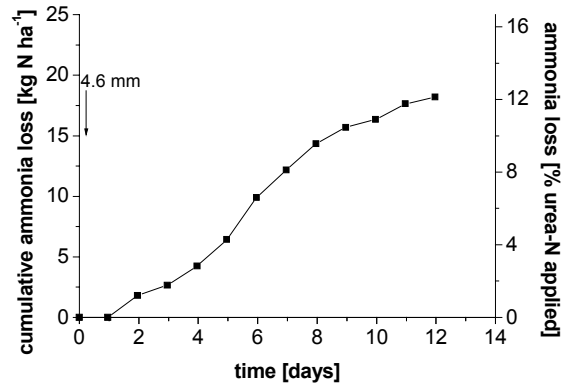
a. DTM (hand pump) ammonia fluxes



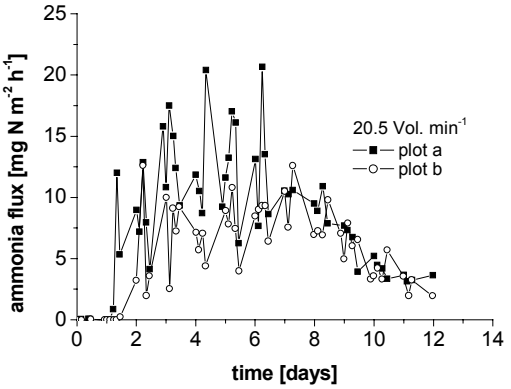
b. DTM (hand pump) cumulative ammonia loss



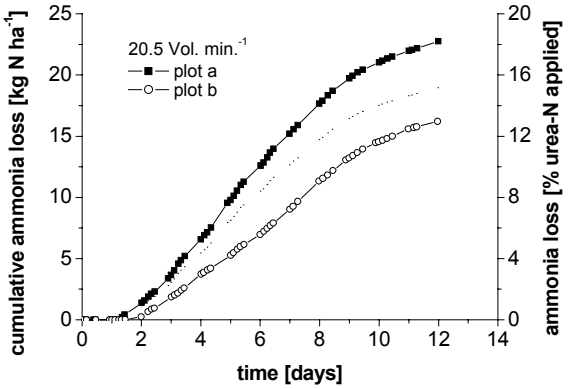
c. SSM ammonia fluxes



d. SSM cumulative ammonia loss



e. DTM (electric pump)ammonia fluxes



f. DTM cumulative ammonia losses

Fig. 34 a – f: Comparison of DTM (hand pump), SSM and DTM (electric pump) ammonia flux measurements, third maize experiment (12.07. – 24.07.1999), deep point placement (150 kg N ha^{-1})

The measurement with DTM (electric pump) yielded about the same cumulative ammonia loss (*a*) as the SSM (Table 15). The other parameters of the SSM and DTM (electric pump) curves agreed also quite well. The curve for DTM (hand pump), however, showed a higher sigmoidality than the other two curves, and cumulative ammonia losses were again lower by a factor of 10. The effect of increased air exchange rates inside the cups underlines the importance of ambient wind speed for both, the absolute amount of ammonia losses measured and sigmoidality of the DTM (hand pump) flux curve. However, in effect, the flux patterns determined by the three measurement approaches were quite similar. This is reflected in the rather small differences between the t_{max} values determined for the three data sets.

The good agreement between SSM results and DTM (20.5 Vol min^{-1}) in this treatment seems to suggest that 20.5 Vol. $min.^{-1}$ is the appropriate air exchange rate for the DTM to match SSM measurement results. However, measurements with the same air exchange rate in the surface broadcast treatment during the same period in July 1999 led to a twofold overestimation of ammonia loss rate. It can be therefore stated, that it was not possible to determine one specific individual air exchange rate in the cups which provides measurement results corresponding SSM ammonia flux measurements. The air exchange rate inside the chambers should be adapted to ambient wind speed, plant height and soil conditions. But it is very hard to carry out an adaptation of the flow rate inside the DTM cups for every specific set of environmental conditions.

As a consequence of the measurement results of the modified DTM with electric pump, the approach for the calibration of the DTM chosen in this study is the indirect consideration of environmental factors by deriving a calibration formula (chapter 4.5) which calculates ammonia losses depending on ammonia losses measured with DTM (hand pump), wind speeds and temperatures. Measurements are made with DTM (hand pump) and later on corrected (scaled up) by taking into account the influence of wind speed and temperatures by applying the calibration formula.

4.2. ^{15}N experiments

The proportioning of recovered ^{15}N between soil and plant as well as total recovery of ^{15}N in the treatments will be discussed in this chapter (Fig. 35). Figure 36 shows the residual ^{15}N in the soil profile for the different experiments.

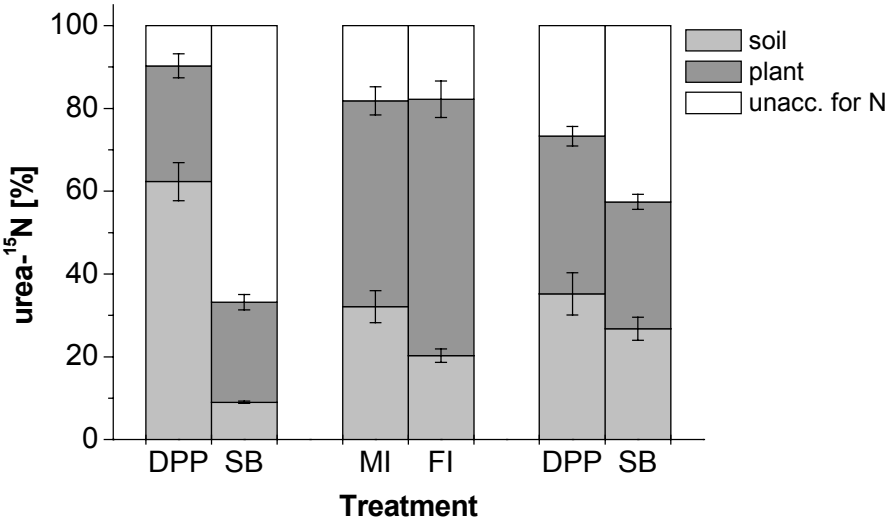


Fig. 35: Recovery of ^{15}N applied in soil and plants (DPP = deep point placement; SB = surface broadcast; MI = mixed incorporation; FI = Fertilization followed by irrigation; ± standard error, n = 4)

4.2.1 Maize treatments

In the two maize experiments ^{15}N recovery in both plant and soil material was higher for the incorporated than for the surface broadcast treatments (Fig. 35). Incorporation of fertilizer (deep point placement, DPP) did thus promote fertilizer uptake by maize as well as decrease total N losses. The main reason for the high total recovery in DPP treatments was the higher recovery in soil compared to the surface broadcast treatments, in particular in the maize 98 experiment. After maize harvest there was still a considerable amount of N beneath the main wheat rooting zone characteristic for the Fengqiu region (< - 60 cm) (Wang 1991) in both deep point placement experiments (Fig. 36 b + f). In the course of the year this N could be leached as nitrate-N to the groundwater by irrigation water or precipitation. The high recovery of ^{15}N in the 98 deep point placement treatment could have been caused by non-appropriate soil sampling using a soil corer for sampling the deeper soil layers as fertilizer was not yet evenly distributed in soil from the fertiliser amended spots.

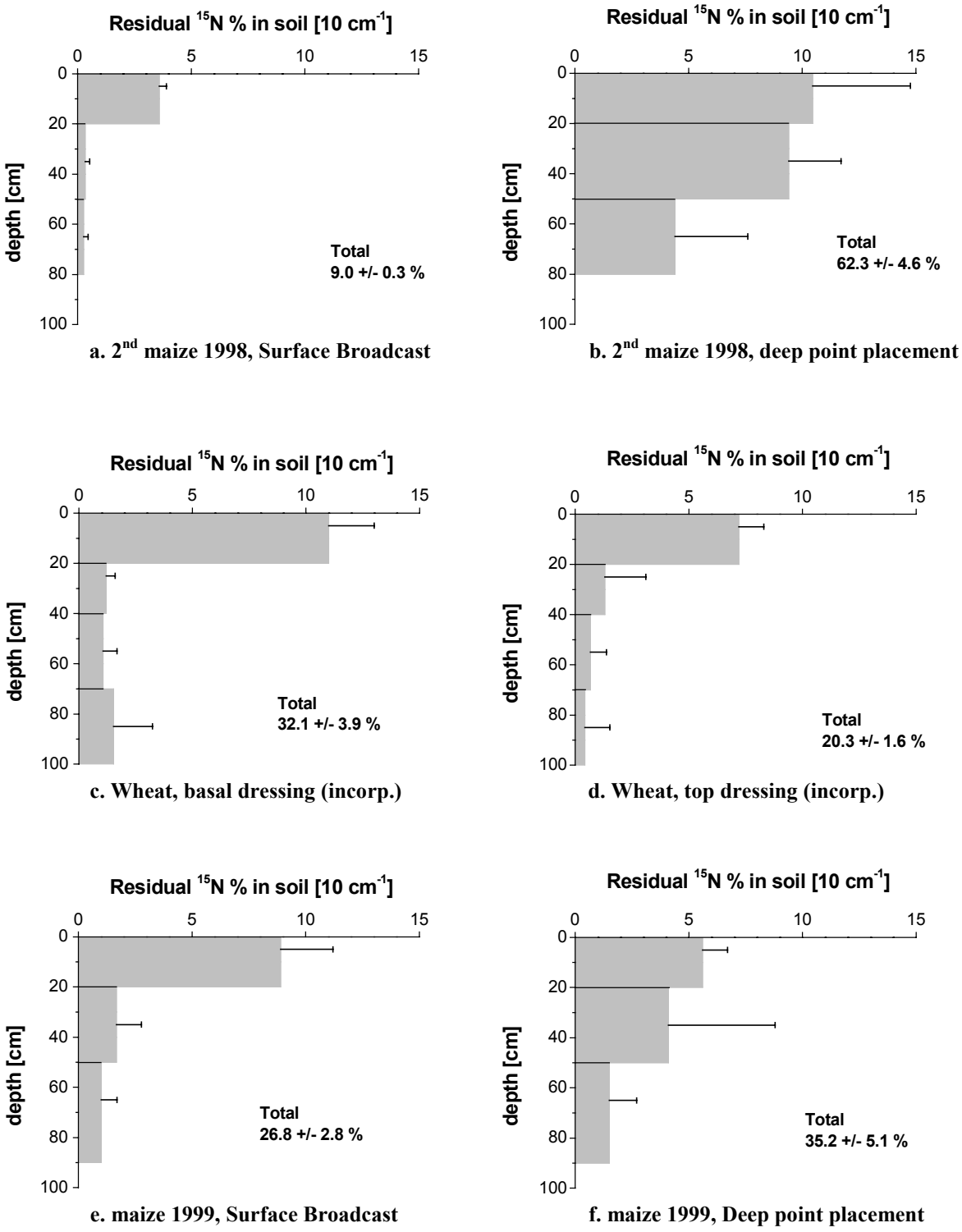


Fig.36 a-f: Residual ^{15}N from labelled urea in the soil profile (± standard error, n = 4)

However, N contents in the deepest sampling layer were highest in both deep point placement treatments for all ^{15}N experiments. Deep point placement of urea did also result in high variability of the ^{15}N contents which is reflected in the comparatively high standard error of the measurements.

The difference in total ^{15}N-recovery between the 1998 and 1999 maize surface broadcast treatments is in good agreement with the ammonia losses determined by the SSM, in the 2 years ammonia volatilisation being the main pathway of N loss in this application method. Due to the higher fertilization rate in the maize 98 experiment and very favourable environmental and soil conditions for ammonia volatilisation, absolute and relative ammonia losses were higher in the 1998 experiment than in 1999. ^{15}N recovery in both plant and soil material was higher in the maize 99 experiment. So, the high N losses in the surface broadcast in 98 can be considered as above average for maize in the region. On average Rees et al. (1997) determined a residual ^{15}N content in soil of about 20 % for surface treatments. ^{15}N recovery in plant material (18% in surface broadcast treatments) was slightly smaller than in the Fengqiu experiment, but in general supports the results. The findings also agree with other measurements in surface broadcast treatments carried out in Fengqiu with 23% and 33% plant and soil recovery, respectively (Zhang et al. 1992).

With regard to the deep point placement treatment with maize the outcomes of the experiments are underpinned by experiments carried out in Fengqiu by Wang (1991) and Zhang et al. (1992). Wang determined residual ^{15}N contents in soil between 65.3% and 26.4% for two different deep point placement experiments which correspond to the results of the 1998 and 1999 experiments, respectively. Plant recoveries are also in good agreement. In contrast, Zhang et al. (1992) detected a soil recovery of 40% , only, and a plant recovery of 31 % which are in line with the maize 99 experiment. To sum up, measurements of plant and soil recovery of ^{15}N (deep point placement) by maize support the argument above that non-appropriate soil sampling might have led to an overestimation of ^{15}N retained in soil in the 98 deep point placement experiment.

4.2.2 Winter wheat treatments

The amounts of fertiliser N unaccounted for in the two wheat treatments (both incorporation of fertilizer) were much lower than for maize except for the maize 1998 deep point placement treatment which was already discussed above. A total ^{15}N recovery of more than 80% in plant and soil material corresponding to only about 20% total loss is relatively high as compared to results reported by other authors.

For a fertilisation followed by irrigation treatment in spring, Rees et al. (1997) determined a total ^{15}N recovery of 64 %, with 30% plant uptake and 34% in soil. The respective values for plant uptake and

soil recovery in the Fengqiu experiment in spring 1999 were 61.9% and 20.3%. Total recovery of ^{15}N for the basal dressing treatment was 54.3% in experiments carried out by Wang (1991). The plant recovery was 30% while soil residual ^{15}N amounted to 22.4%. Corresponding figures for the fertilisation followed by irrigation treatment in Fengqiu 1998/99 were 49.7% and 32.1%, respectively. Thus, the main discrepancy between the Fengqiu 1998/99 experiments and the literature data lies in different amounts of ^{15}N taken up by plants. But the distribution of ^{15}N in relation to soil depth was quite similar compared to the measurements by Rees et al. (1997). However, a total recovery of 98.5% was determined in Fengqiu by Wang (1991) for a top dressing treatment showing a very high ^{15}N recovery in both, plant (54.9%) and soil (43.6%) material. The value for plant uptake in the Fengqiu 99 top dressing treatment (62%) is underpinned by these data while ^{15}N recovery in soil was considerably smaller than the value determined by Wang et al. (1991). For the temperate zone MacDonald et al. (1997) compiled total ^{15}N recoveries (plant and soil) for winter wheat ranging between 66 and 82% (mean 76%) depending on soil type and weather conditions (year). Plant uptake lay between 37% and 63% (mean 52%), and soil recovery between 18 – 36% (mean 23.75%), respectively. Although our values for plant uptake were situated at the upper margin of values observed by the authors cited, the values determined in Fengqiu 98/99 still seem a little high, probably due to measurement or sampling error. They match the small ammonia losses determined by the SSM for the two winter wheat treatments. As amounts of ^{15}N recovered in deeper soil layers were rather small, urea fertiliser applied to winter wheat by incorporation into the soil did not seem to be prone to leaching beneath the root zone or to the ground water.

4.3 Mineral nitrogen

Profiles (0 – 1.2 m) of total mineral N contents sampled before fertilization and after harvest of the crops are presented in Table 16.

Table 16: Measured mineral N contents (NH_4^+-N, NO_3^--N) from soil cores taken from the experimental fields before fertilization and after harvest, and ammonia losses after fertilisation determined with SSM

No.	fertilization rate [kg N ha^{-1}]	time interval	application method	mineral N (0-120 cm) [kg N ha^{-1}]		losses (SSM) [kg N ha^{-1}]
				begin	end	
1.	75 (+125*)	25.06.-25.09.1998	**a.** surface broadcast	112.2	116.7	32.7
			b. fertilization followed by irrigation	125.9	100.3	13.4
2.	200	07.07.-25.09.1998	**a.** surface broadcast	78.6	50.2	95.8
			b. deep point placement	51.7	179.7	21.6
3.+4.	220 (3.: 120, 4.:100)	8.10.1998-03.06.1999	**a.** surface broadcast	92.7	98.7	38.5
			b. mixed fertilization + fertilization followed by irrigation	49.3	67.8	3.4
5.	150	08.07.1999	**a.** surface broadcast	96.5	___	38.3
			b. deep point placement	229.6	___	18.8

*** The second rate of urea was applied after finishing the ammonia measurements of the first maize experiment. Ammonia losses following the second fertilization were not determined on that plot. Therefore, ammonia losses given in the table are only related to the first fertilization.**

Only few profiles which were analysed in the course of the experiments hinted towards a translocation of fertilizer-N as nitrate out of the rooting zone, e.g. recovery of high nitrate contents in deeper layers of the soil (0.9 – 1.2 m) after harvest. Mineral N in this depth of the soil could be leached towards the ground water by irrigation water applied at sowing or fertilization and by strong rainfall or flooding events. In almost all experiments total mineral N contents in the profiles after harvest were nearly as high as prior to fertilization (about 100 kg N ha^{-1} -1.2 m^{-1}). Only exception from this pattern was the 2nd maize experiment, deep point placement, in which total mineral N contents after harvest were 125 kg N

ha^{-1} higher than before fertilizer application. On the other hand, this could also be due to sampling error because mineral N applied at fertilizer points takes quite a long time to disperse evenly through soil (see also Fig. 38). Nevertheless, the high mineral N content and the relatively low ammonia losses (11%) determined during the experiment suggest lower overall N-losses after deep point placement of urea compared to the other fertilization techniques. High mineral N contents after harvest show that N was applied in great excess of the plant uptake, in particular to winter wheat.

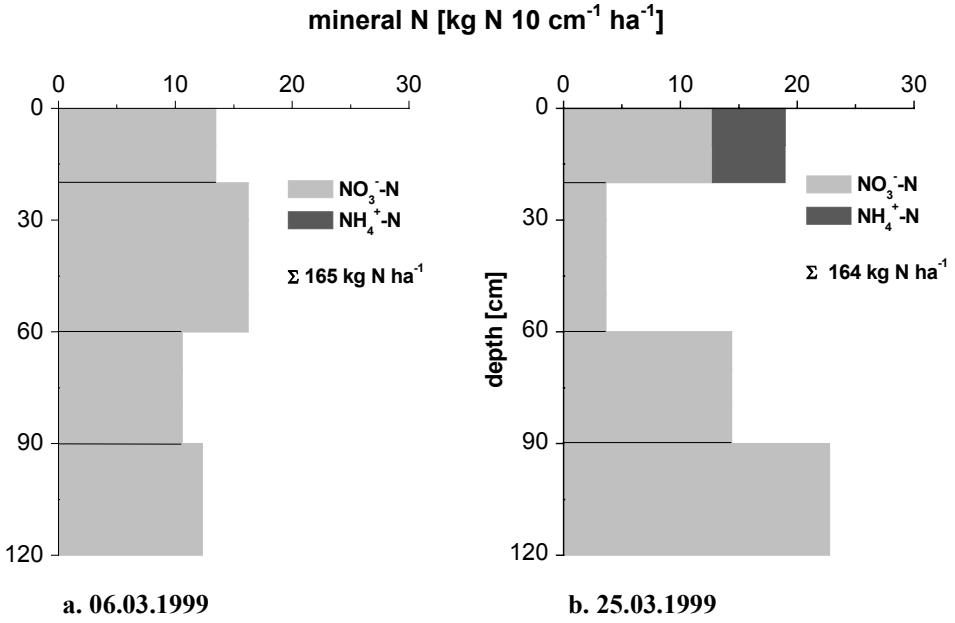


Fig.37 a+b: mineral N contents at the beginning and after finishing of the 2nd winter wheat experiment, surface broadcast treatment (100 kg N ha^{-1}), spring 1999

Throughout both winter wheat experiments (autumn 1998, spring 1999) very high total mineral N contents (mineral N > 100 kg N ha^{-1}) were found in the profiles of both the mixed fertilization and the surface broadcast treatments. The effect of irrigation measures on translocation and leaching of mineral N during the vegetation period of winter wheat could not be determined directly in the experiments. Nevertheless, changes in the distribution of mineral N over depth between the beginning and at the end of the second wheat experiment, surface broadcast treatment, can be interpreted as the effect of mineral N translocation through the profile out of the rooting zone. Before the application of fertilizer the profile contained already 165.5 kg mineral N ha^{-1} (Fig. 37 a). Prior to the surface application of 100 kg urea N ha^{-1}, 50 mm of irrigation water were applied to the experimental sites. About 20 days later, after finishing the ammonia loss measurements, the mineral N profile had a quite different shape as at the beginning of the experiment. Whereas mineral N was almost evenly distributed through the whole

profile without any mineral NH_4^+-content before the fertilization, the mineral N profile at the end of the measurement (164 kg N ha^{-1}) was characterized by two peaks, the first at the plough layer (0 – 0.2 m), the second in the deepest layer analysed (0.9 – 1.2 m) (Fig. 37 b). Moreover, comparatively low ammonia losses were measured in this treatment (14.6 kg N ha^{-1}). As an explanation might serve the following process: some mineral N in the upper layers of the profile was leached to deeper layers of the profile by irrigation water before fertilization. The application of urea resulted in an enrichment of the plough layer with mineral N, in particular with ammonium N. This hypothesis is underpinned by the ^{15}N measurements as only little amounts of the ^{15}N applied in this treatment were recovered in deeper soil layers (see Fig.36 c + d). As mineral N below 0.9 m depth was already outside the main rooting zone of winter wheat in the region (see paragraphs above) it was prone to further translocation to deeper soil layers and towards the groundwater by subsequent rainfall or irrigation. In addition to ammonia volatilisation losses, plant uptake has certainly also contributed to the depletion of mineral N in the surface layers. Nevertheless, the shape of the second profile suggests leaching of nitrate as an additional loss process. The overall recovery of ^{15}N in soil and plant for the mixed fertilization treatments was very high (82%) in the winter wheat experiment. Therefore the leaching of ^{15}N most probably was not very severe. On the other hand, ammonia losses were very low in this treatment suggesting that nitrate leaching might be one of the main pathways of N loss in the winter wheat growing season. But these facts can only be interpreted as hints for an understanding of the processes because mineral N measurements are characterized by a high degree of uncertainty if taken very soon after fertilization (Fink 2001).

Nevertheless, nitrate concentrations in groundwater samples taken from farmers' wells on the fields (about 500 m from the village) were all below the WHO-threshold value of 11,3 mg NO_3^--N l^{-1} (0.2 – 3 mg NO_3^--N l^{-1}). The situation could be different in the village wells (as observed by Zhang et al. (1996)) but those were not sampled. The lowering of the groundwater table in recent years (several decimetres a^{-1}) might also contribute to slowing down of the enrichment of groundwater with nitrate. This hypothesis is supported by NO_3^- -concentrations measured by means of suction cups in the unsaturated zone in fields close to Fengqiu station. NO_3^--concentrations were considerably higher in all sampling depths than those measured in the irrigation wells and increased with depth (NO_3^- content [mg l^{-1}] 0.5 m: 0-30, 1 m: 15-38, 1.5 m: 30-44). Sauer et al. (2002), however, have shown that under dry conditions the rooting depth can reach much deeper than 1 m which is usually considered for an assessment of nitrate leaching to ground water in mineral N investigations. Under water stress plants can take up nutrients from much deeper soil layers. But the authors also admitted that strong precipitation or – in China – irrigation can lead to severe nitrate leaching. Similar was shown by Roelcke et al. (2000) for arable soils at the southern edge of the Chinese loess plateau. Due to high evapotranspiration and limited rainfall excess nitrate was leached to a depth of 1.4 – 2 m, only, which

also moved upwards dissolved in capillary water. A winter wheat rooting depth up to 2.5 m was observed in these Chinese loess soils due to semi-arid conditions. Nevertheless, even under those conditions nitrate might be washed out of the rooting zone in case of intensive rainfall events or excess irrigation. Therefore, apart from nitrate distribution depth, water and rainfall dynamics (distribution and intensity of events) are decisive for the risk of nitrate leaching. The intensive irrigation in Fengqiu may, thus, promote nitrate leaching from arable soils, in particular if the ground water table is raised due to flooding of the canals with water derived from the Yellow River.

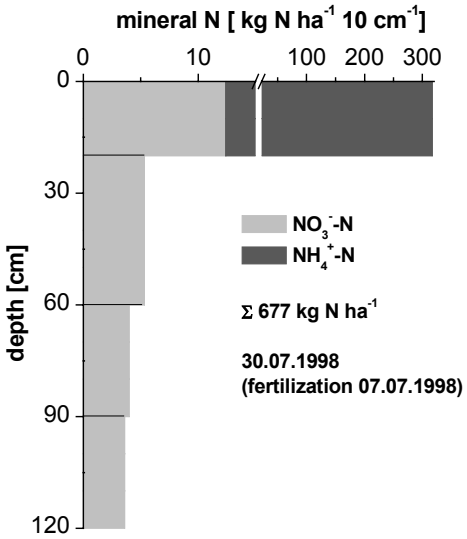


Fig. 38: Mineral N content 3 weeks after fertilization, 2nd maize experiment (200 kg N ha^{-1}, July 1998), deep point placement, on point

Deep point placement of urea resulted in an effective reduction of ammonia volatilisation losses in the 2nd maize experiment. Soil cores taken on the fertilised spots about 3 weeks after fertilisation still showed exceedingly high ammonia concentrations in the plough layer (Fig. 38). As a consequence, most probably further ammonia losses occurred from those points although reduced due to lowered soil pH because of former ammonia volatilisation from these points. Roelcke (1994) observed NH_3-volatilistion on deep point placement treatments for almost 1 month. Nevertheless, if the ammonia-N is not taken up by plants and is transformed to nitrate, high amounts of mineral N could be leached to deeper soil layers by preferential flow, in particular connected to further irrigation measures. Ammonium–N is mostly adsorbed to clay minerals and is only leached in small amounts. The high mineral N contents determined after harvest (Table 16, 2b) in the experimental site support this

hypothesis. They could be explained by a still uneven distribution of mineral N in soil. A former fertilizer point was most probably included in the mixed sample thereby possibly increasing the overall mineral N content. Though effective in reducing ammonia volatilisation losses, deep point placement of urea can, thus, entail nitrate leaching, in particular by preferential flow.

The interpretation of the mineral N profiles is difficult because of the high spatial heterogeneity of the soils texture (Chapter 3.1.2) in the Fengqiu region. Moreover, soil mineral N heterogeneity was increased as the fields were very small and managed by different farmers with varying agricultural practices. Though assumed as homogeneous, the soils of the large circular plots used during one experiment could be characterised by very different mineral N contents before the beginning of the experiment. The soil mineral N profiles prior to the third maize experiment may serve as an example although they were both planted with wheat in winter growing season (96 vs. 229 kg mineral N ha^{-1}).

Average N-uptake by wheat and maize (grain and straw) in Fengqiu is 168 and 154 kg N ha^{-1}, respectively (Fan, pers. communication). Similar values were determined by Richter and Roelcke (2000) for loess soil at the southern edge of the Chinese loess plateau. Considering an annual mineral N fertilization of about 400-420 kg N ha^{-1} as applied in the experiments, a N-balance surplus of about 80-100 kg N ha^{-1} a^{-1} can be calculated for the Fengqiu experimental sites. Mixed fertilization techniques are the urea application methods usually applied by farmers in the region. Annual ammonia losses from these treatments measured with micrometeorological mass balance method (SSM) summed up to 30 kg N ha^{-1}. Moreover, about 5 kg N ha^{-1} a^{-1} are lost from the fields by way of denitrification losses (Xing 1998; Cai et al. 2002). Both ammonia loss as well as denitrification loss measurements exhibit a considerable degree of measurement error. Nevertheless, a surplus of about 45-65 kg of surplus N ha^{-1} remains which is not yet accounted for in the N-balance, prone to leaching to deeper soil layers and the groundwater. In addition, Roelcke et al. (2000) showed that there is a high N mineralisation potential in loess derived soils in Northern China. Simulation results showed that N mineralisation results of about 80 kg N ha^{-1} $crop^{-1}$ (winter wheat growing season) can be calculated for a south Chinese soil with a lower N mineralisation potential as those determined for Northern Chinese loess soils (Roelcke et al. 2002 b). The contribution of N mineralisation to the total mineral N supply was not yet included in the N-balance. As a result, a conservative estimate gives a N surplus in Fengqiu soils of about 150 - 200 kg N ha^{-1} a^{-1} under current management practices. Most probably a high proportion of surplus N is fixed in soil as was shown for German arable soils (Nieder et al. 1996, Nieder and Richter 2000). Due to favourable soil and climatic conditions, ammonia loss was most probably one of the major pathways of surplus N loss in Fengqiu region, besides leaching losses.

Recently, mineral N estimates were included in fertilization recommendations in different Chinese agro-ecosystems. Even strong reductions in mineral N fertilisation (by 50 – 80%) did not lead to significant decreases in grain yield (Chen et al. 2001). Similar findings were reported by Roelcke et al. (1998) and Roelcke et al. (2002 b) when reducing N application rates by 30-40 %. To some extent the high mineralisation potentials reported in these studies might be also caused by excess fertilization in preceding years but mainly due to a long history of applying organic manure. But there should be still considerable N mineralisation in arable soils even after considering the contribution by N mineralisation in reduced fertilisation recommendations for a longer period of time. Farmers in the Chinese Taihu region have already started to reduce mineral N fertilization to winter wheat by 10 – 20 % (Roelcke et al. 2002 b). Altogether, there is a high potential for the reduction of mineral N fertilization in Fengqiu in order to reduce detrimental effects of excess fertilization (nitrate leaching, gaseous N losses etc.) and for a more economically sound use of mineral N fertilisers. This potential for fertilizer N reduction in Fengqiu was also proven by high mineral N contents determined in soil profiles throughout the year.

Table 17: Summary of ammonia volatilisation measurements and weather conditions during the 1998 – 1999 field experiments (DTM values with range of values)

No.	Date	rate [kg N ha^{-1}]	Treatment*	mean wind speed (2 m)[m s^{-1}]	mean wind speed (0.2 m)[m s^{-1}]	mean Air Temp. [°C]	mean Soil Temp. [°C]	cumulative ammonia loss [% urea-N applied]				
								DTM		SSM	ATM	^{15}N§
								hand pump	electric pump			
1	29 June – 07 July 1998	75	**a.** SB	2.00	0.52	27.0	27.8	1.6±0.2	___	43.6	60.8	___
			b. FI	2.32	0.62	27.0	27.9	0.06±0.02	___	17.9	___	___
2	19 – 30 July 1998	200	**a.** SB	0.76	0.05	26.9	29.0	7.8±0.54	___	47.9	___	66.8
			b. DPP	0.78	0.05	27.0	28.9	0.09±0.02	___	10.8	4.1	9.7
3	11 – 23 October1998	120	**a.** SB	1.68	0.95	15.3	17.6	0.8±0.17	___	19.9	17.5	___
			b. MI	1.63	0.89	15.5	16.8	0.15±0.01	___	2.3	___	18.1
4	09 – 24 March 1999	100	**a.** SB	2.79	0.64	4.7	6.7	1.1±0.58	8.7 †	14.6	___	___
			b. FI	2.69	0.46	4.9	7.1	0.09±0.04	1.14 †	0.6	___	10.5
5	12 – 24 July 1999	150	**a.** SB	0.76	0.12	25.8	28.3	1.8±0.003	54±1.77‡	25.5	___	42.5
			b. DPP	0.68	0.06	26.2	27.6	1.3±0.38	13±2.18‡	12.5	5.7	26.8

* **SB** = Surface broadcast
FI = Fertilization followed by irrigation
DPP = Deep point placement
MI = Mixed incorporation

† 16 Vol.min^{-1}
‡ 20.5 Vol.min^{-1}
§ unaccounted for N

4.4. General discussion of ammonia loss measurements and ^{15}N mass-balance results

An overview of the ammonia loss measurement results (DTM, SSM, ATM, ^{15}N) and prevailing average meteorological conditions is given in Tab.17. Particular measurement problems occurring during the experiments are discussed before comparing the data in more detail.

4.4.1 Comparison of ammonia losses measured with DTM (hand pump and electric pump) and SSM

The DTM (hand pump) measurements encountered problems in the course of two experiments. In the first maize experiment in June 1998, fertilization followed by irrigation (No. 1 b), the heads of irrigation tubes were placed very close to the micro-plots set up for DTM measurements. As a consequence, irrigation water spilling out of the tubes was flowing directly over the micro plots washing away urea fertiliser applied to the plots. In addition, measurements could not be carried out immediately following the irrigation because irrigation water was standing on the experimental site for about 1 hour, and the soil was too wet to be tread on. As a result, the good conditions for ammonia volatilisation at the beginning of the experiment (high temperature, high wind speed) and washing away of urea from the plots had the effect of a thorough underestimation of ammonia losses by a delayed onset of the DTM measurements. In fact, the DTM measurements showed the highest discrepancy to the SSM values in this experiment.

In the second maize experiment in July 1998 a thunder storm occurred with heavy rainfall (22.4 mm) already about two days after the beginning of the experiment. The measurement of ammonia losses in the deep point placement treatment (see appendix for details) with the DTM was strongly affected by the heavy rain which washed down urea and ammonium at the fertiliser amended spots to deeper soil layers. This led to strongly reduced ammonia losses determined by the DTM. The measurements with the SSM were also problematic in this experiment. As maize plants grew from a height of about 0.8 m to more than 2 m during the experiment, wind speed was very low inside the plant canopy and thus SSM measurements comparatively unreliable. This might be the explanation for the discrepancy between ammonia losses determined with SSM and ATM. Ammonia losses measured with ATM were about twice as high as SSM results.

Excluded these two treatments, the factors between cumulative ammonia losses measured with SSM and DTM (hand pump) ranged between 6 (2^{nd} maize 1998, surface broadcast) and 27 (1^{st} maize 1998, surface broadcast). SSM and DTM (hand pump) showed the same qualitative differences between treatments in all experiments, i.e. treatments with higher losses were determined by both methods alike

and vice versa. In all experiments ammonia losses following surface broadcast of urea were several times higher than after incorporation of the fertiliser into the soil (as either deep point placement, fertilisation followed by irrigation or mixed incorporation). Despite the limited number of replications of the DTM measurements, for most experiments the difference between the two treatments was statistically significant (experiments 1, 2, 3, 5, t-Test, $p < 0.1$).

Table 18 Ranking (downward) of cumulative ammonia losses [in %] determined by DTM (hand pump) and SSM, treatments 1b and 2b are excluded, indices see Tab.17

Rank	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Method								
SSM	2a	1a	5a	3a	4a	5b	3b	4b
DTM	2a	5a	1a	4a	5b	3a	3b	4b

Ranking of relative cumulative ammonia losses [% urea-N applied] for all experiments determined by SSM and DTM (hand pump) yielded a very similar order of the results (Table 18). The positions of the highest and the lowest losses were the same for both methods. The order in the middle of the whole range of the results was partly interchanged, but for both methods the differences between those fluxes (3a, 4a, 5b) were very low. This discrepancy in the ranking of the results can be attributed to the differing influence of the weather conditions on the two methods. However, in case of considering the absolute losses [kg N ha^{-1}] the agreement of the rankings of the respective results was even better. Even when neglecting the influence of the weather conditions and considering all treatments, DTM (hand pump) measurements reflected the quantitative differences between the different treatments qualitatively good (Spearman Rank Correlation, $R^2 = 0.88$, $p < 0.01$). The DTM with hand pump could also very well account for the qualitative description of ammonia losses depending on different fertilisation methods in studies carried out by Roelcke (Roelcke 1994; Roelcke et al. 2002 a) in China.

DTM (electric pump) yielded results of the same order of magnitude as the SSM. Results for treatments with incorporation of urea into the soil (4b, 5b) were almost the same for the two methods. However, there were considerable discrepancies between the corresponding results for the surface broadcast treatments. While losses in the wheat surface broadcast treatment 1998 were underestimated by about 50% applying DTM (electric pump), losses in the maize surface broadcast treatment 1999 were overestimated by 100%. In all experiments a constant air exchange rate of about 20 Vol. min^{-1} was chosen. This air exchange rate did not necessarily correspond to ambient environmental conditions, in

particular wind speed. The results of DTM (electric pump) strongly corroborate the hypothesis that it is the low air exchange rate inside the cups which led to the underestimation of ammonia losses by DTM (hand pump). To sum up, the DTM using electric pump measurements yielded good qualitative and quantitative accordance with the SSM in several treatments.

A general problem of the comparison of ammonia losses by SSM and DTM lies in the respective reference heights of ammonia measurement. The DTM determines ammonia emissions as ammonia losses *from soil* (i.e. ammonia volatilisation), sampling the atmosphere at the soil surface, whereas SSM measures the whole profile in and above the plant canopy reflecting thus the net ammonia fluxes from the site (i.e. ammonia loss). Farquhar et al. (1980) showed that ammonia can be deposited and emitted by plant leaves from stomata and by deposition /adsorption on leaf cuticles. Denmead et al. (1976) reported that most of the ammonia emitted from the soil surface of an ungrazed clover/ryegrass pasture was absorbed by the plant canopy. Bidirectional fluxes were detected over arable land in temperate climates, i.e. plant canopies emit and take up atmospheric ammonia (Sutton et al. 1995). However, Asman et al. (1998) stated that in general plant communities on arable land well supplied with fertiliser N represent a net source of NH_3 to the atmosphere, and NH_3 emissions might lead to a loss of 5% of the shoot N content. As a result, plant canopy ammonia emissions contribute significantly to atmospheric NH_3 pollution (15 – 20 % of total NH_3 emissions). As our SSM measurements were carried out neither on large plots nor under equilibrium meteorological conditions, they could also contain some uncertainty because part of the ammonia could have been taken up by plants bordering the experimental site. In this case, net ammonia losses from a greater area would have been overestimated by the SSM.

The DTM measurements cannot account for ammonia taken up by the plants after volatilising from the soil surface and, in the opposite case, for ammonia emitted from plant stomata and cuticles above the DTM measurement height. Due to their limited sensitivity, the Draeger Tubes cannot sufficiently reflect ammonia emissions and NH_3-uptake by plants which vary depending on NH_4^+-supply, temperature and humidity. As a consequence, in addition to not properly reflecting the influence of ambient wind speeds on ammonia emissions, non-consideration of ammonia emissions by the plant canopy could be another cause for the underestimation of SSM ammonia losses by DTM. This circumstance may also result in different flux patterns determined by DTM and SSM. Nevertheless, in most treatments ammonia loss patterns determined by the two methods agreed quite well so that the latter consideration does not seem to be that relevant.

4.4.2 Comparison of SSM and ATM ammonia loss measurements

ATM and SSM measurement results also showed some discrepancies. Both methods determined ammonia losses of the same order of magnitude but the ATM measurements deviated up to 50% from ammonia fluxes determined by the SSM. Only for the wheat surface broadcast treatment (Table 17, 3a) the difference between the ammonia losses measured by the two methods was very small (2.4 kg N ha^{-1}). ATM measurements underestimated SSM ammonia losses in treatments 2b and 5b, while losses were overestimated in treatment 1a. In this case varying ambient environmental conditions are sure to have influenced the two measurement methods differently. Experiments first maize 1998 and winter wheat 1998 experiments were characterized by relatively high wind speeds, while wind speeds were low in the second maize 1998 and maize 1999 experiments. Moreover, the ATM samplers were mounted to a higher maximum height (3 m) than the SSM samplers (2 – 2.5 m) which could have had an effect on the measurement results of the maize experiments (1a, 2b, 5b). In particular, in treatments 2b and 5b maize plants grew up to a height > 2 m. These were also the experiments which showed a considerable underestimation of ammonia losses by the ATM as compared to the SSM. As ammonia losses were overestimated in treatment 1a (small maize plants, high wind speeds), the different reaction of SSM and ATM to varying wind speeds and plant heights is likely to have led to the discrepancies in ammonia loss measurements. This result shows that both simplified micrometeorological methods were prone to some measurement error depending on in field and environmental conditions. Harper and Sharpe (1998) reported that comparisons of replicate micrometeorological measurements suggested a nominal error of ± 15% for micrometeorological techniques. The discrepancies of the measurements presented in this article ranged between 0 to 50%. As a result, the discrepancies between the ATM and the SSM measurements observed in the Fengqiu experiments could also be based on intrinsic measurement error of the micrometeorological methods.

4.4.3 Comparison of ammonia losses measured by micrometeorological methods with ^{15}N mass-balance results

In general the comparison of ammonia losses determined by the micrometeorological methods agreed quite well with the 'unaccounted for' ^{15}N-results (Table 17). However, unaccounted for ^{15}N includes all kinds of N losses which could not be recovered in the plant and soil material, i.e. ammonia volatilisation, denitrification (N_2/N_2O losses), nitrate leaching or plant material which was not included/omitted in the analysis (e.g. debris), besides all errors. A proportion of ammonia volatilised from the soil surface can be taken up by plant leaves (Denmead et al. 1976), depending on the ammonia compensation point (Farquhar et al. 1980; Sutton et al. 1995). However, as ammonia concentrations in soil were very high after fertilisation, and plants were well supplied with ammonium, a priori, ammonia

losses measured directly should be smaller than unaccounted-for ^{15}N results of a ^{15}N difference approach. This consideration is also supported by findings of Marshall and Debell (1980) and Reynolds and Wolf (1988). Very close agreement of the measurement results of micrometeorological methods and ^{15}N method suggests that either of the methods is subject to measurement error.

Notwithstanding these considerations ammonia losses determined by the micrometeorological methods and unaccounted-for N were of the same order of magnitude. Other pathways of N loss were not measured directly. Nevertheless, data of other scientists determined at Fengqiu Agroecological Station can be used for an assessment of the importance of other pathways of N-loss. In 1994 N_2O losses following urea fertilisation were determined by Xing (1998). 1-2 % of urea-N applied were lost as N_2O at a fertilisation rate of 200 kg N ha^{-1}. This does not yet include N losses via N_2 emission. Cai et al. (2002) carried out denitrification/nitrification experiments and determined mean gaseous N losses of about 5 % by this process. Mineral nitrogen profiles determined in the course of the experiments gave no evidence that major N losses occurred via nitrate leaching. To sum up, besides ammonia volatilisation other pathways of gaseous N loss account for several percent of fertilizer-N applied altogether.

Except for the maize deep point placement treatment in 1998 ammonia losses determined by micrometeorological measurements were smaller than unaccounted-for ^{15}N. In the maize treatments ammonia volatilisation measured by the SSM accounted for the largest proportion of unaccounted for ^{15}N (47 – 71% of the unaccounted-for N). The greatest discrepancies were found during the winter wheat mixed incorporation treatments suggesting that ammonia volatilisation was not the major process of N loss during the winter season in case of farmers' application practice. However, as the direct ammonia volatilisation measurement periods of the direct methods were much shorter than the ^{15}N measurement period, and the process of ammonia volatilisation was not yet completed at the end of the measurements, direct measurements probably underestimated total ammonia losses. Nevertheless, these omitted ammonia losses should not had been very high because environmental conditions in the winter season were not favourable for ammonia volatilisation, and nitrification of ammonia continued to proceed.

In the second maize deep point placement treatment in 1998 ammonia losses determined by the SSM (10.8 %) were slightly higher than the amount of unaccounted-for N (10±5%) of the ^{15}N-balance study. The ATM determined only less than half of the SSM losses (4.1 %). Although the gaseous NH_3-losses measured were still in the range of the standard error of the ^{15}N-measurements, there are two possible explanations for this circumstance: First, the deeper layers of the ^{15}N micro-plots were sampled by 5 soil cores taken with a soil auger. In case of deep point placement this sampling procedure could result in an underestimation of unaccounted-for N as the fertiliser is not distributed evenly, and samples could

be taken at the 'hot spots' with high mineral N contents. Secondly, as mentioned above, the discrepancy between ATM and SSM results show that these methods are equally prone to measurement error. Either ATM underestimated or SSM overestimated ammonia losses. Low ^{15}N recovery seems to suggest the latter. However, the results of SSM and ^{15}N measurements were in good accordance in the other treatments. As a result, an underestimation of ammonia losses by the ATM in case of low wind speeds and high plant canopy and an underestimation of total N-losses by the ^{15}N-balance approach because of a deficient soil sampling procedure seems to be the appropriate explanation for the discrepancies observed.

4.4.4 Effect of fertiliser application method and growing season on measured ammonia losses in Fengqiu

At large, all the methods determined similar differences of ammonia losses between the treatments. The treatments with incorporated fertilizer, i.e. the farmers' method treatments, showed lower losses than the surface broadcast treatments. With regard to the former treatments, all the methods agreed in determining much stronger reduced ammonia losses in the winter wheat season than in summer maize season. This might be due to higher temperatures and stronger solar radiation in the maize growing period leading to high evaporation and transpiration and, thus to an increased transport of incorporated urea and ammonium to the soil surface. For the same reasons, ammonia losses were generally higher in the summer period than in the winter season, incorporated treatments in summer showing almost the same percentage of ammonia losses as winter surface broadcast treatments. Similar results were observed by Rees et al. (1997) and Roelcke et al. (2002 a) on sites at the Southern edge of the Chinese loess plateau. Another reason for relatively higher ammonia losses in the maize growing period could lie in a positive correlation between relative ammonia losses and fertilisation rate. Such a relationship was also found by Roelcke (1994), Menzi et al. (1998), Sommer and Hutchings (2001), Zhang et al. (1992), whereas Tian et al. (1998) determined no increase in relative ammonia loss with increasing urea fertilisation rates in a Chinese wheat-rice rotation. In two of our three maize experiments higher amounts of urea were applied than in the two wheat treatments. Nevertheless, despite a low fertilisation rate (75 kg N ha^{-1}) in the first maize experiment, very high percentage losses were determined because of environmental conditions favourable for ammonia volatilisation as high wind speed and high temperatures. So the differences in ammonia losses between wheat and maize treatments can be mainly attributed to seasonal (environmental) influences.

To sum up, farmers in Fengqiu County have already taken measures to successfully reduce losses from urea fertiliser applied. However, in summer even after incorporating the fertilizer into the soil still about

15% of fertilizer N applied were lost by way of ammonia volatilisation. In addition, when considering the high application rates even 15% of loss correspond to a considerable amount of N lost from the system. Therefore, the reduction of the overall fertilisation rate and the appropriate timing of fertilisation could be the most effective measures for increasing fertiliser efficiency and thus the reduction of environmental pollution.

4.4.5 Comparison of ammonia losses measured in Fengqiu with literature data

Ammonia losses between a few percent to 50 percent of urea-N applied to maize and wheat depending on treatment, season and environmental conditions are in good agreement with results by other authors and earlier experiments carried out in China. Ammonia losses following urea fertilization of wheat and maize measured in China support the inference that ammonia losses from maize (Zhang et al. 1992; Cai 1997) are higher than from wheat (Cai 1998, Tian et al. 1998, Rees et al. 1997, Roelcke et al., 2002) mainly due to environmental factors (temperatures, rainfall) and – to a lesser extent - higher fertiliser application rates.

Ammonia losses from surface applied urea to wheat determined in Fengqiu corresponded to losses measured in temperate zones as 25% of urea N applied in Denmark (Sommer and Jensen 1994), 21 % in southern USA (Harper 1995) and 15 – 30 % in Canada (Rawluk et al. 2001). Losses determined in Fengqiu were probably slightly smaller because of low soil moisture (autumn 1998) and low temperatures (spring 1999), as compared to the experiments carried out in Denmark and the USA (similar urea application rates as in the Fengqiu experiment). However, ammonia losses following surface broadcast of urea (200 kg N ha^{-1}) determined in Turkey under similar climatic and soil conditions as in Fengqiu (e.g. soil pH 8.44) ranged between 4 and 12% of urea-N applied only. This was mainly due to low soil moisture, the lag phase characterising urea hydrolysis taking up to 20 days. Measurements in Syria on high pH soils and with sufficient water supply also yielded urea-N losses of 49% after 12 days mainly attributed to ammonia volatilisation (Pilbeam and Hutchinson 1998). Similar results were found in laboratory experiments using Indian soils with high pH (Purakayastha et al. 1995). Losses after 15 days measurements reached up to 25% of urea-N applied, the ammonia loss process not yet being completed. In contrast to the Fengqiu experiments, fertilisation with urea followed by irrigation did not reduce ammonia volatilisation. However, measurements of ammonia losses from wheat fertilised with urea followed by irrigation in Fengqiu carried out by Cai (1998) showed that this treatment reduced ammonia losses very effectively (0.9% of urea N applied). ^{15}N Measurements by Katyal (1987) in high pH (pH 7.7 / 7.9) Indian soils yielded similar results. Fertilization of urea followed by irrigation reduced ammonia losses by about 50% while irrigation preceding urea application considerably increased N-losses. Ammonia losses determined following surface

broadcasting of urea in a field experiment (forced-draught system) close to Nanjing (China) reached up to maximum losses of 19% of urea N applied (Tian et al. 1998).

Not many published data of ammonia volatilisation following urea fertilisation of maize exist. Measurements carried out by Zhang et al. (1992) in the early 1990s agree with the measurements carried out in Fengqiu in 1998/99. In case of surface application, ammonia loss amounted to 32% of urea-N applied, accounting for 71% of total N losses. As in the 1998/99 maize experiments ammonia volatilisation was the main pathway of N-loss following surface application of urea. Deep point placement of urea reduced ammonia losses to 12% of N applied (40% of total N losses), other pathways of losses as denitrification were as important as ammonia volatilisation (Cai et al. 1997). These results agree very well with the measurements in Fengqiu 98/99. Ammonia losses from the surface broadcast treatment 1998 were higher (48%) than losses from the other experiments but this was probably due to the very high application rate of urea (200 kg N ha^{-1}) combined with environmental conditions favourable for ammonia volatilisation (high soil moisture, very high temperature). Low losses from maize fertilised using the deep point placement technique were also reported by Wang (1991).

4.5 Calibration of the DTM

4.5.1 Introduction and preliminaries

The relationships between the fluxes measured with DTM and SSM as well as between ammonia fluxes and field variables were examined by means of correlation and regression analysis. Simple linear regression as well as multiple linear regression were applied. The correlation and regression analysis focuses on the data determined by the DTM with hand pump. In the regression SSM values were considered as reference values, as 'true' fluxes, which should be calculated or approximated as close as possible by use of DTM values (hand pump) and environmental data. As described in chapter (3.2.1), experiments by Roelcke et al. (2002 a) using the DTM showed that the DTM could not be calibrated by a single scaling factor. As expected, ammonia measurements in Fengqiu revealed that meteorological conditions as wind speed and temperature had a major impact on the relationship between DTM and SSM fluxes. As a result, the degree of underestimation of SSM fluxes by the DTM is not constant but varies according to the influence of environmental factors. The result of the calibration of the DTM therefore most probably has to be a calibration formula considering environmental variables in place of a single scaling factor.

Two approaches were chosen for the regression and correlation analyses of DTM and SSM ammonia fluxes: firstly single ammonia fluxes (e.g. in mg N m^{-2} h^{-1}) were used, secondly cumulative ammonia losses determined by the two methods (in kg N ha^{-1}) at the end of the experiments were compared. In the latter case, average values of the meteorological variables were calculated for the whole experimental period.

For the calculations according to the first approach it had to be considered that ammonia sampling periods of the DTM and the SSM were quite different. Several DTM ammonia measurements were carried out during one SSM sampling interval. While, as a rule, SSM samplers were kept in place for a time interval of about 1 day, an average of three - in individual situations six – samplings per day were carried out when applying the DTM. In effect, the SSM provided a mean flux rate for the sampling interval while the DTM gave diurnal patterns of ammonia fluxes. In order to compare the two fluxes measured, time weighted means of the DTM fluxes were calculated on the basis of the single SSM sampling intervals. The average flux calculated from two subsequent DTM measurements was assumed to represent the mean flux prevailing in the time interval between the two measurements. DTM measurements were not carried out at regular time intervals. Thus, the time weighted means were calculated using the average DTM ammonia fluxes weighed by the respective duration of the DTM measurement intervals as a proportion of the SSM sampling interval, according to the following formula:

$$\overline{F_{N_g}} = \sum_{i=1}^{i} w_i \cdot F_{\overline{N_g}\,i} \qquad (16)$$

$$w_i = \frac{t_i}{t_{tot}}$$

$\overline{F_{N_g}}$ DTM ammonia flux time weighted average values for single SSM measurement interval [mg N m^{-2} h^{-1}]

$F_{\overline{N_g}\,i}$ mean ammonia flux of two DTM measurements for the time interval (i) between the two measurements [mg N m^{-2} h^{-1})]

w_i weighing factor ($0 < w_i \leq 1$, $\sum_{i=1}^{i} w_i = 1$)

t_i time interval (i) between two DTM measurements within the single SSM sampling interval t_{tot} [h]

t_{tot} time interval of single SSM sampling [h]

Mean values based on SSM sampling periods were also calculated for the meteorological data recorded in 10-minute intervals.

Weighted means were computed for the fluxes determined during the surface broadcast treatments, only. Ammonia fluxes measured by the SSM were quite irregular and discontinuous during winter wheat mixed incorporation treatments (see Chapter 4.1.2.2). Nevertheless, the whole range of ammonia fluxes – from very low to very high ammonia fluxes – was covered by the measurements during the surface broadcast treatments, environmental conditions also being the same as in the mixed incorporation treatments. The measurements not included in the calibration of the DTM could be most usefully applied as test data for the validation of the calibration formula.

4.5.2 Correlation and regression analysis of ammonia fluxes and field variables

A first impression of the relationships between the fluxes and the environmental factors was gained by the calculation of Pearson-correlations. Testing of significance could only be carried out provided that data obeyed normal-distribution. The data were tested for normal distribution applying the Kolmogorov-Smirnov test (significance level $p<0.05$)(Lilliefors 1967). Only wind speed data (2 m and 20 cm) fulfilled the normal distribution requirements. Ammonia fluxes measured with DTM and SSM were both lognormally distributed and their natural logarithms had thus to be formed for the correlation analyses. Altogether three data sets were created: total data set, and two sub-divisions for winter wheat and summer maize seasons. Subdividing allowed for the differentiation between the influences of the respective crop on the ammonia measurements. In addition, weather conditions were quite different in

both growing periods which could result in different degrees of influence of the environmental variables on the fluxes measured. Table 19 gives only significant correlation results.

Table 19: Significant Pearson-correlations (*p<0.05; **p<0.01, n.s. = not significant) between amonia fluxes measured and field variables. Ammonia fluxes were normally distributed in winter season. (n = number of pairs)

Variable	SSM (natural logarithm)	DTM (natural logarithm)
Total (n = 72)		
SSM (natural logarithm)	___	0.779**
DTM (natural logarithm)	0.779**	___
Wind speed (2 m)	n.s.	-0.32**
Summer (maize experiments, n = 46)		
SSM (natural logarithm)	___	0.807**
DTM (natural logarithm)	0.807**	___
air temperature (1 m)	0.473**	0.343*
soil temperature (-0.05 m)	0.422**	0.301*
water content at the soil surface (0-3 mm)	0.461**	0.402**
Winter (wheat experiments, n = 26)	**SSM**	**DTM**
SSM	----	0.647**
DTM	0.647**	----
air temperature (1 m)	0.459*	n.s.
soil temperature (-0.05 m)	0.425*	n.s.

A significant positive correlation between ammonia fluxes measured by DTM and SSM was determined on the basis of the total data set (5 surface broadcast treatments). Likewise positive correlations were determined for the split data set, for winter wheat and summer maize values. A slightly negative correlation with wind speed in 2 meters height was determined for DTM values, only. The negative correlation could be explained by the DTM measurements not accounting for the whole mass flux of ammonia from the field – in contrast to the SSM measurements. Average wind speeds were higher in

winter than in summer. Since temperatures were low in winter season, the overall ammonia volatilisation potential from soil was comparatively small compared to summer season. As the SSM measured the mass flux of ammonia, relatively lower ammonia concentrations in the atmosphere due to the lower ammonia volatilisation from soil in winter were compensated by simultaneously raised wind speeds for the SSM measurements (see average values Table 20). In contrast, DTM measurements just reflected the ammonia volatilisation potential from soil due to ammonia partial pressure at the soil surface (see Chapter 5.1). As ammonia partial pressure was low while average wind speeds were high in winter season, in summer season vice versa, a negative correlation between DTM measurements and wind speed was observed. But this, in a way, can be considered as a nonsense correlation.

For the summer (maize) results, besides the positive correlation between the ammonia fluxes determined by the two methods, significant positive correlations were found between ammonia fluxes and temperature values as well as surface water contents. As was described in Chapter 2.1, the increase in temperature leads to higher urease activity, higher Henry coefficient, lower solubility of NH_3 in soil solution and a higher proportion of NH_3 over NH_4^+ and thus to an increase in ammonia volatilisation. Sufficient water supply in the surface soil is an important precondition for urea hydrolysis and diffusion of ammonia in the soil solution to the soil-atmosphere boundary layer. Therefore, in general soil moisture is a decisive factor with regard to ammonia volatilisation. On the other hand, the relationship between ammonia fluxes and soil moisture could be just another nonsense correlation. In most cases the experimental sites were irrigated prior to or at the beginning of the experiment. Thus, soil moisture was highest at the beginning and ammonia fluxes and soil moisture decreased continuously in the course of the experiment provided there were no subsequent rainfall events. In addition, urea hydrolysis was quite fast at the beginning of the experiments and high ammonia fluxes could be detected from the start of the experiment. The correlation between surface soil moisture and ammonia fluxes could also be interpreted as a synchronic, not causally related decrease in the values of both variables. For the winter season a positive correlation of the ammonia fluxes was detected with the temperature values, only.

It has already been stressed in the discussion of the individual field experiments (chapter 4.1.2) that the wind speed was supposed to have a major influence on the ammonia measurement with the SSM. Strikingly, a slightly negative correlation of ammonia fluxes measured and wind speeds was determined for DTM values only (total data set). However, the effect of wind speed is most important for the comparison of the ammonia fluxes measured by SSM and DTM.

The SSM determines the mass flux of ammonia, which –as a product of wind speed and ammonia concentration – already incorporates the effect of wind speed. However, while wind speeds were oscillating in a similar range during the whole experimental period, ammonia fluxes increased in the beginning and decreased continuously in the course of the experiment. As a result, no significant

relationship was observed between SSM ammonia fluxes and wind speed. On the other hand, the DTM measurements with constant low air exchange rates inside the cups did not sufficiently take into account the influence of wind speed on the ammonia volatilisation process. As a result, the influence of wind speed on ammonia volatilisation was not reflected in the ammonia fluxes measured by both methods. But wind speeds might be very important for more accurately relating the DTM ammonia fluxes to those determined by the SSM as they could influence the degree of the discrepancy between the fluxes measured by the two methods at a specific point in time

Table 20: Average weather conditions during field experiments

Experiment	wind speed (2 m) [m/s]	wind speed (0.2 m)[m/s]	air temperature (1 m)[°C]	soil temperature (-5 cm)[°C]
Maize, June 1998	2.00	0.52	27.02	27.76
Maize, July 1998	0.76	0.05	26.85	28.98
Wheat, October 1998	1.68	0.95	15.32	17.61
Wheat, March 1999	2.79	0.64	4.72	6.74
Maize, July 1999	0.76	0.12	25.84	28.25

4.5.3 Regression analyses

The aim of the regression analyses was the determination of a calibration equation which would allow to calculate sufficiently accurate ammonia loss estimates on the basis of DTM measurements and meteorological data. SSM ammonia flux values were regarded as 'true' ammonia fluxes. Thus, the calibration formula should relate the DTM values to those of the SSM as accurately as possible. In the following several regression approaches to derive the calibration formula are presented.

Simple linear regression between ammonia fluxes determined by DTM and SSM

The linear regression between ammonia fluxes measured with the DTM and the SSM (results not shown) yielded only coefficients of determination (R^2) which were smaller than 0.5 thus not being satisfactory. The comparative field experiments (see Chapter 4.1.2) and the examination of the relationship between ammonia fluxes measured by the two methods and ammonia partial pressure at the soil surface showed (Chapter 5.1) that DTM measurements did not sufficiently take into account the influence of wind speed on ammonia volatilisation while the SSM determined the effective ammonia loss caused by ammonia emission from the soil surface and ammonia transfer by ambient wind. Thus, it could be inferred that the inclusion of wind speed into the calculation of the regression could help to more accurately correlate the ammonia fluxes measured by the DTM to those of the SSM. A direct approach to integrate the wind speed into the DTM measurements similar as in the SSM data is the multiplication of the DTM ammonia fluxes with wind speeds measured at the same time. Fig. 39 depicts the linear regression between ammonia fluxes measured by the SSM (dependent) and the product of wind speed (2 m) and DTM ammonia fluxes (independent) for the treatment winter wheat, autumn 1998, surface broadcast. The regression result improved considerably: the coefficient of determination (R^2) increased to 0.83.

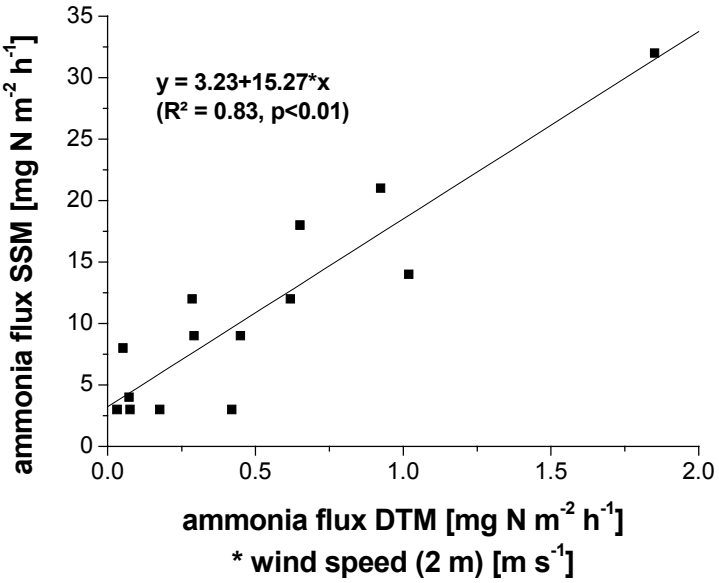


Fig. 39: Linear regression between fluxes determined by SSM (dependent) and ammonia fluxes measured by DTM times wind speed (2 m), winter wheat, October 1998, surface broadcast (120 kg N ha^{-1})

Likewise good regression results were obtained for the other four surface broadcast treatments (Table 21). The regression results did not improve by the same degree for all treatments. The improvement of

the results depended on the intensity of ambient wind (2 m) during the respective measurement period. However, in all cases the combination of ammonia fluxes determined by DTM and wind speed data led to an increase of the coefficient of determination.

Table 21 Coefficients of determination of the regressions between ammonia fluxes measured with SSM and the product of DTM ammonia fluxes and wind speed (2 m) (surface broadcast treatments)

Treatment	June 1998 (first maize)	July (1998) (sec. maize)	October 1998 (first wheat)	March 1999 (sec. wheat)	July 1999 (third maize)
R^2	0.96	0.84	0.79	0.83	0.85

4.5.4 Derivation of a calibration formula by stepwise multiple linear regression of ammonia fluxes determined by SSM and DTM and meteorological variables

So far, the regression analyses considered only ammonia fluxes determined by the two methods and wind speed. In order to include the multiplicative effect of a variable into multiple linear regression analysis, natural logarithms were taken from ammonia flux values and the micrometeorological data. The following data sets were chosen for stepwise multiple linear regression:

1. each single surface broadcast treatment (Table 22)
2. the total data set (surface broadcast treatments) split up into two data sets: winter wheat and summer maize season (Table 22)
3. total data set of all 5 surface broadcast treatments (Table 23)
4. cumulative losses determined with SSM and DTM values and meteorological data (Table 26)

Eq.17 shows the general model of multiple linear regression:

$$Y_i = \alpha + \beta_1 x_i^{(1)} + \beta_2 x_i^{(2)} + ... + \beta_m x_i^{(m)} + \varepsilon_i \quad (17)$$

Y_i target variable (ammonia fluxes SSM)
$x_i^{(m)}$ observed value i of variable m (e.g. wind speed)
β_m coefficient (factor) for variable m
α axis intercept
ε_i error term

Aim of the calculations of the multiple linear regression was to estimate an overall model and the coefficients β_m as accurately as possible. In a first step the general model of multiple linear regression was applied for the estimation of the coefficients. In most of the cases, the regression analyses for data sets 1. and 2. yielded no significant estimate for the parameter α (axis intercept). Consequently, a modified regression model without estimate for the intercept was applied ($\alpha = 0$). For this kind of model the coefficients of determination (R^2) are not comparable to the models estimated with intercept. For that purpose another measure for the model performance 'modelling efficiency *c²*' (Loage and Green 1991) was chosen for the comparison of the parameter estimates.

$$c^2 = \frac{\left(\sum_{i=1}^{n}\left(O_i - \overline{O}\right)^2 - \sum_{i=1}^{n}\left(P_i - O_i\right)^2\right)}{\sum_{i=1}^{n}\left(O_i - \overline{O}\right)^2} \qquad (18)$$

c^2	modelling efficiency ($c^2 \leq 1$)
P_i	i^{th} value predicted by the model
O_i	i^{th} observed value
$\overline{O}$	mean value of observations

c² reflects the proportion of the variance of the observations which can be explained by the values predicted by the model. Both, R^2- and c^2- parameters are shown together with the other estimated model parameters in Table 22. R^2 and c^2 values are identical when the model includes the intercept parameter. 'Backward estimation' was chosen as estimation procedure for assigning variables to be included into the model estimated by stepwise multiple linear regression. This procedure started with a full set of variables from which all variables not significantly ($P > 0.05$) contributing to the overall model estimate (variable coefficient not significantly ($P > 0.05$) different from 0) were successively excluded.

1. Table 22 gives the regression results for the separate data sets. For 4 of the 5 experiments regression results were satisfactory, only the regression for wheat October 1998 yielded a low modelling efficiency value. The factors β_m related to DTM ammonia fluxes were similar (~0.45) for all treatments except for the maize July 1998 treatment with a much lower value. This could be explained by the much higher ammonia losses in this treatment as compared to the other treatments. The ammonia flux pattern was quite different in this treatment as most of the ammonia losses occurred during the first 48 hours of the experiment accompanied by comparatively low wind speeds.

In the regression for the two maize treatments in July 1998 and July only the DTM ammonia fluxes were included as significant variable. Wind speeds were comparatively low during both of those maize experiments (Table 20). For the winter wheat March 1999 and the maize June 1998 experiment the model with the highest performance did also include wind speed at 0.2 m or 2 m height as wind speed was quite pronounced throughout the experiments. The winter wheat October 1998 treatment was particular as there prevailed high wind speeds but low soil moisture contents prevented higher ammonia losses.

Table 22: Results of the multiple linear regression analysis (with $\alpha = 0$) of logarithmic values (natural logarithm) of *target value:* SSM ammonia flux, independent variables: DTM ammonia flux, wind speeds (2 m, 0.2 m), temperatures (-5 cm, 1 m); (n = number of observations)

Experiment	variables included in the model	β_m	standard error	c^2	R^2*
Single treatments					
maize, June 1998 (1a) (n=17)	DTM ammonia flux [mg N m^{-2} h^{-1}]	0.477	0.038	0.74	0.95
	wind speed (2 m) [m s^{-1}]	1.004	0.330		
maize, July 1998 (2a) (n=17)	DTM ammonia flux [mg N m^{-2} h^{-1}]	0.258	0.040	0.61	0.75
wheat, October 1998 (3a) (n=15)	DTM ammonia flux [mg N m^{-2} h^{-1}]	0.432	0.024	0.55	0.96
wheat, March 1999 (4a) (n=11)	DTM ammonia flux [mg N m^{-2} h^{-1}]	0.431	0.033	0.72	0,99
	wind speed (0.2 m) [m s^{-1}]	1.000	0.341		
maize, July 1999 (5a) (n=12)	DTM ammonia flux [mg N m^{-2} h^{-1}]	0.403	0.021	0.64	0.97
Vegetation period					
wheat season	DTM ammonia flux [mg N m^{-2} h^{-1}]	0.444	0.018	0.64	0.97
(2 experiments, n=26)	wind speed (0.2 m) [m s^{-1}]	0.590	0.112		
maize season	DTM ammonia flux [mg N m^{-2} h^{-1}]	0.456	0.033	0.72	0.91
(3 experiments, n=46)	wind speed (2 m) [m s^{-1}]	0.745	0.223		
	wind speed (0.2 m) [m s^{-1}]	-0.280	0.076		

* cannot be compared to the R^2 for linear regression model with intercept.

2. A more comprehensive model approach for the regression analysis was chosen by forming two data sets, for the maize (summer) and wheat (winter) season, containing data of 3 and 2 experiments, respectively (Table 22). In this way the influence of the crops grown and of the specific seasonal conditions could be explicitly considered in the calculations. The winter season was characterised by low temperatures and relatively stable weather conditions, while temperatures in summer were much higher and wind was changing in a diurnal day/night pattern. For both data sets a model (Eq. 19) could be satisfactorily estimated by stepwise multiple linear regression (c^2 0.64 and 0.72, respectively). Both model estimates considered DTM ammonia fluxes and wind speeds for the approximation of SSM ammonia fluxes. In case all treatments of both models were pooled the c^2 equalled 0.86. Thus the combined application of both formulas led to an improved overall performance of the calibration formulas.

'vegetation period' approach **(19)**

winter season:

$$\ln(NH_3 flux_{SSM}) = 0.444 \cdot \ln(NH_3 flux_{DTM}) + 0.590 \cdot \ln(windspeed_{0.2m})$$

summer season:

$$\ln(NH_3 flux_{SSM}) = 0.456 \cdot \ln(NH_3 flux_{DTM}) + 0.745 \cdot \ln(windspeed_{2m}) - 0.280 \cdot \ln(windspeed_{0.2m})$$

3. The model for the whole data set (Table 23) of the five experiments calculated for non-logarithmic values and including the estimation of the axis intercept yielded a satisfactory coefficient of determination (R^2 = 0.83). Apart from the DTM ammonia fluxes this model comprised the variables wind speed (2 m) and soil temperature. By considering soil temperature the model took into account the seasonal impact on ammonia losses.

The main aim of the calibration of the DTM was the determination of a preferably simple calibration formula which can be applied for a sufficiently accurate calculation of "absolute" ammonia losses in the field in a wide range of experimental conditions. The model approaches 'total data set' (Table 23) and 'vegetation period' (Table 22, Eq. 19) were evaluated by comparing ammonia losses calculated on the basis of ammonia fluxes approximated by the two calibration formulas with the 'true' ammonia losses determined by the SSM. In this way, the accuracy of the cumulative ammonia loss estimated by the two calibration models and the average deviation of the estimate error can be calculated (Table 24).

Table 23: Results of the multiple linear regression analysis *target value:* SSM ammonia flux, independent variables: DTM ammonia flux, wind speeds (2 m, 0.2 m), temperatures (-5 cm, 1 m); (n = number of observations)

Experiment	variables included in the model	α	β_m	standard error	R^2
total data set		-0.241		0.105	0.83
(n=72)	DTM ammonia flux		3.944	0.241	
	wind speed (2 m)		0.055	0.026	
	soil temperature (-0.05 m)		0.012	0.003	

Table 24: Cumulative ammonia losses calculated on the basis of ammonia fluxes according to the calibration approaches 'total data set' and 'vegetation period' (Eq. 19) compared to cumulative ammonia losses measured by the SSM (surface broadcast treatments)

Experiment	cumulative loss (kg N ha^{-1})		
	SSM	regression model 'vegetation period'	regression model 'total data set'
Maize, June 1998 (1a)	32.7	27.1	50.6
Maize, July 1998 (2a)	95.8	87.3	94.8
Wheat, October 1998 (3a)	23.9	29.3	22.4
Wheat, March (4a)	14.6	17.3	11.9
Maize, July (5a)	38.2	48.5	52.8
mean absolute error (kg N ha^{-1}) (± Std. dev.)		6.5 ± 2.9	7.5 ± 8.1
mean relative error (% of estimate (± Std. dev.)		17.1 ± 4.7	18.8 ± 6.7

The cumulative ammonia losses estimated on the basis of the 'total data set' approach showed a deviation from the SSM losses which was on average 1 kg N ha^{-1} greater than that determined by the 'vegetation period' approach. Although the former approach yielded very close estimates for three experiments (2a, 3a, 4a) deviations from the SSM data were very high for the other two treatments. Thus, the limits of variation (8.1 kg N ha^{-1}) of the mean absolute deviation (7.5 kg N ha^{-1}) from the SSM were comparatively high. Consequently, when applying this model, the uncertainty of the ammonia loss estimate would be quite high. In contrast to this result, the mean absolute deviation for the 'vegetation period' approach is smaller, and especially its limits of variation are considerably lower (2.9 kg N ha^{-1}). Assuming that the estimation error is normally distributed a mean error of the 'vegetation period' ammonia loss estimate of 6.5 kg N ha^{-1} would result in a maximum absolute error of 12 kg N ha^{-1} (mean relative error 17 ± 5 %). The estimate error is well within the accuracy required for

agronomic purposes. According to Denmead et al. (1977) and Sharpe and Harper (1995) the measurements of standard micrometeorological mass balance methods have an accuracy of ± 20 % of the value measured. For the 5 treatments considered in the comparison of the corrected DTM losses with the SSM losses ranging between 14.6 and 95.8 kg N ha^{-1} a measurement error of 10% would correspond to an absolute measurement error between 1.5 and 9.6 kg N ha^{-1}. This error matches the estimation error obtained by application of the 'vegetation period' calibration formulas very well. The use of this calibration approach would result in an estimation error of the same magnitude as the error obtained by direct SSM measurements. A drawback of these considerations lies in the fact that the calibration formulas were derived from SSM measurements and do thus also implicitly include the SSM measurement errors. In order to check the validity of the 'vegetation period' calibration approach (Eq. 19), the formulas were also applied for the calculation of corrected DTM ammonia fluxes for the three mixed incorporation treatments (excluding the two deep point placement treatments) (Table 25). Simple fluxes measured by the DTM without calculation of weighted averages were used for the calculation of the corrected fluxes and the ammonia losses.

Table 25: Cumulative ammonia losses calculated on the basis of DTM NH_3 fluxes corrected using the 'vegetation period' approach (Eq. 19) compared to cumulative ammonia losses measured by the SSM

Experiment	cumulative loss (kg N ha^{-1})	
	SSM	regression model 'vegetation period'
maize, June 1998 (1b)	13.5 (8)†	5†
wheat, October 1998 (3a)	2.5	8
wheat, March (4a)	1	5

† losses after 3 days of ammonia flux measurements

The results given in Table 25 show that the application of the calibration formula for the mixed incorporation and fertilisation followed by irrigation treatments yielded a satisfactory accuracy. It has to be noted that the DTM fluxes of the mixed incorporation treatments were not considered in the derivation of the calibration formula. Ammonia losses in winter wheat were overestimated by about 5 kg N ha^{-1} which lies well within the range of the measurement error of the SSM. SSM results were discontinuous in the winter wheat mixed incorporation treatments and thus showed some measurement error. The June 1998 fertilization followed by irrigation treatment was difficult to compare due to the reduced urea fertilization on the DTM micro-plots because of inappropriate irrigation (Chapter 4.4.1). Ammonia fluxes from the micro-plots ceased some days earlier than in the SSM measurements. If the whole experimental period is taken as the basis of comparison, the corrected DTM fluxes

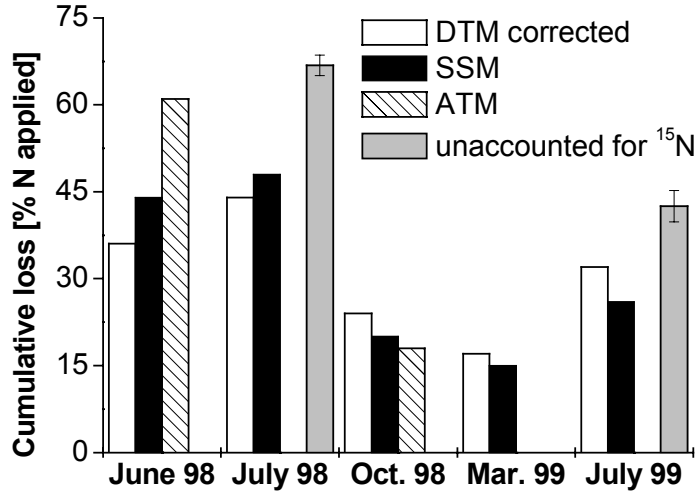


Fig. 40: Cumulative ammonia losses and unaccounted-for ^{15}N determined by SSM, ATM, corrected DTM ammonia fluxes ('vegetation period' model approach) and ^{15}N balance method for surface broadcast treatments Fengqiu 1998 - 99

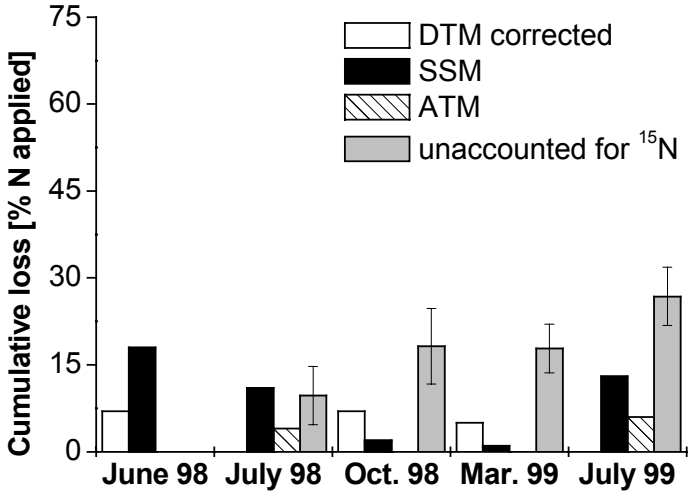


Fig.41: Cumulative ammonia losses and unaccounted-for ^{15}N determined by SSM, ATM, corrected DTM ammonia fluxes ('vegetation period' model approach) and ^{15}N balance method for all the different incorporated fertilizer treatments, Fengqiu 1998 - 99

underestimated SSM ammonia losses by about 9 kg N ha^{-1}. On the other hand, if the losses determined by the two methods are compared until the day after which the DTM could not detect any more

ammonia fluxes (01 July 1998) the SSM determined ammonia losses of 8 kg N ha^{-1} while corrected DTM values gave 5 kg N ha^{-1}. The discrepancy between SSM losses and corrected DTM losses was quite small, including this treatment. Thus, the application of the calibration formula to the mixed incorporation and fertilization followed by irrigation treatment data which were not included in the derivation of the formula validated the applicability of the DTM for the calculation of absolute ammonia losses when corrected by a calibration formula. The comparison of measured ammonia losses (SSM) and corrected DTM values is shown in Figs. 40 and 41, for surface broadcast treatments and mixed incorporations, respectively.

4. Stepwise multiple linear regression between total cumulative ammonia losses determined by the DTM and the SSM method and the meteorological variables averaged for the measurement periods was also applied as a last calibration approach. The general model with axis intercept was fitted by stepwise 'backward' procedure ($P < 0.05$). Nine experiments were considered in the calculation. The maize June 1998 treatment, fertilisation followed by irrigation, was excluded because of the deficient DTM measurements (see Chapter 4.4.1). The deep point placement treatments were also included in the calculation as the difference between the DTM measurements from surface applied and point placed fertilizer is balanced by the calculation of the deep point placement ammonia fluxes on an area basis, i.e. kg N ha^{-1}.

Table 26: Results of the multiple linear regression analysis of cumulative ammonia losses and averaged meteorological variables *target value:* SSM ammonia loss, independent variables: DTM ammonia loss, wind speeds (2 m, 0.2 m), temperatures (-5 cm, 1 m); (n = number of observations)

Experiment	variables included in the model	α	β_m	standard error	R^2
cumulative ammonia losses (n=9)	axis intercept α	0.199		-	0.95
	DTM ammonia loss [kg N ha^{-1}]		4.87	0.56	
	mean air temperature (1 m) [°C]		0.777	0.30	

'cumulative loss' approach **(20)**

$$NH_3\text{-}loss_{SSM}\ [kg\ N\ ha^{-1}] = 0.199 + 4.87 \cdot NH_3\text{-}loss_{DTM}\ [kg\ N\ ha^{-1}] + 0.777 \cdot mean\ T_{air}[°C]$$

The coefficient of determination (Eq. 20, $R^2=0.95$) for this regression was comparatively high and satisfactory. Apart from DTM ammonia losses the average air temperature was included in the

regression model. By considering average air temperature the model takes into account the different temperature levels of the seasons. The positive parameter β_m for average air temperature agrees with the positive theoretical relationship between temperature and ammonia volatilisation described in chapter 2.1. Wind speed was not included. The reason for this may be that this variable is not so as important as temperature for a time period of a whole experiment or season in contrast to the comparison of single ammonia fluxes.

The comparison of the cumulative ammonia losses estimated by DTM losses and the calibration formula with those measured by the SSM reveals that this model provided the lowest mean absolute deviation (5.2± 3.2 kg N ha^{-1}) of the three comprehensive regression models (Tab. 27). The estimates are particularly good for the summer season, while the estimation results are slightly biased for the winter wheat season. On the one hand ammonia losses from treatments with incorporated fertiliser were overestimated, on the other hand losses from the surface broadcast treatments were underestimated. However, the error of estimate was well within the range of the SSM measurement error described above. The high mean relative deviation of simulated values from measured losses (± 37%) does not give very much information as the strong relative overestimation for incorporated treatments resulted in an acceptable absolute estimation error. Because of the low number of data available for this calibration approach a separation of the data set according to single seasons was not considered as suitable here. The comparison of measured ammonia losses and corrected DTM values is shown in Fig. 42 and 43, for surface broadcast treatments and mixed incorporation and deep point placement treatments, respectively.

Table 27: Cumulative ammonia losses calculated from DTM cumulative losses and calibration formula 'cumulative losses' (Eq. 20) compared to those measured by the SSM (number of observations = 9)

Experiment	cumulative loss (kg N ha^{-1})	
	SSM	regression model 'cumulative losses'
Maize, June 1998 (1a)	32.7	26.9
Maize, July 1998 (2a)	95.8	97.0
Wheat, October 1998 (3a)	23.9	16.7
Wheat, March 1999 (4a)	14.6	9.1
Maize, July 1999 (5a)	38.2	33.5
Maize, July 1998 (2b)	21.6	21.4
Wheat, October 1998 (3b)	2.8	12.7
Wheat, March 1999 (4b)	0.6	4.27
Maize, July 1999 (5b)	18.8	26.4
mean absolute error (kg N ha^{-1}) (± Std. dev.)		5.2 ± 3.2

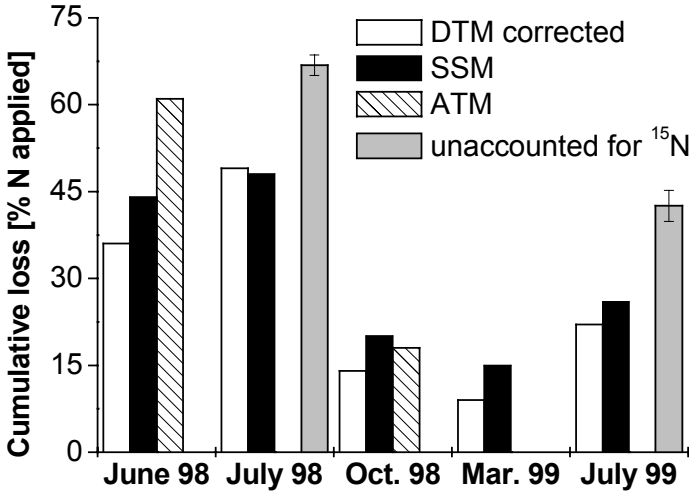


Fig. 42 Cumulative ammonia losses and unaccounted-for ^{15}N determined by SSM, ATM, corrected DTM ammonia fluxes ('cumulative losses' model approach) and ^{15}N balance method for surface broadcast treatments Fengqiu 1998 - 99

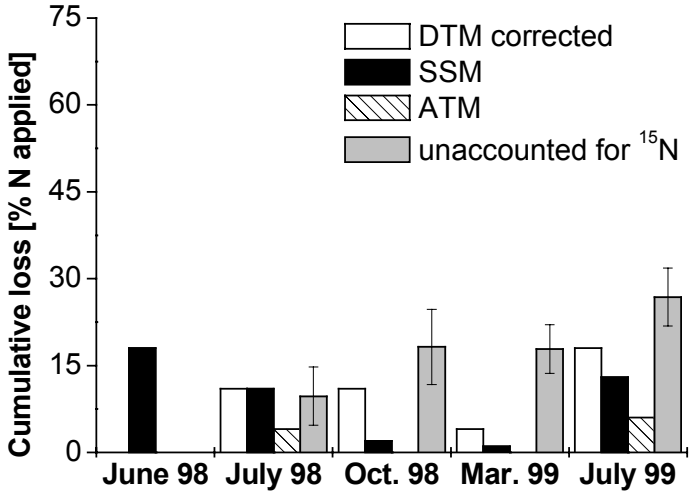


Fig. 43 Cumulative ammonia losses and unaccounted-for ^{15}N determined by SSM, ATM, corrected DTM ammonia fluxes ('cumulative losses' model approach) and ^{15}N balance method for incorporated fertilizer treatments, Fengqiu 1998 - 99

4.5.5 Discussion of the calibration results

Many methods have been developed for the measurement of ammonia volatilisation in the field and under laboratory conditions. Simplified micro-meteorological methods as the methods by Leuning et al. (1985) and Schjoerring et al. (1992) applied in this study have been established as standard methods for the measurement of ammonia losses in the field for agronomic purposes. Recently, more refined micro-meteorological methods like eddy accumulation or relaxed eddy accumulation methods have been introduced for precise and highly frequent measurements. Apart from measurement accuracy, the major advantage of micrometeorological methods is based on the omission of the disturbance of ambient conditions during field measurements. However, their application requires appropriate laboratory and technological facilities as well as trained staff close to the measurement sites.

Chamber methods have been mainly applied for carrying out systematic laboratory and *in situ* experiments under restricted environmental conditions. Because of their construction principle, it is very difficult to use them for the determination of valid ammonia loss data under undisturbed conditions. Major restrictions comprise the controlling of air exchange rates in the chambers, temperature and plant cover effects. Their main advantage is their versatility and comparatively easy 'handling'. Nevertheless, recently developed chamber methods as those by Svensson (1997) and Sommer et al. (2001) or the Standard Comparison Method by Vandré and Kaupenjohann (1998) attempted at overcoming these shortcomings of methods applied on the microscale level.

The development and calibration of the DTM can be seen in line with these recent developments in chamber methods. The DTM was designed to avoid the disturbance of environmental conditions by multiple short-term measurements. The DTM is a simplified chamber method which has no demanding requirements with regard to gas sampling and analysis. During our field measurements in Henan, farmers of the village bordering the experimental sites could carry out the measurements all on their own. Calculations of the ammonia losses could be done later on by accompanying technicians and scientists.

The importance of the air exchange rate inside the DTM cups for the measurement of ammonia volatilisation was supported by the comparison of ammonia fluxes determined by the DTM and ammonia partial pressures calculated from ammoniacal N contents, pH values and temperatures at the soil surface (see Chapter 5.1). It can be said that the DTM with hand pump reflects ammonia volatilisation based on ammonia partial pressure at the soil surface without appropriately considering the influence of atmospheric exchange on the ammonia volatilisation process. The DTM had, thus, to be modified to include the effect of environmental conditions and atmospheric turbulence into the measurements by (a) adapting air exchange rates in the cups to ambient conditions or (b) by calculating corrected ammonia fluxes on the basis of measured environmental variables.

A threshold value for the influence of air exchange rates was determined in plot experiments with DTM and electric vacuum pump (see Chapter 4.1.1). Air exchange rates higher than about 40 volumes minute^{-1} did not lead to a significant increase in measured ammonia losses. This threshold value was considerably larger than air exchange rates of 15 – 20 Vol. min.$^{-1}$ determined for other chamber methods. While the latter were designed to establish laminar air flux through the chambers the DTM chambers can be characterized by turbulent flux.

However, ammonia losses determined at air exchange rates close to the threshold value correspond to potential ammonia losses from soil related to the respective soil (pH, urease activity, CEC etc.) and environmental conditions (temperature, soil moisture etc.). For this reason, air exchange rates lower than 40 Vol. min^{-1} in the cups were applied during field measurements in order to match losses determined with the SSM. Ammonia losses were partly under- and partly overestimated using different constant exchange rates but exhibited the same order of magnitude as the SSM losses (see Chapter 4.4.1). This points out the difficulty of using constant flow rates in chamber techniques, which would theoretically have to be frequently adapted to actual wind conditions.

As a consequence, the calibration of the DTM and adaptation of the DTM measurements to ambient conditions were carried out by an indirect approach. Ambient conditions were not directly reproduced by modifying the DTM measurement set-up but rather taken into account by including them in the calculations of corrected DTM ammonia losses. The former approach was successfully applied for the optimisation of chamber methods by Svensson and Ferm (1993) and Sommer et al. (2001). Two indirect calibration approaches, the 'vegetation period' approach (Eq. 19) and the 'cumulative loss' approach (Eq. 20), were successfully applied for the calculation of sufficiently accurate ammonia loss estimates on the basis of DTM measurement results as compared to losses determined with the SSM.

SSM and ATM measurements showed good agreement as well as major discrepancies (see Chapter 4.4.2). Consequently, one or both micrometeorological methods exhibited a considerable degree of measurement error, which according to Harper and Sharpe (1998) amounts to at least ± 15% up to 50% for micrometeorological measurements. Similar values for the measurement error of micrometeorological measurements were presented by Denmead et al. (1977) and Sharpe and Harper (1995). Besides the intrinsic measurement error of the DTM (15-20 %, see Chapter 4.1.1), this renders the calibration result to an additional degree of uncertainty. Nevertheless, Wood et al. (2000) also used the SSM for the calibration of an improved method of field-scale measurement of ammonia volatilisation which basically is a combination of the ATM and the SSM method.

The Draeger-Tube method has been validated as a simple measurement tool for the quantitative estimation of ammonia losses under field conditions. The method is not as accurate as micrometeorological methods for quantitatively determining total losses but is very useful for the

determination of ammonia losses *in situ* under all kind of experimental facilities and conditions, in particular for low scale comparison of different fertilisation approaches connected to varying environmental conditions with many replications. The indirect approach for the calibration of the DTM proved to be feasible and more elegant than a direct modification of the method.

The calibration of the DTM could be strengthened by further laboratory and field studies. Ammoniacal solutions have different ammonia loss characteristics than soils. But the decrease of ammoniacal N concentrations in the solution (with nitrification inhibitor) can serve as a more accurate measure of ammonia loss than micrometeorological measurements which are also prone to a considerable degree of measurement error. The measurement of ammoniacal N concentrations in solutions is more accurate then the indirect measurement of its depletion by micrometeorological measurements. Applying this approach, the effect of pH, temperature and ammoniacal N concentrations in the solution and of air exchange rates in the cups on DTM ammonia volatilisation measurements could be studied systematically in laboratory experiments. As a second step, the results obtained from such experiments could be extended and checked by the measurement of ammonia losses from ammoniacal solutions in the field.

4.5.6 Summary of the calibration results

The improvement of regression results between SSM and DTM ammonia fluxes when considering wind speeds in the calculation ($R^2 = 0.79 – 0.96$) showed the importance of ambient wind conditions for the correction of DTM ammonia fluxes. Wind speeds were also considered in the multiple linear regression for the derivation of a calibration formula for the correction of the DTM based on time weighted ammonia fluxes. Both the 'vegetation period' (Eq. 19) and the 'cumulative loss' (Eq. 20) regression models provided satisfactory ammonia loss estimates when compared to the SSM measurements (mean absolute deviation 6.5 resp. 5.2 kg N ha^{-1}). With regard to simplicity the 'cumulative loss' model should be preferred. However, when considering the number of data used for the calculation of the formulas as well as the direct comparison of the fluxes measured by the two methods, the 'vegetation period' approach is more accurate and reliable than the cumulative loss model. The regression for the whole data set ('total data set' model) also based on the ammonia flux measurement by the two methods did not provide satisfactory estimates (7.5 ± 8.1 kg N ha^{-1}). The combined application of the two calibration formulas of the 'vegetation period' approach facilitates a sufficiently accurate absolute estimate of ammonia losses by using the corrected DTM ammonia fluxes. This was corroborated by the validation with corrected DTM values for the mixed incorporation treatments and SSM measurements.

5. Modelling ammonia loss

5.1 Ammonia partial pressure at the soil surface as a basic parameter of ammonia volatilisation

In our field experiments the SSM measurements reflect the product of wind speed and ammonia concentration in the atmosphere while the DTM does not sufficiently take into account the influence of wind speed on ammonia volatilisation. On the contrary, as the DTM determines ammonia fluxes at a constant, low air exchange rate close to the soil surface, hypothetically, ammonia fluxes measured by the DTM should be closely related to the concentration of gaseous ammonia in the atmospheric layer immediately bordering the soil surface. Ammonia partial pressure at the soil surface is the driving force of ammonia volatilisation. The above given hypothesis can be tested by examining the relationship of ammonia partial pressure at the soil surface and ammonia fluxes determined by the DTM and the SSM, respectively.

On the basis of the basic equilibria described in Chapter 2.1 Denmead et al. (1982) gave a set of equations for the calculation of ammonia partial pressure in equilibrium with ammonia concentration in aqueous solution (Eq. 21 and 22). Soil pH, soil temperature and total ammoniacal nitrogen content (TAN) were the input information needed for the calculation. The formulas hold for aqueous solutions but can also be applied to soils, provided the soil moisture content is sufficient. In a first step, NH_3 concentration in the aqueous solution was calculated from TAN concentration, soil pH value and soil temperature (Eq. 21). In the second step ammonia partial pressure is computed depending on soil temperature (Eq. 22)

$$\left[NH_3\right]_{solution} = \frac{\left[NH_3 + NH_4\right]_{solution}}{1 + 10^{(0.09018 + 2729.92/T - pH)}} \tag{21}$$

$$p\left(NH_3\right) = \frac{0.488 \cdot \left[NH_3\right]_{solution} \cdot T}{10^{(1477.8/T - 1.6937)}} \tag{22}$$

$[NH_3]_{solution}$	NH_3-N concentration in solution [mg l^{-1}]
$[NH_3+NH_4^+]_{solution}$	concentration of total ammoniacal N (TAN) in solution [mg l^{-1}]
T	temperature [°K]
$p(NH_3)$	ammonia partial pressure [Pa]

The TAN concentrations (extraction with 1 M KCl), pH and soil moisture contents of surface soil samples (0 – 3 mm) sampled during the field experiments in Fengqiu were used for the application of the calculation scheme in order to obtain the ammonia partial pressure at the soil surface. Soil moisture contents were needed for the calculation of the TAN concentration in soil solution. An important characteristic of ammonium is its adsorption to sorption sites in soil. For this reason, not the total amount of soil ammonium is in solution. For that purpose the ammonium adsorption isotherm presented in Chapter 5.4.1 was used to derive the partitioning of ammonium between sorbed phase and soil solution. Soil solution TAN concentrations were iteratively calculated on the basis of total ammonium (sorbed and in liquid phase) and soil moisture contents and used as input values for equation 21. Soil temperatures (- 0.05 m) were taken from the continuous measurements provided by the meteorological stations set up on the SSM measurement sites.

Ammonia partial pressure varies according to diurnal changes of temperature. As surface soil sampling was carried out only once a day (usually at 10 – 12:00), the calculated ammonia partial pressures gave only punctual information about the development of ammonia partial pressure in the course of a day, a 'snap-shot' of the ammonia volatilisation process. For the comparison of the calculated ammonia partial pressures and the ammonia fluxes measured by the two methods the ammonia volatilisation measurement events and surface soil samplings should be as close as possible. There was no problem with the DTM measurements for this requirement, as DTM sampling was frequent and short. However, SSM samplers were kept continuously in the experimental site and only exchanged once a day. Nevertheless, the results given below can be used for the interpretation and explanation of the differences in ammonia volatilisation losses determined by the two methods.

Fig. 44 depicts the linear regression between ammonia fluxes determined by DTM and the calculated surface soil ammonia partial pressures for the wheat 1999, spring surface broadcast treatment (4a). The coefficient of determination (R^2) of 0.79 was satisfactory. Ammonia partial pressure at the soil surface characterises the situation in the soil/atmosphere boundary layer preceding the impact of advective wind on the transfer of ammonia to the ambient atmosphere. This result supports the hypothesis that ammonia volatilisation measurements by the DTM basically reflect the ammonia concentrations in the atmosphere close to the soil surface. The regression analyses for the other surface broadcast treatments yielded results of similar significance (Table 28). The winter wheat October 1998 surface broadcast treatment was not included as the soil moisture was too low for the calculation of TAN concentration in soil solution. In autumn, the surface soil was very dry, and no irrigation was applied.

Table 28: linear regression between calculated ammonia partial pressure at the soil surface and ammonia fluxes measured by DTM

Experiment	number of pairs	R^2	significance level p
Maize June 1998, 1 a	10	0.88	<0.01
Maize July 1998, 2 a	7	0.97	<0.01
Winter wheat March 1999, 3a	12	0.79	<0.01
Maize July 1999, 4a	8	0.82	<0.01
total data set (decadic logarithm)	**34**	**0.86**	<0.01

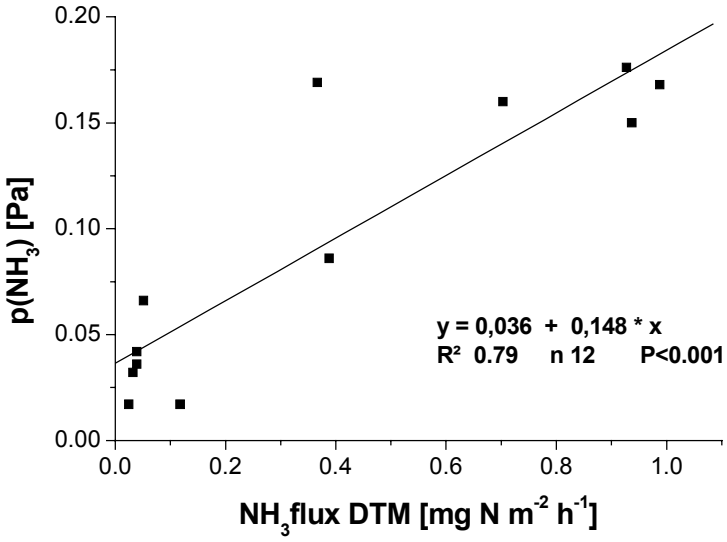


Fig.44: Linear regression between ammonia fluxes measured by DTM (independent) and calculated surface soil (0-3 mm) ammonia partial pressures (dependent), wheat, spring 1999, surface broadcast (100 kg N ha^{-1})

As the whole data set comprised a wide range of ammonia partial pressures and ammonia fluxes, no significant regression could be determined for the unmodified data set. However, after plotting the data on a scale of decadic logarithm a significant linear relationship was determined (R^2 0.82, Fig. 45, Tab.

28). The data supported the hypothesis that DTM ammonia measurements can be regarded as a measure for ammonia partial pressure at the soil surface.

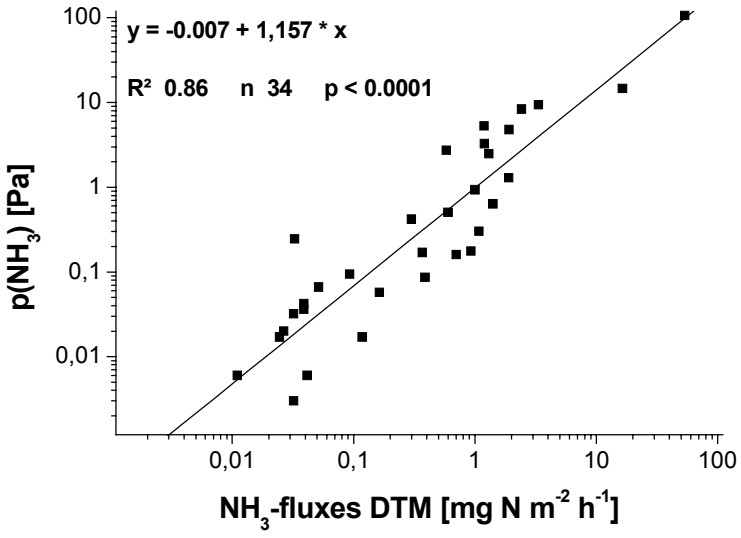


Fig.45: Linear regression between the logarithms of ammonia fluxes measured by DTM (independent) and calculated surface soil (0-3 mm) ammonia partial pressures (dependent) for the whole data set

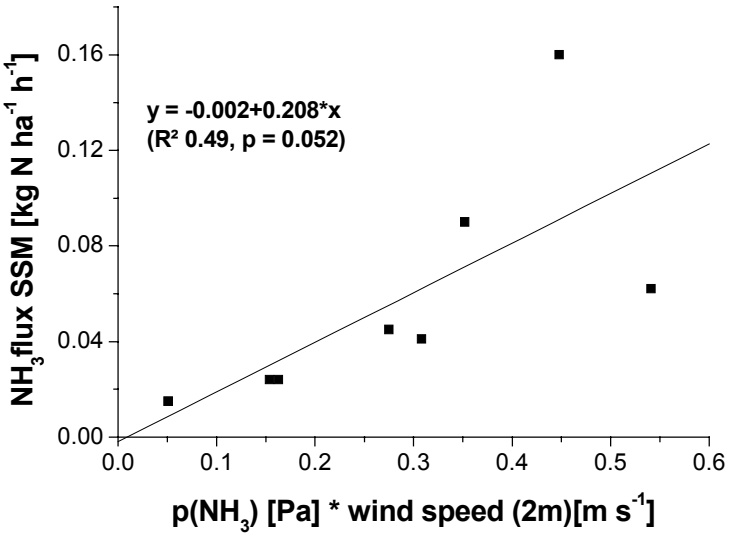


Fig.46: Linear regression between ammonia fluxes determined by SSM (dependent) and the product of calculated ammonia partial pressure at the soil surface and wind speed at 2 m height (independent), wheat, spring 1999, surface broadcast (100 kg N ha^{-1})

As expected, a regression between ammonia partial pressure at the soil surface and SSM ammonia fluxes yielded no significant result (R^2 0.22, not shown). Multiplying the calculated ammonia partial pressures with wind speeds prevailing at the moment of soil sampling yielded a significant improvement of the regression result (Fig. 46, R^2 0.49, $p < 0.1$). Similar results were determined for the other treatments. This outcome validates the fact that SSM measurements reflect the product of wind speed and ammonia concentration in the atmosphere. This is valid despite the problem of fittingly assigning SSM ammonia fluxes which are average values for longer time periods to calculated punctual ammonia partial pressures with regard to time resulting in a blurred relationship of the data. As a result, SSM measurements can be characterised as a measure for the joint effect of ammonia evolution processes at the soil surface and the air exchange caused by wind. In contrast to the SSM, DTM results were closely related to ammonia partial pressure at the soil surface without sufficiently taking into account the effect of wind speed on ammonia volatilisation.

5.2 Model by Rachhpal-Singh and Nye

The 'model of ammonia volatilisation from applied urea' (DUPAV) developed by Rachhpal-Singh and Nye (1986 a-c; Rachhpal-Singh and Nye 1988) was chosen for the simulation of ammonia losses measured during the field experiments in Fengqiu. The model, which was written in FORTRAN programming language, was developed on the basis of independent laboratory measurements. It is mainly based on three continuity equations describing the diffusion and reactions of urea, ammoniacal nitrogen and soil base. The mechanistic model thus combines the process of ammonia volatilisation with the simultaneous transformation and movement of urea and its products in soil for predicting the concentration profiles of urea, ammoniacal nitrogen and soil pH, as well as ammonia volatilisation, following application of urea (Rachhpal-Singh and Nye 1986a).

The calculation of ammonia fluxes from soil following urea application is based on the difference between ammonia concentrations in the soil air and in the immediate atmosphere (processes related to ammonia volatilisation see Chapter 2.1). In general, ammonia concentrations in the ambient atmosphere can be neglected. Therefore, ammonia volatilisation was considered to principally depend on the ammonia concentration in the surface soil:

$$F_{Ng} = K_a [N_g]_0 \qquad (23)$$

F_{Ng}	flux of ammonia gas [mol dm^{-2} h^{-1}]
K_a	empirical one-dimensional transfer coefficient for ammonia volatilisation [dm h^{-1}]
$[N_g]_0$	concentration of ammonia gas at the soil surface [mol dm^{-3}]

Under field conditions the transfer coefficient K_a depends on many factors, of which surface roughness, temperature and the wind velocity over the soil surface are the most important. In case of the laboratory chamber experiments used for the validation of the model by Rachhpal-Singh and Nye (1986b) K_a mainly depended on the laminar air flux rate through the chambers determined by the authors in an independent experiment.

Most processes related to ammonia volatilisation following urea application described in chapter 2.1 are considered in the model. All of the three equations are complex differential equations which were simultaneously solved using the Crank-Nicholson implicit finite difference method (Richtmeyer algorithm). In the course of a time step (originally 6 minutes), the concentration profiles are calculated in the sequence: urea, bicarbonate (soil base) and ammoniacal nitrogen. Integration of ammonia fluxes to cumulative ammonia losses is iteratively calculated by Simpson's rule. The core model, consisting of the continuity equations and the calculation of the boundary and initial conditions, was not modified in this study. Therefore, the continuity equations for urea, ammoniacal nitrogen and soil base shall not be described in detail here. Details can be found in Rachhpal-Singh and Nye (1986 a-c).

The model calculates the ammonia loss as one-dimensional flux out of a 'representative' soil core of the same size as the diffusion cell used by the authors for experimentally deriving the diffusion parameters (circular cell, 4 cm diameter, 5 cm depth) (Rachhpal-Singh and Nye 1984 a). Transport of urea, ammoniacal nitrogen and soil base through soil is based on diffusion in the gaseous and aqueous phases of the soil, while convective transport (mass flux) is not considered in the model. In the original model calculations were carried out using constant water contents and temperatures corresponding to the laboratory conditions of the experiments. As a consequence, temperature or soil moisture dependent parameters for diffusion (e.g. diffusion impedance factors), urease activity and dissociation constants were kept constant, equally. The working units for the calculations are mole (concentrations), dm (volume, depth) and hour (time). The following paragraphs give a short description of the initial and boundary conditions of the unmodified model.

Urea

The urea content depends mainly on the surface application of urea to soil at the start of the simulation. Concentrations decrease due to the hydrolysis of urea by urease to ammonium, bicarbonate and hydroxide (see Chapter 2.1). The initial distribution of urea in the soil profile is calculated after a

negligibly small diffusion time δt with an equation given by Crank (1975) (also cited in Rachhpal-Singh and Nye (1986a)). The surface boundary condition for urea is that the urea concentration at the soil surface (x = 0) is zero. There is no transfer of urea across the soil surface.

Ammoniacal nitrogen

In the model ammonium and ammonia are treated together as one working variable: ammoniacal nitrogen. The concentration of ammoniacal nitrogen in soil solution depends on initial content, ammonium released in the course of urea hydrolysis, adsorption of ammonium at soil particles and removal of ammonia from soil via ammonia volatilisation. The initial distribution of ammoniacal nitrogen is the uniform initial content of the soil. Adsorption of ammonium to soil particles is considered by applying an ammonium adsorption isotherm of the Freundlich type.

The boundary condition at the soil surface for ammoniacal nitrogen is more complicated than for urea due to ammonia volatilisation in the course of the simulation. As ammonia gas is lost from the soil surface, more ammoniacal nitrogen within the soil must diffuse upwards to maintain the continuity. At the surface boundary the total flux of ammoniacal nitrogen in the soil moving upward both in the liquid phase and in the gaseous phase is equal to the flux of ammonia gas moving out of the soil.

Soil alkalinity

As described in chapter 2.1 soil pH and pH changes are decisive for extent and course of the ammonia volatilisation process. Therefore, soil alkalinity is considered by the most complex continuity equation in the model. Soil alkalinity is treated as a function of initial soil pH, pH buffer capacity, soil respiration (CO_2 production), urea hydrolysis (release of HCO_3^- and OH^-) and ammonia volatilisation (loss of base, H^+ release). Moreover, the equilibria between partial pressure of CO_2 and H_2CO_3 concentration, and between H_2CO_3 and HCO_3^- and H^+ are included. The original model does not include the precipitation of calcium carbonate at high pH-levels. The initial distribution of soil base is the uniform initial content of the soil (uniform soil pH).

The loss of ammonia gas due to volatilisation represents a loss of base from the soil. Similar as for ammoniacal nitrogen, there must be continuity of flux of base across the surface plane. Therefore, the amount of ammonia volatilised equals the loss of base from the soil as upper boundary condition.

Lower boundary condition

No loss of urea, ammoniacal nitrogen, soil base, hydrogen ion and ammonia in aqueous solution across the bottom of the soil column is assumed as the boundary condition at the lower end of the column.

Shortcomings of the model

At large, the major shortcoming of the model with regard to the simulation of field data lies in its design for the estimation of data obtained from laboratory experiments. For this reason, the model does not take into account the effects of changing field conditions as water content, temperature, or wind speed on the ammonia volatilisation process. In addition, the model does not include several other important transformation and transport processes related to soil nitrogen. Nitrification and denitrification processes, ammonium fixation by clay minerals, nitrogen uptake by plants, nitrogen immobilization and convective transport of nitrogen in soil solution are not considered. With regard to soil pH, carbonate precipitation is not included in the model. The process of $CaCO_3$ precipitation and solution and the dissociation of HCO_3^- were incorporated as part of a modification of the model carried out by Roelcke et al. (1996) but yielded only little improvement of the simulation results.

The original model was used in the present study. The model by Rachhpal-Singh and Nye (1986 a) is the most appropriate approach for the deterministic modelling of ammonia volatilisation following urea application to upland soils when compared to other models available for the simulation of ammonia losses. Most models developed for the situation of industrialised countries of the temperate zone calculate ammonia losses following the application of slurry or animal manure (Van der Molen et al. 1990, Génermont and Cellier 1997, Mannheim et al. 1997, Hengnirun et al. 1999, Sommer and Olesen 2000). The model by Génermont and Cellier (1997) is the most refined model for the calculation of ammonia volatilisation from upland soils under field conditions. In effect, the model is a combination of the models by Van der Molen et al. (1990) and Rachhpal-Singh and Nye (1986a), but does not include the calculation of ammonia losses following urea application. On the other hand, only validated ammonia volatilisation models for ammonia volatilisation under field conditions following urea application to flooded (paddy) soils exist, e.g. Jayaweera and Mikkelsen (1990).

With regard to models designed for the calculation of ammonia losses following urea application to upland soils, the approach by Ismail et al. (1991) offers just a statistical response surface for the estimation of ammonia losses. The model by Fleisher et al. (1987) has the same shortcomings as the model used in this study but includes less processes related to ammonia volatilisation. The model by Sadeghi et al. (1988) does not offer any advantages over that by Rachhpal-Singh and Nye (1986 a) (see also Ladewig 1993) and was not validated in laboratory studies.

The model used in this study was successfully applied by the authors to calculate ammonia losses from soils under laboratory conditions (Rachhpal-Singh and Nye 1986 b, Rachhpal-Singh and Nye 1988). Moreover, the model also proved very suitable for the description of laboratory ammonia loss experiments by Roelcke et al. (1996). For this reason the model by Rachhpal-Singh and Nye (1986 a) was considered as the most appropriate basis for the deterministic simulation of ammonia losses measured under field conditions in Fengqiu.

5.3 Modification of the model

In order to overcome some of the shortcomings described in the paragraph above, the model was modified with regard to the influence of temperature, water content and wind speed on the model parameters and, thus, on the ammonia volatilisation process. The sensitivity analysis by the model authors (Rachhpal-Singh and Nye 1986 c) revealed, that initial soil pH, urease activity, water content, urea application rate and pH buffer capacity were the most sensitive parameters in the model. Therefore, the input of the variables mentioned above was modified in order to account for the influence of environmental conditions on the parameters.

Meteorological data

The model was enlarged by a routine reading and storing meteorological data measured *in situ* in Fengqiu (Chapter 3.4.4.1). The file consisted of five data columns including air temperature (1 m), soil temperature (-0.05 m), wind speed (2 m), wind speed (0.2 m) measured at 10 minute intervals, and surface water contents (0 – 3 mm) measured at daily intervals. As moisture content at the soil surface was too low in the first winter wheat surface broadcast treatment (autumn 1998), water contents of 0-0.2 m soil cores measured at 1- 2 days intervals were used instead of those of surface soil samples. The time step of the model was changed from 6 minutes to 10 minutes (field sampling interval) in order to use unmodified data in the model runs.

Modification of the model with regard to temperature

The temperature influence on urease activity, Henry constant and ammonium dissociation constant in aqueous solution was adapted. The diffusion coefficients for urea, ammoniacal nitrogen etc. were kept constant. Soil temperatures (-0.05 m) were used in the calculations.

Urease activity was one of the most sensitive parameters in the sensitivity analysis. Therefore, the effect of urea concentration and temperature on urease activity was investigated in a laboratory batch experiment. A simplified Michaelis-Menten equation combined with an Arrhenius-relationship was successfully fitted to the data. The set-up of the experiment and the results of the parameter estimation are presented in chapters 3.4.4.2 and 5.4.1.

The temperature dependencies of Henry's law constant and of the dissociation constant of ammonium in aqueous solution were described by common equations used in the models by Van der Molen et al. (1990) and thereafter by Génermont and Cellier (1997) and Sommer and Olesen (2000).

The Henry's law constant was calculated according to the empirical relation given by Sander (1999):

$$\ln K_H = -\frac{4200}{T} + 3.133 \tag{24}$$

K_H Henry's law constant [atm m³ mol^{-1}]
T Temperature [K]

As required by the model, the Henry law constant (K_H) was transformed to its dimensionless form (K'_H) by:

$$K'_H = \frac{K_H}{RT} \tag{25}$$

R universal gas constant [8.206 10^{-5} atm mol^{-1} K^{-1}]

The temperature dependency of the equilibrium ammonia dissociation constant (K_N) was calculated as follows (Génermont and Cellier 1997; Sommer and Olesen 2000):

$$\ln K_N = -177.95292 - \frac{1843.22}{T} + 31.4335 \ln(T) + 0.0544943 \cdot T \tag{26}$$

K_N equilibrium constant for the dissociation of NH_4^+ in aqueous solution [mol dm^{-3}]

Modification of the model with regard to water content

Water content and the partitioning of the pore space into gaseous and aqueous phase are important parameters concerning the diffusive transport of urea, ammoniacal-nitrogen and soil base in soil. Surface soil samples (0 – 3 mm) taken at daily intervals were used for the determination of gravimetric water (GR_l) contents. Volumetric water contents (θ_L) were calculated from the gravimetric water

contents in order to derive diffusion impedance factors for gaseous (f_g) and aqueous (f_L) phase used during the simulation runs.

$\theta_l = GR_l \rho$ (27)

θ_l volumetric water content [cm³ cm^{-3}]
GR_l gravimetric water content [cm³ g^{-1}]
ρ soil bulk density [1.45 g cm^{-3}, determined in Fengqiu]

The volumetric gas content (θ_g) was calculated from soil bulk density (ρ), soil particle density (ρ_p) and volumetric water content (θ_l):

$$\theta_g = 1 - \frac{\rho}{\rho_p} - \theta_l \quad (28)$$

ρ_p soil particle density [2.65 g cm^{-3}]

The diffusion impedance factor in aqueous solution in soil (f_l, reciprocal value of the tortuosity factor in aqueous solution) was calculated using an empirical relationship given by Barraclough and Tinker (1981). In that laboratory study solution diffusion impedance factors from soils were determined with textures ranging from clay loam to sandy loam.

$$f_l = 1.58 \cdot \theta_l - 0.17 \quad (29)$$

f_l solution diffusion impedance factor [dimensionless]

Two approaches Millington and Quirk (1961) (Eq.30) and Kirk and Nye (1991) (Eq.31), were tested for the calculation of gaseous diffusion impedance factors in soil (f_g, reciprocal value of the tortuosity factor in gaseous phase). The latter formula was also applied in the ammonia volatilisation model by Génermont and Cellier (1997). Equation 31 (f_g2) gave considerably higher values for f_g than equation 30 (f_g1). Therefore both equations were used and compared in the simulation runs.

$$f_g = \frac{\theta_g^{10/3}}{\phi^2} \quad (f_g1) \quad (30)$$

$$f_g = (1.7\theta_g)^2 \quad (f_g2) \quad (31)$$

f_g gaseous diffusion impedance factor [dimensionless]
ϕ soil porosity [vol. %]

By application of the approaches described above the most sensitive parameters of the model were adapted for the simulation of ammonia losses in the field. However, the limitatons of the model with regard to nitrogen transformation and transport processes were not overcome by these changes. It will be discussed in chapter 5.4.3 in how far the modifications of the model were sufficient to estimate ammonia losses following urea application to the soil surface.

In addition to the modification of the model which is based on the insertion of new equations into the model, model parameters were also adapted to Fengqiu conditions by carrying out laboratory experiments as described in Chapter 3.4.4.2.

Simulation runs

Ammonia losses following urea application were calculated for the 5 surface broadcast treatments which were carried out using the modified volatilisation model by Rachhpal-Singh and Nye. Simulations of the incorporation treatments (mixed incorporation and fertilization followed by irrigation excluding deep point placement) were run including a new initial condition for the distribution of urea in soil according to Rachhpal-Singh and Nye (1988):

$$U(I) = \frac{M_U}{d}, \quad 0<x_d<d \qquad (33)$$

U(I)	urea-N concentration in total soil volume (solid, gaseous, liquid) in the I^{th} depth increment (mol dm^{-3})
M_U	amount of urea-N applied to surface unit area (mol dm^{-2})
d	depth of the soil layer mixed with fertilizer (dm, here 0.5 dm)
x_d	soil depths increments (dm, here 0.005 dm)

It was assumed that all urea-N applied was evenly mixed with the soil to a depth of 0.5 dm used in the simulations. A soil depth of 0.5 dm corresponding to the original simulations by Rachhpal-Singh and Nye (1986a) was chosen, as only surface soil (0 – 3 mm) characteristics (temperature, soil moisture) were determined at daily sampling intervals during the Fengqiu field experiments. In addition, preliminary simulations including higher soil depths (2 dm) showed that the decisive processes with regard to ammonia volatilisation (diffusion of urea, ammonia and soil base) occurred mainly in the uppermost centimetres of the soil. A more detailed description of the individual simulation runs is given in chapter 5.4.2. Simulations were carried out assuming that the lower end of the soil column was closed for the gaseous diffusion of CO_2.

5.4 Simulation results and discussion

5.4.1 Parameter estimation

The results of the parameter estimation for ammonium adsorption isotherm, pH-buffer capacity and urease activity (see Chapter 3.3.3) are presented in the following.

Ammonium adsorption isotherm

Fig. 47 depicts the relationship between NH_4^+-equilibrium concentrations in aqueous and sorbed phase. The data were successfully fitted with a Freundlich adsorption isotherm (R^2 0.992):

$$S = k\, C^m \qquad (34)$$

S	NH_4^+ in sorbed phase	[mmol kg^{-1} dry soil]
C	NH_4^+ equilibrium concentration in aqueous phase	[mmol l^{-1}]
k	Freundlich coefficient	3.64 [$mmol^{1-m} l^m kg^{-1}$] (std.err. 0.40)
m	Freundlich exponent	0.66 [dimensionless] (std.err. 0.02)

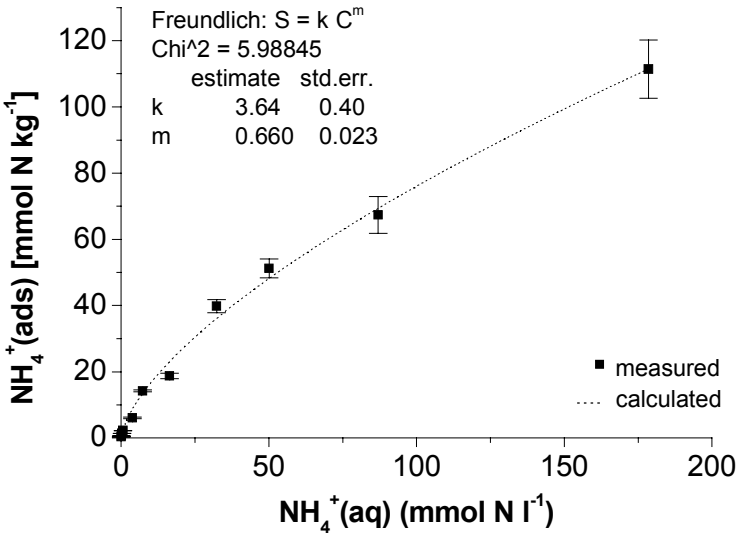


Fig.47: Relationship between NH_4^+ in aqueous and sorbed phase determined from field fresh samples of Fengqiu top soil and fitted Freundlich adsorption isotherm

The Freundlich exponent m smaller than 1 (m < 1) indicates that a proportion of the ammonium in aqueous phase was specifically sorbed at the inner lattice structure of clay minerals. Fengqiu topsoils had a clay content of 10 % (see Chapter 3.1.3).

pH buffer capacity

Fig. 48 shows the response of the soil pH to the stepwise addition of acidic and alkaline solution. The pH response curve presented in Fig. 48 shows that the buffering of the soil against pH changes was distinctly lower in the pH range of pH 8 – 10. Linear regression of the data points yielded a pH buffer capacity of 0.016 Mol OH^- resp. H^+ kg^{-1} dry soil in that pH range. A pH buffer capacity of 0.033 Mol OH^- resp. H^+ kg^{-1} dry soil was determined for the whole range of pH values measured. The initial pH of 8.8 (H_2O) was very high, well above the range of pH values typical for the soil carbonat buffer system (pH 7.2 – 8.3; (Gisi 1997)). These values were multiplied with the soil bulk density (1.45 g cm^{-3}) in order to obtain volume based pH buffer (Mol dm^{-3} soil) capacities required to run the model. Both pH buffer capacities were tested when applying the modified model of Rachhpal-Singh and Nye.

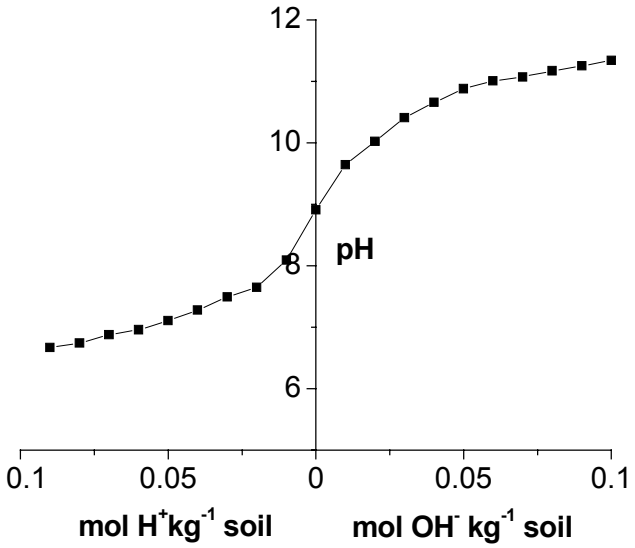


Fig. 48: pH buffer curve after 3 days incubation of field moist Fengqiu top soil with several aliquots of acidic and basic solution

Urease activity

The urease activity is decisive for the intensity of the hydrolysis of urea to ammonium, bicarbonate-anion and hydroxile-anion. Urease activity should be determined as accurately as possible for the estimation of ammonia volatilisation losses using the model by Rachhpal-Singh and Nye. As described in chapter 3.4.4.2, urease activity was determined with regard to the influence of urea concentration and temperature on the urea hydrolysis process.

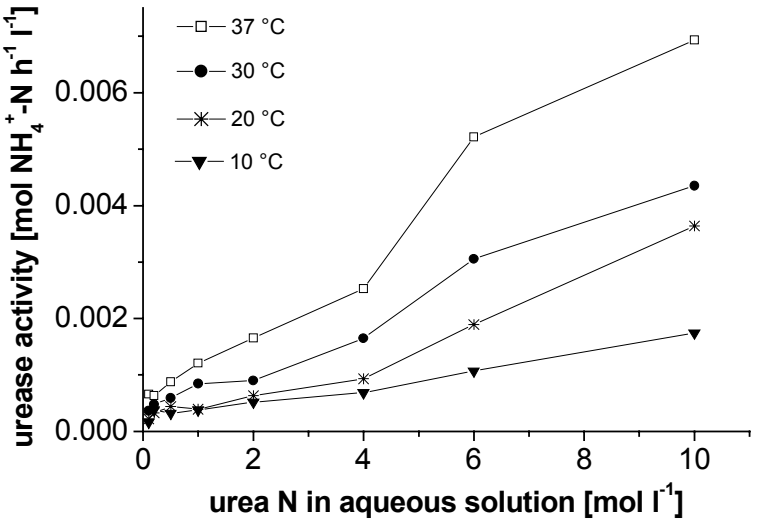


Fig. 49: Urease activity depending on urea concentration and temperature determined in a batch experiment

An urease activity of 0.00121 Mol N h^{-1} l^{-1} (17 µg NH_4^+-N h^{-1} g^{-1} soil) at standard conditions (37°C and 1 Mol urea N l^{-1}, as commonly used by other scientists) was comparatively low (Bremner and Mulvaney 1978). Fig. 49 shows that there was a significant increase of urease activity with increasing temperatures and urea concentrations. The 30 and 37 °C curves for urease activities are flattening out at high urea-N concentrations, but no maximum urease activity, i.e. substrate saturation of the enzymatic reaction was reached. The graphs can be separated into two different sections. The first section ranges from urea concentrations between 0 and 2 Mol l^{-1} while the second section ranges between 2 and 10 Mol l^{-1}. The first section is characterized by a steep increase of urease activity with urease concentration and temperature until a transitory plateau reached at a concentration of about 0.5 Mol l^{-1}. Starting from an urea concentration of about 2 Mol l^{-1} urease activity increases again in a linear way. Urease activity was similar to the one in the soil investigated in the original experiment by Rachhpal-Singh and Nye (1986b). It was possible to fit a combined Michaelis-Menten and Arrhenius kinetics to the whole data set (similar to Eq. 33, results not shown). However, first simulation runs with the modified model revealed that the fitted model underestimated urease activities, as it did not reflect the steep increase in urease activity for low urea concentrations (see Fig. 50). For that reason the data set was subdivided into two sections described above. An equation was fitted to each of the two data sets to describe the dependency of urease activity on temperature and substrate concentration. Data points which showed a

high deviation from a plausible course of the hydrolysis curve (probably due to measurement error) were not considered in the fitting process in order to obtain a urease activity model estimate as accurate as possible.

Eq. 35 was fitted to the data set with low urea concentrations. It is a simplified Michaelis-Menten approach combined with an Arrhenius relationship for the description of the temperature dependency. The coefficient of determination (R^2) of 0.884 was satisfactory (the modelling efficiency c^2 - see Chapter 4.5.1 - also 0.884). In the fitting of the Michaelis-Menten equation the parameter V_{max} (maximum rate of hydrolysis) was omitted as it was not possible to estimate it with sufficient accuracy. This could be explained by the fact that the urease activity curves still showed slightly increasing slopes at the plateau between 0.5 and 2 mol l^{-1}. In addition, the small number of data points might have restricted the fitting of a more complex model. Nevertheless, the comparison of measured and simulated urease activity shows a satisfactory agreement (Fig. 50).

Simplified Michaelis-Menten-Arrhenius equation (applied for urea concentration < 0.5 Mol l^{-1})

$$a_{urease} = \frac{C_{urea}}{(C_{urea} + k_m)} \cdot e^{\left(\frac{-a}{T}\right)} \qquad (R^2\ 0.884,\ a\ 2074.5,\ k_m\ 0.252) \qquad (35)$$

Simplified Arrhenius-equation (applied for urea concentration > 0.5 Mol l^{-1})

$$a_{urease} = C_{urea} \cdot e^{\left(\frac{-a}{T}\right)} \qquad (R^2\ 0.873,\ a\ 2303.8) \qquad (36)$$

a_{urease}	urease activity [Mol N h^{-1} l^{-1}]
C_{urea}	urea concentration [Mol l^{-1}]
k_m	Michaelis-Menten constant [Mol l^{-1}]
a	Arrhenius constant
T	temperature in °K

There was a more or less linear increase in urease activity for urea concentrations greater than 2 Mol l^{-1} for all temperatures. Therefore, urease concentrations and Arrhenius approach were linearly related for the calculation of urease activities at higher urea concentrations (Eq.36). The fit was likewise satisfactory (R^2 0.873). No figure comparing measured and simulated data is presented for that model as urea concentrations occurring during the simulation runs were almost always below the threshold value chosen for the application of the equation for higher urea concentrations (Eq. 36). Equation 35 fitted for lower urea concentrations was applied below a threshold urea concentration of 0.5 [Mol l^{-1}].

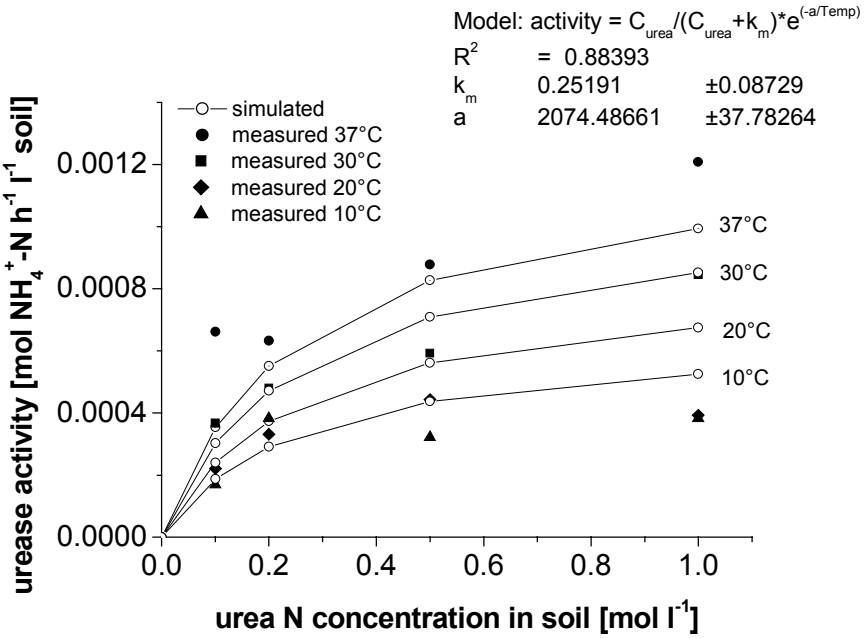


Fig. 50: Measured and simulated urease activity depending on temperature and urea concentration fitted with a simplified Michaelis-Menten-equation (concentration) combined with an Arrhenius equation (temperature) for low urea concentrations

5.4.2 Comparison of simulation results with field measurements

Soil temperatures and soil moisture contents measured in situ were used as input variables for the simulations. Several sets of boundary conditions and parameters were compared in the course of the simulations.

As was described in Chapter 5.4.1, two pH buffer capacities could be derived from the pH buffer curve determined in a laboratory batch experiment: an average buffer capacity (0.033 Mol H^+/OH^- kg^{-1} soil) for the whole range of pH-values and a lower pH buffer capacity in the interval between pH 8 and 10 (0.016 Mol H^+/OH^- kg^{-1} soil). The effect of both buffer capacities on the calculation of ammonia losses was studied in the simulation runs.

Furthermore, both approaches for the calculation of the gaseous diffusion impedance factor in soil presented in chapter 5.3 (Eq. 30 and 31) were compared during the simulations. As a third aspect of the simulations, surface soil moisture values changing at daily intervals were compared to that of average surface soil moistures of the whole experimental period. Altogether three features of the model were varied in the course of the simulations:

1) Low and high pH-buffer capacities (0.016 (low bc) vs. 0.033 (high bc) Mol H^+ respective OH^- kg^{-1} soil), initial pH of 8.5 (average pH value determined at Fengqiu)
2) Two approaches for the soil gaseous diffusion impedance factor (f_g1, Eq. 30 + f_g2, Eq. 31)
3) Daily measured surface soil moisture vs. average soil moisture for the whole experiment

For two experiments exceptions were made from the general design of the simulations. In the first wheat experiment with surface broadcast urea (120 kg N ha^{-1}, October 1998), surface soil moistures were too low for a stable simulation, the simulations breaking off when low surface soil moistures were reached. Therefore, soil moisture values determined for the top 0 – 0.2 m soil layer taken at 2 –3 day intervals were used during the simulations. In the 3rd maize experiment with surface broadcast urea the same problems occurred. Average 0 – 0.2 m soil moisture values were used for these calculations as the surface soil layer was only sampled at the beginning and at the end of the experiment.

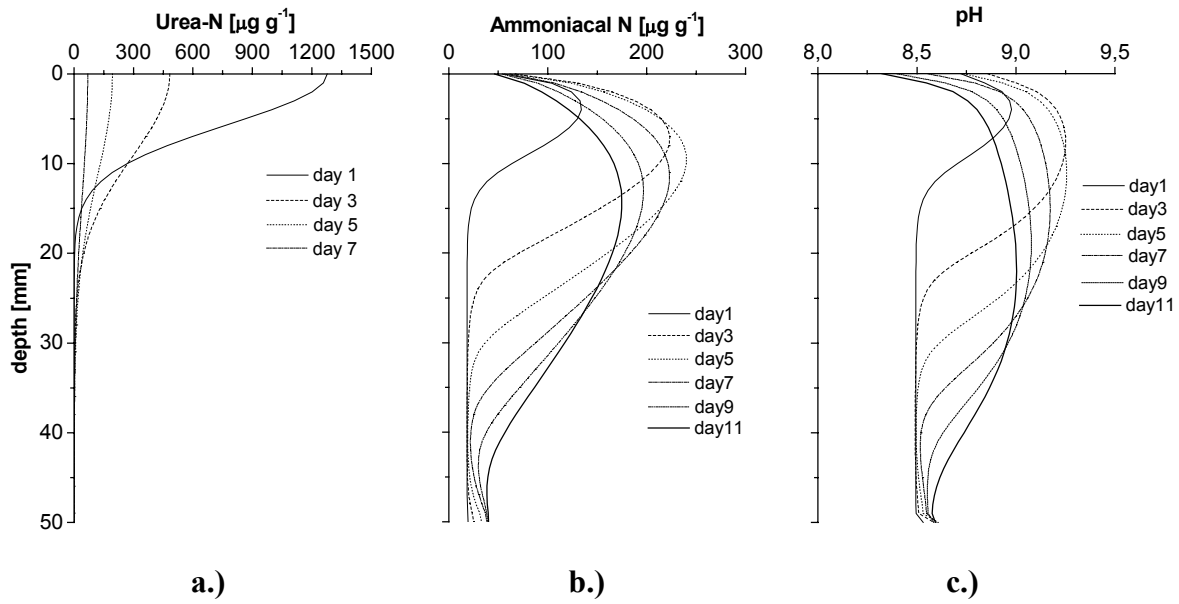


Fig. 51: Example: simulated distributions of urea-N (a), ammoniacal-N (b) and pH (c) for the 3rd maize experiment (summer 1999; 150 kg N ha^{-1}), surface broadcast urea (average water content, buffer capacity low)

The estimation of ammonia losses from urea was based on the calculation of the diffusion and reactions of urea-N, ammoniacal N and soil base in soil. Only one set of simulated profiles in soil shall be discussed in detail here.

Fig. 51 gives example profiles calculated for the third maize experiment, surface broadcast treatment (summer 1999, 150 kg N ha^{-1}). The figures are arranged in a sort of synchronous order although the processes also progress simultaneously. As a first step urea is placed on the soil surface and diffuses in the liquid phase into the deeper layers of the surface soil (Fig. 51 a). The simulated urea distributions did not reach depths beyond 0.03 m. As urea is hydrolysed to ammonium, HCO_3^- and OH^-, the total amount of urea decreases rapidly in the course of the simulation. Ammonium released by urea hydrolysis diffuses in the soil towards deeper soil layers (Fig. 51 b). As ammonia is lost by the process of ammonia volatilisation there is an upward diffusion of ammonia back to the soil surface from the deeper soil layers. The ammonia concentration decreases towards the surface of the soil as it is lost as ammonia to the atmosphere. With proceeding ammonia volatilisation ammonium contents at the surface of the soil column are further decreasing while it also diffuses deeper into the soil. Hydrolysis (release of OH^- and HCO_3^-) of urea leads to an increase in soil pH in the uppermost soil which then decreases in the course of time due to NH_3 volatilisation (release of H^+) and diffusion of soil base towards the deeper

layers of the soil column (Fig. 51 c). At the end of the simulation, when balancing over the whole profile, the initial pH at the soil surface was not re-established in the whole profile. This is due to the fact that not all ammonium has volatilised as ammonia. The amounts of base and acid released by urea hydrolysis and ammonia volatilisation, respectively, would be equal if all urea-N applied had be volatilised. As NH_3 is emitted from the soil surface, the surface soil pH is lower than the initial pH-value at the end of the simulation. Decreasing soil pH entails a reduced dissociation of ammonium to NH_3 and H^+ and, thus, a reduction and fading out of ammonia emissions as was observed in most of the simulation runs.

5.4.2.1 First maize experiment (June 1998, 75 kg N ha^{-1})

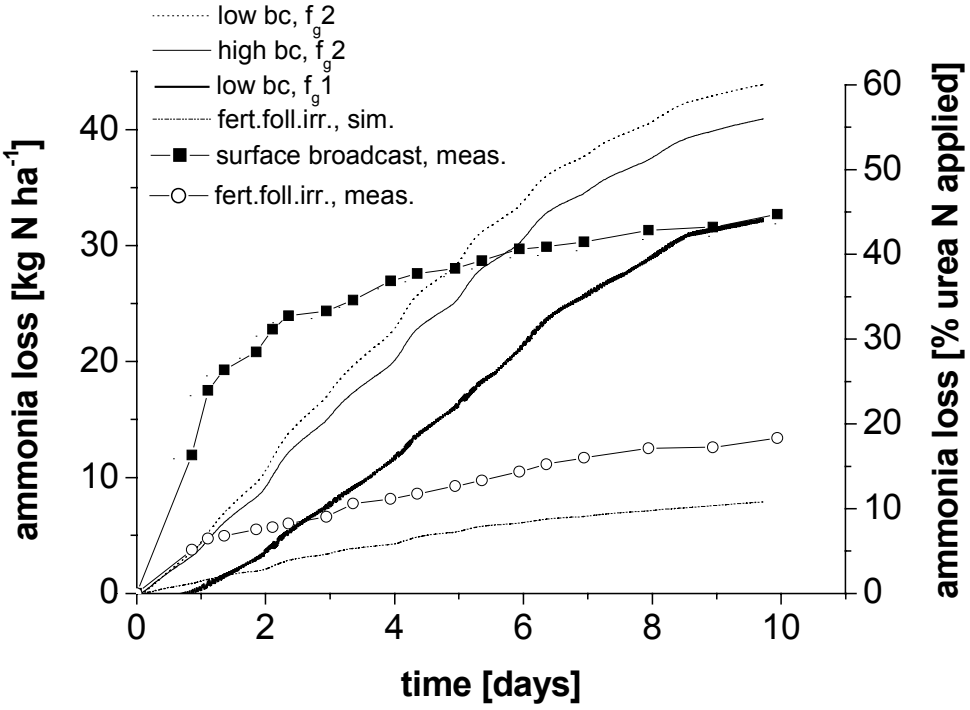


Fig. 52: 1st maize experiment (75 kg N ha^{-1}), measured (SSM method) and simulated cumulative ammonia losses for surface broadcast treatment and fertilization followed by irrigation treatment using different sets of parameters (bc = buffer capacity)

Fig.52 shows the comparison of measured (SSM method) and simulated cumulative ammonia losses for the first maize experiment, surface broadcast treatment and fertilization followed by irrigation treatment. Focussing on the surface broadcast treatment, the figure shows that the courses of cumulative

ammonia losses determined by the simulations did not agree well with the course of losses measured in the field. This was true for the three simulation approaches presented in the Fig. 52, which basically all describe the kinetics of the NH_3- volatilisation process by a sigmoidal curve. Nevertheless, the cumulative ammonia losses calculated by the model had the same order of magnitude as the measured losses, with a positive maximum deviation from the measured values of 10% of the urea-N applied. In general, ammonia fluxes determined in the field were higher in the beginning than those simulated by the model, i.e. the highest proportion of the measured losses occurred during the first two days. In contrast relatively constant ammonia fluxes were calculated by the model during most of the simulation time. As a result, the overall shapes of the measured and simulated ammonia loss curves were quite different. However, the simulated curves reflected the influence of oscillating day and night temperatures on the course of ammonia volatilisation also given in measured data (e.g. on days 1- 2).

The differences in the general shape of the curves can be explained by the influence of evaporating water on ammonia loss. This process is not included in the model by Rachhpal-Singh and Nye (1986a). As described by Kirk and Nye (1991), in case of intensive evaporation the mass flux of ammonium in the aqueous phase is a very important transfer mechanism for ammonium through soil compared to aqueous and gaseous diffusion. The water flux is directed towards the soil surface and transports dissolved urea, ammoniacal N and soil base (HCO_3^-) to the soil surface. As a result, ammonium and urea concentrations at the soil surface are comparatively higher than in case of solely diffusive transfer through soil. In addition, soil base transported to the soil surface sustains a high soil pH, and a high proportion of ammonium dissociated to NH_3 and H^+. All these processes provide favourable conditions for ammonia volatilisation. The evaporation of water from the soil surface is also causes the co-transfer of NH_3 with water to the atmosphere because the molecular weight of NH_3 and water are almost the same. In the 1st maize experiment, surface broadcast treatment, temperatures were quite high (see Table 20) and the experimental sites had been irrigated one day before fertilization. Therefore, soil was saturated with water at fertilization time, and, due to high temperatures, a strong water flux to the soil surface took place, and high ammonia losses inter-linked with intensive evaporation of water occurred. Consequently, in the first few days high temperatures and very high water contents following irrigation were conditions resulting in ammonia losses mainly based on convective transport processes and evaporation which dominated losses in contrast to solely gaseous and aqueous diffusion as simulated in the deterministic model.

Three different simulation runs are presented in Fig. 52. The simulation using f_g1 (Millington and Quirk 1961, Eq. 30) for the calculation of the soil gaseous diffusion impedance factor did not run stable. In case of high pH-buffer capacity the simulation broke off while the values for the approach f_g1 and low buffer capacity were flickering and gave no continuous curve. Nevertheless, for the cumulative loss at the end of the experiment almost the same amount was calculated by this approach as what was

measured in the field. The flickering of the simulation results could have been due the increased time step used in the simulations (from 6 minutes to 10 minutes) resulting in instability of the numerical algorithm. This problem mainly occurred when f_g1 was used in the calculations. The other two simulated curves for the surface broadcast treatment show cumulative ammonia losses calculated using f_g2 (Eq. 31) as soil gaseous diffusion impedance factor and high and low pH-buffer capacities. f_g2 gave quite higher values than f_g1 which means a lower tortuosity of the soil and thus led to an enhanced gaseous diffusion through soil. As a consequence, simulation using the f_g2 always resulted in higher ammonia losses than those using f_g1 because diffusion of ammoniacal N through the aqueous phase is much slower than its diffusion through the gaseous phase. In addition, the values derived using f_g2 led to more stable calculations of the model. The use of the low pH buffer capacity resulted in higher calculated ammonia losses as compared to the model with high pH buffer capacities. A lower pH buffer capacity results in a higher increase of soil pH following urea hydrolysis and, thus, in a larger proportion of ammonium dissociated to H^+ and ammonia which can volatilise to the atmosphere. The difference between the two model runs amounted to 3 % of urea-N applied, their curves running in parallel. Similar observations were made by Roelcke et al. (1996). Both simulations using the f_g2 calculated higher ammonia losses than those determined in the field. But this is in line with the considerations about the shortcomings of the model presented in chapter 5.2 and 5.3. As the model does not include other processes of ammonium loss or transformation as plant uptake or nitrification, ammonia losses calculated by the model should be higher than those measured in the field. A major drawback of these simulations lies in the fact that the overall kinetics of the measured ammonia loss process was quite different from the simulated curve. This can be explained by the fact that the model does not include the most important pathway of ammonia volatilisation observed in the June 1998 field experiment, i.e. mass flux of ammonium and ammonia connected to the evaporation of water.

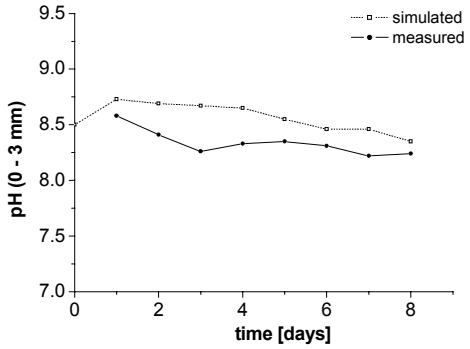


Fig.53 a: simulated and measured pH (0 - 3mm), surface broadcast treatment

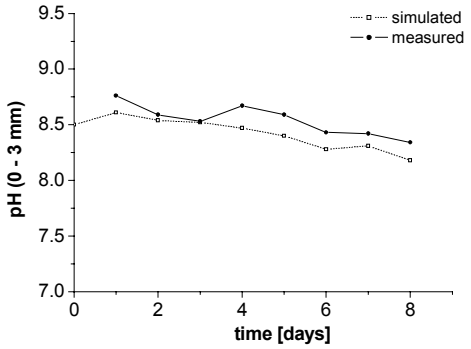


Fig.53 b: simulated and measured pH (0 - 3mm), fertilization followed by irrigation

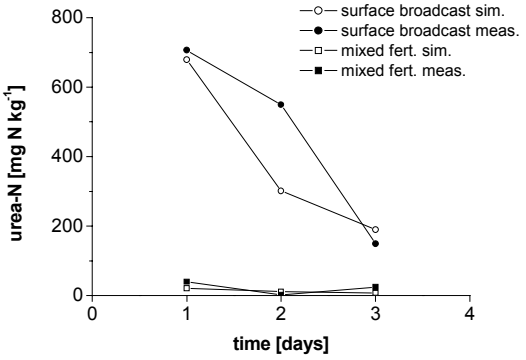


Fig.53 c: simulated and measured urea contents at the soil surface (0 – 3 mm), surface broadcast treatment and fertilization followed by irrigation

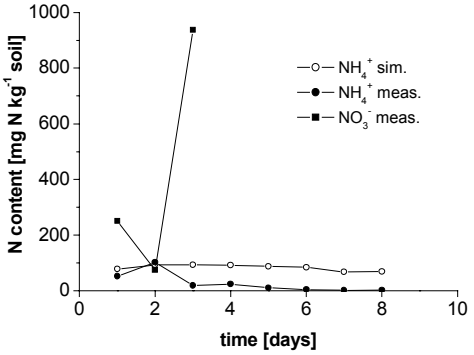


Fig.53 d: simulated NH_4^+- and measured NH_4^+- and NO_3^-- contents (0 - 3mm), surface broadcast

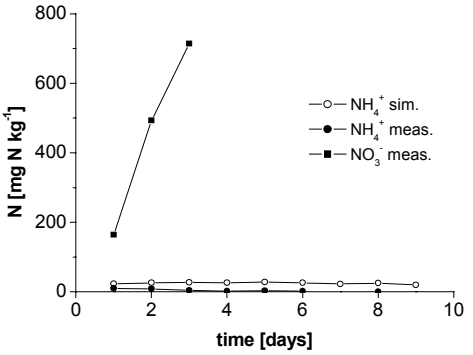


Fig.53 e: simulated NH_4^+- and measured NH_4^+- and NO_3^-- contents (0 - 3mm), fert. foll. by irrigation

Fig. 53 (a-e): Simulated and measured mineral N- and water contents and soil pH in surface soil (0 – 3 mm) samples, 1st maize experiment

Similar holds true for the comparison of simulated and measured ammonia losses for the treatment fertilization followed by irrigation (Fig.52). The simulation was carried out applying f_g2, high pH buffer capacity, and temperature and moisture data at 10 minutes intervals. Apart from the very beginning of the experiment the shape of simulated and measured ammonia loss curves is quite similar. Total simulated and measured ammonia losses at the end of the experiment were both considerably smaller than those determined for the surface broadcast treatment. However, simulated ammonia losses were about 5 % of urea-N applied smaller than those measured in the field although the simulated losses should theoretically be higher than the measured values. A possible reason can be found at the beginning of the curve where a kind of off-set in the measured ammonia losses can be observed. This can be explained by the intensive volatilisation of ammonia from dissolved and hydrolysed urea in stagnating water on the field after irrigation. In this treatment urea was placed on the soil surface and afterwards washed into the soil by means of irrigation water. But irrigation water did not infiltrate in the soil at once. It took about 1 – 2 hours before no stagnating water was left on the field. Weather conditions being favourable for ammonia volatilisation (mean soil temperature 27.5 °C) , this resulted in comparatively high initial ammonia losses from ammonium dissolved in the water. The largest proportion of ammonium, however, was washed into deeper layers of the soil leading to a reduced ammonia loss as compared to the surface broadcast treatment. Similar to the discussion of the surface broadcast treatment, the model does not include ammonia volatilisation from an ammoniacal solution over the soil surface and could, therefore, not reflect all ammonia losses occurring at that time interval. Except for this underestimation of ammonia fluxes at the beginning of the experiment, the model was in good agreement with the losses measured in situ.

The discussion of the curves above is underpinned by the comparison of simulated and measured surface soil characteristics (pH, urea-, NH_4^+-, NO_3^-- contents in 0 – 3 mm soil). Fig. 53 a – e shows the results for the fertilization followed by irrigation and surface broadcast treatments. The pH-values were simulated with satisfying results for both treatments (Fig. 53 a + b). In both cases simulated and measured data were about the same magnitude and courses of the curves were similar with regard to the overall trend of the pH (decline of pH values after the first day). As the model could not account for the higher ammonia losses in the surface broadcast treatment at the beginning of the experiment causing a high release of H^+ in the course of NH_3- volatilisation, simulated pH values ought to be higher than those measured in the field. As was discussed above, theoretically, the same should hold true for the mixed fertilization treatment but to a lesser extent. But pH values were slightly underestimated by the model for the mixed treatment. The differences between measured and simulated pH values, however, were smaller in this case than for the surface broadcast treatment and could be explained by sampling and measurement error and inaccuracy in the determination of the pH-buffer capacity.

Surface soil urea contents were only determined for the first three days following urea application, assuming that urea would quickly be hydrolysed after fertilisation. Similar as for the pH values, measured and simulated surface urea contents showed good agreement (Fig. 53 c). For both treatments the order of magnitude and the curve of the urea changes were well reflected in the simulated data. Therefore, the determination of the fitted kinetics for urease activity proved to be valid for the soils in Fengqiu. In the surface broadcast treatment, only one major discrepancy could be observed, for the second day of the experiment. The measured urea content was considerably higher than the simulated value. Besides a possible sampling or measurement error, this could be also explained by the intensive evaporation of water leading to a mass flux of urea back to the soil surface which was not considered in the model.

The most pronounced discrepancies between measured and simulated surface soil characteristics could be stated with regard to soil ammoniacal N (Fig. 53 d + e). Due to non-inclusion of the process of nitrification in the model, the simulation runs calculated higher ammoniacal N contents than those measured in the field for both treatments. Nevertheless, simulated and measured contents were still of the same order of magnitude and showed even good agreement in the fertilization followed by irrigation treatment. Only measured NO_3^--values for the first three days were included in the graph because strong dilution of the samples during the measurements with the auto-analyser led to an overestimation of the ammonia concentrations in the samples taken after the third day. The data show that nitrification in Fengqiu soils occurred at a very high rate. Higher ammonium concentrations in the simulated soil resulted in higher calculated ammonia losses at later stages of the experiment than observed in the field (Figure 52). It is an inherent feature of the model that ammonia fluxes are not decreased by ammonium transformations in soil but solely by the reduction in soil pH at the soil surface and reduced ammonium concentrations due to volatilisation of ammonia.

5.4.2.2 Second maize experiment (July 1998, 200 kg N ha^{-1})

Fig. 54 shows the results of one simulation run and the measurement results (SSM method) of the second maize experiment surface broadcast treatment. The incorporation treatment (deep point placement) was not included in the simulations. The weather conditions at the beginning of the experiment were more extreme than in the maize experiment (mean soil temperature during the first days 31.5 °C). As a result, only one simulation approach ran stable. In particular when surface soil water contents at 10 minutes intervals and low buffer capacity were chosen, the simulations broke off. A simulation approach applying time-averaged surface (0-3 mm) water contents over the duration of the experiment and f_g2 as soil gaseous diffusion impedance factor gave the best results. Similar as for the

same treatment in the first maize experiment, the courses of simulated and measured ammonia losses were quite different. This discrepancy can be explained in the same way as for the 1st maize experiment surface broadcast treatment. The main difference between the two experiments lies in the fact that ammonia losses related to evaporation of irrigation water were more pronounced in the second experiment because temperatures were higher as well as the fertilization rate. The sensitivity analysis by Rachhpal-Singh and Nye (1986c) and experimental results (see Chapter 2.2) showed that there is a positive relationship between the amount of fertilser-N applied and relative ammonia loss (% of fertiliser-N applied). Therefore, simulated ammonia losses were always lower than those measured in the field even at the end of the experimental period. While about 90 % of the ammonia losses occurred in the first two days during field measurement, the model calculated almost constant ammonia fluxes throughout most of the experiment and slowly decreasing at the very end of the simulation. Regarding surface soil characteristics similar relationships as for the maize experiment, e.g. simulated surface soil pH was lower than that measured in the field, could be found. This shall not be discussed in detail here.

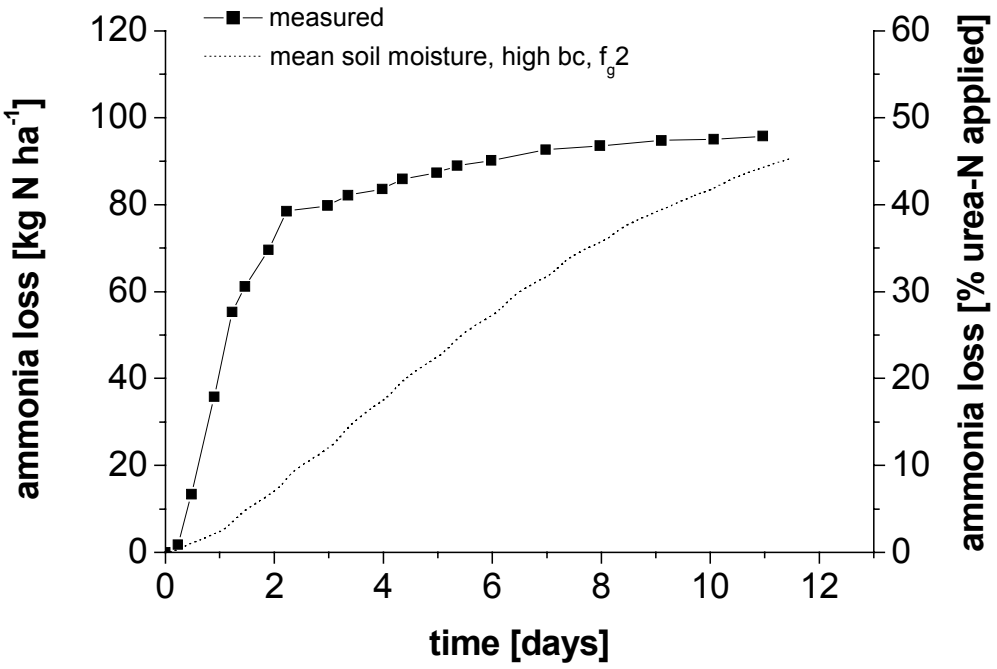


Fig. 54: 2nd maize experiment (200 kg N ha^{-1}), measured and simulated cumulative ammonia losses for surface broadcast treatment (bc = buffer capacity)

5.4.2.3 First wheat experiment (October 1998, 120 kg N ha^{-1})

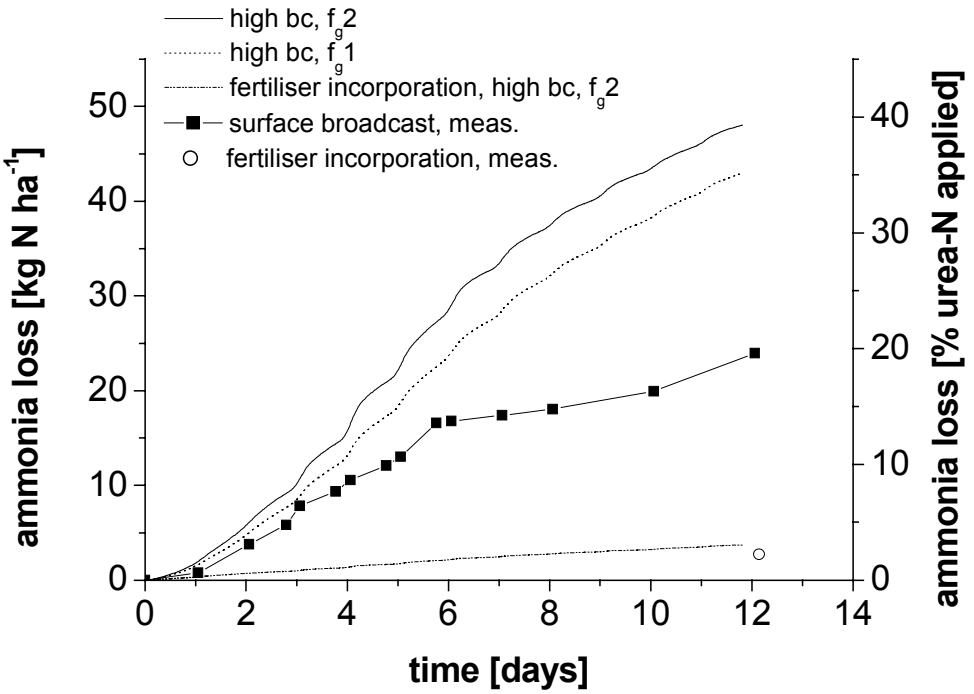


Fig. 55: 1st wheat experiment (120 kg N ha^{-1}), measured and simulated cumulative ammonia losses for surface broadcast treatment and mixed incorporation treatment using different sets of parameters (bc = buffer capacity)

Fig. 55 gives the results of measured and calculated cumulative ammonia losses for the first wheat experiment (October 1998), surface broadcast and mixed fertilization treatment. As shown in Chapter 4.1.2.2 ammonia loss measurements using the SSM yielded only discrete (discontinuous) ammonia fluxes and no continuous curve for the mixed fertilization treatments in both wheat experiments. For this reason only the cumulative loss determined at the end of the experiment is presented in the graph for this treatment. Because of the low soil moisture content at the soil surface and the resulting instability of the model, water contents determined for the whole plough layer (0 – 0.2 m) were used in the simulation runs of both surface broadcast and mixed incorporation treatment.

The comparison of simulated and measured ammonia losses for the surface broadcast treatment is in strong contrast to the differences discussed so far for the two maize experiments. While simulated and measured values agree quite well for the time interval up to the 5th day of the experiment, the gap between measured and simulated data widened steadily thereafter simulated losses being distinctly higher than measured ones. The kinetics of ammonia loss is well described for the first time interval clearly depicting the day/night oscillation of ammonia fluxes which are also indicated in the curve of

the measured values. In the time following measured values reached a plateau with only slightly increasing cumulative ammonia losses towards the end of the measurements. In contrast simulated ammonia losses are further increasing after the 6th day.

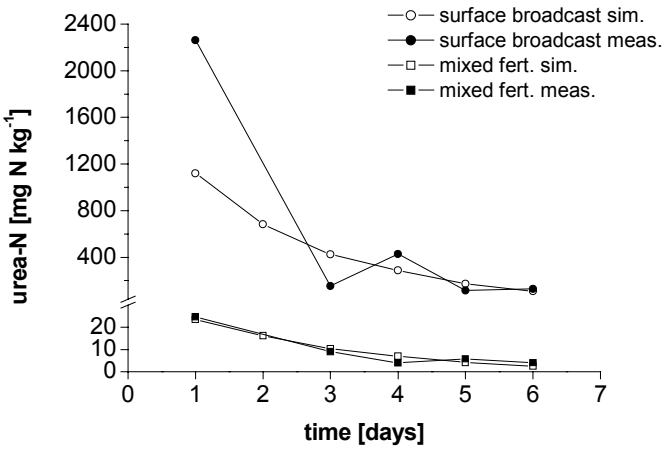


Fig. 56: Simulated and measured urea contents at the soil surface (0 – 3 mm), first wheat experiment, surface broadcast treatment and mixed incorporation

This discrepancy could be explained by the omission of the influence of soil moisture on urea hydrolysis in the model. Fig. 56 depicts simulated and measured urea contents in the surface soil layer (0 – 3 mm) for surface broadcast and mixed fertilization treatment, respectively. While the values for the mixed incorporation treatments agree almost perfectly, major discrepancies can be observed for the surface broadcast treatment. In particular, at the beginning of the experiment simulated values thoroughly underestimated urea contents, suggesting that the model overestimated the rates of urea hydrolysis. With a gravimetric water content of only 3% at the beginning of the experiment most of the urea was not hydrolysed. This also implies problems for soil sampling because urea was not evenly distributed on the soil surface. On the second day 3.3 mm of rainfall occurred which resulted in the dissolution of urea granules and a better contact of urea with the soil. It can be seen from Fig. 56 that there was still some urea not yet hydrolysed after the 6th day of the experiment. In addition, ammonium and urea dissolved in soil solution were not transported deeper soil layers due to lack of continuity of water filled pore space. As a result, low measured ammonia losses (SSM) can most probably be explained by the low soil moisture content. As mentioned the simulation runs were carried out using water contents in the 0 – 0.2 m soil layer. Future urease activity determination should include kinetics considering the influence of soil moisture on urease activity. This kinetics could also contain a lower limit below which no urea hydrolysis takes place. As for the maize experiments the overestimation of ammonia losses by the simulations is a general feature of the model as it does not include several

processes of N-transformation and –transport. But in contrast to former two maize experiments, the kinetics of the simulated ammonia losses did generally correspond to that of the measured ammonia loss process during the first six days. The initial ammonia losses calculated by the modified model corresponded to actual ammonia losses.

The difference between the two simulations for the surface broadcast treatment resulted from the two approaches for the calculation of the soil gaseous diffusion impedance factor (f_g1 and f_g2), respectively. Although f_g1-values were about 5 times smaller than those calculated as f_g2, this had no effect on the general shape of the curve and resulted in approximately 10% lower cumulative ammonia losses than using f_g2. It is hard to decide which approach is closer to the 'true' ammonia losses. This could only be determined in laboratory experiments with inhibited nitrification under controlled conditions.

The simulation of the mixed fertilization treatment using high pH buffer capacity and f_g2 yielded satisfying result with regard to both cumulative ammonia loss at the end of the experiment (Fig. 55) and surface soil urea content (Fig. 56). This supports the hypothesis formulated above that the modified model can calculate actual ammonia losses realised under field conditions if actual temperature and soil moisture condition are taken into account. The model can, thus be used to estimate the magnitude of ammonia losses under different meteorological conditions and fertilizer application methods. Relative ammonia losses were smaller in winter wheat in October (35% of urea N applied) than from maize in summer season (> 40% of urea n applied). The reduction of ammonia losses by mixed fertilization was also well reflected by the model calculations.

5.4.2.4 Second wheat experiment (March 1999, 100 kg N ha^{-1})

The conclusions given above are supported by measurement and simulation results for the second wheat experiment (Fig. 57). Both, the measured and simulated cumulative ammonia losses in early spring were the lowest of all treatments compared. This exemplifies the major impact of temperatures on ammonia losses. The basic pattern of the volatilisation process is reflected in the simulated losses although the measured curve has a much slower onset than the simulated course of ammonia losses. After day 6 a stronger increase in measured ammonia losses than in simulated losses was found. Very high wind speeds prevailing between day 6 and 8 (see appendix) could account for this discrepancy as the SSM measurements reflect the product of concentration and wind speed while the model considers soil processes only. At day 8 the simulated as well as the measured curves show an inflection which is more pronounced for the measured values. This reduction in ammonia fluxes, can be explained by a pronounced drop in temperatures which even fell below 0 °C at night time and early morning. The more

pronounced flattening out of the measured losses compared to the simulated ones could be accounted for by snowfall accompanying the temperature drop and covering the soil surface in the morning hours the days following the 8th day, respectively. In addition to the impact of dramatically decreased temperatures the snow cover very effectively reduced ammonia losses from soil. The effect of snow cover on ammonia losses was also not considered in the model. Apart from the inaccuracy of the SSM in case of low ammonia losses, this might also account for the more pronounced overestimation of ammonia losses from the mixed fertilization treatment as compared to the first wheat experiment (Fig. 55). Simulated cumulative ammonia losses from mixed fertilization were significantly smaller than from surface broadcast treatment which agrees well with the measurement results. Moreover, the consideration of snow cover in an ammonia volatilisation model is not a very important feature because ammonia losses are usually not determined under such weather conditions.

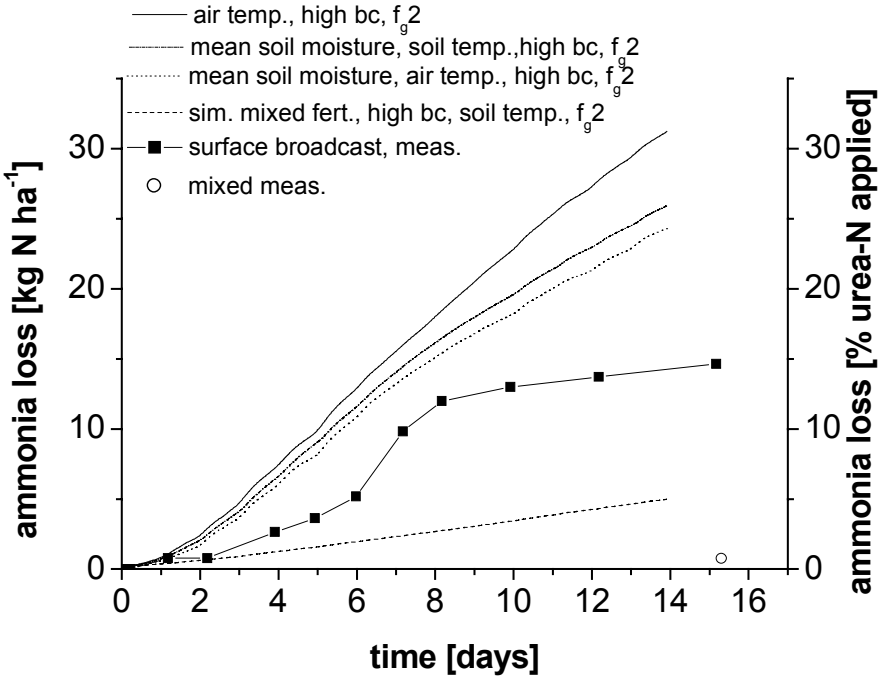


Fig.57: 2nd wheat experiment (100 kg N ha^{-1}), measured and simulated cumulative ammonia losses for surface broadcast treatment and fertilization followed by irrigation (mixed) treatment using different sets of parameters (bc = buffer capacity)

The simulation approaches presented in Fig. 57 show the effect of air and soil temperature and the influence of average and actual soil moisture contents on the simulation results. In this experiment a large discrepancy between soil and air temperatures was observed, in particular after day 8. While

above-ground temperatures (1 m height) dropped below 0°C, soil temperatures (-0.05 m depth) were always higher than 0°C. However, soil temperature at the very surface could be assumed to be lower or to be at least at the same level as air temperature as the snow cover lasted only a few hours a day. For this reason air temperature was included in the simulation runs. The application of time averaged surface soil moisture contents did effectively reduce cumulative ammonia losses calculated by the model. The difference between ammonia losses calculated using air and soil temperatures was not very pronounced. Thus, the difference in both temperatures did not seem to be very important as long as both temperatures were at a very low level. The influence of soil moisture content, however, was stronger. Almost in all experiments simulated mean surface soil water contents resulted in lower ammonia losses than actual contents. This can be mainly explained by the strong increase of f_g2 values as a result of even minor decreases in soil moisture. The f_g2-values have a strong effect on gaseous diffusion which is the most important transfer process for ammonia loss considered in the model.

5.4.2.5 Third maize experiment (July 1999, 150 kg N ha^{-1})

Fig. 58 presents the results for the 3rd maize experiment (July 1999). As the incorporated fertilization treatment was carried out as deep point placement, it was not included in the simulations. The simulations encountered similar problems as in the 1st wheat experiment surface broadcast treatment. Surface soil was drying considerably in the course of the experiment. At about the 8th day a surface moisture content was reached which caused a break-off of the simulation. High pH buffer capacity and f_g2 were chosen for the simulation runs because they yielded the most stable and reliable simulation results similar to the simulations of the other experiments. For this reason average surface moisture contents were also used for the simulation. The two simulated curves (Fig. 58) show only a small discrepancy until the break-off of the simulation using surface soil moistures taken at daily intervals.

Because of abundant precipitation prior to the experiment, irrigation was omitted in this experiment. Although meteorological conditions during the experiment were similar (mean air temperature 26 °C) to those in the other two maize experiments (27 °C), the course of ammonia fluxes was quite different from those determined for the 1998 maize experiments. However, temperatures at the beginning of the experiment were higher in the first two experiments than in the third experiment, in particular in the second experiment (see Fig. 18 b). Because of the flood irrigation prior to the first two maize experiment initial surface water contents (0 – 3 mm) were also higher in these experiments (20 and 22%) than in the third experiment (15%). This corroborates the hypothesis at the beginning of this chapter that high evaporation rates due to irrigation under high temperature conditions were decisive for

the shift of the dominant pathway of ammonia loss from liquid and gaseous diffusion to the mass flux of urea, soil base and ammonia to the soil surface by the intensive water flux in the same direction

The latter processes are less important for the third experiment because no irrigation was applied leading to very high water contents. As a result, the general kinetics of the simulated losses agreed well with measured losses because diffusive fluxes seemed to be the dominant pathway of ammonia loss in this experiment. In this case, similar to the winter wheat experiments, ammonia losses were overestimated by the simulations after day 3 becoming more pronounced towards the second half of the experiment. This can be mainly explained by the omission of the simulation of nitrification and plant uptake in the model. Fig. 59 shows the development of simulated and measured mineral N contents in the surface soil layer (0 – 3 mm).

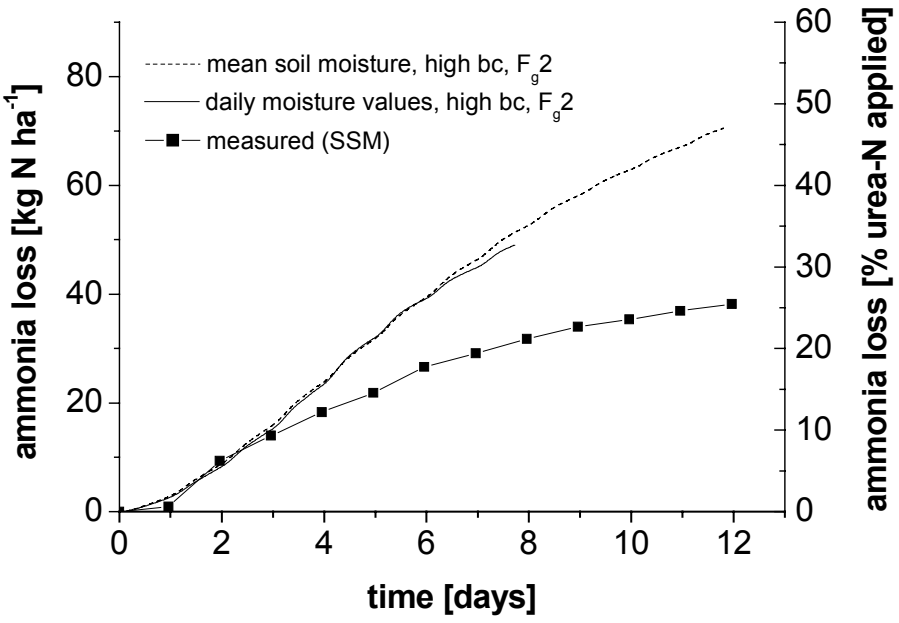


Fig.58: Third maize experiment (150 kg N ha^{-1}), measured and simulated cumulative ammonia losses for surface broadcast treatment using different sets of parameters (bc = buffer capacity)

In the beginning of the experiment there was a striking discrepancy between measured and simulated ammonium contents, simulated values being markedly higher than measured contents. This was due to rainfall (4.6 mm) at the first day of the experiment washing dissolved urea and ammonia into deeper layers of the soil. However, afterwards urea ammonium were transported to the soil surface by evaporating water exceeding simulated ammonium contents. Thereafter, simulated and measured ammonium contents were of about the same magnitude entailing very similar ammonia losses. At the same time, ammonium was increasingly nitrified lowering measured ammonium contents below the simulated values in the second half of the experiment. After the third day of the experiment NO_3^- - contents exceeded ammonium contents. Therefore, the model simulations yielded higher ammonia losses towards the end of the experiment than those determined in the field. In addition, comparatively high surface soil pH-values simulated by the model might have contributed to the overestimation of ammonia losses. However, the calibration of the pH-electrode encountered problems in this experiment (Cai, pers. communication) so that simulated and measured pH values cannot be compared in this case. Moreover, drying of the surface soil towards the end of the experiment might have also contributed to decreasing volatilisation rates which was not accounted for in the simulations.

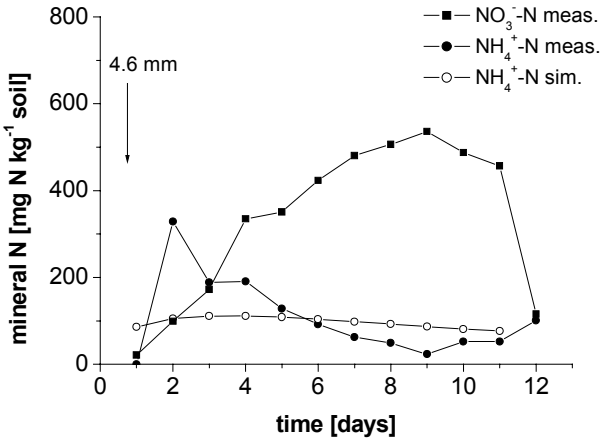


Fig. 59: Simulated NH_4^+- and measured NH_4^+- and NO_3^-- contents (0 - 3mm), 3rd maize experiment, surface broadcast treatment

5.4.3 Discussion of the simulation approach

The curves of cumulative ammonia losses could not be modelled with high accuracy by the model by Rachhpal-Singh and Nye (1986a) modified for the inclusion of natural temperature- and soil moisture changes on the simulation of ammonia losses. For three of the 5 experiments (both winter wheat experiments, third maize experiment) the general kinetics of the ammonia volatilisation process was

reflected in the simulated curves at least for part of the experimental period. Nevertheless, ammonia losses were generally overestimated by the model, probably mainly due to the omission of plant uptake and nitrification of ammonium in the model. Drying of the soil surface and snow cover led to additional deviations of the measured ammonia losses from the general simulated ammonia loss pattern in the first and second wheat experiment, respectively.

The most pronounced discrepancies between measured and simulated curves occurred in the first two maize experiments with surface broadcast treatment. Here, the overall kinetics of the ammonia volatilisation process was missed by the modelling approach. Ammonia losses measured in the field were dominated by high evaporation of water from soil following irrigation connected to high ambient temperatures. While more than 90% of measured ammonia losses occurred during the first 2 days of the experiments, the cumulative ammonia loss curve displaying almost no sigmoidality, the simulated curves showed much slower ammonia losses and a sigmoidal shape. The same differences between the curves were found in the first maize experiment with fertilization followed by irrigation.

In most cases the model simulated ammonia losses with the similar kinetics as the measured losses but missed the experimentally determined curves in several respects. This supports the hypothesis that ammonium transport by gaseous and aqueous diffusion, which are the transfer processes of ammonia included in the model, are the dominant transport mechanisms with regard to ammonia loss following fertilization of urea under most of the conditions observed *in situ*. In particular situations e.g., high water saturation of the soil and high temperatures, these processes can be dominated by ammonia transported via massflux connected to strong soil water evaporation.

The importance of considering ambient wind speeds in the calculation of ammonia losses following urea fertilisation can be discussed on the basis of the considerations given above. Although the calculation of the influence of ambient wind speed on ammonia losses could not be successfully included in the model, this did not have major impacts on the comparison of measured and simulated results. Only in one case, second wheat experiment surface broadcast treatment, the influence of high wind speeds on the measured ammonia loss curve could be detected. This is also in line with the sensitivity analysis by Rachhpal-Singh and Nye (1986 c) which revealed that changes in the transfer coefficient for ammonia (K_a) had very limited effect on calculated ammonia losses above a threshold value. In the modelling approach by Hengnirun et al. (1999) the effect of wind speed on ammonia losses was also limited to situations with very low wind speeds (wind speed < 0.016 m s^{-1}). Therefore, complicated approaches used in other ammonia loss models by Van der Molen et al. (1990), Génermont and Cellier (1997) or Sommer and Olesen (2000), which are often based on empirical relationships in particular with regard to plant cover, do not seem to be essential for a reasonable estimate of ammonia

losses following urea application. Nevertheless, the mechanisms might be slightly different following surface application of slurry or animal manure which were in focus of the models cited above.

The overestimation of ammonia losses could have also occurred because of the application of an improper parameter-function for the calculation of the gaseous diffusion impedance factor (f_g) which had a major influence on overall ammonia losses. The approach using f_g1 (Millington and Quirk 1961, Eq. 30) entailed lower ammonia losses than the approach using a f_g2 value (Kirk and Nye 1991, Eq. 31). As both formulas are based on empirical studies they are only valid for are limited range of situations. Nevertheless, the application of the formulas gave reasonable results, and in most instances it would not be worth the effort to determine a formula for the soil investigated.

The urease activity approach (combination of simplified Michaelis-Menten and Arrhenius function) fitted to the measured laboratory data proved to be valid for the simulation of field data. Urease activity was a decisive parameter for the calculation of ammonia losses as was also shown by Rachhpal-Singh and Nye (1986c) and should be determined explicitly for the respective soil under investigation. It was a shortcoming of this approach that it did not take into account the influence of soil moisture content on urea hydrolysis. Future analysis of urease activity should, thus, include this factor. Such a model could contain a threshold value below which no urea hydrolysis occurs as was observed in field measurements.

The pH module included in the model in combination with pH buffer capacities determined in laboratory batch experiments gave satisfactory estimates for most experiments. It was the higher pH-buffer capacity, however, which resulted in more accurate and stable simulation results. The lower pH buffer capacity which was determined for the particular range of pH values (8 – 10) observed in Fengqiu fields gave a more pronounced overestimation of the results and an unstable calculation of surface soil pH values. The experimental approach for the derivation of pH buffer capacities was based on the assumption of soil base and soil acid equilibrium after 72 hours. Most empirical pH systems, however, are not in equilibrium state. Moreover, investigated soil samples were over-saturated with base and acid solution. Thus, other experimental approaches, e.g. shorter incubation time and reduced saturation with solution, should be tested in future modelling. The good performance of the pH module can be contrasted to the difficulties of pH modelling related to ammonia volatilisation from surface applied animal slurry by Génermont and Cellier (1997) or Sommer and Olesen (2000). The pH systems in pure soil seem to be, thus, quite different from those established in slurry/soil mixtures.

In general, the approach chosen in this study could account for the effect of temperature (growing season) on the overall ammonia losses at the end of the experiments. Thus, temperature appeared to be a crucial factor determining the height of overall ammonia losses and the ammonia volatilisation rate. Lower ammonia losses due to incorporation of urea into the soil were also calculated in good agreement

with measured losses. The modified model can, thus, help to estimate the effect of soil characteristics, temperature and moisture conditions and management practices on ammonia losses following urea application. Average plant uptake and nitrification rates could be applied for a correction of overestimated losses.

To sum up, three major modifications of the model would seem necessary for a more appropriate and accurate modelling of ammonia losses as those obtained in this study. A more detailed description of soil water dynamics, in particular of evaporative processes, is crucial for a valid description of the kinetics of ammonia losses. However, it might be doubtful whether a purely deterministic approach would be feasible on the time scale necessary for a detailed calculation of ammonia losses. Secondly, the nitrification of ammonium and plant uptake should be included in the model. Simplified approaches might be sufficient for satisfactory ammonia loss estimates. Thirdly, a more refined approach for the calculation of urease activity, in particular the consideration of soil moisture on urea hydrolysis, should be included. Additional modifications could consider a more empirically based description of diffusion impedance factors and detailed investigation of non-equilibrium pH buffer capacity. The influence of ambient temperatures and at least simplified soil moisture contents on ammonia losses are crucial features of future ammonia loss modelling.

5.4.4 Summary of the simulation results

Simulation of the field experiments using the modified model by Rachhpal-Singh and Nye, developed for the simulation of ammonia losses and related soil processes in laboratory chamber experiments, encountered several problems. Although the influence of temperature and soil moisture were included as new routines in the model, the dominating pattern of ammonia loss could not be reconstructed by the model under several soil and environmental conditions. In particular soil irrigation connected with high ambient temperatures resulting in high evaporation rates in summer caused ammonia loss patterns which could not be matched by simulated losses. Moreover, pronounced drying of the surface soil in autumn and snow-cover in spring entailed major deviations of simulated values from measured ammonia losses. Though sometimes for only part of the experimental period, the model simulations could well account for the order of magnitude of ammonia losses, in particular with regard to the influence of fertilizer application method (surface broadcast/mixed fertilization) and the influence of temperatures (effect of season). In general, urease activity and soil pH were described satisfactorily by the model. As plant uptake and nitrification of ammonium are not included in the model, simulated ammonia losses exceeded measured values in most of the experiments. The model includes a much less complex description of the ammonia loss process than what was observed under field conditions. Nevertheless, the comparison of simulated and measured ammonia loss patterns proved that diffusive

ammonia loss processes, on which the calculation by the model are based, were an important pathway of ammonia loss in many situations. Keeping in mind its limitations, the modified model could be used to estimate ammonia losses under different temperature regimes and fertilizer application techniques.

6. Conclusions

6.1 Introduction of the DTM as a simple method for determination of ammonia losses

The DTM is a simplified chamber method for the measurement of ammonia volatilisation which has no demanding requirements with regard to gas sampling and analysis. The DTM was designed to avoid the disturbance of environmental conditions by multiple short-term measurements. Systematic microplot experiments showed that the DTM yielded reproducible measurement results. The general shape of the ammonia loss curves determined by DTM and SSM (micrometeorological mass balance method) agreed very well for most of the experiments. The qualitative and relative differences between cumulative ammonia losses following various fertilization methods, fertilization rates and growing seasons were well reflected in DTM results – except for the absolute amount of ammonia losses. The low air exchange rate inside the measurement cups induced by simple hand pumps resulted in an underestimation of ammonia losses by about one order of magnitude. A significant linear relationship was observed between ammonia partial pressure and ammonia fluxes determined by the DTM. It can be said that the DTM with hand pump reflects ammonia volatilisation based on ammonia partial pressure at the soil surface without appropriately considering the influence of atmospheric exchange on the ammonia volatilisation process. The comparison of the influence of different cup sizes and air exchange rates in the cups revealed that only the variation in air exchange rates inside the cups resulted in significantly different ammonia losses. Air exchange rates higher than about 40 volumes minute^{-1} did not lead to a further significant increase in measured ammonia losses. Ammonia losses measured during the field experiments were partly under- and partly overestimated using different constant exchange rates in the DTM cups but exhibited the same order of magnitude as the SSM losses. This points out the difficulty of using constant flow rates in chamber techniques, which would theoretically have to be frequently adapted to actual wind conditions.

The calibration of the DTM and adaptation of the DTM measurements to ambient conditions were carried out by an indirect approach. Ambient conditions were not directly reproduced by modifying the DTM measurement set-up but rather taken into account by including them in the calculations of corrected DTM ammonia losses. A calibration approach based on the individual fluxes measured by the SSM, time weighted mean meteorological data and time weighted average fluxes of the DTM calculated on the basis of SSM sampling intervals ('vegetation period' approach) yielded satisfactory results quantified by an overall modelling efficiency (Loage and Green 1991) c^2 of 0.86. Two calibration formulas were calculated by multiple linear regressions for each growing season (crop), respectively. Applying the formulas of the 'vegetation period' approach resulted in an absolute estimate

error of cumulative ammonia losses of ± 6.5 kg N ha^{-1} or 17 % of the ammonia losses determined by the SSM. The 'vegetation period' approach was validated by the successful estimation of ammonia fluxes (mixed fertilization treatments) not included in the calculation of the calibration formula. A second calibration approach was based on total cumulative ammonia losses determined by both methods and average micrometeorological variables calculated for each experimental period. The multiple linear regression yielded a calibration formula with high coefficient of determination (r^2 0.95) based on cumulative DTM ammonia losses and mean air temperature. The indirect approach for the calibration of the DTM proved to be feasible and more elegant than a direct modification of the method.

The Draeger-Tube method has been validated as a simple measurement tool for the quantitative estimation of ammonia losses under field conditions. The DTM is very useful for the determination of ammonia losses *in situ* under all kind of experimental facilities and conditions, in particular for low scale comparison of different fertilisation approaches connected to varying environmental conditions with replications.

6.2 Simulation of the ammonia volatilisation process

The curves of cumulative ammonia losses measured by the SSM could not be modelled with high accuracy by the deterministic model by Rachhpal-Singh and Nye modified for the simulation of ammonia losses in the field. For three of the 5 experiments (both winter wheat experiments, third maize experiment) the general kinetics of the ammonia volatilisation process was reflected in the simulated curves at least for part of the experimental period. Ammonia losses were generally overestimated by the model, probably mainly due to the omission of plant uptake and nitrification of ammonium in the model. Drying of the soil surface and snow cover led to additional deviations of the measured ammonia losses from the general simulated ammonia loss pattern. Ammonium transport by gaseous and aqueous diffusion, which are the transfer processes of ammonia included in the model, can account for ammonia loss following fertilization of urea under many of the conditions observed *in situ*. However, in particular situations e.g., high water saturation of the soil and high temperatures, these processes can be dominated by ammonia transported via massflux due to strong soil water evaporation. In this case simulated ammonia loss patterns showed a strong deviation from measured ammonia loss kinetics. A more detailed description of soil water dynamics, in particular of evaporative processes, is crucial for a valid description of the kinetics of ammonia losses.

The urease activity approach (combination of simplified Michaelis-Menten and Arrhenius function) fitted to the measured laboratory data proved to be valid for the simulation of field data. Future analysis

of urease activity should consider the effect of soil moisture contents on urease activity. The pH module included in the model in combination with pH buffer capacities determined in laboratory batch experiments gave satisfactory estimates for most experiments. Other experimental approaches, e.g. shorter incubation time and reduced saturation with solution, should be tested in future modelling.

In general, the approach chosen in this study could account for the effect of temperature (growing season) on the overall ammonia losses at the end of the experiments. Lower ammonia losses due to incorporation of urea into the soil were also calculated in good agreement with measured losses. Average plant uptake and nitrification rates could be applied for a correction of overestimated losses.

6.3 Consequences for N fertilization strategies

The prevalent fertilizer application methods (fertilisation followed by irrigation, mixed incorporation and deep point placement) applied by the farmers did significantly reduce ammonia losses. Ammonia losses from fertilizer incorporation treatments (deep point placement and fertilisation followed by irrigation) in summer growing season were still considerably high, ranging between 10.8 and 18 % of urea-N applied. Higher ammonia losses observed in maize growing seasons were connected to intensive flood irrigation prior to fertilization and high ambient temperatures resulting in intensive evaporation of soil water. Optimised irrigation practices would be beneficial for both reduction of ground water depletion and limiting ammonia volatilisation losses. The application of plant demand oriented irrigation techniques as drip irrigation would be a very effective measure for the reduction of ammonia losses in summer growing season. Research on improved and plant demand oriented irrigation techniques should be intensified with the aim of identifying techniques which are applicable to the conditions of average Chinese villages. A better control of the amount of irrigation applied by flood irrigation would also result in an improved fertiliser efficiency. A careful increase of water prices could induce a more effective application of irrigation water.

^{15}N experiments and analysis of the mineral N dynamics revealed that there was an annual N surplus of at least 100 kg N ha^{-1}. Ammonia volatilisation losses could be thus diminished by an overall reduction of application rates and a better timing of urea fertilization. Some ^{15}N and mineral N distribution profiles suggested that leaching of nitrate was also a pathway of fertilizer loss in the region. Improved irrigation techniques would be helpful to decrease these losses, too. The mineralisation of soil born organic N should be included in the calculation of mineral N fertilization rates. It was shown in other experiments in northern China that this can help to reduce mineral N surpluses to a considerable extent without concomitant reductions in grain yield.

7. Summary

A simple method for the measurement of ammonia volatilisation in the field (Draeger Tube Method DTM, (Roelcke 1994; Roelcke et al. 2002 a)), a special type of dynamic chamber method, was calibrated by comparison with micrometeorological standard methods. Two set-ups of the DTM were tested including air exchange with hand pump and electric vacuum pump. Micrometeorological methods comprised the methods by Leuning et al. (1985) and Sherlock (1989) (Space Shuttle method, SSM) and Schjoerring et al. (1992) (Ammonia Tube Method, ATM), both specimen of integrated horizontal flux methods (mass balance method) applying passive flux samplers. SSM measurement results were particularly applied for the calibration of the DTM (hand pump). Results were checked by the indirect ^{15}N mass balance approach.

Experiments were carried out close to the Yellow River in Fengqiu Agroecological Experimental Station, Henan province, P.R. China. This location was selected due to the predominant application of ammonium based N fertilisers in China (urea, ammonia bicarbonate) and because of semi-humid climate and high pH (8.5 (H_2O)) soils providing favourable conditions for high ammonia volatilisation losses. Five field experiments, 3 in maize and 2 in winter wheat, were carried out in the years 1998-1999, each with a duration of 2-3 weeks. Ammonia volatilisation was measured synchronically by the different methods following the application of urea. Each experiment included two treatments regarding urea application method, incorporation ('farmers' methods': fertilisation followed by irrigation, mixed incorporation and deep point placement) and surface broadcasting of urea fertiliser. The experimental set-up consisted of two circular plots (500 m²) for application of the micrometeorological methods surrounded by unfertilised fields. Each of the circles contained two microplots (4 m^2) for synchronic DTM ammonia volatilisation measurements and an on-site meteorological station (wind speeds, temperatures), respectively. In addition to ammonia loss measurements, mineral N-, urea- and soil moisture contents and pH in soil cores and surface soil samples (0 – 3 mm) were analysed.
The influence of covered surface area and air exchange rates in the DTM measurement chambers ('cups') on measured ammonia losses was tested by systematic microplot experiments employing the DTM with hand pump and electric pump including different numbers of cups, cup sizes and air exchange rates inside the cups.

Ammonia volatilisation determined by the DTM and the SSM showed very similar ammonia loss patterns in all experiments and for all treatments. The qualitative differences in ammonia losses between urea fertilisation methods, fertilisation rates and growing seasons were well reflected in the results of both methods. This was also proven by fitting a sigmoidal logistic function (Demeyer et al.

1995) to the cumulative ammonia loss curves determined by SSM and DTM, respectively. However, DTM (hand pump) underestimated ammonia losses measured by the SSM by about one order of magnitude. The discrepancy between ammonia fluxes determined by SSM and DTM depended mainly on ambient temperature in maize growing season or on ambient temperature and wind speed in wheat growing season (effect of season). The DTM was calibrated by an indirect approach calculating corrected ammonia fluxes by a calibration formula based on time weighted average DTM ammonia measurements, temperatures and wind speeds related to SSM ammonia sampling intervals. An approach applying two different calibration formulas for maize growing season and wheat growing season, respectively, yielded satisfactory results (modelling efficiency c² 0.86) resulting in an average estimation error for cumulative ammonia losses of 6.5 kg N ha^{-1} (absolute) and 17% (relative). A second calibration approach based on cumulative ammonia losses determined by SSM and DTM at the end of the experiments and averaged meteorological variables (r² 0.95) yielded an equally good agreement. As the former approach was based on a high number of ammonia flux measurements it is preferable to the second calibration formula which considered 9 treatments, only.

SSM and ATM measurements showed good agreement as well as major discrepancies. Consequently, one or both micrometeorological methods exhibited a considerable degree of measurement error, which according to Harper and Sharpe (1998) amounts to at least ± 15% up to 50% for micrometeorological measurements. Replicate ammonia volatilisation measurements with the DTM (hand pump) on microplots without vegetation cover yielded a mean measurement error of 20 %. Unfortunately, this renders the calibration result to an additional degree of uncertainty.

The calibration approaches were supported by comparison of ammonia fluxes measured with the DTM and the SSM with ammonia partial pressures at the soil surface. Ammonia partial pressures were calculated by equations given in Denmead et al. (1982) using total ammoniacal N contents, pH values and soil moisture contents of surface soil samples (0 - 3 mm) taken at the study sites as well as in situ soil temperatures. Regression analysis showed that the DTM ammonia fluxes agreed very well with calculated ammonia partial pressures, while there was considerable discrepancy between ammonia partial pressures and SSM ammonia fluxes. These results underlined that the DTM (hand pump) reflects the ammonia partial pressure at the soil surface and neglects the influence of ambient wind on the ammonia volatilisation processes. On the other hand, the effect of wind speed on ammonia losses was fully accounted for by the SSM which determines the product of ammonia concentration in the atmosphere and wind speed. Therefore, the discrepancy between ambient wind speeds and air exchange rates inside the DTM chambers primarily determines the differences between the ammonia fluxes obtained from both methods.

The major impact of low air exchange rates (1 Vol.min^{-1}) in the DTM chambers with hand pump on the underestimation of ammonia losses was also proven by the application of the DTM with increased air exchange rates by means of an electric vacuum pump in microplot and field experiments. Microplot experiments revealed that the air exchange rate in the cups and not their volume or the surface area covered is decisive for the determination of ammonia losses by the DTM. Successively increasing air exchange rates in the cups, an air exchange rate of 40 Vol. min^{-1} was determined as threshold value above which only minor increases in ammonia losses occur. Air exchange rates of about 20 Vol. min^{-1} applied in the field yielded cumulative ammonia losses of the same order of magnitude as those determined by the SSM. However, the measurement results showed very good agreement as well as major discrepancies depending on growing season and fertiliser application method. This points out the difficulty of using constant flow rates in chamber techniques, which would theoretically have to be frequently adapted to actual wind conditions. The problems in properly adapting air exchange rates in the cups to ambient wind conditions underlined the validity of the indirect calibration approach.

Incorporation of urea significantly reduced ammonia losses, in particular in wheat growing season. Ammonia losses ranged in between 47.9 and 0.6 % of urea N applied (SSM measurements), the highest losses occurring after surface application of 200 kg urea-N ha^{-1} to maize in July 1998, the lowest following urea fertilisation followed by irrigation in March 1999 (winter wheat, 100 kg N ha^{-1}). High soil moisture contents and high evaporation rates, high pH values and hot temperatures in maize growing season resulted in considerable ammonia losses even following incorporation of urea into the soil (10.8 - 19.9 % of urea N applied). These outcomes of the ammonia loss measurements agreed well with ^{15}N mass balance analyses which proved that ammonia volatilisation is one of the major pathways of fertiliser-N loss in the region, in particular in maize growing season. Mineral N sampling revealed very high mineral N contents in the root zone throughout the year even after harvest (about 100 kg mineral N ha^{-1}). Supported by ^{15}N measurements, mineral N results showed that fertiliser was applied in excess in the region.

Ammonia volatilisation and related soil processes were simulated applying the deterministic computer model by Rachhpal-Singh and Nye (1986 a). The model was modified by including new routines for the calculation of temperature dependencies of urease activity, ammonium dissociation constant, Henry's law constant and moisture dependency of gaseous and aqueous diffusion impedance factors. Temperatures and soil moisture contents at ten minutes intervals measured in the study sites were used in the simulation runs. Additional model parameters, ammonium adsorption isotherm, pH buffer capacity and urease activity, were determined in laboratory batch experiments.

The simulation of ammonia volatilisation losses measured in Fengqiu using the modified model encountered several problems. In wheat growing season and in the third maize growing season without irrigation prior to the fertilisation the general kinetics of simulated ammonia losses showed good agreement with measured losses (SSM). However, when irrigation was applied shortly before or after urea fertilisation in maize growing season (first and second maize experiment) characterised by high temperatures, ammonia losses were dominated by ammonium and urea transport due to convective mass flux caused by intensive water evaporation. The kinetics of these ammonia losses was not matched by simulated data, because the simulations were based on the diffusion of the N species in gaseous and aqueous phase without considering the transport by convective mass flux. In general, simulated ammonia losses were higher than those measured in the field as other pathways of the depletion of ammonium N in soil as nitrification and plant N uptake were not considered in the model. Nevertheless, the amount of ammonia losses due to different fertilisation methods and seasons was reflected in simulated ammonia losses. The approaches chosen for the calculation of soil pH and urease activity proved to be valid in the course of the simulations. Notwithstanding the discrepancies from measured data in the first two maize experiments, the simulations revealed that the diffusion in aqueous and gaseous phase was the dominant transfer process for mineral N species related to ammonia volatilisation in a high proportion of experiments and treatments. Therefore, the model should be further improved by including convective mass transfer in aqueous solution, nitrification of ammonium and plant N uptake in the calculation of ammoniacal N dynamics in the simulations.

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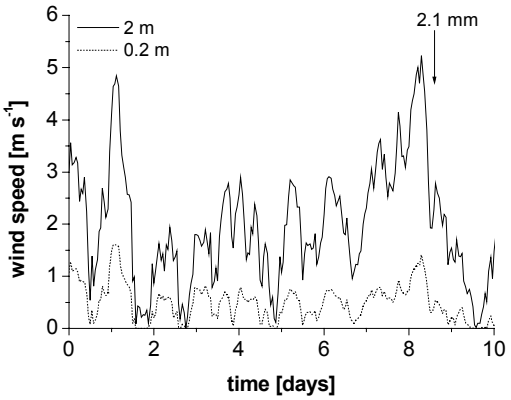
Notations

$\bar{u}$	average horizontal wind speed	m s^{-1}
$\overline{\rho_g}$	average concentration (density) of the gas less background concentration	mg m^{-3}
$\overline{u\rho_g}$	time based averaged horizontal flux densities in each sampled air layer above the vertical plane	mg NH_3-N m^{-2} h^{-1}
$\overline{u}\,\overline{\rho}_A$	mean horizontal flux density of ammonia	mg NH_3-N m^{-2} h^{-1}
$\overline{u}\,\overline{\rho}_{AC}$	mean horizontal flux density of ammonia from the fertilised area	mg NH_3-N m^{-2} h^{-1}
$\overline{u}\,\overline{\rho}_{AB}$	background mean horizontal flux densities measured in the unfertilised area	mg NH_3-N m^{-2} h^{-1}
$\overline{F_{N_g}}$	DTM ammonia flux time weighted average values for single SSM measurement interval	mg N m^{-2} h^{-1}
$F_{\overline{N_g}\,i}$	mean ammonia flux of two DTM measurements for the time interval (i) between the two measurements	mg N m^{-2} h^{-1}
A	surface area of land enclosed	m^2
A_e	effective cross-sectional area of the SSM sampler determined in wind tunnel experiments	$2.42 \cdot 10^{-5}$ m^2
a	asymptotic ammonia loss	kg N ha^{-1}
A_1	NH_3 collected in ATM tube A1	µg
A_2	NH_3 collected in ATM tube A2 (with stainless steel disc)	µg
ATM	Ammonia Tube Method (Schjoerring et al. 1992)	
c	ammonia loss rate constant	
CEC_{pot}	potential cation exchange capacity	$mmol_c$ kg^{-1}
conc	NH_3-Vol.-concentration	ppm
C_{org}	organic C in soil	%
d	depth of the soil layer mixed with fertilizer (0.5 dm)	dm
DTM	Draeger Tube Method (Roelcke et al. 2002 a)	
F	vertical ammonia flux density	kg N ha^{-1} h^{-1}
F_g	flux density of the gas	
f_g	gaseous diffusion impedance factor	dimensionless
F_{Ng}	ammonia flux from the soil surface	kg N ha^{-1} h^{-1}
F_{χ}	Flux of the trace gas with the concentration χ	
GR_l	gravimetric water content	cm^3 g^{-1}
i	parameter of sigmoidality	
K_N	ammonium dissociation constant	mol dm^{-3}

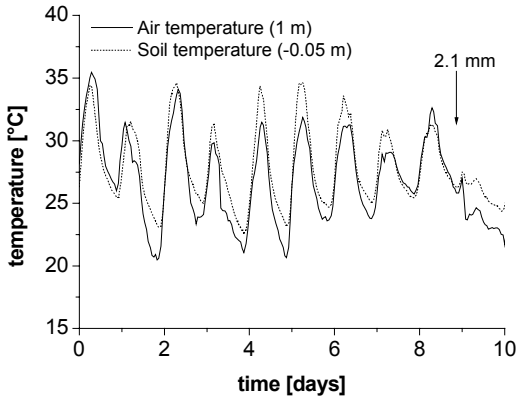
K_a	ammonia transfer coefficient	dm h^{-1}
K_c	dimensionless correction factor for ATM sampler [0.77]	
K_H	Henry's law constant	atm m^3 mol^{-1}
K'_H	Henry's law constant (dimensionless form)	
K_χ	Exchange coefficient (eddy diffusivity)	
M	measured mass of ammonia collected in the SSM sampler	mg
M_U	amount of urea-N applied to surface unit area	mol dm^{-2}
N_{tot}	total N content	%
$p(NH_3)$	ammonia partial pressure	Pa
r	air exchange rate in the chamber	Vol. min^{-1}
R	universal gas constant	8.206 10^{-5} atm mol^{-1} K^{-1}
r_T	radius of the ATM tube	0.5 mm
SSM	Space Shuttle Method (Leuning et al. 1985)	
T	temperature	K
TAN	Total Ammoniacal Nitrogen	mg l^{-1}
t_i	time interval (i) between two DTM measurements within the single SSM sampling interval t_{tot}	h
t_{max}	point in time of maximum ammonia flux	days after beginning of the process
t_{tot}	time interval of single SSM sampling	h
U(I)	urea-N concentration in total soil volume (solid, gaseous, liquid) in the I^{th} depth increment	mol dm^{-3}
U_F	surface area conversion factor (10000 cm² m^{-2}/415.5 cm² , 415.5 cm² = surface area covered by 4 cups)	m^{-2}
U_N	molecular weight conversion factor (14/17 = g N/g NH_3)	
U_Z	time conversion factor (3600 s h^{-1}/DTM measurement interval s)	h^{-1}
V	volume of the headspace	l
w_i	weighing factor ($0 < w_i \leq 1$, $\sum_{i=1}^{i} w_i = 1$)	
x	fetch	m
x_d	soil depths increments (0.005 dm)	dm
Y	cumulative ammonia loss (kg N ha^{-1})	kg N ha^{-1}
z	height above ground (m)	m
α	impact angle of the wind	
χ	concentration of the trace gas	µg l^{-1}
ϕ	soil porosity	vol. %
ν	gas flow rate	Vol. s^{-1}
θ_L	volumetric water content [cm^3 cm^{-3}]	

ρ	soil bulk density (determined in Fengqiu)	1.45 g cm^{-3}
ρ_b	background gas concentration	µg l^{-1}
ρ_g	gas density within a ammonia measurement chamber	µg l^{-1}
ρ_{NH3}	temperature dependent density of NH_3 ()	mg l^{-1}
ρ_p	soil particle density	2.65 g cm^{-3}

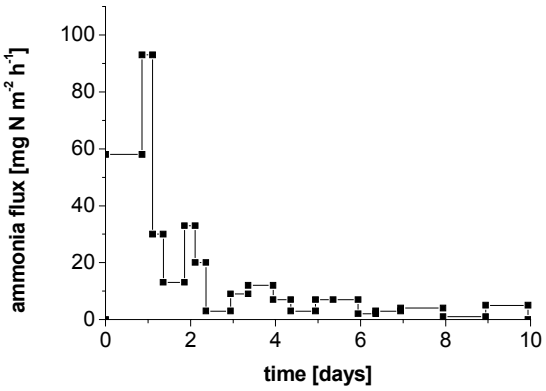
First maize experiment (28 June – 08 July 1998), surface broadcast treatment (75 kg N ha^{-1}), DTM hand pump and SSM



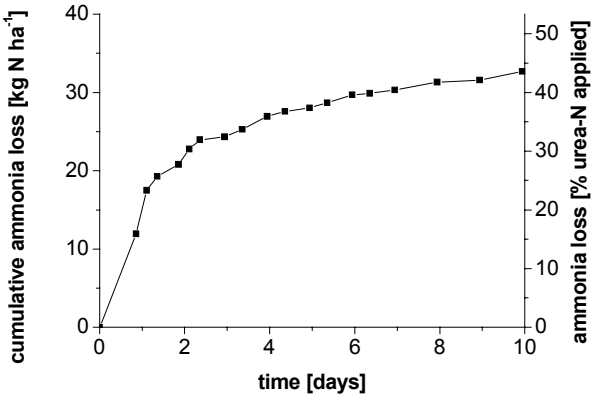
a. wind speeds (2 m and 0.02 m)



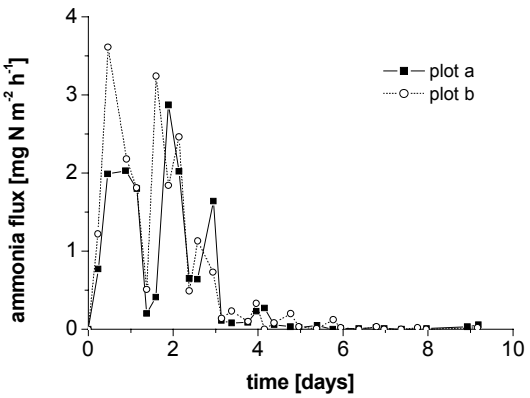
b. temperatures (1 m and -0.05.m)



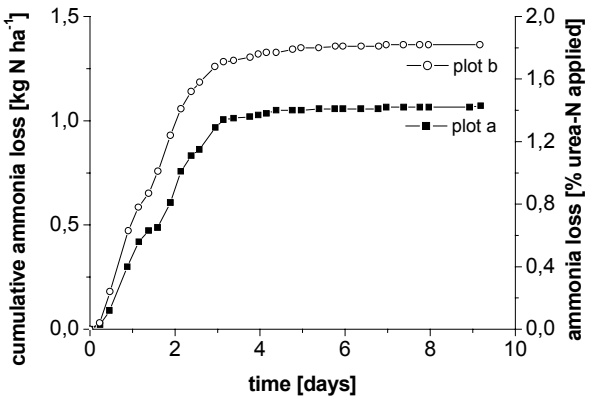
c. SSM ammonia fluxes



d. SSM cumulative ammonia loss

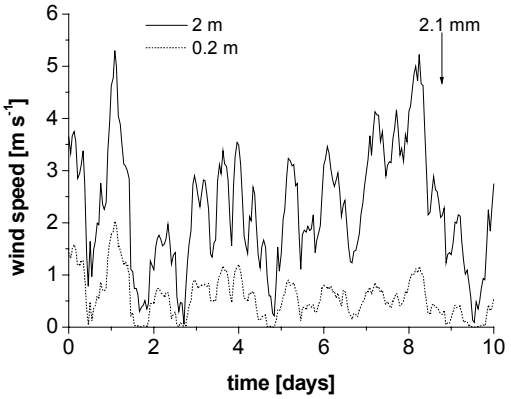


e. DTM ammonia fluxes

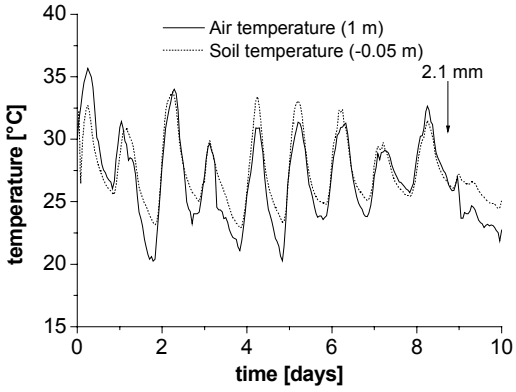


f. DTM cumulative ammonia loss

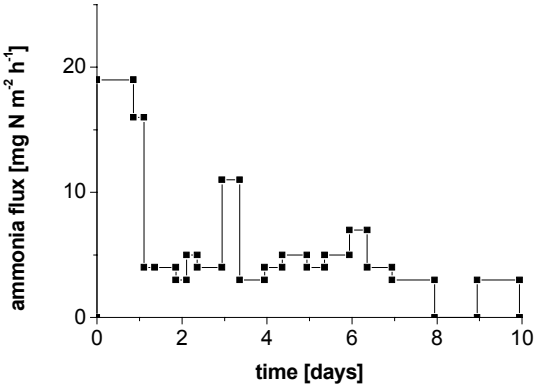
First maize experiment (28 June – 08 July 1998), fertilization foll. by irrigation (75 kg N ha^{-1}), DTM hand pump and SSM



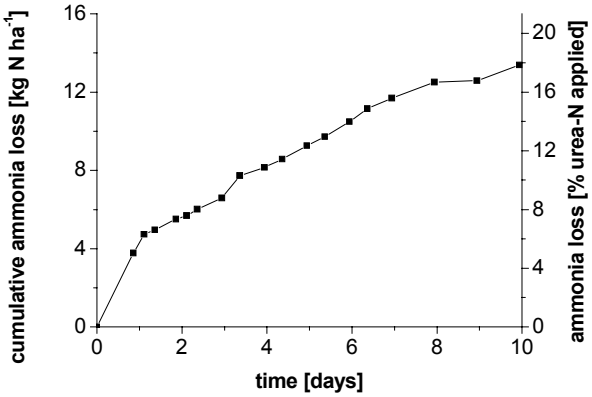
a. wind speeds (2 m and 0.02 m)



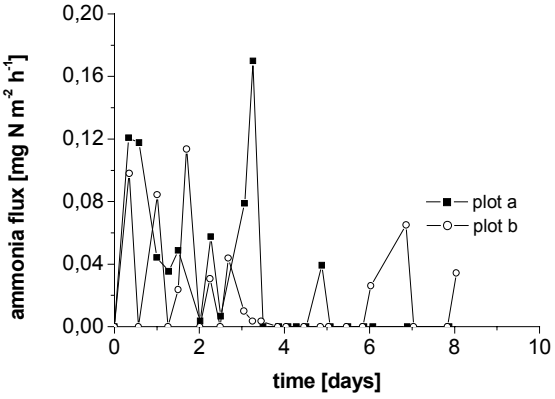
b. temperatures (1 m and -0.05.m)



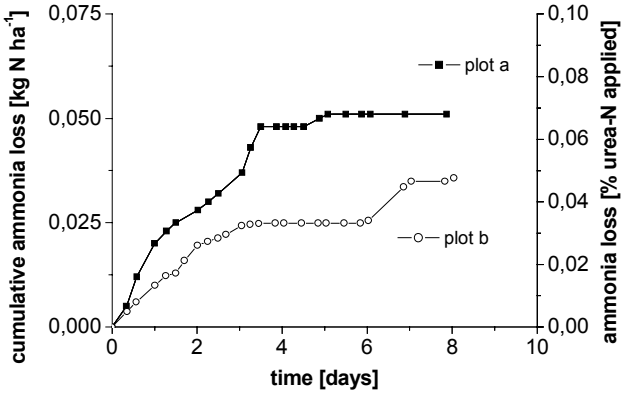
c. SSM ammonia fluxes



d. SSM cumulative ammonia loss

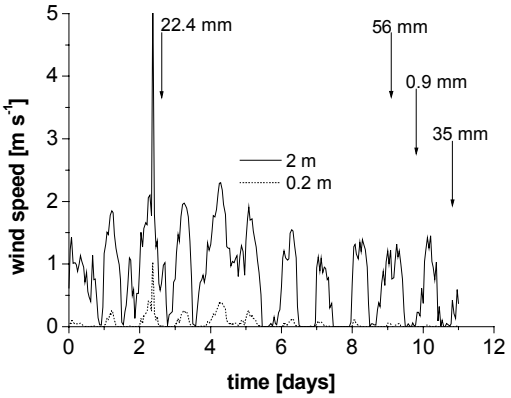


e. DTM ammonia fluxes

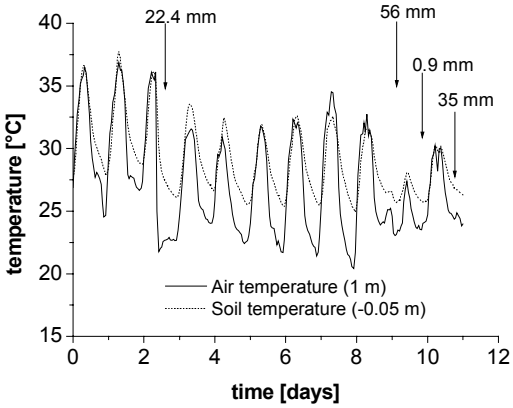


f. DTM cumulative ammonia loss

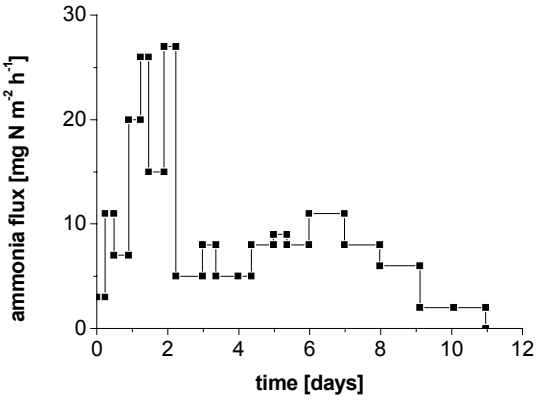
Second maize experiment (19 – 30 July 1998), deep point placement (200 kg N ha^{-1}), DTM hand pump and SSM



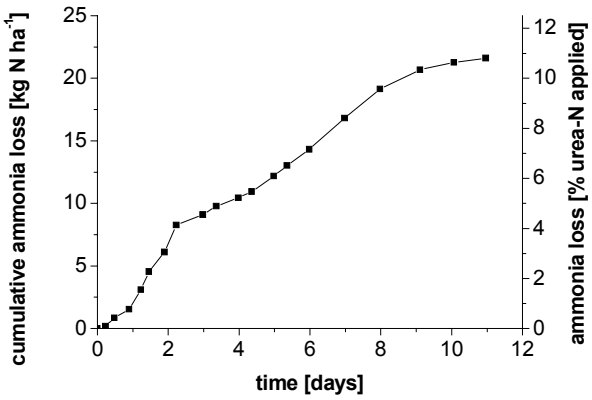
a. wind speeds (2 m and 0.02 m)



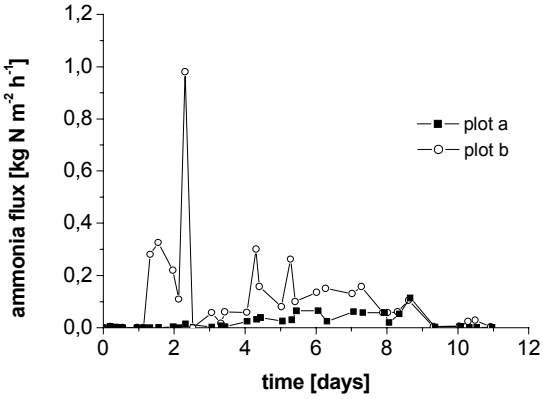
b. temperatures (1 m and -0.05.m)



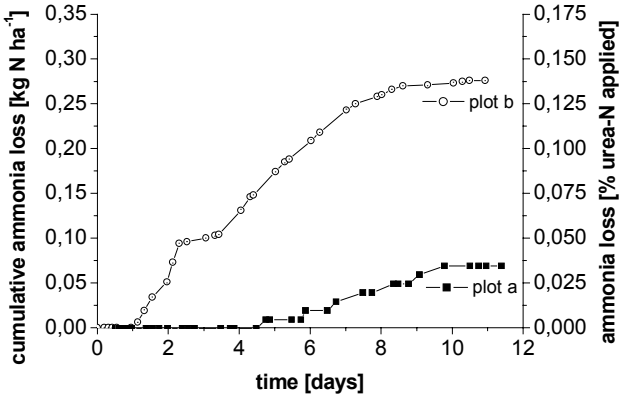
c. SSM ammonia fluxes



d. SSM cumulative ammonia loss

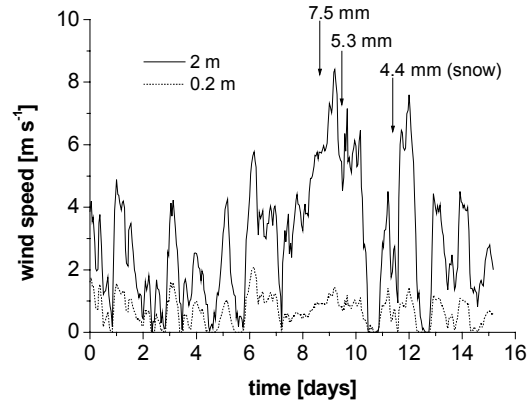


e. DTM ammonia fluxes

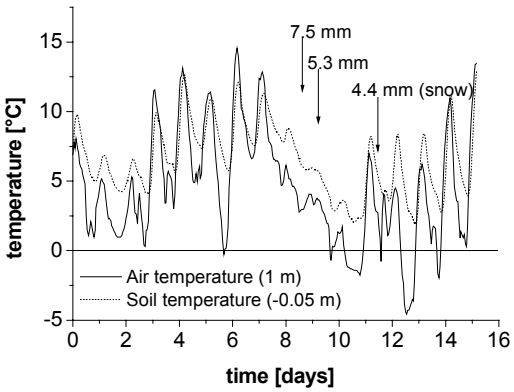


f. DTM cumulative ammonia loss

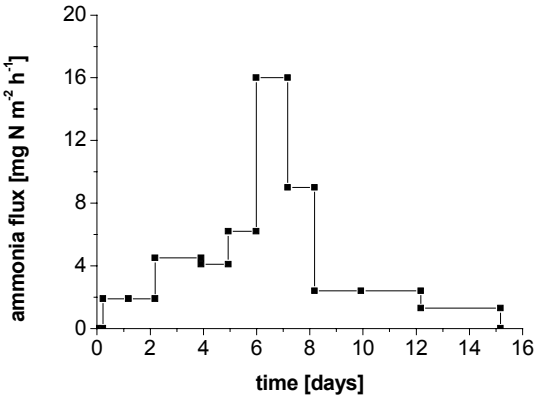
Second Wheat Experiment (09 – 21 March 1999), surface broadcast treatment (100 kg N ha^{-1}), DTM hand pump and SSM



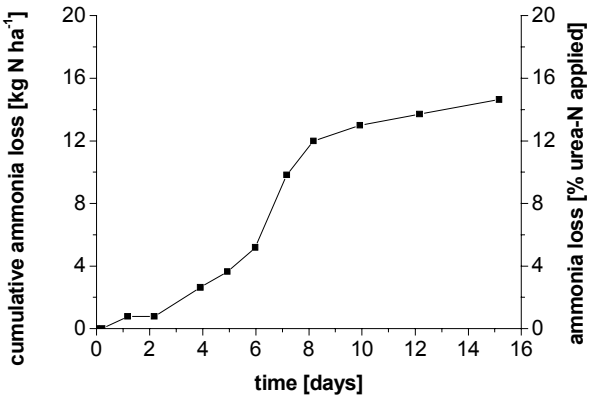
a. wind speeds (2 m and 0.02 m)



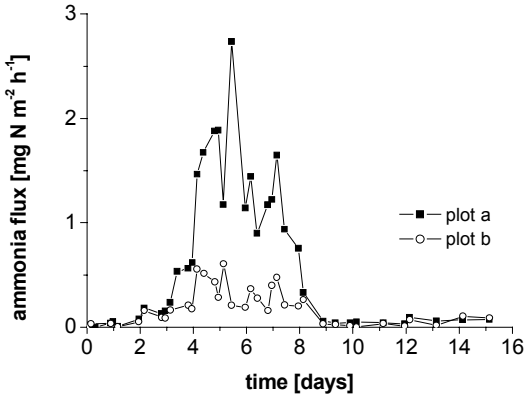
b. temperatures (1 m and -0.05.m)



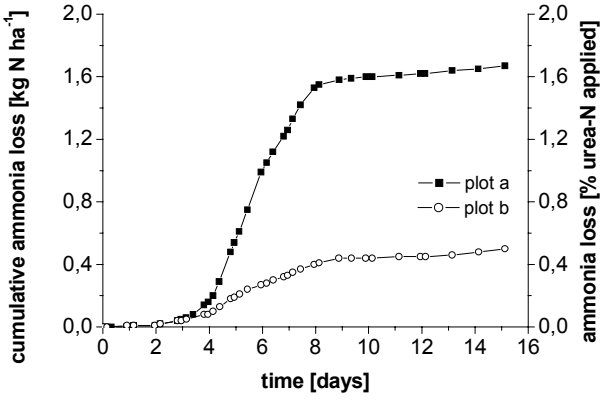
c. SSM ammonia fluxes



d. SSM cumulative ammonia loss

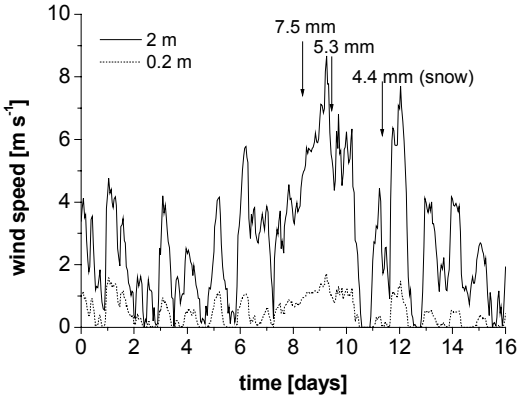


e. DTM ammonia fluxes

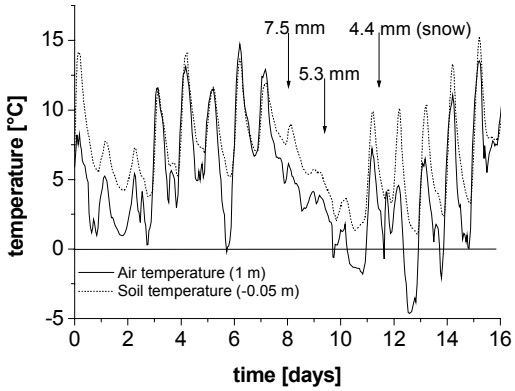


f. DTM cumulative ammonia loss

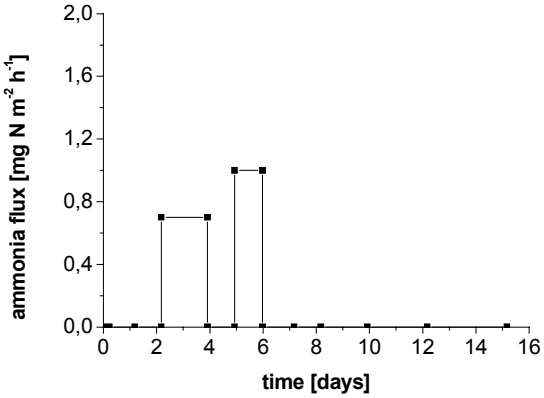
Second Wheat Experiment (09 – 21 March1999), fertilization followed by irrigation (100 kg N ha^{-1}), DTM (hand pump) and SSM



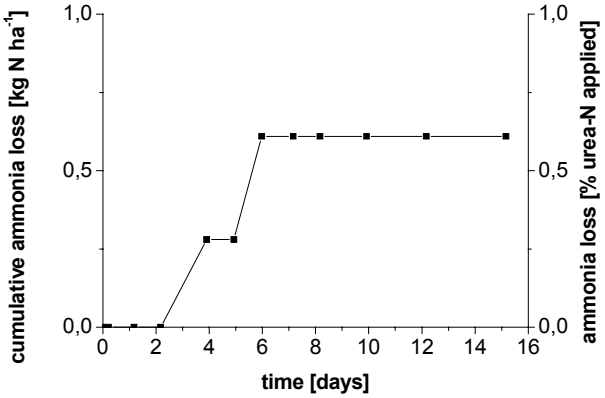
a. wind speeds (2 m and 0.02 m)



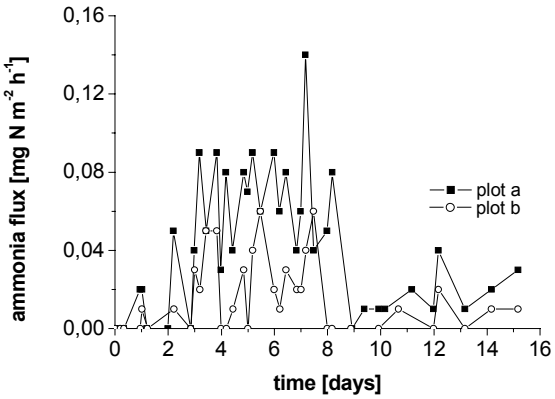
b. temperatures (1 m and -0.05.m)



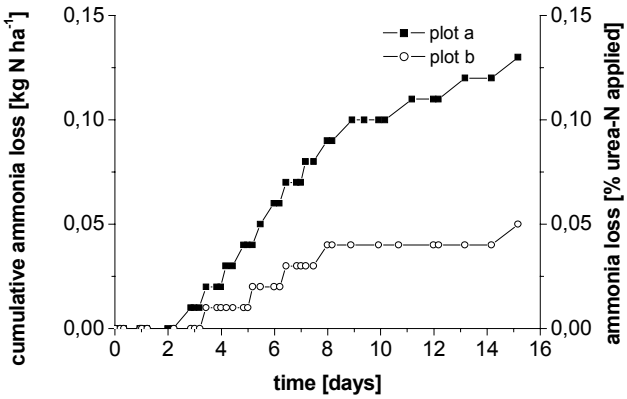
c. SSM ammonia fluxes



d. SSM cumulative ammonia loss

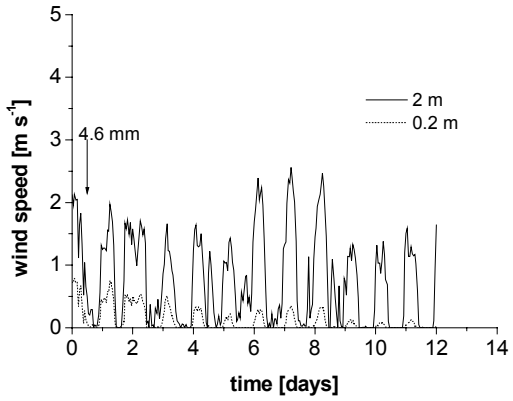


e. DTM ammonia fluxes

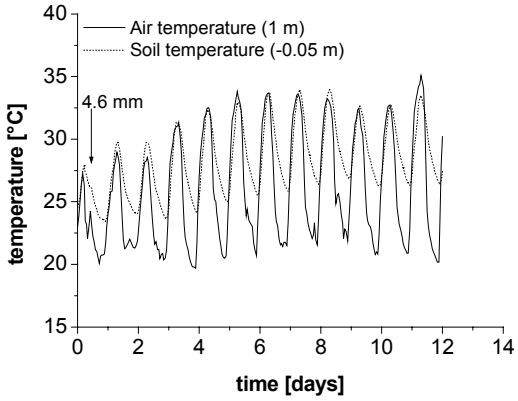


f. DTM cumulative ammonia loss

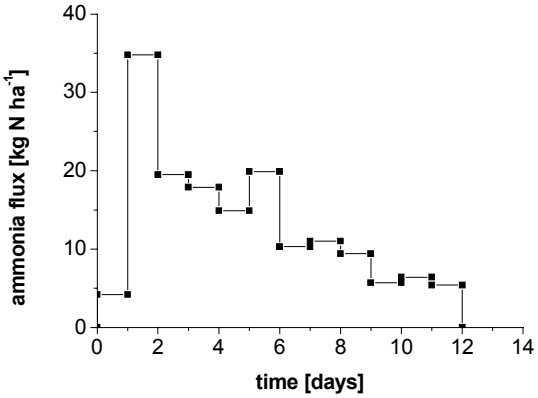
Third Maize Experiment (12. – 24 July 1999), surface broadcast treatment, (150 kg N ha^{-1}), SSM and DTM electric pump



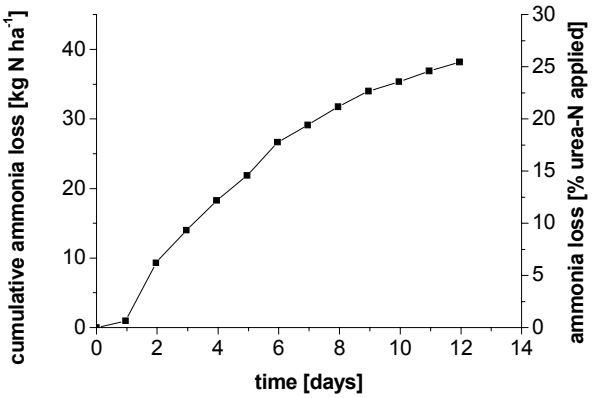
a. wind speeds (2 m and 0.02.m)



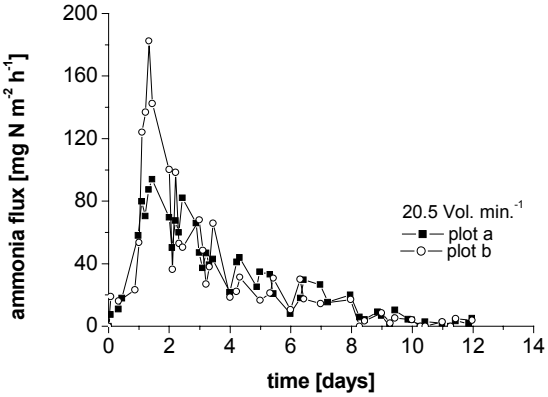
b. temperatures (1 m and -0.05.m)



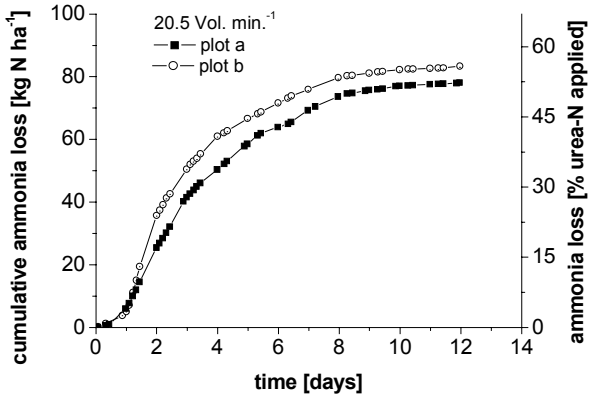
c. SSM ammonia fluxes



d. SSM cumulative ammonia loss



e. DTM (electric pump) ammonia fluxes



f. DTM (electric pump) cumulative ammonia loss

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