Net N mineralization in agricultural soils – Experimentally parameterized modelling for N fertilizer recommendations and inhibition effects in soils with specific former land-uses

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von Dr. rer. hort. Sabine Heumann
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Für Frederik.

God, grant me the serenity to accept the things I cannot change,
the courage to change the things I can,
and wisdom to know the difference.

(Karl P. R. Niebuhr)

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I Zusammenfassung

Diese Habilitationsschrift befasst sich mit der Verbesserung der standort- und jahresspezifischen N-Nettomineralisation in norddeutschen Ackerböden zum Zweck von Online-N-Düngeempfehlungen. Sogar auf europäischem Ackerland wird etwa die Hälfte des ausgebrachten N in mineralischen und organischen Düngern nicht von den Pflanzen aufgenommen und bewirkt so zu hohe Nitratgehalte im Grundwasser und klimarelevante gasförmige N-Verluste an die Atmosphäre. Die effizientere Ausnutzung von N-Düngern könnte durch eine Absenkung der Düngung auf das optimale N-Düngungsniveau erreicht werden, jedoch bleibt es schwierig das N-Angebot von Boden und Düngern mit dem Pflanzenbedarf zu synchronisieren. Eine sicherere Bestimmung des N-Angebots des Bodens würde die N-Düngerkosten im Weizenanbau um 10-30% und im Maisanbau sogar um 20-40% reduzieren – ohne die Erträge zu vermindern. Es wird angenommen, dass die Vorhersage der standort- und jahresspezifischen N-Nettomineralisation, d.h. Bruttomineralisation minus N-Immobilisation, am wichtigsten für adäquate N-Düngeempfehlungen ist, neben der Vorhersage des Pflanzenbedarfs. Die größten Herausforderungen bezüglich einer breiten Anwendung von N-Simulationsmodellen für Düngeempfehlungen sind, dass sie meistens nicht speziell für eine Abschätzung der N-Nettomineralisation evaluiert wurden und dass es einen Mangel an guten Felddaten gibt, z.B. aus durchdachten Bilanzansätzen. Daher können Teilmodelle zur N-Mineralisation signifikante Über- und Unterschätzungen bewirken, obwohl das Gesamtmodell zufriedenstellende Simulationsergebnisse liefert. Außerdem können Modelle nicht einfach an unterschiedliche Boden- und Standortbedingungen angepasst werden. Das übergeordnete Ziel dieser Arbeit war die experimentelle Entwicklung und Evaluierung eines Modells zur N-Nettomineralisation, das eine standortspezifische Online-Parametrisierung erlaubt. Für das gewählte, doppelt-exponentielle Modell wurde eine genaue Zuordnung von adäquaten Temperatur- und Wassergehaltsfunktionen für die Reaktionskoeffizienten sowie Pedotransferfunktionen (PTFs) für die Poolgrößen zu bestimmten Vornutzungen der Äcker, zu Bodentypen oder Gruppen von Böden („Mineralisationstypen“) anhand digital verfügbarer Boden- Wetter- und Managementdaten benötigt. Es wurde außerdem angestrebt, wichtige, möglicherweise hemmende Substanzen innerhalb der organischen Bodensubstanz in sandigen Ackerböden mit speziellen Vornutzungen, die oft eine sehr geringe Mineralisierbarkeit zeigten, zu ermitteln (**Kapitel 1**).

In den beiden ersten Veröffentlichungen geht es um die experimentelle Parametrisierung des Modells. Langzeitlaborinkubationen, zum Teil bei verschiedenen Temperaturen und

Bodenwassergehalten, wurden mit Freilandevaluationen anhand ungestörter Bodensäulen kombiniert. Die Studie erfolgte an einer großen Reihe von typischen Böden, Parabraunerden, Braunerden, Schwarzerden, Podsolen, Gleyen und Übergangstypen, die die Hauptanbaugebiete für Winterweizen in Niedersachsen abdecken. **Kapitel 2** beschreibt Teil 1 dieses kombinierten Ansatzes: Es war tatsächlich möglich spezifische Temperatur- und Bodenwassergehaltsfunktionen für die beiden Reaktionskoeffizienten k_{fast} und k_{slow} zu ermitteln, und dazu war eine Differenzierung zwischen nicht mehr als drei Mineralisationstypen bzw. Bodengruppen notwendig. Die beiden Gruppierungskriterien, die Bodenartenklasse und die Humusgehaltsklasse, können digitalen Bodenkarten (Maßstab 1:5000 für Niedersachsen) entnommen werden. Für die Bodenwassergehaltsfunktionen wurde nur ein Kriterium benötigt (Schluffböden vs. Sand- und Lehmböden), für die Temperaturfunktionen wurde die Gruppe der Sand- und Lehmböden anhand der Humusgehaltsklasse weiter unterteilt. Die Bodenwassergehaltsfunktionen sind dimensionslose Ratenfunktionen, skaliert zwischen 0 und 1, wie sie oft in Simulationsmodellen benutzt werden. Die Temperaturfunktionen sind relativ komplexe, multiple Gleichungen, die am besten die gemessenen Temperatureffekte berücksichtigen konnten. Dieses Ergebnis stimmt mit anderen Studien überein, die zeigten, dass einfache Arrhenius- und Q_{10}-Funktionen wegen der Komplexität der Mineralisationsprozesse oft nicht geeignet sind. Die in ungestörten Bodensäulen im Feld gemessene N-Nettomineralisation war hoch signifikant korreliert mit Simulationsergebnissen unter Benutzung dieser Funktionen, und die Ergebnisse lagen auch in derselben Größenordnung (r^2=0.87, P<0.001; RMSE= 23 kg N ha^{-1}, n-RMSE= 29%). Teil 2 dieses kombinierten Ansatzes wurde in **Kapitel 3** ausgearbeitet, das von den experimentell bestimmten und evaluierten PTFs für die Poolgrößen der beiden organischen N-Pools N_{fast} und N_{slow} berichtet. Insgesamt wurden dazu 179 Bodenproben inkubiert. Die wichtigsten Inputdaten für beide PTFs waren die mittleren Tongehalte der jeweiligen Bodenartenklasse, die man auch digital verfügbaren Bodenkarten entnehmen kann. Dennoch dürften die zugrunde liegenden Wirkmechanismen bei den beiden Pools unterschiedlich sein. Ein weiterer Faktor war für N_{slow} die Humusgehaltsklasse, die für bessere Simulationsergebnisse in die PTF integriert werden sollte. Für N_{fast} war es wichtig die mittlere Herbsttemperatur des Vorjahres, genauer gesagt von September bis November, einzubeziehen, wahrscheinlich aufgrund ihres Einflusses auf den Abbau der Ernterückstände vor dem Winter (negative Korrelation). Die Korrelation der simulierten (mit PTFs) mit der gemessenen N-Nettomineralisation in den Bodensäulen war nahezu genau so eng wie die mit aus Inkubationen abgeleiteten Poolgrößen, jedoch waren RMSE und n-RMSE etwas höher (r^2=0.79; P<0.001; RMSE= 36 kg N ha^{-1}; n-RMSE= 46%).

Das parametrisierte N-Nettomineralisationsmodell wurde *‚Net N‘* genannt und **Kapitel 4** der notwendigen Evaluation während der Wachstums von Winterweizen in einer Reihe von typischen nordwestdeutschen Böden mit unterschiedlicher Bodenart gewidmet. Dazu wurden zunächst ungedüngte Versuchsparzellen in den Blick genommen, da unterschiedliche Anteile des N-Düngers immobilisiert werden können und dadurch die Auswertung der Ergebnisse erschweren. Ein detaillierter Bilanzansatz, der auf Feldmessungen von N_{min}-Gehalten im Boden (im Frühling, zur Ernte und an mehreren Terminen dazwischen), auf Abschätzungen des N im Spross und auf der getrennt hiervon modellierten N-Auswaschung basierte, ergab Werte von bis zu 185 kg N ha^{-1}. Die mit *NET N* simulierte N-Nettomineralisation war hoch signifikant mit den Abschätzungen des Bilanzansatzes korreliert (r^2=0.58; P<0.0001; RMSE= 24 kg N ha^{-1}; n-RMSE= 24%). Interessanterweise lassen Korrelationen der simulierten N-Nettomineralisation mit Abschätzungen aus einfacheren Bilanzansätzen aufgrund eines niedrigeren RMSE und n-RMSE erkennen, dass die Wahl eines detaillierten Bilanzansatzes geeignetere Abschätzungen der wahren N-Nettomineralisation im Feld ermöglicht. Das mag nicht überraschend sein, aber beachtenswert, da einfachere Ansätze in der Literatur immer noch oft benutzt werden.

In **Kapitel 5** verhalf das ausgearbeitete Modell zu verstehen, ob und warum Unterschiede in Ertrag und Nitratauswaschung von unterschiedlichen landwirtschaftlichen Kulturarten von der pflanzenspezifischen Aufnahme von mineralisiertem N abhängen. Es wurde außerdem angestrebt die Kulturart(en) zu benennen, für die verbesserte N-Düngeempfehlungen den größten Nutzen bringen. Ergebnisse von 12 Jahren eines Feldexperiments mit unterschiedlichen N-Raten und einer Fruchtfolge aus Silomais, Wintergerste und Winterroggen wurden dazu herangezogen. Die mittlere N-Auswaschung war innerhalb jeder Kulturart unterhalb eines N-Angebots von 150 kg N ha^{-1} einigermaßen konstant, wodurch sich bestätigte, dass eine N-Auswaschung sogar ohne jegliche N-Düngung nicht völlig verhindert werden kann. Für höhere N-Angebote stieg die N-Auswaschung spezifisch je nach Pflanzenart an. Der relative Anstieg beim höchsten N-Angebot (ca. 200 kg N ha^{-1}) war bei Mais am stärksten ausgeprägt (Anstieg auf das Sechsfache im Vergleich zu den geringsten, konstanten Auswaschungsraten), während die Raten für die beiden Getreidearten auf weniger als das Doppelte anstiegen. Der Ertrag hing auch sehr stark von der Kulturart ab, und für die beiden Getreidearten war der relative Ertrag als Funktion des N-Angebots fast identisch. Er nahm hier exponentiell auf weniger als 30% des Maximalertrags in den Plots ohne N-Düngung ab, während er für Silomais nur auf etwa 60% des Maximalertrags absank. Aufgrund der zeitlichen Verläufe der mit *NET N* simulierten N-Nettomineralisation ließ sich herausfinden, dass ohne N-Düngung Silomais etwa dreimal so viel N aufgenommen haben dürfte wie z.B. Wintergerste (im Mittel 87 kg N ha^{-1} statt 31 kg N ha^{-1}) - aus wahrscheinlich zwei Gründen. Der eine, offensichtliche Grund ist das spätere Erntedatum. Der zweite Grund hängt mit der Pflanzenphysiologie zusammen: In ungedüngten Plots mit Wintergetreide dürfte aufgrund geringer N-Mineralisation im Frühjahr beim Schossen ein gewisser N-Mangel geherrscht haben, so dass möglicherweise nicht genug Sprosse ausgebildet wurden, die den später mineralisierten N aufnehmen können. Als Folgerung daraus ist das extrem hohe Auswaschungspotential nach Mais überwiegend bedingt durch relativ starke Überdüngung, weil Mais mineralisierten N sehr effizient nutzt. Daher sind für Mais verbesserte N-Düngeempfehlungen tatsächlich dringender als für die beiden untersuchten Getreidearten. Nach den Ergebnissen der Studie ist es im Maisanbau möglich eine Minimierung der Nitratauswaschung mit einer gleichzeitig mäßigen Ertragsreduktion (≤ 10% des Maximalertrags) zu kombinieren, während bedeutende N-Düngemengen eingespart werden können (ca. 100 kg N ha^{-1}). Umsetzungsschwierigkeiten bestehen noch aufgrund der allgemeinen Praxis, Mais nur einmal, beim Drillen, zu düngen.

Eine ungewöhnlich niedrige N-Nettomineralisation in Böden mit relativ hohen Gehalten an organischem C wurde wiederholt von sandigen Ackerböden NW-Europas berichtet. Um dies adäquat in Simulationen berücksichtigen zu können, ist es notwendig die verursachenden Substanzen und die dahinterliegenden Prozesse zu verstehen. **Kapitel 6** befasst sich mit neun landwirtschaftlichen Oberböden (< 6% Ton) mit einer breiten Spanne von Gehalten an organischem C (1.1 - 5.2%) und von C:N-Verhältnissen (12 - 35). Die Böden variierten sehr stark in der Mineralisierbarkeit ihres organischen N, die über Langzeitlaborinkubationen bestimmt wurde. Pyrolysis-Feldionisationsmassenspektrometrie (Py-FIMS) wurde angewendet, um den möglichen Einfluss der chemischen Zusammensetzung der organischen Bodensubstanz auf molekularer Ebene zu untersuchen. Überraschend war, dass die Stoffklasse der Sterole aus der Py-FIMS-Untersuchung am engsten und negativ korreliert war mit der Mineralisierbarkeit des organischen N ($r^2=0.75$, $P=0.003$). Dies war wahrscheinlich kein antioxidativer Effekt - wie kürzlich vorgeschlagen, weil die gemessene antioxidative Kapazität (AOC) nicht ausreichend mit der Mineralisierbarkeit und den Sterolionenintensitäten (aus Py-FIMS) korrelierte. Die negative Korrelation der Mineralisierbarkeit mit den Sterolen könnte trotzdem kausal sein, weil die Korrelation mit dem Hauptpflanzensterol β-sitosterol noch enger war (r^2=0.84, *P*=0.001) und mit anderen Bestandteilen aus der Stoffklasse der Sterole fast genauso eng. Außerdem wurde die Variabilität innerhalb der Proben sehr stark vom Anteil der Sterole bestimmt, und diese hatten auch eine große Trennschärfe in der Hauptkomponentenanalyse. Die Anteile der Sterole waren außergewöhnlich hoch in den ackerbaulich genutzten Podsolen, die sich unter ehemaliger Heide und ehemaligem Wald gebildet hatten und meistens reich an organischem C sind (bis 10.2% der gesamten Ionenintensität). Die Studie warf außerdem die Frage nach einem geeigneten Extraktionsmittel für Antioxidantien in Böden auf.

In der Publikation in **Kapitel 7** wurde der Einfluss von potentiell hemmend wirkenden Substanzen auf die C- und N-Nettomineralisation experimentell untersucht. Einer Braunerde, die nur wenige mögliche Hemmstoffe enthält, wurden verschiedene Substanzen mit bekannter AOC und/oder mit antimikrobiellen Eigenschaften zugesetzt und 7 bzw. 14 Tage inkubiert: zwei Phenolsäuren mit keiner (Acetovanillon) oder großer (Ferulasäure) AOC; Trolox, ein Analogon von Vitamin E, weil es das Standardantioxidant bei der Messung der AOC ist; β-sitosterol wegen seiner berichteten antimikrobiellen Eigenschaften und keiner AOC. Überraschenderweise zeigten die beiden Substanzen mit hoher AOC keine signifikante Hemmung der C- oder N-Nettomineralisation. Die Ergebnisse mit Acetovanillon lassen vermuten, dass diese Substanz schnell abgebaut wird (hohe C-Mineralisation) und dadurch eine N-Immobilisation bewirkt. Nur β-sitosterol bewirkte eine starke Hemmung der N-Nettomineralisation nach 7 und 14 Tagen (-59% bzw. -26%), die nicht als N-Immobilisation interpretiert wurde, da es keinen gleichzeitigen Anstieg der C-Mineralisation gab. Daher dürfte die extrem geringe Mineralisierbarkeit des organischen N in stark podsolierten Ackerböden mit ehemaliger Heide- oder Waldvegetation möglicherweise durch einen hemmenden antimikrobiellen Einfluss von Sterolen hervorgerufen werden.

Die Synopse in **Kapitel 8** wurde der Zusammenfügung der Ergebnisse der sechs Publikationen gewidmet, plus einer Beschreibung der erreichten Modellanwendungen, der möglichen Grenzen des Modells (beides unter Berücksichtigung weiterer Versuchsergebnisse) sowie der aktuellen Arbeitshypothese über die Wirkungsweise der Bodensterole gewidmet. Die primäre Anwendung von *NET N* war die Implementierung in einen neuen Online-Service für N-Düngeempfehlungen zu Winterweizen unter www.ISIP.de. Außerdem wurde angeregt, dass die Poolgröße N_{slow} hilfreich sein könnte als ein integrierter Indikator für die Bodenfruchtbarkeit in existierenden Bewertungssystemen für Bodenfunktionen. Vereinfachte Gleichungen des Modells *NET N* wurden auch einbezogen in eine Broschüre für Landwirte und landwirtschaftliche Berater. Bislang nicht publizierte Ergebnisse von gedüngten Böden demonstrieren, dass Simulationen mit *NET N* ohne explizite Berücksichtigung der Immobilisation von Dünger-N für Empfehlungen geeignet sind, solange Unterschiede in der N-Nettomineralisation zwischen den Jahren (z. B. zum Mittelwert der letzten 10 Jahre) verwendet werden. Für Simulationen mit *NET N* in Kulturen, die später im Jahr angebaut werden als Wintergetreide, wurde vorgeschlagen, die Simulationen im Februar zu beginnen, um insbesondere Poolgröße N_{fast} durch die bis zum eigentlichen Kulturbeginn stattfindende Nettomineralisation zu reduzieren. Eine große Übereinstimmung zwischen Simulationsergebnissen mit *NET N* und zwei anderen bekannten Modellansätzen wurde in einer Studie eines landwirtschaftlichen Beratungsinstituts auf acht landwirtschaftlichen Praxisflächen mit unterschiedlichen Vorfrüchten und Bodenarten in den Bundesländern Nordrhein-Westfalen und Hessen festgestellt. Jedoch betonte die Evaluierung von Feldinkubationen ungestörter Bodensäulen aus lehmigen Böden in Rheinland-Pfalz mit höheren Tongehalten als in unserer Hauptstudie, dass die ermittelten PTFs nicht einfach auf Bodenarten, die noch nicht untersucht wurden, übertragen werden sollten und dass PTFs, die auf zwei Bodeneigenschaften basieren, im Allgemeinen sehr zu empfehlen sind. Die oft verlangte Kombination von anderen aufkommenden Technologien für automatisierte N-Düngeempfehlungen (z. B. GPS-geführte Präzisionslandwirtschaft, Fernerkundungsmethoden, Luft-/Satellitenfotos) mit Simulationsmodellen wurde auch umrissen. Die Synopse erläutert zudem unsere gegenwärtige Arbeitshypothese zum übergeordneten Hemmmechanismus der Bodensterole und mögliche Hemmprozesse auf zellulärer Ebene. Generell werden noch mehr Untersuchungen benötigt, bevor Analysen von hemmenden Substanzen effektiv für eine Zuweisung von (neuen) Mineralisationstypen für *NET N* genutzt werden können. Das letzte Kapitel schließt mit einem Ausblick, worauf neue Experimente zur Verbesserung von *NET N* fokussieren sollten.

II Abstract

This habilitation thesis is focusing on improving site- and year-specific modelling of net N mineralization in agricultural soils of Northern Germany for online N fertilizer recommendation purposes. Even on European cropland about half of the applied N in fertilizers and manure is not taken up by plants and this over-fertilization induces too high nitrate loads in the groundwater and climate-relevant gaseous N losses to the atmosphere. A more efficient N fertilizer use could be accomplished by lowering N application from surplus to optimum levels, but it remains difficult to synchronize N supply from soil and fertilizers with plant N demand. Eliminating uncertainty in soil N supply was estimated to reduce N fertilizer costs by about 10-30% in wheat production and even 20-40% in corn production - without lowering crop yields. The prediction of site- and year-specific net N mineralization, i.e. gross N mineralization minus immobilized N, is assumed to be most important for adequate N fertilizer recommendations besides predictions of plant N demand. Major challenges to a widespread use of N simulation models for N recommendation purposes are that they are usually not specifically evaluated for estimating net N mineralization and that there is a lack of good field data, e.g. from sophisticated balance sheet approaches. Thus N mineralization sub models could produce significant over- and underestimations, even though the whole model could give satisfactory simulation results. Further, models are not easily adjustable to different soil and site characteristics. The overall goal of the study was to experimentally parameterize and evaluate a net N mineralization model that allows a site-specific online parameterization. For this double-exponential kinetic model, a precise assignment of adequate temperature and soil water functions for the rate coefficients as well as pedotransfer functions (PTFs) for the pool sizes to specific former land-uses, soil types, or groups of soils (“mineralization types”) via digitally available soil, weather and management data was needed. It was further aimed to elucidate important, possibly inhibiting substances within the soil organic matter (SOM) in sandy arable soils with certain former land-uses that have often shown a very low mineralizability (**chapter 1**).

The first two papers deal with the experimental parameterization of the model. Long-term laboratory incubations, partly at different temperatures and soil water contents, were combined with field evaluations using undisturbed soil columns. The study took place on a large set of typical soils, Luvisols, Cambisols, Chernozems, Podzols, Gleysols and intermediates, which represent the main areas for wheat production in Lower Saxony. **Chapter 2** describes part 1 of the combined approach: It was indeed possible to derive specific temperature and

soil water reduction functions for the two rate coefficients k_{fast} and k_{slow} and a differentiation between not more than three mineralization types/soil groups was necessary. The two criteria for grouping, soil texture class and humus content class, can be taken from digitally available soil maps (scale 1:5000 for Lower Saxony). For the water functions just one criterion was needed (loess *vs.* sandy/loamy texture classes), for the temperature functions the group of sandy/loamy soils was further separated by their humus content class. The soil water function is a dimensionless function, scaled between 0 and 1, as often used in simulation models. The temperature functions are relatively complex multiple equations that could most adequately account for the measured temperature effects. This is in accordance with other studies which showed that simple Arrhenius and Q_{10}-functions are often not suitable due to the complexity of mineralization processes. Field net N mineralization in undisturbed soil columns was highly significantly correlated to simulations using these derived functions and the results were also in the same range (r^2=0.87, P<0.001; RMSE= 23 kg N ha^{-1}, n-RMSE= 29%). Part 2 of this combined approach was elaborated in **chapter 3** which refers to experimentally determined and evaluated PTFs for the pool sizes of the two organic N pools, N_{fast} and N_{slow}. A total of 179 soil samples was studied by incubations. The most important input data for both PTFs were the mean clay contents of the respective texture class that could also be taken from digitally available soil maps. Nevertheless, the underlying mechanisms might be different for the two pools. For N_{slow} the humus class was another factor that should be included in the PTF in order to improve the simulations. For N_{fast} it was important to include the mean fall temperature of the preceding year, explicitly from September to November, probably due to its influence on residue degradation before winter (negative correlation). The correlation of simulated (using PTFs) with measured net N mineralization in soil columns was almost as close as with pool sizes from incubations, just RSME and n-RMSE were somewhat higher (r^2=0.79; P<0.001; RMSE= 36 kg N ha^{-1}; n-RMSE= 46%).

The parameterized net N mineralization model was named '*NET N*' and **chapter 4** was dedicated to its necessary evaluation during the growing season of winter wheat for a set of typical NW German soils differing in texture. In the first instance it was focused on unfertilized field plots as variable proportions of the fertilizer N could get immobilized which would complicate data interpretation. A detailed balance approach estimate basing on field measurements of soil mineral N (in spring, at harvest, and on several dates in between), on estimates for shoot N, and on separately modelled N leaching amounted to up to 185 kg N ha^{-1}. Simulated net N mineralization with *NET N* was highly significantly correlated with the balance estimate ($r^2=0.58$; $P<0.0001$; RMSE= 24 kg N ha^{-1}; n-RMSE= 24%). Interestingly, comparing these results to correlations of simulated net N mineralization with more simple balance estimates revealed that choosing a more detailed balance approach might be more appropriate for estimating the real amount of net N mineralization in the field due to lower RMSE and n-RMSE. This might not be surprising - but notable - as much simpler approaches are still quite often used in the literature.

In **chapter 5** the elaborated *NET N* model helped to understand if and how differences in yield and nitrate leaching of different agricultural crops could depend upon crop-specific use of mineralized N. It was also aimed to identify the crop(s) for which improved N fertilizer recommendations are most beneficial. Results from 12 years of an N-rate field experiment with a crop rotation of silage corn, winter barley and winter rye were used. Mean N leaching was relatively constant for each crop below an N supply of 150 kg N ha^{-1} which confirmed that N leaching cannot be totally avoided even without any N fertilization. For higher N supplies N leaching crop-specifically increased. The relative increase for highest experimental N supply (ca. 200 kg N ha^{-1}) was most pronounced for corn (six fold increase compared to minimum leaching rates), whereas the rates for the two cereals increased less than twofold. Crop yield also strongly depended upon crop type, and the relative yield as a function of N supply was almost the same for the two winter cereals. Here, it exponentially decreased to less than 30% of maximum yield in zero N plots, whereas for silage corn it decreased to just 60% of maximum yield. Using time courses of net mineralization simulated with *NET N*, we found that in unfertilized plots silage corn might have taken up about three times as much mineralized N than e.g. winter barley (on average 87 kg N ha^{-1} compared to 31 kg N ha^{-1}) - for probably two reasons. One obvious reason is the much later harvest date. The second reason is connected with plant physiology: In unfertilized plots with winter cereals there might have been some N shortage at tillering due to low N mineralization in spring with the possible consequence that not enough shoots were developed to use all N which was mineralized later on. As a conclusion, the extremely high leaching potential after corn is mostly caused by relatively high over-fertilization, as corn very efficiently uses mineralized N. Thus, for corn improved N fertilizer recommendations are actually more urgent than for the two winter cereals studied. According to the results of the study, for corn production it is possible to combine minimization of nitrate leaching with concurrent modest reduction in yield (≤ 10% of maximum yield) while saving considerable amounts of N fertilizer (ca. 100 kg N ha^{-1}). Difficulties due to the common practice to fertilize corn only once at drilling still need to be overcome.

Unusually low net N mineralization in soils relatively rich in total organic C and N was repeatedly reported for sandy arable soils in NW Europe. In order to adequately account for it in simulations, it is necessary to know the involved substances and understand the processes behind it. **Chapter 6** deals with nine arable top soils (< 6% clay) with a wide range of total organic C (1.1 - 5.2%) and C:N-ratios (12 - 35). The soils varied strongly in their mineralizability of soil organic N as determined via long-term laboratory incubations. Pyrolysis-field ionization mass spectrometry (Py-FIMS) was applied to investigate a possible influence of the molecular-chemical composition of the SOM. Surprisingly, the compound class of sterols from Py-FIMS was most closely and negatively correlated with the mineralizability of soil organic N ($r^2=0.75$, $P=0.003$). This was probably not an antioxidative effect as was recently suggested, because the measured antioxidative capacity (AOC) did not sufficiently correlate with the mineralizability and the sterol ion intensities (from Py-FIMS). The negative correlation between mineralizability and sterols could still be causal, since the correlation was even closer with the main plant sterol β-sitosterol ($r^2=0.84$, $P=0.001$) and about as close with other components of the compound class of sterols. In addition, the variability among samples was strongly governed by the proportions of sterols, and they had a high discriminating power in principle component analysis. The proportions of sterols were extraordinary in these arable podzol soils that developed under previous heath- or woodland (up to 10.2%) and are usually rich in organic matter. The study also raised the question about an adequate extractant for soil antioxidants.

In the paper in **chapter 7** the effect of potentially inhibiting substances on soil C and net N mineralization was experimentally tested. A Cambisol low in potentially inhibiting substances was amended with different substances of known AOC and/or with potential antimicrobial properties and incubated for 7 and 14 days: two phenolic acids with no (acetovanillone) or large (ferulic acid) AOC; Trolox, an analogue of vitamin E, because it is the standard antioxidant for determining AOC; β-sitosterol due to its reported antimicrobial properties and no AOC. Surprisingly, the two substances with large AOC showed no significant inhibition of C or net N mineralization. Results from Acetovanillone suggest that this substance was easily degraded (high C mineralization) and thereby caused N immobilization. Only β-sitosterol showed strong inhibition of net N mineralization after 7 and after 14 days (-59% and -26% respectively) which was not interpreted as N immobilization, since there was no concomitant increase in C mineralization. Consequently, the extremely low mineralizability of soil organic N in strongly podzolized arable soils with former heath- or woodland vegetation probably might be caused by an inhibitory, antimicrobial effect of sterols.

The synopsis in **chapter 8** is dedicated to merge the results from the six papers plus a description of the achieved model applications, potential model limitations (both considering further experimental results) as well as the current working hypothesis on the mode of action of soil sterols. The primary application of *NET N* was its implementation in a new online-service for N fertilizer recommendations under winter wheat at www.ISIP.de. In addition, pool size N_{slow} was suggested to be helpful as an integrated indicator for soil fertility in existing rating systems for soil functions. Simplified equations of the *NET N* model were also included in a booklet for farmers and advisors working in agricultural extension services. Not yet published results in fertilized soils demonstrate that simulations with *NET N* without explicit consideration of N fertilizer immobilization are adequate for recommendations as long as inter-annual differences of net N mineralization (e.g. to the mean of the last ten years) are used. For *NET N* simulations in crops that start later in the year than winter cereals it was suggested to begin simulations in February in order to especially reduce pool size N_{fast} through current mineralization until the actual start of crop growth. A high analogy of simulation results of *NET N* and two other known model approaches was detected in a study from agricultural consulting engineers on eight farmers' fields with varying preceding crops and texture in the German states North Rhine-Westphalia and Hesse. However, the evaluation of field incubations of undisturbed soils columns from loamy soils in Rhineland-Palatinate with higher clay contents than in our main study stressed that the derived PTFs should not simply be transferred to texture classes that were not yet tested and that PTFs basing on two soil characteristics are generally highly recommended. The often requested combination of other emerging technologies for automated site-specific N fertilization (e.g. GPS-guided precision farming, remote sensing, airborne satellite images) with simulation models was also outlined. The synopsis further explicates our current working hypothesis on the overall mode of inhibition of soil sterols and possible inhibition processes on a cellular level. In general, more research is still needed before analyses of inhibiting substances could be effectively used for an assignment of (new) mineralization types for *NET N*. Last but not least, this chapter closes with perspectives on some points that new experiments for improving *NET N* should focus on.

1 Introduction

1.1 Motivation

1.1.1 Significance of net N mineralization for N fertilizer recommendations

Worldwide, agricultural crop production is the most important anthropogenic cause for changes in the nitrogen (N) cycle (Liu et al. 2010, Smil 1999). Unfavorably, even on European cropland about half of the applied N in fertilizers and manure is not taken up by plants (Sutton et al. 2011). The main adverse ecological effects of over-fertilization are nitrate leaching into the groundwater and gaseous nitrous oxide (N_2O) and nitric oxide (NO) losses to the atmosphere. Residual soil nitrate at harvest is mostly leached and can easily lead to a transgression of the critical drinking-water threshold (Cameron et al. 2013). It can yet be assumed that this problem might exacerbate with the proposed lower seepage water rates due to climate change (Stuart et al. 2011). Microbial transformations of ammonium (via nitrification) and nitrate (via denitrification) generally also lead to formation and losses of N_2O and NO to the atmosphere. N_2O is a potent greenhouse gas with a mean lifetime of 114 years and a global warming potential of 298 times that of carbon dioxide (CO_2). It is also responsible for about 6% of the current global greenhouse effect (IPCC 2007; Bouwman et al. 1995). Furthermore, N_2O and NO are both highly relevant due to their importance in processes of ozone production and consumption (Ravishankara et al. 2009). Globally, N_2O from soils accounts for about 60% of the natural and about 37% of the total N_2O sources (IPCC 2013).

A more efficient N fertilizer use due to a reduction of N losses could be accomplished by lowering N application from surplus to about optimum levels which generally decreased nitrate leaching for different crops (Cameron et al. 2013; Oenema et al. 2009). Further lowering N fertilization below the optimum levels seemed to be not as likely to additionally reduce nitrate leaching (Köhler et al. 2006; Beaudoin et al. 2005). Similarly, gaseous N_2O losses could be reduced as the amount of fertilizer N showed the strongest influence on the size of N_2O emissions (Stehfest and Bouwman 2006), especially when it exceeded plant N demand (Shcherbak et al. 2014; Kim et al. 2013). However, just about 1% (up to 3%) of fertilizer N is usually lost as N_2O (Saggar et al. 2009 2009).

Synchronizing N supply from soil and fertilizers with plant N demand would not only help minimizing N losses caused by over-fertilization; it was estimated to also have a significant economic advantage for farmers. Eliminating uncertainty in soil N supply would reduce average N rates and, thus, N fertilizer costs by 10 to 30% in today's wheat production and even

20 to 40% in corn production - without lowering crop yields (Lobell 2007). These reductions might be much more pronounced for circumstances where current N fertilizer rates are still far above optimum rates, as reported for instance from vegetable production (Soto et al. 2015) or in countries like China (Cui et al. 2008). Especially for winter sown crops, future fertilizer N rates were predicted to become even more variable with increasing water stress situations (Webber et al. 2015). However, in current N fertilizer recommendation systems there is a vast variety of balance approaches for soil N supply that differ in complexity and in the way single components are measured or estimated (e.g. Sylvester-Bradley 2009; Olfs et al. 2005; Jarvis et al. 1996).

In the work reported here, soil N supply is defined as soil mineral N (nitrate plus ammonium) within the rooting zone (defined depth) in spring and possible plant N in spring (e.g. for winter cereals) plus soil net N release during plant growth (equation 1). Then, for unfertilized conditions the soil net N release is the sum of the change in the soil mineral N content from spring to harvest plus N taken up by the plant within this period (equation 2). This sum can also be expressed as the result from several processes: gross N mineralization from soil organic matter (SOM) including plant residues, N immobilization in microbial biomass, N leaching to the groundwater, gaseous N losses and N additions from deposition (equation 3; after Cameron et al. 2013).

$$SNS = (\,SMN^{spring} + N_{plant}^{spring}\,) + \,SnetNR \qquad \text{(Eq. 1)}$$

$$SnetNR = \,\Delta\,SMN + \Delta\,N_{plant} \qquad \text{(Eq. 2)}$$

$$\Delta\,SMN + \Delta\,N_{plant} = N_{gm} - N_i - N_l - N_g + N_d \qquad \text{(Eq. 3)}$$

Here, SNS is soil N supply, SMN the soil mineral N content, N_{plant} plant N uptake, $SnetNR$ soil net N release, N_{gm} gross N mineralization, N_i immobilized N, N_l leached N, N_g gaseous N losses, and N_d is N deposition (compare Fig. 1).

In this balance approach, 'net N mineralization' (N_{gm} minus N_i) during plant growth is the component with the strongest impact on soil net N release *SnetNR* and therefore - besides SMN^{spring} and possible N_{plant}^{spring} - on soil N supply *SNS*. Firstly, negative gaseous losses N_g (often below 5 kg N ha^{-1} y^{-1} after Shcherbak et al. 2014) can be assumed to about outweigh positive deposition N_d (about 10 kg N ha^{-1} y^{-1} in Lower Saxony after Keuffel-Türk et al. 2012). This assumption is often made for mere agricultural N balances (e.g. Justes et al. 1997), since specific values are mostly very low and measurements usually not available. The term 'net N mineralization' (N_{gm} minus N_i) is generally used, because it is more interesting from an agronomic point of view. It is the N amount which is available to plants, as gross mineralized N (N_{gm}) is depleted when microorganisms take up part of this N in their cell biomass (immobilization, N_i).

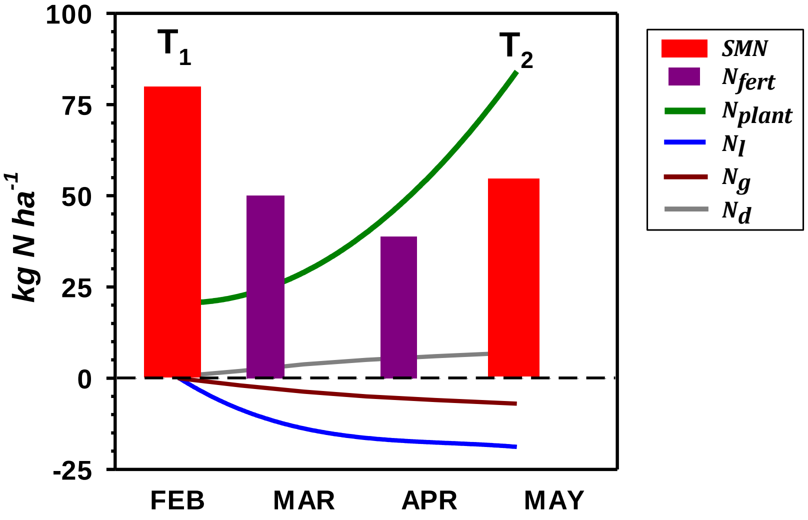


Fig. 1: Components of a balance sheet approach for calculating net N mineralization between the two dates T_1 and T_2 (N_{fert} is fertilizer N; for other abbreviations see equation 3).

Consequently, the balance approach called 'apparent net N mineralization' (*ANM*, equation 4 for unfertilized plots) does not include the balance approach components gaseous N losses and N deposition. This approach was further simplified to equation 5 (Hartmann et al. 2014; Willekens et al. 2014; Schröder 1999; Appel 1994; Engels and Kuhlmann 1993) as in most cases N_{plant}^{spring} is not known and leaching losses N_l during plant growth are negligibly low. The latter even seems to apply to susceptible sandy arable soils, because e.g. during twelve years of lysimeter measurements on a coarse sandy soil nitrate leaching between spring and harvest under cereals and corn only ranged from only 0 to 10 kg N ha^{-1} (Heumann et al. 2013a). As measured soil mineral N contents are known to vary considerably (Köhler et al. 2006; Ilsemann et al. 2001), all approaches including *SMN* might still be rather rough measures. However, there are even much more simple balance approaches in use, e.g. plant N uptake plus residual soil mineral N in 0-30 cm at harvest for unfertilized plots (Dessureault-Rompré et al. 2012; Sharifi et al. 2007) and aboveground plant N uptake at harvest reduced by 75% of starter fertilizer N, which amounted to 15 - 50 kg N ha^{-1} (St. Luce et al. 2013; Nyiraneza et al. 2012).

$$ANM = \Delta SMN + \Delta N_{plant} + N_l \qquad \text{(Eq. 4)}$$

$$ANM = \Delta SMN + N_{plant} \qquad \text{(Eq. 5)}$$

The prominent role of net N mineralization for adequate N fertilizer recommendations is also supported by the finding that the optimal N fertilization is highly sensitive to mineralized N (McKenzie et al. 2004; Webb et al. 2000). The so-called 'economic optimum N supply' (N^{opt}) can be obtained *ex post* from N rate experiments (Sieling et al. 2011; Olfs et al. 2005) and is, from the producers' perspective, the actual target of N fertilization. Furthermore, in humid environments with coarse soils where carry-over of soil nitrate from the previous growing season is limited and, thus, SMN^{spring} is negligibly low, net N mineralization is - according to equation 1 - even more important for estimating soil N supply (Zebarth et al. 2007).

Estimates of field net N mineralization in cropped soils via balance approaches as *ANM* and more simple ones (see above) are relatively scarce, despite their high relevance for more precise N fertilizer recommendations. This scarcity might be due to the high number of required input variables as well as the many factors that are causing a high variability - even on unfertilized fields with the same crop type. The strong influence of the crop type might probably be primarily attributed to the varying length and timing of the growth period. Published estimates for apparent net N mineralization varied from 7 - 119 (mean = 62) kg N ha^{-1} for winter barley, 27 to 163 (mean = 70) kg N ha^{-1} for winter wheat, and 42 - 316 (mean = 160) kg N ha^{-1} for sugar beet (30 to 60 plots for each crop, after Engels and Kuhlmann 1993). Moreover, for cereals about 36 kg N ha^{-1} (Appel 1994), and for corn 110 to 130 kg N ha^{-1} were assessed (Schröder 1999). With more simple balance approaches, a soil N supply of 47 - 185 (mean = 106) kg N ha^{-1} was estimated for potatoes (Sharifi et al. 2007), of 13 - 198 (mean = 76) kg N ha^{-1} for corn (Nyiraneza et al. 2012), and of 26 - 229 kg N ha^{-1} for canola (St. Luce et al. 2013) in Canadian soils. These values might be not fully comparable due to some differences in the kind and number of balance sheet components used. However, the variability within each study and crop type is extraordinarily, implying the high importance of other factors than crop type.

In addition to crop type, net N mineralization in the field is known to also be strongly site- and year-specific. Site factors can be principally considered to be rather stable features like soil characteristics (Khanna and Raison 2013; Zebarth et al. 2009; Cui et al. 2008), climate (Dessureault-Rompré et al. 2010), tillage system (Willekens et al. 2014; Malhi et al. 2001; Brye et al. 2003), the history of organic manuring (Watts and Torbert 2014; Gutser et al. 2005; Schröder 1999), and land-use history (Brye et al. 2003; Heumann 2003). Highly variable features that are changing from year to year are - besides the main crop - weather, the preceding crop (Sharifi et al. 2009; Webb et al. 1997), and current fertilizer activities (see below). Furthermore, there are interactions between various factors (e.g. Thomas et al. 2015; Watts and Torbert 2014; Kay et al. 2006), and there is a high spatial in-field variability of net N mineralization as well as of soil characteristics (Córdova et al. 2012; Karlsson et al. 2011). As a consequence, prediction models have often focused on the most significant, rather direct factors which are in turn influenced by site factors as well as factors changing with time: the availability of mineralizable organic N, and temperature as well as soil water response (Watts and Torbert 2014; Manzoni and Porporato 2009; Benbi and Richter 2002; Wu and McGechan 1998).

Accordingly, site- and year-specific prediction of net N mineralization is a great challenge even in unfertilized plots. Applying fertilizer N generally further complicates predictions as it yields lower net N mineralization compared to unfertilized plots (e.g. Appel 1994; Engels and Kuhlmann 1993). This decrease is mainly induced by microbial immobilization of fertilizer N rather than a reduction in gross N mineralization (Blankenau et al. 2000a; Nieder et al. 1995a, 1995b; Recous et al. 1992). As a result, balance approach values for apparent net N mineralization in fertilized fields, ANM_{fert}, could even get negative (Engels and Kuhlmann 1993), since the applied amount of N fertilizer (N_{fert}, Fig. 1) would have to be subtracted on the right side of equations 4 and 5. This result particularly applies to vegetable crops with a relatively short growing period, a high N demand and, consequently, high fertilizer N applications (Willekens et al. 2014; Feller et al. 2011). On average, apparent net N mineralization ANM_{fert} was reduced by 40 to 50% of the mineral fertilizer N rate compared to ANM without fertilization (Appel 1994; Engels and Kuhlmann 1993). However, the percentage which is immobilized by microorganisms is highly variable (e.g. 7 - 55% of fertilizer N after Olfs et al. 2005). This implies that immobilization is not strictly proportional to the fertilizer N rate applied (Lam et al. 2012; Blankenau et al. 2000b; Nieder et al. 1995a, 1995b; Rao et al. 1991). Instead, rates of N fertilizer immobilization were shown to be strongly influenced by weather, management, and soil properties (Lam et al. 2012; Nieder et al. 1995a, 1995b; Rao et al. 1991), and by the crop type itself (Engels and Kuhlmann 1993).

1.1.2 Experimentally parameterized modelling of net N mineralization

A furthermore greater challenge than *ex post* estimations is the implementation of year- and site-specific estimates of net N mineralization, besides plant N demand, into N fertilizer recommendation tools (Olfs et al. 2005). Simple soil-based recommendation methods in Europe and North America (Zebarth et al. 2009) usually include measurements of soil mineral N in spring (Fig. 2), target values from look-up tables, and some kind of N credit system (± 10 to 50 kg N ha^{-1} after Olfs et al. 2005) for specific catch crops or crop residues. These methods might indeed give reliable estimates for "average" soil and weather conditions, but they are generally still limited in their ability to adjust to the full range in year- and site-specific variations, especially in N released by mineralization (Burns 2006). This also refers to the German N_{min}-method which considers an average soil net N mineralization, because the target values were derived a) from various sites and b) in many years. As a consequence of the mentioned soil, site, weather, and management factors, it can be assumed that these simple soil-based recommendation tools do not fully acknowledge site- and year-specific N mineralization when calculating fertilizer N recommendations in order to not risk costly yield losses. Thus they might often lead to over-fertilization. Therefore, especially in the course of precision farming on large sites with high in-field variability, different plant analytical procedures and devices, e.g. optical measurement of crop canopy, have been developed to be used mounted on a tractor (Olfs et al. 2005). However, these methods would have to be annually calibrated under field conditions and might still be too costly and thus less applicable to rather small-scale farming (Hüter et al. 2007) like in the West of Germany.

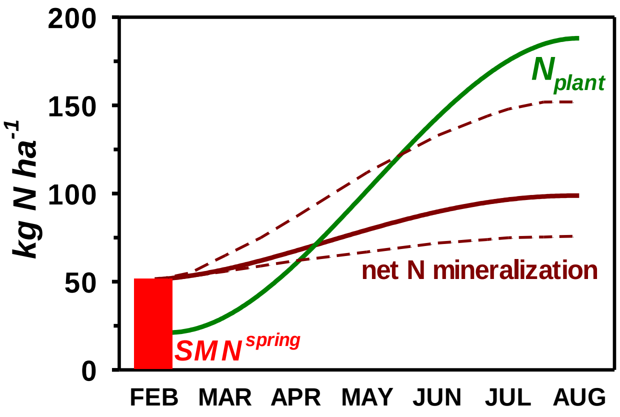


Fig. 2: Simple soil-based N fertilizer recommendations consider measured SMN^{spring} and include within their target values a mean net N mineralization (thick brown line; possible range within thin brown lines).

Possible other soil-based tools for the site-specific estimation of soil N supply or net N mineralization could be chemical and biological indices, i.e. chemical soil extraction and soil incubation methods, respectively (Nyiraneza et al. 2012; St. Luce et al. 2011; Ros et al. 2011, Schomberg et al. 2009). Here, any balance method can be helpful for calibrating or evaluating these more simple methods and tools via regression analyses, although any balance method is - as an *ex post* method - not directly useful for predictions. Over the years, a vast variety of chemical and biological indices have been tested and evaluated. But measurements are mostly too labor intensive for practical use (Weaver 2008; Jarvis et al. 1996). In addition, the most appropriate predictor strongly differs among datasets and the correlation between laboratory indices and net N mineralization decreases from laboratory studies to field studies (Ros et al. 2011). The obvious reason for this decreasing correlation is that these indices might include site-specific variability, but do not include year-specific variations due to current weather conditions. Therefore, these indices cannot fully simulate the microbial-mediated release of plant-available N under field conditions (St. Luce et al. 2011).

In addition, dynamic N simulation models have been developed that allow the quantification of many, rather year-specific factors influencing net N mineralization, especially temperature and soil water content (Benbi and Richter 2002). Some of these models have also been adapted to calculate N fertilizer recommendations (e.g. Kersebaum et al. 2005). However, there are two major challenges for a widespread use of N simulation models for N recommendation purposes. Firstly, they are usually not specifically evaluated for the process of net N mineralization and there is a lack of good field data (e.g. values determined via sophisticated balance approaches) that could be used for improving existing dynamic N simulation models regarding this deficit. Many models just have merely conceptual pools that are calibrated by optimization procedures using measured soil mineral N contents (Mary et al. 1999), results from incubation studies (Nicolardot et al. 1994) or SOM contents from long-term field trials (Jenkinson 1990). In some other models, N flows are coupled to C transformations and N mineralization is not directly simulated (e.g. Franko et al. 1995; Jenkinson 1990). Thus, N mineralization sub models would produce significant under- or overestimations (e.g. Gabrielle et al. 2002), even though the whole model could give satisfactory simulation results (He et al. 2006). Secondly, N models are usually not easily adjustable to different soil and site characteristics and a major challenge is to free simulations for recommendations from site-specific calibration in advance of any model application (Benbi and Richter 2002).

A combined approach of experimental parameterization and field evaluations for an N simulation model would meet the first challenge. This approach has already been used by some research groups (Wang et al. 2004; Heumann 2003; Kersebaum 1995; Campbell et al. 1995) - with different profundity. Generally, the long-term incubation-leaching technique first proposed by Stanford and Smith (1972) allows to experimentally derive the pool sizes (N_{fast} and N_{slow}) and their first-order rate coefficients (k_{fast} and k_{slow}) of two organic N pools differing in mineralizability (equation 6; Fig. 3). Therefore, equation 6 is simply fitted to curves of cumulative net N mineralization from these incubations (NM_{sim} *(t, T),* as net N mineralization does depend upon time *t* and temperature *T).* To take into account suboptimum temperature conditions in the field, specific functions for the rate coefficients, k_{fast} *(T)* and k_{slow} *(T),* were also experimentally determined. Nevertheless, only in one combined approach (Heumann 2003) parameters and functions derived in the laboratory (Heumann and Böttcher 2004a) were evaluated in greater detail using, at least, *in situ* measurements of net N mineralization in undisturbed soil columns (Heumann and Böttcher 2004b). In these studies, only relatively complex multiple equations could account for the temperature dependencies of two rate coefficients derived from long-term incubation experiments at different temperatures. This finding is confirmed by growing evidence from other studies that simple Arrhenius and Q_{10}-functions are often not the best choice due to the complexity of mineralization processes (Bauer et al. 2008; Ågren and Wetterstedt 2007).

$$NM_{sim}(t,T) = N_{fast}\left(1 - e^{-k_{fast}(T)t}\right) + N_{slow}\left(1 - e^{-k_{slow}(T)t}\right) \qquad \text{(Eq. 6)}$$

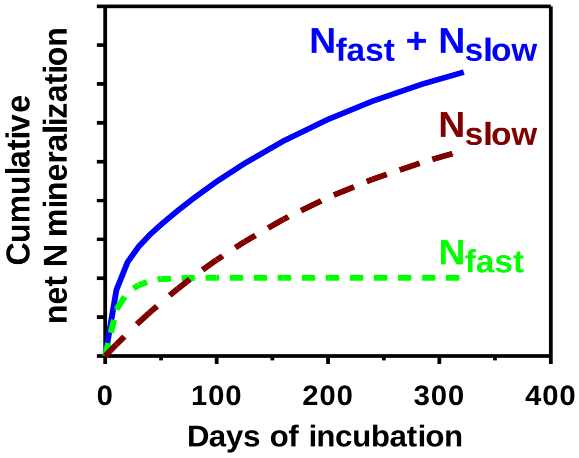


Fig. 3: Splitting cumulative net N mineralization from a long-term incubation-leaching technique into two organic N pools differing in mineralizability (see equation 6).

Besides temperature, the soil water content strongly affects the rates of net N mineralization as the availability of water and oxygen are both controlling factors. Many predictive models currently use a dimensionless scaling function (e.g. $WF(\Theta)$; equation 7) which is scaled between 0 and 1 to simulate the effect of the soil water content Θ on net N mineralization (Paul et al. 2003), but models have different water functions and units to express the soil water content (Wu and McGechan 1998; Rodrigo et al. 1997). The mentioned combined approach (Heumann 2003) has still awaited further experimental parameterization and evaluation of water functions. Furthermore, it has only been tested in one catchment with sandy arable soils and evaluations for planted fields have still been missing.

$$NM_{sim}(t,T,\theta) = NM_{sim}(t,T) \times WF(\theta) \qquad \text{(Eq. 7)}$$

For the second challenge, the site- and soil-specific derivation of parameters, which is of increasing importance for precision farming, digitally available online data bases might be helpful nowadays. These data bases comprise small-scale soil maps, (e.g. 1:5000 for the state of Lower Saxony; www.LBEG.niedersachsen.de), weather data (e.g. in the online service 'ISIP' for German farmers; www.ISIP.de), and management data from digital farmers' field records. Adequate site-specific temperature and soil water functions need to get digitally assigned by soil data bases, as considerable differences were already found between the temperature dependencies in loess and in sandy arable soils (Fig. 4; Heumann and Böttcher 2004a, 2004b).

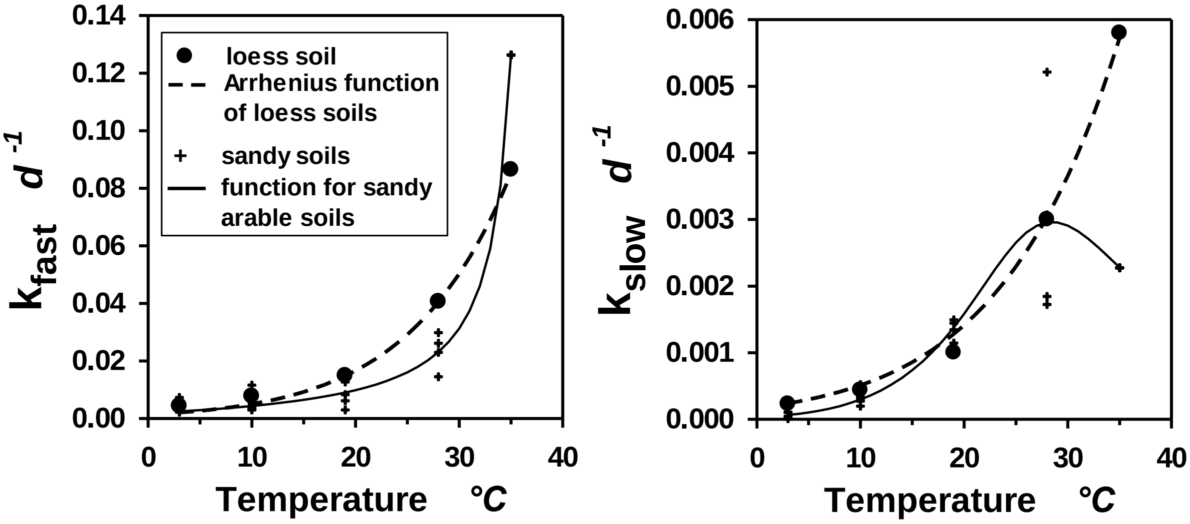


Fig. 4: Temperature functions of k_{fast} (left) and k_{slow} (right) in sandy arable soils compared to Arrhenius functions derived for loess soils (Nordmeyer and Richter 1985). From Heumann and Böttcher (2004a).

Furthermore, so-called pedotransfer functions (PTFs) are useful tools to derive values of soil properties and model parameters, which are difficult to obtain, from regression equations using more easily accessible soil characteristics (Bouma 1989). PTFs were already determined for soil water properties (e.g. Rawls et al. 1991) or heavy metal sorption (e.g. Streck and Richter 1997), and also for the pool size N_{slow} in a drinking water catchment with sandy arable soils (Heumann et al. 2003). In the latter case, the PTFs included one or two measured soil characteristics (organic C, total N, C: N, mineral fraction < 20 µm) and were relatively accurate (r^2 ranged from 0.55 to 0.83). This accuracy was yet subject to the condition that sites were grouped by former land-use (grassland, wood- and heathland, old arable land).

1.1.3 Inhibition effects on net N mineralization in specific sandy arable soils

Besides different temperature functions for k_{fast} and k_{slow} (Heumann and Böttcher 2004a, 2004b) and very specific PTFs for pool size N_{slow} (Heumann 2003), the mineralizability of soil organic N was generally found to be much lower in sandy compared to loess soils (Fig. 5; Heumann et al. 2002). Mean daily mineralization rates from N_{slow} relative to total N were about 30% of what was found in Luvisols from loess. Actually, this mineralizability showed a very high variability, as for some sandy soils it was less than 10% of the mean value for loess soils and for some other sandy soils it was about the same as for loess soils (Fig. 5).

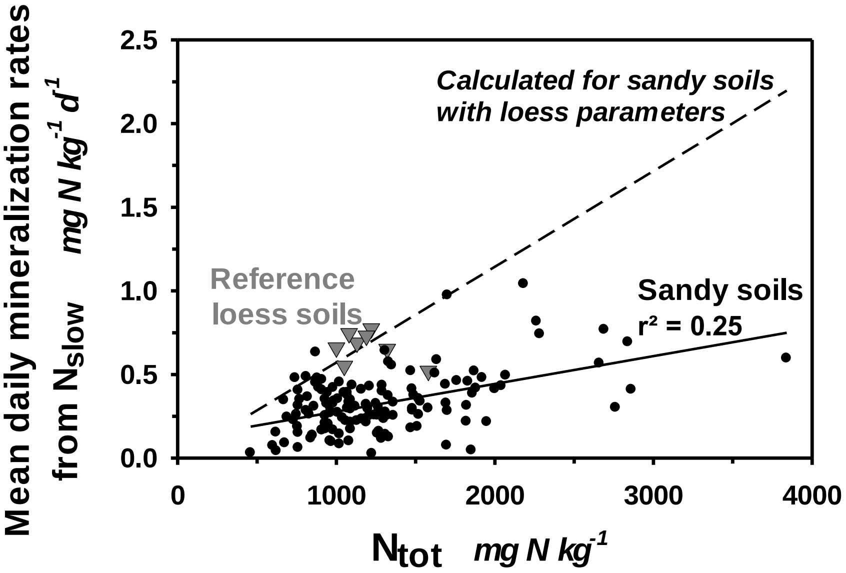


Fig. 5: Mean daily N_{slow} mineralization rates of 137 sandy arable soils *(circles, solid line)* compared to 8 reference loess soils *(triangles)* and rates calculated with 'standard' loess parameters (Nordmeyer and Richter 1985) for the range of total N in the sandy soils *(dashed line)*. From Heumann et al. (2002).

Looking closer, it could be concluded that the lower mineralizability might be related to a former land-use of sandy arable soils as heath- or woodland. The former land-uses were identified by digital releases of topographical maps from 1901 to 1995 and of a historical map from 1780 (for details see Heumann et al. 2003). In the former heath- and woodland soils, N_{slow} amounted on average to just about 7.1% of total N compared to about 9.3% of total N in old (> 220 years) arable soils (Heumann et al. 2003). Furthermore, it was possible to conclude that in soils with former heathland cover even the light density fraction contains a lot organic N with very low mineralizability in contrast to the old arable soils (Fig. 6; Heumann et al. 2003). Usually, N in the light density fraction is supposed to be an indicator of easily mineralizable N in arable soils (Curtin and Wen 1999; Cambardella and Elliott 1992). Besides historical land-use as heathland, external factors like a generally podzolization-enhancing climate combined with plaggen fertilization and a high groundwater table were named to cause remarkably high SOM levels in sandy arable soils of NW Germany (Springob and Kirchmann 2002). These conditions generated high amounts of non-texture-stabilized SOM with very low C and N mineralization rates (Springob and Kirchmann 2010, 2003). Another evidence for the influence of podzolization is the finding that - among old arable soils - the mineralizability of organic N was about twice as high in soils with only light podzolization features compared to strongly podzolized soils of the same area (Heumann et al. 2003).

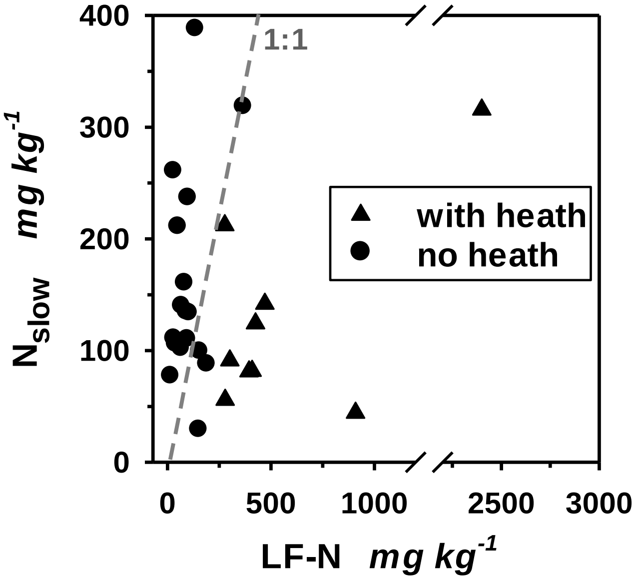


Fig. 6: N in the light fraction (LF-N) compared to pool size N_{slow} of sandy arable soils with resp. without heathland cover within the past 220 years according to land-use maps. From Heumann et al. (2003).

As a consequence, a precise assignment of adequate temperature and water functions and/or PTFs for the pool sizes to specific former land-uses, soil types or groups of soils is needed. As one prerequisite, a better understanding of the “somehow” inhibiting factors on mineralizability might be necessary for improving the use of N simulation models that consider net N mineralization. This ought to be of even special importance for sandy arable soils rich in SOM like in NW Germany (Springob and Kirchmann 2002) that are often planted to corn. This is a crop which might use mineralized N much better than e.g. grain crops. This preferential use was deduced from yield data of N fertilizer rate experiments where yield losses appeared to depend upon the crop type, especially grain crops versus silage corn. For winter cereals without N fertilization, yields were reduced to about 50% of maximum yield (Köhler et al. 2006; Sieling 2004) or even less than 40% (Zimmer et al. 2005; Thomsen et al. 2003). In contrast, yields of silage corn without N fertilization still reached 70 to 90% of maximum yield (Kayser et al. 2011; Zimmer et al. 2005; Schröder 1999). As a consequence, fields could get over- or under-fertilized when simulating inappropriate N mineralization rates and, thus, lead to either adverse environmental impacts (nitrate leaching, gaseous N losses; see above) or yield losses. The effect of over-fertilization could even get aggravated by the buildup of a high N mineralization potential due to a long history of very high loads of organic manure from intensive animal husbandry like in NW Germany.

However, the named factors like specific former land-use and soil forming processes have been mostly deduced from regression analyses (Heumann et al. 2003, 2002; Springob and Kirchmann 2002). It has not yet been possible to discover possible substances or processes that cause a low mineralizability. So far, SOM stabilization, which was defined as processes or mechanisms that lead to prolonged turnover times, was usually explained by just three processes: binding to soil minerals and metals, chemical recalcitrance, and spatial inaccessibility (Kögel-Knabner et al. 2008). Lately, soils were shown to contain plant-derived and newly synthesized antioxidants (Rimmer and Smith 2009) which were hypothesized to also slow down the oxidative decomposition of SOM (Rimmer 2006). Just as well as C mineralization, antioxidative compounds could actively inhibit nitrate formation, although ammonification, the first step in N mineralization, is not an oxidation process. But it depends on oxidative processes, since it is basically due to heterotrophic organisms that gain energy by oxidation of organic substrates.

There are different kinds of plant compounds which are potential antioxidants, e.g. polyphenols, tannins and flavonoids (Podsedek 2007; Hagerman et al. 1998). Additionally, pharmaceutical studies have shown that microbial activity can be inhibited by plant compounds like terpenoids (Dickson et al. 2007) and sterols (Bouhadjera et al. 2005). Polyphenols with high molecular weights like tannins could have various effects, e.g. inhibition of extracellular enzymes, toxic effects or complexation of protein substrates (Fierer et al. 2001; Hättenschwiler and Vitousek 2000). Regarding the possible substances that are enriched in the named specific soils, there are first hints from sandy relict heathland and cultivated former heathland soils in Belgium (Sleutel et al. 2008). These soils showed an accumulation of SOM rich in aliphatics which was linked to high inputs of lipids, long-chain aliphatics and sterols from heathland vegetation, low soil pH, and low microbial activity (Sleutel et al. 2008). Nevertheless, experimental evidence has still been lacking about which organic molecules in SOM exert antioxidative or otherwise inhibitory effects, and if these effects directly slow down N (and maybe also C) mineralization rates.

1.2 Objectives and thesis outline

The overall goal of these studies was to improve site- and year-specific modelling of net N mineralization in agricultural soils of Northern Germany for online N fertilizer recommendation purposes. Therefore, it was aimed to experimentally parameterize and evaluate a net N mineralization model (two organic N pools with first-order kinetics) that allows a site-specific online parameterization. For this model, a precise assignment of adequate temperature and water functions and pedotransfer functions for the pool sizes (“mineralization types”) to specific former land-uses, soil types, or groups of soils via digitally available data was needed. It was also aimed to elucidate important, possibly inhibiting substances within the soil organic matter in sandy arable soils with certain former land-uses that have already shown a relatively low mineralizability.

In detail, the first two papers (chapter 2 and 3) deal with the experimental parameterization of a net N mineralization model. A promising combined approach of experimental parameterization and field evaluations with undisturbed soil columns was used in order to specifically evaluate the simulation of net N mineralization. Therefore, a large set of typical North German soils, Luvisols, Cambisols, Chernozems, Podzols, Gleysols and intermediates, which represented the main areas for wheat production in Lower Saxony, was studied. **Chapter 2**

(Heumann et al. 2011a) describes part 1 of the approach: to experimentally determine field-specific temperature functions as well as soil water dependency functions for the two rate coefficients of net N mineralization that could be allocated via digitally mapped data, and to find out the least necessary discrimination of soils/soil groups in order to obtain adequate simulation results of *in situ* net N mineralization in undisturbed soil columns. Part 2 of this combined approach was elaborated in **chapter 3** (Heumann et al. 2011b) which refers to the experimental determination of pedotransfer functions for the pool sizes of the two organic N pools. These PTFs ought to be calculated via digitally mapped data, to also need just a minimum set of easily accessible management data, and to be applicable to the variety of different soil and site characteristics under winter wheat in NW-Germany.

After that, the parameterized net N mineralization model allowed site-specific calculations solely on the basis of weather and soil data that are digitally available in small-scale maps, and it was named *NET N.* **Chapter 4** (Heumann et al. 2014) was dedicated to its further necessary evaluation during the growing season of winter wheat for a set of typical NW German soils with different texture. It focused on unfertilized field plots as variable proportions of the fertilizer N could get immobilized which would complicate modelling and data interpretation and might be a task for follow-up evaluations. The objectives of this study were to evaluate, if soil net N mineralization under unfertilized winter wheat (deduced from a relatively detailed balance approach) can be satisfactorily simulated with the mineralization model *NET N*, and to examine the variation in the time patterns of simulated net N mineralization from two functional N pools within years and sites.

The elaborated model with its specific functions was further used for understanding if and how differences in yield and nitrate leaching of different agricultural crops could depend upon crop-specific use of mineralized N. As mentioned above, corn might use mineralized N much better than grain crops which might lead to higher uncertainties and therefore might impose a higher risk of over-fertilization and of Nitrate leaching. Therefore, in **chapter 5** (Heumann et al. 2013a) it was determined how nitrate leaching and yield of different crops (silage corn, winter rye, and winter barley) vary with N supply and whether differences between these crops could depend upon crop-specific use of mineralized N as estimated with *NET N*. It was also aimed to identify the crop(s) for which improved N fertilizer recommendations are most urgent, i.e. savings of fertilizer N and reductions in nitrate leaching are most probable while minimizing yield losses.

The next two chapters concentrated on possibly inhibiting substances within the SOM of sandy arable soils with certain former land-uses (heath- and woodland). The long-term goal was to enable a clearer discrimination between soil mineralization types for modelling with *NET N*. The objectives in **chapter 6** (Heumann et al. 2011c) were to explain differences in the mineralizability of soil organic N among a set of sandy arable soils by differences in the molecular-chemical composition of the SOM and their antioxidant capacity (AOC). The second objective was related to the earlier findings that sterols are enriched in soils with former heathland vegetation (Sleutel et al. 2008) and inhibit microbial activity (Bouhadjera et al. 2005) and to the hypothesis that antioxidants slow down mineralization processes in soil (Rimmer 2006). It was investigated whether sterols could have an (a) negative and (b) anti-oxidative effect on net N mineralizability of soil organic N.

In **chapter 7** (Heumann et al. 2013b) it was finally experimentally tested whether there are antioxidant or rather antimicrobial effects of selected substances on soil C and net N mineralization. A Cambisol low in potentially inhibiting substances was amended with different substances of known AOC or with potential antimicrobial properties: two phenolic acids with no (acetovanillone) or large (ferulic acid) AOC (Rimmer and Abbott 2011); Trolox, an analogue of vitamin E, because it is a standard antioxidant for determining AOC (e.g. Re et al. 1999); and β-sitosterol due to its potential antimicrobial properties (Bouhadjera et al. 2005) and no AOC (Heumann et al. 2011c).

The synopsis in **chapter 8** is dedicated to merge the results from the six papers plus a description of the achieved model applications, potential model limitations as well as the current working hypothesis on the mode of action of soil sterols.

2

Heumann S, Ringe H, Böttcher J (2011)

Field-specific simulations of net N mineralization based on digitally available soil and weather data. I. Temperature and soil water dependency of the rate coefficients.

Nutrient Cycling in Agroecosystems 91: 219–234
DOI: 10.1007/s10705-011-9457-x

Abstract

Including field- or even site-specific estimates of current net N mineralization into N fertilizer strategy is essential in order to further reduce N surpluses while maintaining crop yields, but adequate estimates are not available. Simulation models could account for many influencing factors, yet are not easily adjustable to different soil and site characteristics. Nowadays important input data for N mineralization models are digitally available. Thus, our objectives were (i) to experimentally determine specific temperature and soil water dependency functions for the rate coefficients of net N mineralization that could be allocated via digitally mapped data and (ii) to find out the least necessary discrimination between soils. Specific and general functions for the rate coefficients of two organic N pools with first-order kinetics were derived using laboratory long- and short-term incubations from a broad variety of soils. Functions were evaluated using comparisons to field incubations of undisturbed soil columns from 27 sites. Interestingly, a differentiation between specific functions of not more than three soil groups was necessary for quite accurate simulations (r^2=0.87, P<0.001; RMSE= 23 kg N ha^{-1}, n-RMSE= 29%). The two criteria for grouping, soil texture (loess *vs.* sandy/loamy classes) and humus content class (applies only to temperature functions for sandy textures), can be taken from digital soil maps. Field studies, especially under suboptimal water contents, with plant cover and N-fertilization, will have to further prove the applicability of the derived functions. Pedotransfer functions for the pool sizes also based on digitally available data are needed for automatically calculating specific estimates of net N mineralization.

3

Heumann S, Ringe H, Böttcher J (2011)

Field-specific simulations of net N mineralization based on digitally available soil and weather data: II. Pedotransfer functions for the pool sizes.

Nutrient Cycling in Agroecosystems 91: 339–350
DOI: 10.1007/s10705-011-9465-x

Abstract

Avoiding surplus N fertilization without reducing crop yields could be accomplished by accounting for current net N mineralization in N fertilizer recommendations. N simulation models would allow a quantitative consideration of important factors and could be based upon digitally mapped data. Soil-specific temperature and water functions that were derived in part I of the paper needed a differentiation between only three soil groups and the two allocating criteria were taken from digital soil maps. Here, the objectives were to experimentally determine pedotransfer functions (PTFs) for the pool sizes of two organic N pools (N_{fast}, N_{slow}) that could be calculated via digitally available data and need a minimum set of easily accessible management data. Interestingly, most important input data for the PTFs of both pool sizes were mean clay contents of the texture class (German soil classification system). However, the underlying mechanisms might be different, as N_{slow} could be positively influenced by clay-associated mineralizable SOM, whereas N_{fast} could be positively related to clay content due to higher yield potential and thus more residues on finer-textured soils. For N_{slow} including the humus class improved the accuracy of the PTF ($r^2=0.60$; $P<0.050$). For N_{fast} it was important to include a negative influence of the mean fall temperature of the preceding year ($r^2=0.42$; $P<0.010$), probably due to its influence on residue degradation before winter. Surprisingly, easily accessible management data, e.g. previous crop, did not improve the predictions in this study. Field studies with plant cover will have to further prove the applicability of the derived PTFs.

4

Heumann S, Ratjen AM, Kage H, Böttcher J (2014)

Estimating net N mineralization under unfertilized winter wheat using simulations with *NET N* and a balance approach.

Nutrient Cycling in Agroecosystems 99: 31-44
DOI: 10.1007/s10705-014-9616-y

Abstract

Eliminating uncertainty in soil N supply could reduce fertilizer input, but the amount of N mineralized during plant growth is usually still unknown. We aimed to test the relatively simple two-pool net N mineralization model *NET N* that uses site-specific temperature and soil water functions as well as pedotransfer functions (PTFs) for deriving the pool sizes in NW Germany. The objectives were to (i) evaluate, if field net N mineralization under unfertilized winter wheat could be satisfactorily simulated, and to (ii) examine the variation in time patterns of net N mineralization within years and sites and from two functional N pools: a rather small, fast mineralizable N pool (N_{fast}) and a much greater, slowly mineralizable N pool (N_{slow}). *NET N* simulations for 36 site-year-combinations and up to five dates within the growing season were evaluated with detailed N balance approaches (calculated from: soil mineral N contents, plant N uptake using estimates of green area index, simulated N leaching). Simulated net N mineralization was highly significantly correlated (r^2=0.58; RMSE= 24.2 kg N ha^{-1}) to estimations from the most detailed balance approach, with total simulated net N mineralization until mid August ranging from 62.1 to 196.5 kg N ha^{-1}. It also became evident that N mineralization from pool N_{slow} - in contrast to pool N_{fast} - was considerably higher for loess soils than for sandy or loamy soils. The results suggest that *NET N* was adequate for simulations in unfertilized winter wheat. However, further field studies are necessary for proving its applicability under fertilized conditions.

5

Heumann S, Fier A, Haßdenteufel M, Höper H, Schäfer W, Eiler T, Böttcher J (2013)

Minimizing nitrate leaching while maintaining crop yields: Insights by simulating net N mineralization.

Nutrient Cycling in Agroecosystems 95: 395–408
DOI: 10.1007/s10705-013-9572-y

Abstract

Nitrate leaching from agricultural fields still is a serious threat in temperate regions, as it often causes an exceeding of the legal nitrate threshold in the groundwater. It was often proposed to lower mineral nitrogen (N) fertilization, but suboptimal N rates are usually associated with severe yield losses. Here it was hypothesized that the crop type has a strong impact on the relation between N leaching and yield, besides N fertilizer rates, due to crop-specific use of N mineralized from soil organic matter. We analyzed N leaching and yield data of a field trial in NW-Germany with five mineral N fertilizer levels and a crop rotation of silage corn, winter barley and winter rye from 12 years. Net N mineralization was calculated with an N mineralization model, that allowed site-specific estimations, and with a balance approach based on measured field data. Yield and N leaching of the three crops strongly depended upon N supply, but N leaching could not be totally avoided even without any N fertilization, since for each crop type N leaching showed relatively constant values below an N supply of ca. 150 kg N ha^{-1}. Secondly, the possibility of minimizing N leaching with concurrent modest reduction in yield (not more than 10%) depended upon crop-specific use of mineralized N. Thirdly, these reductions appear to be most probable for silage corn due to 2 to 4 times higher N uptake in unfertilized plots (mean: 87 kg N ha^{-1}) compared to the cereals (mean: 31 kg N ha^{-1}). Thus there is a strong need to include estimates for net N mineralization in fertilizer recommendations, especially for corn, in order to more efficiently use mineralized N and reduce nitrate leaching. This is evident for the kind of sandy soil studied, and even stronger for soils with finer texture and consequently higher net N mineralization potential.

6

Heumann S, Schlichting A, Böttcher J, Leinweber P (2011)

Sterols in soil organic matter in relation to nitrogen mineralization in sandy arable soils.

Journal of Plant Nutrition and Soil Science 174: 576-586
DOI: 10.1002/jpln.200900273

Abstract

Unusually low net N mineralization in soils relatively rich in total organic C and N was repeatedly reported for sandy arable soils in North-Western Europe. In order to adequately account for it in simulation models, it is necessary to know the involved substances and processes. Therefore, nine arable top soils (< 6% clay) with a wide range of total organic C (1.1 - 5.2%) and C:N-ratios (12 - 35) were studied. The soils varied strongly in the mineralizability of soil organic N which was determined via long-term laboratory incubations (> 200 days). It was hypothesized that mineralization was controlled by antioxidants, and the Trolox Equivalent Antioxidant Capacity (TEAC) of the soils was measured. In addition, pyrolysis-field ionization mass spectrometry (Py-FIMS) was applied to investigate the influence of the molecular-chemical composition of SOM. In these soils, the compound class of sterols from Py-FIMS analysis was most closely, negatively correlated with the mineralizability of soil organic N ($r^2=0.75$, $P=0.003$). This was probably not an antioxidative effect, because the TEAC values did not correlate sufficiently with the mineralizability and the sterol intensities. However, the negative relation with sterols could be causal, since the correlation was about as close with other components of the compound class of sterols and even closer with the main plant sterol beta-sitosterol ($r^2=0.84$, $P=0.001$). In addition, the variability among samples was strongly governed by the proportions of sterols, and sterols also had a high discriminating power in principle component analysis. Furthermore, the proportions of sterols were extraordinary in those arable podzol soils that developed under previous heath- or woodland (up to 10.2% of total ion intensity from Py-FIMS). In conclusion, the inhibitory effect of these compounds needs to be investigated in more detail in order to optimize parameterization of N as well as C simulation models especially for podzolized, sandy arable soils with former heath- or woodland vegetation.

7

Heumann S, Rimmer DL, Schlichting A, Abbott GD, Leinweber P, Böttcher J (2013)

Effects of potentially inhibiting substances on C and net N mineralization of a sandy soil - a case study.

Journal of Plant Nutrition and Soil Science 176: 35-39
DOI: 10.1002/jpln.201200353

Abstract

Recently, indirect evidence was obtained for inhibition of soil net N mineralization by sterols in soil organic matter (SOM), which could have been caused by their antioxidant or anti-microbial properties. The objective of this study was to test the effect of potential inhibitors (i.e. individual compounds with known antioxidant and/or antimicrobial properties) on soil microbial mineralization processes during incubation for 7 and 14 days. A sandy agricultural soil was amended with four substances: two phenolic acids differing in their antioxidant capacity (AOC) (acetovanillone with no AOC, ferulic acid with large AOC), Trolox, an analogue of vitamin E (large AOC), and β-sitosterol (no AOC, but potential antimicrobial properties). The two compounds with large AOC (ferulic acid and Trolox) showed no significant inhibition of C and net N mineralization; and the Trolox amendment actually caused a significant increase in C and net N mineralization after 7 days of incubation. Acetovanillone with no measurable AOC caused a significant increase in C mineralization (109% of substance C added), indicating degradation of the substance, and a very pronounced negative net N mineralization within 7 days (-356%), which was interpreted as N immobilization. Only β-sitosterol showed strong inhibition of net N mineralization after 7 and 14 days (-59% and -26% respectively) which was not interpreted as N immobilization, since there was no concomitant increase in C mineralization. Thus, an antimicrobial effect of β-sitosterol specifically on microorganisms of the N cycle was suggested, but there was no clear inhibitory effect caused by the antioxidant compounds.

8 Synopsis

This thesis mainly aimed to improve site- and year-specific modelling of net N mineralization in agricultural soils of Northern Germany for online N fertilizer recommendation purposes. As sandy arable soils with certain former land-uses (former heath- and woodland) have shown a relatively low mineralizability, it was also aimed to elucidate important, possibly inhibiting substances within the SOM of these kinds of soils. The Synopsis is dedicated to merge the results from the six papers presented in chapters 2 to 7, including an essential description of the achieved model applications as well as potential model limitations. For both aspects further, partly unpublished experimental results will be considered. In addition, the current working hypothesis on the mode of action of soil sterols and its usefulness for modelling will be elaborated.

8.1 Parameterizing and evaluating the net N mineralization model *NET N* for fertilizer recommendation purposes

8.1.1 The mineralization model *NET N*

For the first time it was possible to generate a net N mineralization model that can be site-specifically parameterized using an online allocation of specific functions:

Firstly, short- and long-term laboratory incubations from a variety of typical soil types in Northern Germany with varying texture indeed allowed to derive specific temperature and soil water reduction functions for the two first-order rate coefficients k_{fast} and k_{slow} (Heumann et al. 2011a). Interestingly, a differentiation between not more than three mineralization types (soil groups) was necessary. The two criteria for grouping, soil texture class and humus content class, can be taken - at least for Lower Saxony in NW-Germany - from digital soil maps (scale 1:5000). For the water functions just one criterion was needed (loess *vs.* sandy/loamy texture classes), for the temperature functions the group of sandy/loamy soils was further separated by their humus content class. For both kinds of functions, general equations which apply to all studied soils were also determined, but - as expected - distinct deviations (up- or downward) from the specific equations would occur.

Secondly, PTFs for the pool sizes N_{fast} and N_{slow} were also experimentally determined using a total of 179 soil samples from this area (Heumann et al. 2011b). The most important input data for both PTFs were the mean clay contents of the respective texture class. Nevertheless, the underlying mechanism was assumed to be different for the two pools. Whereas pool size

N_{slow} might be positively influenced by clay-associated and/or aggregate-protected mineralizable SOM, pool size N_{fast} could be positively related due to higher yield potential and, thus, more organic N in crop residues on finer-textured soils. For N_{slow} the humus class is another factor that should be included in the PTF in order to improve the simulations. For N_{fast} it is important to include the mean fall temperature of the preceding year, explicitly from September to November, probably due to its influence on residue degradation before winter (negative correlation). Three PTFs were derived for both pools: a simple plus a multiple linear regression equation using digital data plus a multiple equation using measured data. All multiple equations just included two input data, more than these were not significant in the calculated stepwise linear regressions. Surprisingly, involvement of easily accessible management data, e.g. the previous crop, did not improve the predictions. Sandy arable soils with the suspect specific former land-uses (heath- or woodland) and proposed low mineralizability were not among the here studied main areas for wheat production in Lower Saxony.

These derived functions were evaluated in two steps using measurements of net N mineralization within several months in undisturbed unplanted soil columns from 27 field plots, representing a broad variety of NW-German soils (Heumann et al. 2011a, 2011b). In a first step, the temperature and water functions were evaluated (Heumann et al. 2011a) still using pool sizes directly obtained from incubations. Here, the general functions gave already relatively close significant correlations (r^2=0.85; P<0.001; RMSE= 36 kg N ha^{-1}; n-RMSE= 46%), but RSME and n-RMSE (RMSE relative to the mean) were much lower with specific temperature and water functions (r^2=0.87; P<0.001; RMSE= 23 kg N ha^{-1}; n-RMSE= 29%). In the second step, these specific functions were also used and pool sizes were obtained from PTFs basing on two digitally available input data (Heumann et al. 2011b). In the latter case, the correlation was almost as close as with pool sizes from incubations, and RSME and n-RMSE were somewhat higher (r^2=0.79; P<0.001; RMSE= 36 kg N ha^{-1}; n-RMSE= 46%). The combination of these temperature and soil water functions as well as PTFs was named '*NET N*'.

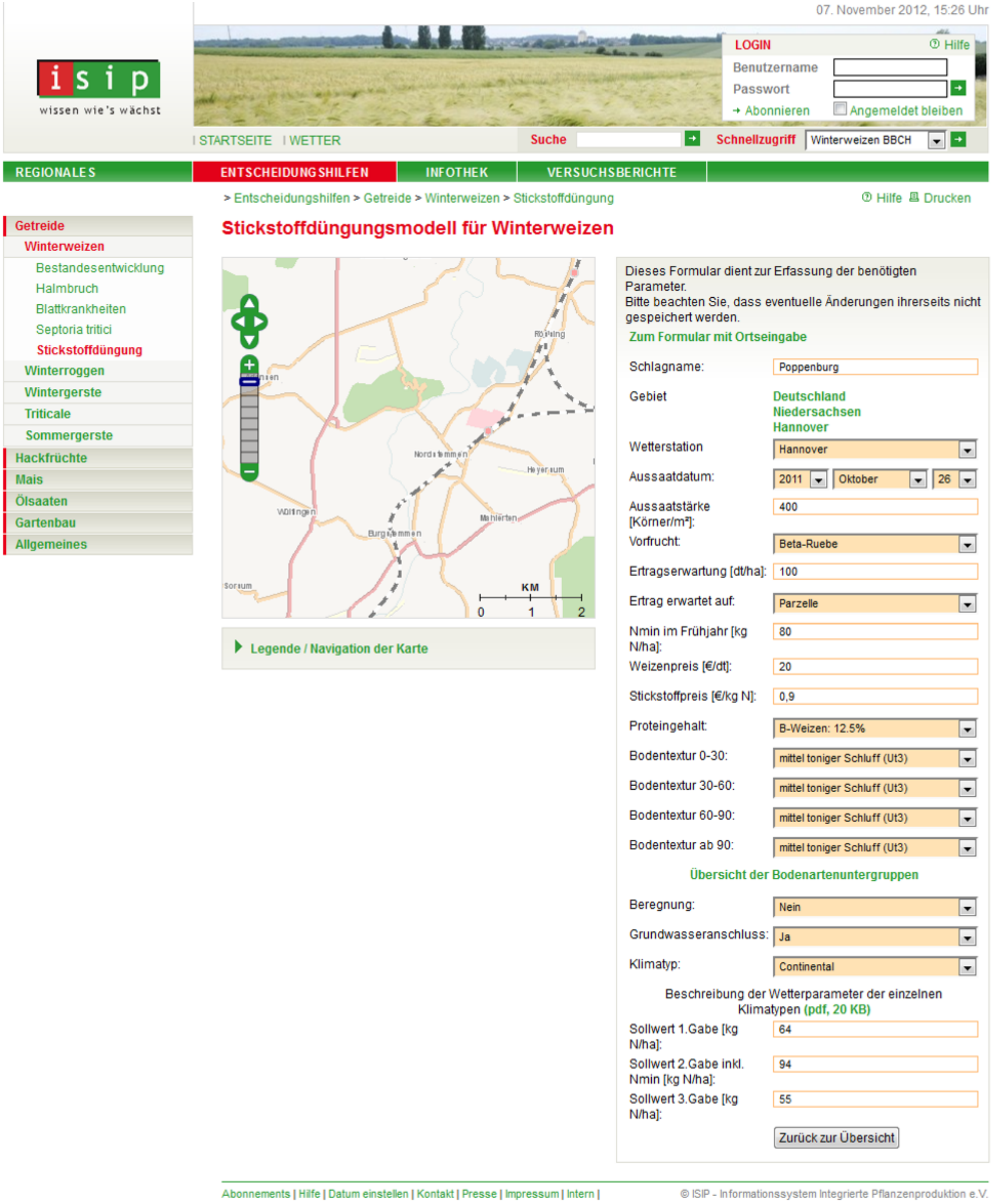
A further evaluation of *NET N* was done comparing simulations with measurements of net N mineralization from a detailed balance approach for unfertilized plots of NW-German winter wheat trials (Heumann et al. 2014). The balance approach estimate (up to 185 kg N ha^{-1} from early spring to harvest) based on field measurements of soil mineral N (in spring, in the end of the growing season, and on several dates in between), on estimates for shoot N (from green area index measurements during the vegetative growth period combined with modelling;

after Ratjen 2012), and on modelled N leaching (after Kage et al. 2003). Simulated net N mineralization with *NET N* was highly significantly correlated with the balance approach estimate (r^2=0.58; P<0.0001; RMSE= 24 kg N ha^{-1}; n-RMSE= 24%). Interestingly, comparing these results to correlations of simulated net N mineralization with more simple estimates suggests that choosing a more detailed balance approach might be more appropriate for estimating the real amount of net N mineralization in the field. This might not be surprising - but notable - as much simpler approaches are still quite often used. In detail, estimates without considering leached N (comparable to "apparent net N mineralization" after Engels and Kuhlmann 1993) appeared to be less suitable, especially due to significantly larger n-RMSE, although N leaching only ranged between 3 and 28 kg N ha^{-1} with a mean of 11 kg N ha^{-1}. An estimate neither considering leached N nor soil mineral N in spring (comparable to "soil N supply" after Dessureault-Rompré et al. 2012) was even less suitable, because r^2 was lower (r^2=0.45) and the RMSE more than twice as high. As a consequence, values for initial soil mineral N in February, that ranged from 18 to 102 kg N ha^{-1} with a mean of about 56 kg N ha^{-1}, should be subtracted when calculating net N mineralization from a balance approach (Heumann et al. 2014). Nevertheless, measured soil mineral N contents could also be erroneous due to their common high spatial variability (Köhler et al. 2006), especially in spring, when contents were not measured on individual plots, but averaged across the whole experimental site. It also became evident that mean simulated net N mineralization from pool N_{fast} was similar in sandy/ loamy and in loess soils, whereas simulated net N mineralization from pool N_{slow} was on average considerably higher for loess soils than for the group of sandy/loamy soils (Heumann et al. 2014). As a conclusion, the results suggest that *NET N* with its specific functions is adequate for simulations under the studied conditions in NW-Germany.

8.1.2 Achieved model applications

Installing an online-service for N fertilizer recommendations at www.ISIP.de

The primary application of the designed net N mineralization model *NET N* was an internet-service for N fertilizer recommendations in winter wheat at www.ISIP.de (Fig. 1). The joint recommendation model was set up together with three other groups (Tab. 1). The Chamber of Agriculture of Lower Saxony provided the sites, the field experiments, and most outside plant and soil samplings and measurements. The Institute of Crop Production and Crop Breeding, division Agronomy and Crop Production, of the Christian-Albrechts-Universität of Kiel developed a model for growth and N uptake of winter wheat. Finally, the State Authority for Mining, Energy and Geology of Lower Saxony contributed a regional soil water model, which allowed to calculate the input soil water data for the other two models and estimates for N leaching, as well as access to digitally available soil data bases (scale 1:5000).



Stickstoffdüngungsmodell für Winterweizen

Dieses Formular dient zur Erfassung der benötigten Parameter.
Bitte beachten Sie, dass eventuelle Änderungen ihrerseits nicht gespeichert werden.

Zum Formular mit Ortseingabe

Schlagname:	Poppenburg
Gebiet	Deutschland Niedersachsen Hannover
Wetterstation	Hannover
Aussaatdatum:	2011 Oktober 26
Aussaatstärke [Körner/m²]:	400
Vorfrucht:	Beta-Ruebe
Ertragserwartung [dt/ha]:	100
Ertrag erwartet auf:	Parzelle
Nmin im Frühjahr [kg N/ha]:	80
Weizenpreis [€/dt]:	20
Stickstoffpreis [€/kg N]:	0,9
Proteingehalt:	B-Weizen: 12.5%
Bodentextur 0-30:	mittel toniger Schluff (Ut3)
Bodentextur 30-60:	mittel toniger Schluff (Ut3)
Bodentextur 60-90:	mittel toniger Schluff (Ut3)
Bodentextur ab 90:	mittel toniger Schluff (Ut3)

Übersicht der Bodenartenuntergruppen

Beregnung:	Nein
Grundwasseranschluss:	Ja
Klimatyp:	Continental

Beschreibung der Wetterparameter der einzelnen Klimatypen (pdf, 20 KB)

Sollwert 1.Gabe [kg N/ha]:	64
Sollwert 2.Gabe inkl. Nmin [kg N/ha]:	94
Sollwert 3.Gabe [kg N/ha]:	55

Zurück zur Übersicht

Fig. 1: The first page of the internet-service for N fertilizer recommendations at www.ISIP.de asks for all input parameters including the location on an interactive map, the allocation of a weather station, management data, and a set of soil data that could also be taken from a soil map linked to this page.

Tab. 1: Project collaboration partners and joint model structure.

Partner	Chamber of Agriculture of Lower Saxony	Institute of Soil Science, Leibniz University of Hannover	Institute of Crop Production and Breeding, University of Kiel	State Authority for Mining, Energy and Geology
Task	Field experiments	Net N mineralization model	Plant growth and N uptake model	Regional soil water model

The project partners worked together for five years on the experimental sites shown on Fig. 1 in chapter 4. There were several field experiments on research stations operated by the Chamber of Agriculture as well as smaller studies on farmers' fields in vicinity to the research stations.

For obtaining N fertilizer recommendations, the online user has to locate the field on an interactive map and to fill in some input parameters including the reasonable allocation of a weather station and management data (Fig. 1). It is planned to import these data from digital farmers' field record systems. Preferably, the user should also fill in a set of individual soil data that could also be taken from soil maps (State Authority for Mining, Energy and Geology of Lower Saxony) linked to this page. Users may also store input data and results in a personal area of the internet-service.

The recommendation output is divided into graphs (Fig. 2) and an explanatory text. Explanatory comments for the third fertilizer rate could be like this: "… According to preceding crop, mineralization type, expected yield and pursued protein content a total N supply of 237 kg N ha^{-1} is recommended. For the third fertilizer application, a scenario for the future N uptake was calculated (Fig. 2, top) also considering the current water content and the current plant growth. Current net N mineralization is close to the average of the last ten years, i.e. 'reference years' (Fig. 2, middle). Calculated N leaching is below average and, actually, negligible (Fig. 2, bottom). Due to all these points an N uptake below average is expected and a third fertilizer application should be below average as well. The year-specific modification is minus 16 kg N ha^{-1} compared to average recommendations."

Currently, the joint model is tested under the guidance of the project partners from the University of Kiel by more German farmers and agricultural extension specialists in order to transfer it to all German states whose chambers of agriculture take part in www.ISIP.de.

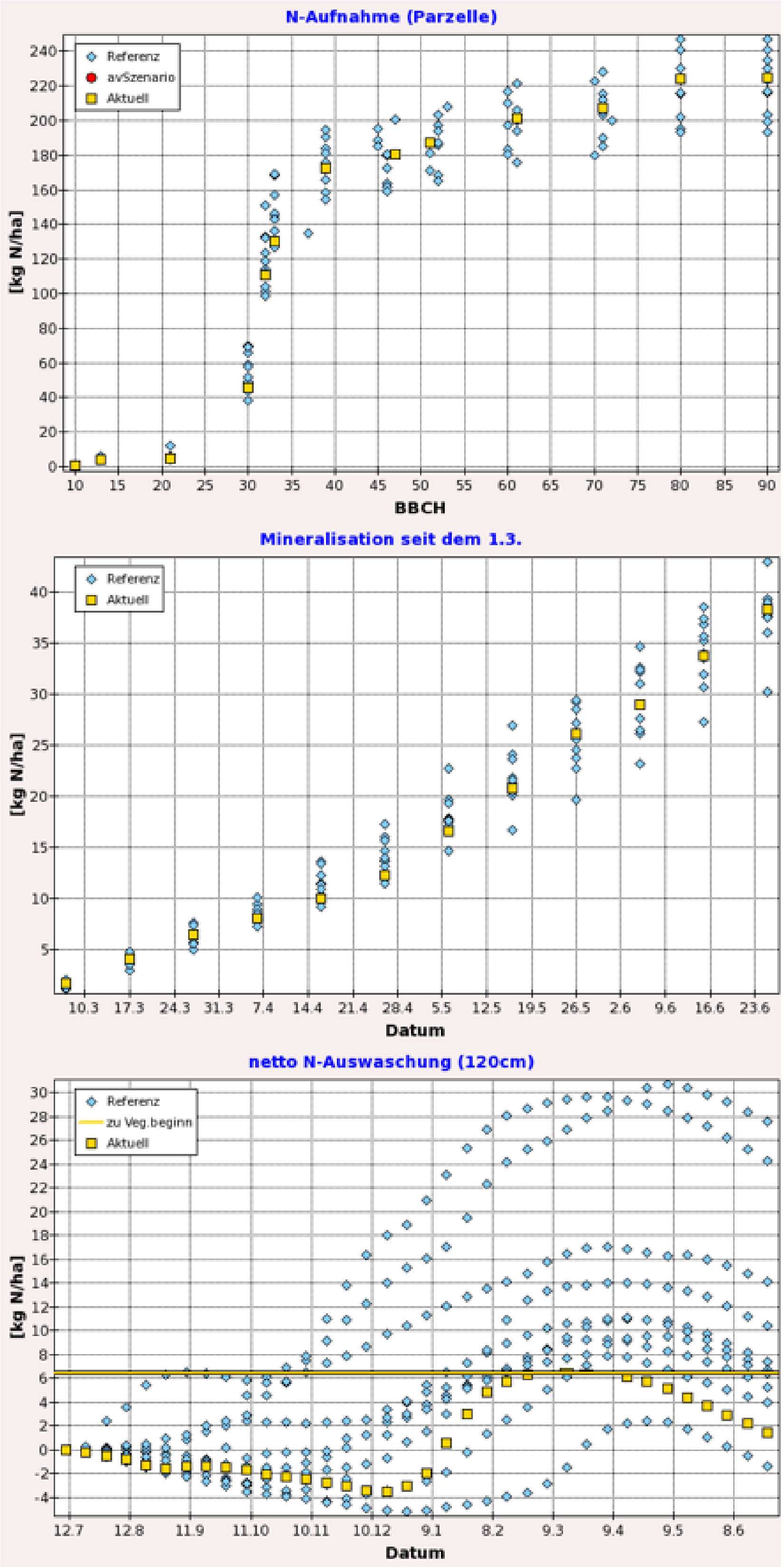


Fig. 2: An example for the output for N fertilizer recommendations at www.ISIP.de (in German): plant N uptake, net N mineralization since the 1st of March, and N leaching below 120 cm depth (from top to bottom) for the current year (large yellow squares) and the last ten years (i.e. 'reference years'; light blue diamonds). From www.ISIP.de.

Insights into minimizing nitrate leaching while maintaining crop yields

The simulations presented in the paper in chapter 5 (Heumann et al. 2013a) were originally intended to - *ex post* – explain differences between crop types in their relation of N fertilizer rate to crop yield and N leaching. An elaborate field experiment had been conducted for 12 years by the Chamber of Agriculture of Lower Saxony and the State Authority for Mining, Energy and Geology of Lower Saxony. Yield and N leaching of silage corn, winter barley and winter rye have strongly depended upon N supply, but the interrelationships had not been understood. Thus, recommendations in order to lower N leaching on susceptible sandy arable soils while largely maintaining crop yields had been difficult.

Within the 12 years under study, mean N leaching has shown relatively constant values for each crop below an N supply of 150 kg N ha^{-1} which had confirmed that N leaching cannot be totally avoided even without any N fertilization (Kayser et al. 2011; Henke et al. 2008; Köhler et al. 2006; Sieling and Kage 2006). For an N supply of more than 150 kg N ha^{-1}, N leaching crop-specifically increased. The relative increase for highest experimental N supply (ca. 200 kg N ha^{-1}) has been by far most pronounced for corn where leaching rates have increased six fold from minimum leaching rates, whereas rates for the two cereals have increased less than twofold. These relative increases in leaching rates for all crops corresponded to other leaching data from Northern Germany (Kayser et al. 2011; Sieling and Kage 2006), the extremely high rates under corn also corresponded to data from Canada and the USA (Syswerda et al. 2012; Jayasundara et al. 2007).

Crop yield also strongly depended upon crop type and followed typical optimum curves with maximum yields at highest experimental N supply. The relative yield (maximum yield = 100%) as a function of N supply has been almost the same for the two winter cereals, and has exponentially decreased to less than 30% of maximum yield in zero N plots. For silage corn without N fertilization, it has exponentially decreased to just about twice as much, i.e. 60% of maximum yield. These crop-specific reductions without N fertilizer were in accordance with other results for cereals (Köhler et al. 2006; Zimmer et al. 2005; Sieling 2004) and for corn (Zimmer et al. 2005) on sandy arable soils. Reductions for corn have been reported to be even less severe on more productive sandy soils with relatively high organic matter contents, approximately 80 - 96% of maximum yields (Kayser et al. 2011; Schröder 1999).

Actually after this precursory analysis, we hypothesized that the pronounced differences between the crops depend upon crop-specific use of mineralized N and calculated time courses of net mineralization with the *NET N* model. In addition, we hypothesized that for corn improved N fertilizer recommendations are most urgent, i.e. savings of fertilizer N and reductions in nitrate leaching are most probable while minimizing yield losses.

Interestingly, we found that in unfertilized plots silage corn might have taken up about three times as much mineralized N than e.g. winter barley - for probably two reasons. One obvious reason is the much later harvest date, since the two winter cereals were harvested between Mid July and the first days of August and silage corn 1.5 to 2 months later. A similar relation in N uptake has already been found for sugar beet *vs.* cereals (Engels and Kuhlmann 1993). The second reason is connected with plant physiology: In unfertilized plots with cereals there might have been some N shortage at tillering (around March/April) due to low N mineralization early in the year - with the possible consequence that not enough shoots were developed to use all N which was mineralized later on. This has also been indicated by Sylvester-Bradley et al. (2001) and Blankenau and Kuhlmann (2000). As a conclusion, the extremely high leaching potential after corn is mostly caused by relatively high over-fertilization, quite beyond optimum, as corn very efficiently uses mineralized N. Thus it was also confirmed that for corn improved N fertilizer recommendations are actually more urgent than for the two winter cereals studied. According to the results of the study, for corn production it is possible to combine minimization of nitrate-N leaching with concurrent modest reduction in yield (not more than 10% of maximum yield) while saving considerable amounts of N fertilizer (ca. 100 kg N ha^{-1}).

Consequently, a further testing and optimization of prediction models for net N mineralization is needed, especially for corn production, in order to more efficiently use mineralized N and thus minimize nitrate leaching. This need is evident for the kind of sandy soil studied here (2% clay, 1.7% organic C) and might be even greater for soils with finer texture and, thus, probably higher net N mineralization potential. Notably, a close synchrony of N uptake with the time course of soil N mineralization could possibly also be applicable to sugar beet. Another difficulty of adequate fertilizer recommendations for the two crops, corn and sugar beet, might probably arise from the common practice to fertilize both crops only once at drilling.

Long-term net N mineralization potential as an indicator for soil fertility

In addition to using the pool sizes for modelling, a further application could be to use at least pool size N_{slow} from long-term laboratory incubations as an indicator for soil fertility (Heumann et al. 2012). Such an indicator might be useful in rating systems for soil functions that address not only multiple soil functions but also threats, e.g. degradation by erosion or humus loss. In Germany, such rating systems have been developed and are in use in different federal states and major cities (Ad-hoc-AG Boden 2003). They combine the rating of selected and widely available soil and site parameters by easy-to-use algorithms for the assessment of individual soil functions. However, there is no standardized minimum data set, instead soil data inputs largely differ among systems, so that evaluation ratings are not transferable (Mueller et al. 2010). Even more, several oversimplifications and deficits are found in the existing systems also regarding the soil function agricultural soil productivity (Ad-hoc-AG Boden 2003) which is closely related with soil fertility.

The soils' capacity to supply N to crops through decomposition could be a main indicator for soil fertility, but due to the many factors influencing the N dynamics in soils there is currently no reference method to assess this capacity. The measurement of the soil's net N mineralization potential using long-term laboratory incubations accounts for many possible factors. Besides SOM quantity and chemical composition, it integrates the activity of soil microorganisms and the physical accessibility of SOM. In addition, the curve-splitting technique has the advantage that the mineralization from easily degradable fresh residues (pool N_{fast}) can be experimentally separated from the rather inherent N supplying capacity of the soil (pool N_{slow}). The derived PTFs for N_{slow} (Heumann et al. 2011b; 2003) might be helpful for rating a soil's long-term N supply and, thus, its fertility. Similarly, long-term incubations of Arenosols from Botswana revealed their low fertility due to low N_{slow} values, and N mineralization appeared to be too low in these soils to significantly contribute to nitrate pollution of the groundwater (Schwiede 2007).

However, it is important to stress here that pool size N_{slow} is merely a relative measure suitable for simulations and for comparing different soils, but it is not an absolute mineralization "potential" (Heumann et al. 2012). This limitation originates from the course of the cumulative net N mineralization curves, since in most of the studied soils cumulative net N mineralization did not reach an asymptotic value within the incubation time (Heumann et al. 2002). Thus, the rate coefficients of both pools have usually been fixed to mean observed values in all soils in order to eliminate the confounding effect on pool size estimates (Wang et al. 2004; Heumann and Böttcher 2004a) as the rate coefficient and the respective pool size of first-order kinetics are reciprocally related (Bonde and Rosswall 1987). In summary, this procedure allows the soil net N mineralization capacity to be explicitly expressed by its pool size which is an advantage for using it as an indicator for soil fertility.

Simplified calculations of net N mineralization for e.g. agricultural extension

Even an online-model could take too much time for some practical applications, e.g. for just getting an idea of a soil's net N mineralization within a certain time span. Such more simple estimations could be helpful for farmers and for advisors working in agricultural extension services.

The ‚Deutsche Vereinigung für Wasserwirtschaft, Abwasser und Abfall e.V.' (DWA) edits book series which generally describe evaluation schemes and soil rating methods as well as their scientific bases complemented by current research. The DWA working group that addresses soil functions compiled a booklet called 'Funktion des Bodens im Nährstoffhaushalt (N, P, K, Ca, Mg, S) landwirtschaftlich genutzter Standorte'. For one of the chapters, which deals with estimating net N mineralization of agricultural soils, simplified equations of the *NET N* model were set up. This booklet is currently being reviewed by relevant institutions and extension services before being finally printed and sold.

8.1.3 Potential model limitations

Simulations with NET N in fertilized soils

As stated above, *NET N* was found to be appropriate for typical NW-German soils with winter wheat without N fertilization, but 'the goodness of prediction could be different for fertilized crops, since mineralization and immobilization processes are strongly influenced by mineral N supply, especially in combination with plant roots' (Heumann et al. 2014). The uniformly fertilized counterparts of the unfertilized sites from chapter 4 were also studied, but the results have not yet been published.

Balance approach values for apparent net N mineralization in the adjacent fertilized sites were calculated as outlined in chapter 1.1.1 of the introduction with the applied amount of N fertilizer (N_{fert}) being subtracted on the right side of the equation (equation 1, see below). The resulting values were partly even strongly negative (Fig. 3, yet unpublished results) as already experienced before (Engels and Kuhlmann 1993). Here, some values were negative and extremely low (down to -100 kg N ha^{-1}) which is probably due to the short time spans of this study, including i.e. the short period from February until April. In the beginning of the growth period, high fertilizer N applications usually take place and are subtracted. The correlation with simulated net N mineralization was significant, but not close (Fig. 3). The main reason for this low correlation might be that the percentage of the fertilizer N which is immobilized by microorganisms is highly variable (e.g. 7 to 55% of fertilizer N after Olfs et al. 2005) as it is strongly influenced by weather, management, soil properties (Lam et al. 2012; Nieder et al. 1995a, 1995b; Rao et al. 1991), and by the crop type itself (Engels and Kuhlmann 1993).

$$ANM = \varDelta SMN + \varDelta N_{plant} + N_l - N_{fert} \qquad \text{(Eq. 1)}$$

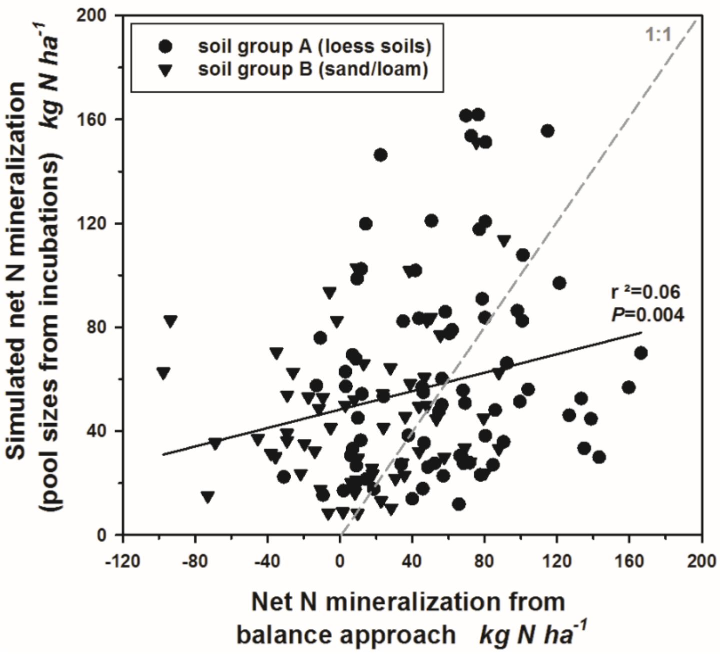


Fig. 3: Net N mineralization from the balance approach *vs.* simulated net N mineralization for the fertilized counterparts of the unfertilized sites studied in chapter 4 (compare to its Fig. 5). Unpublished results.

Nevertheless, calculations with *NET N* at www.ISIP.de are here argued to be adequate for the prevailing fertilized conditions as well. The rationale is based on (a) the argument, that N_{opt}, the economically optimized N supply, is the farmers' actual target of N fertilization and that this value is sensitive to mineralized N (McKenzie et al. 2004; Webb et al. 2000), on (b) the assumption, that the better the in-season prediction of net N release, the closer the recommendation to the *ex post* determinable N_{opt} and the lower the immobilization of fertilizer N, and on (c) the strategy that www.ISIP.de deals with 'inter-annual' differences between net N mineralization calculated for the current year and net N mineralization calculated for the last 10 years (i.e. 'reference years'). As a consequence, inter-annual differences in net N mineralization without N fertilization should be proportional or even transferable to inter-annual differences in net N mineralization at N^{opt}. A proportionality would implicate that an explicit consideration of N immobilization processes driven by N fertilization might be not strictly necessary for the prediction of inter-annual differences in net N mineralization. Arne M. Ratjen, a colleague in the joint research project from the Institute of Crop Production and Breeding at the University of Kiel (see Tab. 1), developed this rationale and we systematically analyzed it, but our manuscript has not yet been published. Nevertheless, the main result regarding this rationale will be explained here as it is a prerequisite for using *NET N*.

For systematically developing and evaluating the rationale, at first Ratjen had to define a new approach for estimating soil N release at N^{opt}. This is due to the fact that N^{opt} is a theoretical N supply, which is determined *ex post* from N rate field experiments and is usually in-between practical N supplies ($SMN^{spring} + N_{fert}$). Consequently, there are usually no plots in field N rate experiments with this theoretical N supply and, thus, there are also no measurements of soil mineral N at harvest which would be needed for calculating net N mineralization from a common balance approach (see above and chapter 1.1.1). Measurements of soil mineral N in spring, however, are regularly studied in many field experiments and could be taken from the unfertilized counterparts, because the first fertilization step usually would not have been taken place in early spring. N taken up by the plants could be derived from measurements of grain yield and their protein content, and estimated for N^{opt} by fitting quadratic N response curves to the observations (left and middle graphs in Figure 4; after Ratjen 2012).

Ratjen's new approach is based on a simple balance sheet method similar to the 'Düngeverordnung', the current German ordinance for fertilization (Bundesministerium der Justiz und für Verbraucherschutz 2007), for which four different balance components are distinguished. His so-called 'effective mineralization', Min^{eff}, is the fraction of plant N at harvest which exceeds the sum of fertilizer N, N_{fert}, and soil mineral N in spring, SMN^{spring} (equation 2; right graphs in Fig. 4). Thus the term Min^{eff} is rather focused on crop response to N release and gives an estimate for the fraction of plant N which originates from soil N mineralization.

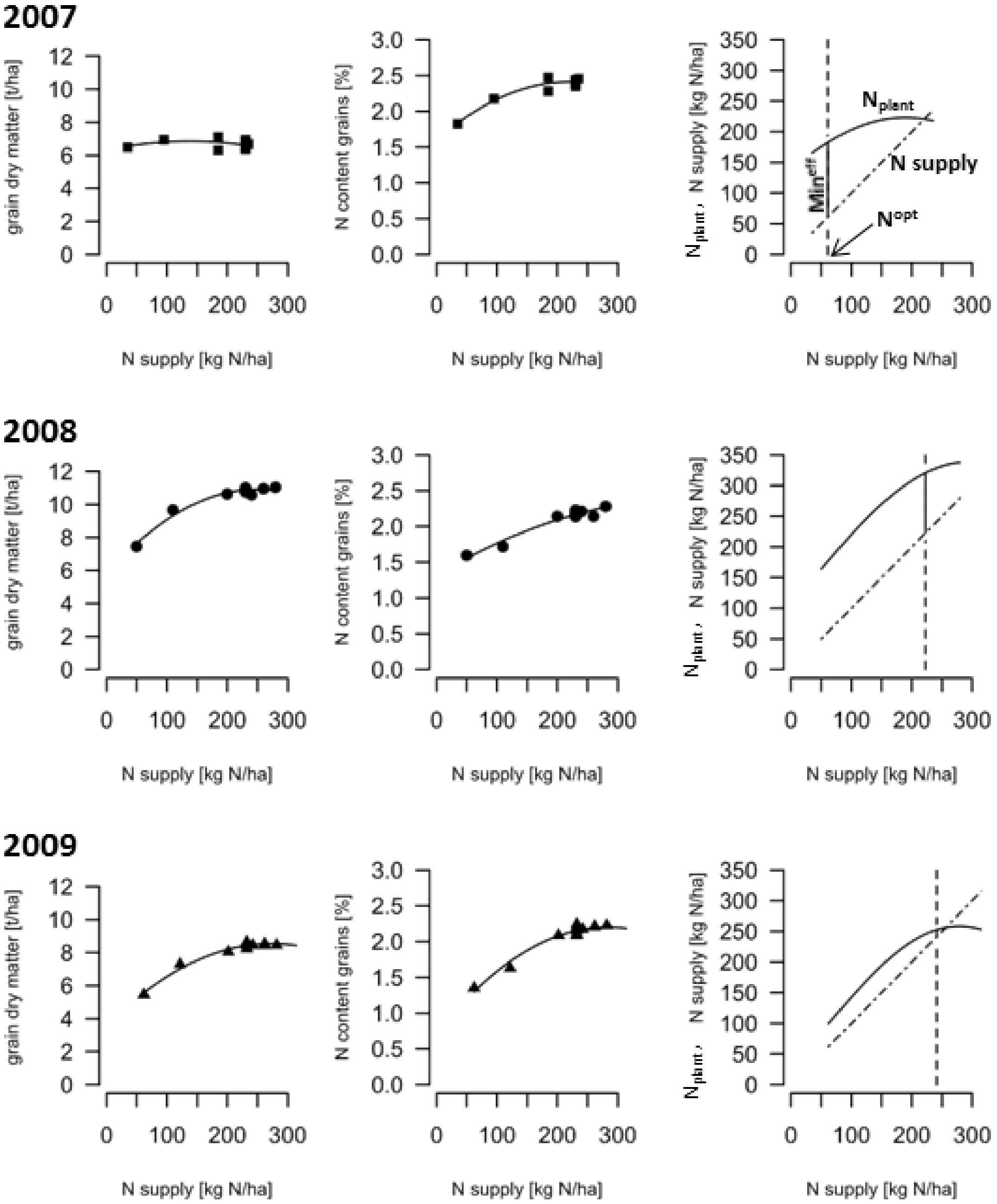


Fig. 4: Steps of the Min^{eff} calculation on the example of one experimental site (2007-2009, from top to bottom). Observed grain dry matter, grain N content and N_{plant} for several N treatments were plotted against N supply (N response curves; left, middle and right graphs respectively). Each data point represents the average of four replications. At the right side, the year-specific N^{opt} is signified by the x-coordinate of the vertical straight line. The amount of the annual Min^{eff} at N^{opt} is signified by the length of the vertical solid line. Min^{eff} (Eq. 2) is the difference between the N_{plant}-curve and N supply (SMN^{spring}+N_{fert}; diagonal line). After Ratjen (2012).

Yet it does not include soil mineral N at harvest which is not taken up by plants, but could anyway not get measured for a theoretical N supply like N^{opt}. The calculation is illustrated in Figure 4 (right graphs) for three subsequent years of an experimental site which reveals the high variability within subsequent years. Generally, it can be expected that Min^{eff} is only a valid estimator for N release from soil N mineralization as long as N_{plant} is well below its maximum. Thus this approach is only applicable when N supply is well below over-fertilization. This is guaranteed by the positive marginal yield increase at N^{opt}. Min^{eff} at N^{opt} was calculated and also Min^{eff} at a uniform N supply comparable to the data in Figure 3. At the chosen uniform N supply, N^{230} ($SMN^{spring} + N_{fert} = 230$ kg N ha^{-1}) yield was as well below maximum in all situations.

$$Min^{eff} = N_{plant} - (N_{fert} + SMN^{spring}) \tag{Eq. 2}$$

Field data from a large set of field experiments with winter wheat were used for the so far unpublished study. The experiments were also located across the state of Lower Saxony and represent main areas of wheat production (Heumann et al. 2014). There were 50 site-season combinations altogether (much more than in Heumann et al. 2014) containing 6 to 17 levels of different inorganic N fertilizers. All analyzes were done according to standard methods.

The main result is that there was no significant correlation between unfertilized treatments and uniform N supply, N^{230}, when calculating annual differences from Min^{eff} (ΔMin^{eff}) by pooling all locations (Fig. 5a; in accordance with Fig. 3). In contrast, a highly significant and very close correlation ($r^2=0.92$; $P<0.001$) was observed for ΔMin^{eff} at N^{opt} (Fig. 5b). Both regression lines do not have an intercept due to the fact that inter-annual differences in Min^{eff} were calculated by subtracting the mean over all years from Min^{eff} of the specific year. The slope of the regression line (Fig. 5) can be interpreted as a weighting factor for the transferability of ΔMin^{eff} from unfertilized to fertilized conditions. For ΔMin^{eff} at N^{opt}, this slope was very close to one, indicating a high transferability. These findings are in conformity with the observations for particular combinations of site and preceding crop with at least six experimental years. These site-specific correlations were significant with optimum N supply for all situations (r^2 from 0.69 to 0.90). With uniform N supply there was, again, no significant correlation between ΔMin^{eff} of fertilized and unfertilized treatments for these specific combinations. In summary, simulations with *NET N*, e.g. at www.ISIP.de, are adequate for calculating N fertilizer recommendations as long as inter-annual differences of net N mineralization are used.

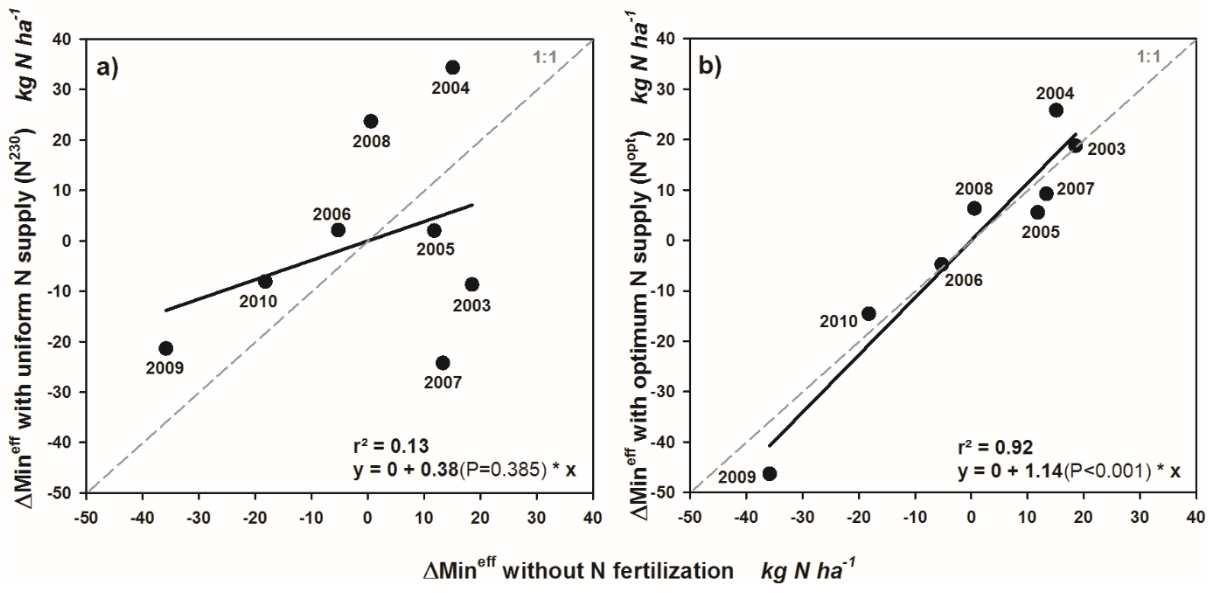


Fig. 5: Correlation of mean inter-annual differences of Min^{eff} (ΔMin^{eff}) for zero N fertilization *vs.* (a) uniform N supply (N^{230}) and (b) optimum N supply (N^{opt}). Ratjen et al. (unpublished).

Simulations with NET N for crops other than wheat

The *NET N* model was developed with the intention to be used under winter wheat which is the main crop in Northern Germany. Thus, typical soils were sampled for determining temperature and water functions (Heumann et al. 2011a) as well as the PTFs for the pool sizes (Heumann et al. 2011b). For pool size N_{slow}, a somewhat broader variety of soils than that of the main experimental stations of the Chamber of Agriculture of Lower Saxony was sampled, because N_{slow} is generally assumed to mostly depend upon soil characteristics.

The part of the model that could indeed have to be adopted when using it for crops other than wheat would be the PTF(s) for N_{fast}. This pool contains - per definition - fast mineralizable organic N and is usually assumed to mostly depend upon the prevailing plant residues and maybe soil characteristics. For its determination, sites under winter wheat with different preceding crops (winter rape, sugar beet, corn, winter cereals) have been sampled in February in order to mimic natural conditions (Heumann et al. 2011b). However, the PTFs for pool size N_{fast} did not appear to strongly depend upon the previous crop, the clay content was more important (see 8.1.1). Classes of previous crops were also significantly correlated with mean clay contents of the texture class (r=0.40, *P*=0.001). This might be caused by the local practice that potatoes, the preceding crop with the lowest mean values for N_{fast}, are only grown on sandy soils with rather low clay contents, whereas sugar beets, the preceding crop with the highest mean values for N_{fast}, are usually grown on loess soils with generally higher clay contents. Further, the mean fall temperature of the preceding year (September to November) had a significant, negative correlation in the PTF(s) for N_{fast}. Higher fall temperatures probably increase degradation of organic N in crop residues resulting in lower pool sizes in spring which is supported by an earlier finding: the higher the temperature in October the higher the soil mineral N content thereafter (Schweigert et al. 2004).

These findings imply that the derived PTFs for N_{fast} might be most adequate for simulations starting in February or March, because later on the pool sizes might be more diminished through mineralization on warm spring days. In contrast, crop growth of corn, sugar beet, and many vegetables do not start earlier than April or even May or June. Nevertheless, simulations with *NET N* were found to be also quite adequate for field experiments with corn, although in one of the four years under study, the agreement with balance approach values was not close (Heumann et al. 2013a). Interestingly, no further similar comparisons of simulated net N mineralization and balance approaches for net N mineralization under real plant cover are available in the literature, probably indicating the challenges regarding time and efforts connected with this procedure. In practice, one might be able to use the original PTFs from *NET N* for N_{fast} also for later crops like corn and sugar beet. It is suggested to start simulations in February or at least March in order to reduce pool sizes through mineralization until the actual start of crop growth.

A high analogy of net N mineralization simulated with *NET N* and two other approaches was found in a study from agricultural consulting engineers and farmers. In that study, eight fields with varying preceding crops and texture (clay contents from 3 – 366 mg kg^{-1}, mean 130 mg kg^{-1}) in the German states North Rhine-Westphalia and Hesse were studied over two years (Beisecker et al. 2015a). Simulations with *NET N* were compared to the approaches of Nordmeyer and Richter (1985) and of the N model HERMES (Kersebaum 2007). The comparison resulted in a high analogy of total simulated N mineralization from N_{fast} plus N_{slow} for all three approaches (Tab. 2) with e.g. a Spearman correlation coefficient of ca. 0.63 for N_{slow}-values ($P<0.001$; Tab. 21 of Beisecker et al. 2015b). Interestingly, the contribution of the two pools to total N mineralization differed - with *NET N* showing a higher contribution from N_{fast}. The other two approaches showed very close results, since the HERMES approach has been originally developed from the results from Nordmeyer and Richter (1985). Significant correlations with net N mineralization from a balance approach were also found for all three tested approaches (r_S of 0.57 – 0.63, $P<0.001$; Tab. 30 of Beisecker et al. 2015b), but it was not possible to really favor one of them.

Tab. 2: Ranges, means and medians of simulated net N mineralization from two organic N pools using three approaches for two subsequent years. From Tables 18 and 19 of Beisecker et al. (2015a).

	NET N			**Nordmeyer and Richter (1985)**			**Kersebaum (2007)**		
	from N_{slow}	**from N_{fast}**	**total**	**from N_{slow}**	**from N_{fast}**	**total**	**from N_{slow}**	**from N_{fast}**	**total**
2012									
Min	19	32	59	48	5	49	53	1	64
Max	166	176	336	220	23	221	209	59	217
Mean	47	78	125	103	13	110	101	14	114
Median	31	58	100	92	13	99	94	10	100
2013									
Min	8	24	37	28	4	32	28	1	34
Max	113	151	229	124	86	206	135	111	246
Mean	34	62	96	66	45	111	64	38	101
Median	27	50	69	53	50	118	60	7	76

Simulations for loamy soils with higher clay contents than originally tested

The clay content (class) is needed besides the humus content class for the site-specific allocation of adequate temperature and water functions for the studied soils (three soil groups/ mineralization types; see chapters 2 and 3). Also for the PTFs, the most important input data was the mean clay content of the texture class (Heumann et al. 2011b) which implies a high relevance. Thus it was recommended to use PTFs with two input data. For N_{slow}, the humus class was another factor that was included in the PTF in order to improve the simulations. For N_{fast}, the mean fall temperature of the preceding year was included.

Nevertheless, the boundaries for the soil criteria/soil groups should be recapitulated here. As a matter of fact, the range of studied texture classes and especially their clay contents were typical for the areas in Lower Saxony with winter wheat production, but it was not very broad when looking at main texture classes (after Sponagel 2005). Thus, in the first evaluation it could only be tentatively recognized that simulations with PTFs only basing on clay contents might not be adequate for loamy soils with clay contents above 100 mg kg^{-1} (Heumann et al.

2011b; see chapter 3). Here, measured and simulated net N mineralization in the undisturbed soil columns was generally closely and significantly linearly related and, even when both pool sizes were derived from PTFs, r^2 was around 0.80. But, within the 27 sites with mineralization measurements in field-incubated soils columns, there was one soil where measured net N mineralization was strongly overestimated by simulations (see Fig. 3 in chapter 3). This specific soil was the only soil from the sandy/loamy soil groups with clay contents above 64 g kg^{-1}, namely a loamy soil with 139 g kg^{-1} clay. The relatively high clay content resulted in large values for both, N_{fast} and N_{slow}, just as both PTFs largely depend upon clay contents. The arising large overestimation by a factor of about 2 would have been even 19 kg N ha^{-1} greater, when an equation for pool N_{slow} solely basing on clay content would have been used. This was a first hint to be careful with using the PTFs for loamy soils with clay contents of more than about 100 g kg^{-1}.

In a recent study at the LUFA Speyer in the German state Rhineland-Palatinate (A. Heger, unpublished results), undisturbed soil columns were similarly sampled also on 10 loamy vegetable production sites with clay contents of 125 to 338 g kg^{-1} (mean value = 202 g kg^{-1}). First results showed that using the standard PTFs would generate high overestimations (by a factor of 2 to 3) on these sites (A. Heger, unpublished results). In addition, the factor of over-estimation appeared to be positively related to the clay content and was actually similar to that of the one loamy soil in the study of Heumann et al. (2011b). Thus, these preliminary results suggest that for loamy soils with a clay content above ca. 100 g kg^{-1} pool size N_{slow} (and maybe also N_{fast}) might not at all increase with clay content. Instead it may stay almost constant despite increasing clay contents.

Looking closer at the originally developed PTF for N_{slow} and marking the different main texture classes (Fig. 6), it is striking that pool size N_{slow} from incubations of the few included loamy soils - strictly spoken - did not necessarily increase with clay content. In the first evaluation (Heumann et al. 2011b) this did not became obvious as the few soils with loamy texture classes fell within the range of the silty texture classes. But it would be revealed when e.g. erasing all dots from silty soils and from the one clayey soil in Fig. 6. Further,

The reasons for this lower mineralizability are not yet clear, but could be due to different quality of the SOM and/or different binding to clay particles and/or oxides. Because of the many possible interactions between these three counterparts (Mikutta 2015) this topic needs further research. Yet the high variability in pool size N_{slow} for sandy soils - and maybe as well for loamy soils - might stress the need for investigating the underlying reasons, e.g. possibly inhibiting substances (see 8.2).

As a practical consequence, it should be emphasized here that the derived PTFs should not be transferred to soil types or texture classes that were not yet tested. Additionally, PTFs basing on two soil characteristics are generally highly recommended.

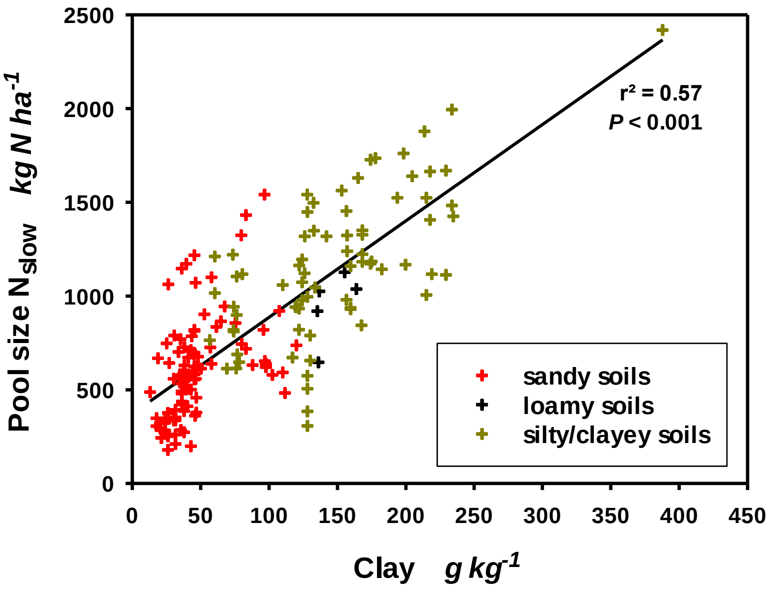


Fig. 6: Correlation of pool size N_{slow} *vs.* measured clay contents. Similar to the pedotransfer function for N_{slow} shown in Fig. 1 of Heumann et al. (2011b) (see chapter 3), but main texture classes (after Sponagel 2005) are differently colored here and mean clay contents of texture classes are removed.

Other emerging technologies for automated site-specific N fertilization

Since the beginning of the outlined experiments, various technical developments in GPS-guided precision farming with variable-rate fertilizer applications have also taken place. There are optical measurements of crop canopy (biomass, chlorophyll content) by different spectral indices (remote sensing) that are often mounted on a tractor (Olfs et al. 2005). These online approaches can combined with offline generated soil or yield maps or with airborne satellite images (Wójtowicz et al. 2016; Diacono et al. 2013). But despite the many techniques it is still challenging to gain up-to-date, high-quality, and high-resolution data showing the spatial as well as the temporal variability for these purposes (Grunwald et al. 2015).

Difficulties arise from variations in reflectance caused by solar illumination angles, sensor viewing direction, or plant row orientation as well as from “noise” introduced by soil and non-photosynthetically active plant material (Wójtowicz et al. 2016). Thus, the fusion of lab- and field-based soil measurements is being evaluated and greatly expected to enhance the capabilities to assess specific soil properties (Grunwald et al. 2015).

Besides measurements, also an understanding of soil spatial variability is needed (Diacono et al. 2013) where the use of models could strongly benefit. It was also postulated to further combine various remotely acquired data with existing simulation models in order to improve the reliability of the needed complex decision support systems (Wójtowicz et al. 2016).

Nevertheless, the greatest practical drawbacks of these methods are that they are still often too costly (Obenauf et al. 2013) or advantegous only for fields with high yield potential (Hüter et al. 2007) and for large farms like in the Eastern part of Germany. It has also been taken into consideration that even sophisticated combinations of these methods would be most useful for crops that are fertilized several times during their growth period like cereals - and not just once at drilling like corn or sugar beet. However, fully considering net N mineralization in fertilizer recommendations might be most useful for minimizing nitrate leaching under crops with high uptake of mineralized N like corn or sugar beet (chapter 5; Heumann et al. 2013a).

8.2 Elucidating possibly inhibiting substances within the SOM of sandy arable soils with specific former land-uses

8.2.1 Assignment of further mineralization types for *NET N*

Sandy arable soils with low clay contents and specific former land-uses (i.e. heath- and woodland) as well as podzolization features were not among the here studied main areas for winter wheat production in Lower Saxony. Thus no further mineralization types have been assigned, yet one could argue that it might still be advisable to use earlier PTFs for estimating pool size N_{slow} (Heumann et al. 2003) in these specific kinds of soils. Therefore, soils would have to be grouped by former land-use: former heath- or woodland *vs.* former grassland *vs.* old arable land (> 200 years). But these earlier PTFs are not helpful in their current state, as there is in fact a corresponding temperature function (Heumann and Böttcher 2004a, 2004b) to these specific PTFs, but no corresponding soil water function. And they would also not match with the newly derived temperature and soil water functions (Heumann et al. 2011a, 2011b), because rate coefficients and pool sizes have to be fitted together to the cumulative net N mineralization curves from incubations. Therefore, one option would be to recalculate the earlier derived PTFs in order to match the new temperature and soil water functions.

Otherwise, as in most cases information on former land-uses are not available, it could be more helpful to find out if there are generally inhibiting substances in the specific soils before simulating with *NET N*. New insights into substances and mechanisms that might be responsible for the relatively low mineralizability of soil organic N were gained (see below). This is in contrast to the situation with the earlier mentioned loamy soils, which showed a much lower mineralizability than loess soils with the same clay content, and where reasons are not yet clear.

The suspected substance(s) in sandy arable soils with specific former land-uses appeared to be a more general factor determining the low mineralizability of soil organic N than other soil characteristics (Heumann et al. 2011c). Nevertheless, one has to keep in mind the high analytical costs of Py-FIMS and more research is still needed before analyses of inhibiting substances could be effectively used for an assignment of new mineralization types for *NET N*. The following chapters about nature, accumulation and mechanisms of inhibiting substance(s) should merely be quoted as first results.

8.2.2 Possible nature and accumulation of inhibiting substances

Differences in the mineralizability of slowly mineralizable soil organic N could be largely explained by differences in the molecular-chemical composition of the SOM as measured by Pyrolysis-field ionization mass spectrometry (Py-FIMS) (Heumann et al. 2011c). More precisely, the proportions of total ion intensity (% TII) of the compound class of sterols revealed the closest correlations with the N_{slow} mineralization rates per total N (0.10 - 0.41 mg N g^{-1} N_{tot}^{-1} d^{-1}) among a set of sandy arable soils (r^2=0.75, P=0.003). In contrast, there were no correlations with organic C, C:N-ratio, pH, or texture.

We considered the negative relation to the Py-FIMS class of sterols to be causal, since the correlation was even closer just for the main plant sterol β-sitosterol (r^2=0.84, P=0.001) and about as close with other compounds of the class of sterols. Further, the variability among samples was strongly governed by the proportions of sterols (1.0 – 10.2% of TII). Sterols also had a high discriminating power in principle component analysis which clearly separated podzolized from non-podzolized soils.

Remarkably, the two samples with lowest N mineralizability had the largest proportions of sterols and for one of these arable top soils it was even higher than in present heathland soils in Belgium (Sleutel et al. 2008) and as high as in B_h-horizons of forest Podzols in Germany

(Wilcken et al. 1997). According to land-use maps these two specific soils have been under heath- or woodland until about 50 years ago, when the farmers started to use them for agriculture and plowed them. Therefore it is postulated that sterol accumulation is caused by former land-uses like heath- and woodland which both also support podzolization. For the other sites, however, either reliable information about the former land-use type is not available or there has been a temporary use as grassland in between. Permanent grasslands are enriched in organic N (Strebel et al. 1988), since otherwise decomposable organic substrate is physically protected from microorganisms within soil aggregates (Cambardella and Elliott 1992). As a consequence, former use as grassland remarkably increases soil mineralization rates in plowed soils and can also be traced back for mixtures of land-use types (Heumann et al. 2003). For the sandy podzolic soil in Thülsfelde (chapter 5) a good approximation between simulated net N mineralization and balance approach values was obtained despite its podzolization features and, thus, maybe low mineralizability. This could be due to reported high slurry application in the past decades, since it is known that N is still mineralized from slurry that has already been applied several years ago (Dittert et al. 1998).

The detected sterols maybe directly originate from the former heath- or woodland vegetation, because β-sitosterol is the main sterol of higher plants (Weete 1974). Besides, it could be possible that an enrichment also occurred during humification through build-up of new substances, as was shown when analyzing extracts of soil and associated vegetation samples for antioxidative compounds (Schlichting et al. 2013).

8.2.3 Proposed inhibition mechanism(s)

The extremely low mineralizability of soil organic N especially in strongly podzolized arable soils with former heath- or woodland vegetation might be caused by a - somehow - inhibitory effect of sterols. Until now no definite statement regarding the mode of action is possible. It could only be shown that, in contrast to the hypothesis that antioxidants slow down mineralization processes (Rimmer 2006) in these soils, it is probably not an antioxidative effect.

Nevertheless, the study in chapter 6 raised the general question about appropriate soil extraction methods for antioxidants within the SOM. An assay taken from food analysis, the widely-used Trolox equivalent antioxidant capacity (TEAC) (Re et al. 1999) had been transferred to soils (Rimmer and Smith 2009). To this end, an adequate extraction method for antioxidants in soils had to be found. NaOH, which had been previously used for extracting phenolic acids from soils (Martens 2002), has been more effective in solving antioxidants than deionized water, $CaCl_2$, and methanol (Rimmer and Smith 2009), and some of the compounds extracted also had antioxidant properties (Kim and Lee 2004). Our results question that NaOH is an adequate general extractant for antioxidants, since TEAC values were much closer correlated with the total ion intensity than with the ion intensity from sterols, including β-sitosterol, alone. According to the TEAC method, β-sitosterol showed anyway no antioxidant capacity (Heumann et al. 2011c) which is in contrast to earlier results from pharmaceutical studies that, however, have used different methods than TEAC (Paniagua-Perez et al. 2008; Vivancos and Moreno 2005).

The possibility of an antioxidant effect on C and net N mineralization was also excluded for two substances with known antioxidant capacity, ferulic acid (TEAC by Rimmer and Abbott 2011) and the TEAC-standard Trolox (TEAC by Re et al. 1999). Adding them to a Cambisol which was low in potentially inhibiting substances did not reduce, and partly even increased, mineralization rates after 7 and 14 days (Heumann et al. 2013b).

Our current working hypothesis is that the overall mode of inhibition by sterols is an "antimicrobial" effect. Adding β-sitosterol to the above mentioned Cambisol showed a strong significant inhibition of net N mineralization after both 7 and 14 days of incubation (-59% and -26% respectively) with no concomitant significant increase in C mineralization (Heumann et al. 2013b). The latter would otherwise lead to the interpretation that mainly an enhanced microbial degradation of the substance itself caused N immobilization. This has been assumed for the also studied Acetovanillone, a substance without any antioxidant or antimicrobial properties (Heumann et al. 2013b). From pharmaceutical studies it is just as well known that the microbial activity is inhibited by plant extracts that are rich in sterols (Smania et al. 2006), especially β-sitosterol (Bouhadjera et al. 2005). As reduced values were found for the mineralizability of organic N (Heumann et al. 2011c) as well as for net N mineralization in short-term incubations (Heumann et al. 2013b), an "overall antimicrobial effect" was hypothesized to affect mineralization from pool N_{fast} and from pool N_{slow}. Although in long-term incubations inhibition effects on pool N_{fast} could not been detected, those might have been covered by effects of different plant residues in the studied soil samples (Heumann et al. 2013b).

Similar studies but with organic layers from forest soils revealed inhibitions of 10 to 90% (often 30 to 40%) by addition of β-sitosterol as well as diterpenes on net N mineralization (Adamczyk et al. 2011), on nitrification (Adamczyk et al. 2013) as well as on different enzyme activities *in vivo* and *in vitro* (Adamczyk et al. 2015). Effects were mostly stronger for higher additions, but the increase was not proportional. Partly, even an increased respiration was measured (Adamczyk et al. 2011) and effects were not always constant throughout the incubation (Adamczyk et al. 2015). Those authors also claimed studies focusing on the process(es) behind these many pronounced effects.

There appear to be several possibilities for an antimicrobial effect of sterols on a cellular level. We currently suspect that it is a rather unspecific inhibition of the microbial metabolism, because various organic N compounds are mineralized from different microorganisms in different ways. Due to their hydrophobicity, sterols are part of biological membranes (Hannich et al. 2011; Aparicio and Aparicio-Ruíz 2000). Therefore, they could accumulate in membranes of soil microorganisms during degradation of SOM. Some sterols could, maybe only in uncommon high concentrations, have an inhibitory effect by disturbing membrane-bound transport or maybe also respiration processes. These aspects have not yet been studied for sterols. Suggested antimicrobial effects of sterols and terpenoid plant substances are inactivation of membrane-bound proteins (Engels et al. 2011) as well as disruption of cell membranes and walls (Akinpelu et al. 2008; Lim et al. 2006).

Besides an active inhibition process, strong binding and cross-linking between different components of the SOM, including sterols, has also been suggested to cause SOM recalcitrance depending upon sterol concentration (Sleutel et al. 2008). However, the measured inhibitory effect of sterol additions to short-term incubations (Heumann et al. 2013b) would be contradictory to this hypothesis. In either case, the substances as well as the activity and mode of action of these substances would have to be investigated in more detail on a cellular level, maybe in combination with enzymatic studies, in order to achieve more precise and reliable conclusions.

8.3 Perspectives

New experiments for improving *NET N* should focus on mainly five points. First, the estimation of N_{fast} for crops with later start of the growing season (e.g. corn, sugar beets, and various vegetables) is needed, as well as the systematic experimental estimation of N_{fast} by laboratory incubations for different preceding crops in a set of soils with different texture. The latter implies that there is no correlation of type of preceding crop and soil texture like it happened in the current study (Heumann et al. 2011b). Second, *NET N* should be further evaluated with measurements of field net N mineralization in undisturbed soil columns from loamy sites with clay contents > 100 mg kg^{-1} (e.g. texture classes Sl4, Ls2 to Ls4, etc.) and, preferably, from other missing texture classes of agricultural soils that did not occur within the sampled experimental stations in Lower Saxony. Third, an in-depth investigation on fertilizer immobilization at N^{opt} and on the Min^{eff}-concept is desirable in order to prove the transferability of simulations of net N mineralization from unfertilized sites to conditions of optimum fertilization. Fourth, the combination of *NET N* with remote precision farming technologies for crops like corn and sugar beet is highly requested due to a high potential for minimizing nitrate leaching while retaining yield losses at less than 10%. Last but not least, more research on a cellular level on the substances as well as the involved (e.g. antimicrobial) inhibition mechanisms is needed before this information could be effectively used for an assignment of new mineralization types for *NET N*.

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Eidesstattliche Erklärung

Hiermit erkläre ich, dass ich die vorliegende Arbeit selbstständig verfasst und nur unter Verwendung der angegebenen Quellen und Hilfsmittel angefertigt habe.

Hannover, 29.03.2016

Dr. Sabine Heumann