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NIFLUM – Nitrogen Flux Method Evaluation – Outcomes and Recommendations of an International Expert Workshop

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NIFLUM – Nitrogen Flux Method Evaluation – Outcomes and Recommendations of an International Expert Workshop

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Abstract

With financial support of the German Federal Environment Agency the **NIFLUM International Expert Workshop,** attended by European experts experienced in recording gaseous N emissions following the application of synthetic fertilizers, took place on the 28th and 29th of September 2017 in Berlin. On the workshop challenges and uncertainties involved in generating the N fertilizer emission factors (EF) for ammonia (NH_3) and nitrogen oxide (N_2O and NO_x) emissions for the EMEP Guidebook were discussed.

The workshop resulted in the following recommendations:

(1) Country-specific EF for NH_3 emissions from synthetic N fertilizers are needed for Germany. An ad hoc national expert group should be nominated examining wether or not the international results on NH_3 emissions for synthetic N fertilizers respect the agricultural production conditions in Germany. The plans for the establishment of a statewide representative measuring program for NH_3 emissions resulting from the application of synthetic fertilizers are supported, their integration into international research activities is recommended.

(2) Within the frame of a European expert group standardized emission recording methods should be set up. This group should also develop EU-wide balanced data acquisition programs in order to cover missing information. Of particular importance and urgency is the standardization of plot-applicable measurement methods enabling replicated fertilization studies. With respect to NO_x, generally agreed protocols are available, which should be considered as well.

(3) A Germany-wide well designed and coordinated complementary inventory of NH_3 emissions from synthetic fertilizers along with model development is indispensible for the derivation of resilient national and regional EF. For this purpose, a national research program addressing both the methodical development as well as the data acquisition for NH_3 emissions resulting from N mineral fertilizer application including the proposal of mitigation measures is absolutely required.

Kurzbeschreibung

Mit finanzieller Unterstützung durch das Umweltbundesamt fand am 28. und 29. September 2017 in Berlin der **Internationale Expertenworkshop NIFLUM** statt, an dem europäische Experten für die Emissionsmessung von gasförmigen N-Spezies nach dem Einsatz von synthetischen Düngern in der Landwirtschaft teilnahmen. Auf dem Workshop wurden Probleme und Unsicherheiten diskutiert, die bei der Generierung der EMEP-Guidebook-Emissionsfaktoren (EF) für Ammoniak (NH_3) und Stickstoffoxide (N_2O und NO_x) nach N-Düngemittelausbringung auftreten.

Aus dem Workshop ergeben sich folgende Empfehlungen:

(1) Für Deutschland werden länderspezifische EF für Ammoniakemissionen bei der Anwendung synthetischer N-Düngemittel benötigt. Eine nationale ad-hoc-Expertengruppe sollte etabliert werden, die prüft, inwieweit internationale Messergebnisse zu NH_3-Emissionen aus der Anwendung synthetischer Stickstoffdünger die landwirtschaftlichen Produktionsbedingungen in Deutschland zutreffend berücksichtigen. Die Planungen zur Etablierung eines landesweiten repräsentativen Messprogramms zu NH_3-Emissionen aus der Anwendung synthetischer Stickstoffdünger werden unterstützt, ihre Einbindung in internationale Forschungsaktivitäten wird empfohlen.

(2) Im Rahmen einer einzuberufenden internationalen Expertengruppe sollten standardisierte Emissionsmessverfahren auf europäischer Ebene entwickelt werden. Diese Gruppe sollte auch EU-weit Datenerfassungsprogramme durchführen, um Informationslücken zu schließen. Von besonderer Be-

deutung und Dringlichkeit ist die Standardisierung parzellentauglicher Messverfahren, die es ermöglichen, Düngevarianten repliziert zu untersuchen. In Bezug auf N_2O sind allgemein anerkannte Messprotokolle verfügbar, die ebenfalls berücksichtigt werden sollten.

(3) Eine deutschlandweit gut abgestimmte und repräsentative Quantifizierung der NH_3-Emissionen aus synthetischen Düngemitteln sowie die Modellentwicklung ist für die Ableitung belastbarer landesweiter aber auch regionaler EF zwingend erforderlich. Ein entsprechendes nationales Forschungsprogramm sollte sich sowohl mit der methodischen Entwicklung als auch mit der Datenerfassung für NH_3-Emissionen aus der N-Mineraldüngeranwendung befassen, wobei Maßnahmen zur Emissionsminderung eingeschlossen werden müssen.

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List of Abbreviations

ABC	Ammonium Bicarbonate
AS	Ammonium Sulfate
bLS	backward Langrangian Stochastic model
BMEL	Federal Ministry of Food and Agriculture
CAN	Calcium Ammonium Nitrate
CEC	Cation Exchange Capacity
CHPT	Cyclohexylphosphorictriamide
CLRTAP	Convention on Long–Range Transboundary Air Pollution
COST	Cooperation in Science and Technology
CPS	Calibrated Passive Sampling Method
CRDS	Cavity Ring Down Spectroscopy
DAP	Diammonium Phosphate
EEA	European Environment Agency
EF	Emission Factor
EMEP	European Monitoring and Evaluation Programme
EPMAN	Expert Panel on Mitigating Agricultural Nitrogen of the Task Force of Reactive Nitrogen (TFRN)
FYM	Farmyard Manure
GHG	Greenhouse Gas
IHF	Integrated Horizontal Flux Method
IPCC	Intergovernmental Panel on Climate Change
LAI	Leaf Area Index
MANOVA	Multivariate Analysis of Variance
MAP	Mono Ammonium Phosphate
NBPT	Urease Inhibitor (N-(n-butyl) thiophosphoric triamide)
NEC	National Emission Ceilings
PPD	Phenylphosphorodiamidate
QCLTDLAS	Quantum Cascade Laser Tunable Diode Laser Absorbtion Spectroscopy
SCM	Standard Comparison Method
SFP	Soil Flux Processor
TAN	Technical Ammonium Nitrate
TFEIP	Task Force on Emission Inventories and Projections
UI	Urease Inhibitor

UNECE	United Nations Economic Commission for Europe
UNFCCC	United Nations Framework Convention on Climate Change
VERA	Multinational Cooperation for the Verification of Environmental Technologies for Agricultural Production
VOC	Volatile Organic Compounds

Summary

Introduction and background

Germany is subject to numerous international, European and national commitments aimed at reducing emissions of greenhouse gases and air pollutants. These include obligations under the United Nations Framework Convention on Climate Change (UNFCCC), the Paris Agreement succeeding the Kyoto Protocol and the Geneva Convention on Long-range Transboundary Air Pollution (CLRTAP 1979). The multi-component-protocol of the United Nations Economic Commission for Europe (UNECE) and the National Emissions Ceiling Directive (NEC Directive) at EU level are setting challenging targets for the reduction of air pollutants such as, for example, ammonia and nitrogen oxides.

In order to identify and quantify emissions and emission-mitigation measures in agriculture and forestry, sources and sinks for greenhouse gases and air pollutants are calculated and published annually. Due to various information sources and evaluation methods, the ammonia emission factors in the EMEP/EEA air pollutant emission inventory guidebook – 2016 (EMEP Guidebook) have been changed several times within the last years leading to general uncertainty regarding the credibility of the resulting ammonia emission values. The application of the new EF in the German inventory resulted in significant increases of the ammonia emission values and concurrently to massive exceedances of the national emission ceilings. In consequence, a fierce debate arose among experts in the fields of plant nutrition, soil science, air pollution and climate protection as well as the industrial sectors. The correctness of the EF for Germany and the calculated emission values were seriously called into question.

Workshop objectives and methods

For overcoming the challenges of the EF and emission values, the Federal Environment Agency has launched a call for tender for convening an international workshop to be attended by German and European experts experienced in recording N species following the application of synthetic fertilizers in agriculture. The workshop had the following objectives:

- determining factors for ammonia and nitrogen oxides
- assessing the available measurement techniques and their suitability for generating datasets dedicated for the deduction of EF
- identifying knowledge gaps
- identifying and recommending reference and standard emission recording methods
- developing a roadmap for the application of suitable recording methods.

The **NIFLUM International Expert Workshop 2017** finally took place on the 28th and 29th of September in Berlin. Its main objective was to discuss challenges and uncertainties involved in generating the N fertilizer emission factors for the EMEP Guidebook. Mechanisms of gaseous nitrogen emissions (NH_3, N_2O and NO_x) from synthetic fertilizer application as well as methods for recording emissions of ammonia and nitrous oxide were discussed and evaluated in order to provide the basis for the generation of a standardized recording method for Germany and, if appropriate for Europe, with the aim of international recognition.

Basically, the workshop consisted of keynote lectures reviewing a) the influencing factors on gaseous nitrogen emissions, the underlying processes and the mitigation options, and b) in the experiences with the recording methods for nitrogen gases including the strengths, weaknesses and the require-

ments for a precise and correct N release monitoring. Each lecture section was followed by an intensive discussion using the world café discussion method.

Key questions to be dealt with in the world café session 1 included

- the identification of most relevant N release processes
- challenges involved with the recording of emissions
- requirements on an appropriate emission recording method of ammonia fluxes
- requirements on an appropriate emission recording method of nitrogen oxide fluxes.

Key questions of the world café session 2 involved

- requirements on ammonia emission recording techniques from the user's perspective
- requirements on nitrogen oxide emission recording techniques from the user's perspective
- consequences for the modeling of gaseous nitrogen
- assessing the most appropriate emission recording method for the deduction of EF.

The world café results were finally introduced by the conclusion discussion panel using the fishbowl discussion method. In doing so, the information gathered in the world café discussion panels 1 and 2 were summarized by the moderator and initially discussed by a group of four debaters. The moderator documented and visualized the key points. The conclusion panel worked out again strengths and weaknesses of emission recording techniques and gave recommendations for a standardized measurement method and recording method alternatives.

Results, conclusions and recommendations

The establishment of national N-emission inventories is based on the utilization of empiric and modeled EF. It has to be considered, however, that the empirical data base for the deduction of EF for emissions of gaseous N along with the application of synthetic N fertilizers under practical conditions has to be regarded as weak. In the course of the international NIFLUM expert workshop both various available recording and measurement methods for collecting these data and respective modeling approaches have been critically assessed.

For NH_3 the data base for the deduction of EF is especially uncertain, which resulted in up to two times larger EF in the current EMEP Guidebook, compared to those in the previous version, while at the same time the EF for mineral nitrogen fertilizers, in particular urea, determined at German sites are significantly below the ones currently in force for the EU. On the one hand, the uncertainty is resulting from a lack of sufficient spatially and temporally explicit data on NH_3 volatilization resulting from mineral fertilizer application. For the calculation of NH_3-EF 2012, for example, which were intended to be applied European-wide, data from the UK were heavily overrepresented, and NH_3 emission data from measurements at times when no fertilization took place in agricultural practice were used (experiments in summer at high temperatures with high NH_3 emissions being not relevant in practice). In particular, the available data base is not sufficient for the derivation of regionally differentiated EF, e.g. according to the twelve soil regions established in Germany (using modeling techniques).

On the other hand, the available NH_3 emission data are based on recording methods with differing precision and accuracy. Generally, a distinction is made between "open" methods which do not or hardly impact the weather parameters, and chamber methods. The first group mentioned includes micrometeorological methods which are generally regarded as reference methods although to date no empirical assessments on the precision and accuracy of these methods exist. The second group includes wind tunnels which deliver results comparable to those of micrometeorological measurements, if the wind speed inside the tunnels is controlled in accordance with the ambient wind speed. However, it can be said restrictively, that the published accuracy controls of the wind tunnel recordings tested only the functionality of the wind tunnels themselves and not the precision of the emission recordings under ambient environmental conditions. For the other methods discussed the uncertainties are even larger. Further, one of the main constraints of wind tunnels is, that rainfall, which largely affects NH_3 emissions cannot be taken into account.

For N_2O largely consistent measurement protocols exist. Due to the - compared to NH_3 - small influence of atmospheric N_2O-partial pressure on the emissions from soils, emission recordings using closed chambers can easily be conducted by evaluating the short-term linear increase of N_2O concentrations inside the chambers. Thus, the more elaborative open techniques (e.g. Eddy-covariance) which also have been proven do not necessarily have to be deployed. However, there is a need for coordination with respect to the design of the chambers, and in particular with regard to the temporal resolution of the measurements.

Against the background of this state of the art, the international NIFLUM workshop encourages the establishment of an EU-wide, coordinated research program to develop standardized methods for the precise quantification of NH_3 emissions under ambient agricultural-practice conditions.

The central goal must be to generate a broadly agreed method which considers the country specific climatic and soil properties, as well as differences in agricultural management practices. With respect to the final target (reliable, generally accepted EF for the whole of Europe) it has to be assured that the method must be proven according to both precise and accurate measurements under ambient weather and soil conditions. At the same time it has to be considered that multi plot experiments are needed to study the effects of different fertilizer types under different site conditions on the emission of NH_3. Thus, the methods to be developed have to be robust as well as cheap and must be applicable in multi plot research experiments. Both the calibrated passive sampler method and the standard comparison method may come into consideration for this purpose. However, the weaknesses of these methods, which were identified at the workshop, such as the instrumentation of the standard plots or the required distances between the differently treated experimental plots in order to avoid artifacts, have to be overcome. Integrated horizontal flux methods (IHFM) may be used for the validation of these methods; however, the IHF methods themselves need to be further tested. A central point of that matter is the development of scientifically sound approaches for testing the precision of the methods. In this regard, the ^{15}N based mass balance method might be promising.

In summary, the following is recommended:

(1) The expert group agrees that country-specific EF for ammonia could be developed and are needed for Germany. To this end, a short-term national expert group should be nominated which examines if the international results on NH_3 emissions for synthetic N fertilizers respect the agricultural production conditions in Germany and proposes EF for synthetic N fertilizers on the basis of all available data in Germany until the end of 2018. These EF should be valid until an EU-wide procedure is agreed upon.

(2) The expert group further recommends to establish an international expert group (e.g. in the frame of a COST action (cooperation in science and technology)) which should set up standardized emission recording methods at the level of the European Union. Particular important and urgent is the development and standardization of plot-applicable measurement methods enabling replicated fertilization studies. This group should, besides the methodical work, also develop EU-wide balanced data acquisition programs in order to cover missing information (including ring trials). Besides considering the scientific basis, the expert group should also take into account the profound preliminary work of VERA. With respect to N_2O, generally agreed protocols are available, which should be considered as well. When establishing the international group, it should be assured that members of the national expert groups are represented.

(3) In order to cover existing knowledge gaps with respect to NH_3 emissions in Germany, a Germany-wide well designed and coordinated complementary inventory of NH_3 emissions from synthetic fertilizers along with model development is mandatory for the derivation of resilient national and regional EF. For this purpose, a national research program addressing both the methodical development as well as the data acquisition for NH_3 emissions resulting from N mineral fertilizer application is absolutely required.

Zusammenfassung

Einleitung und Hintergrund

Deutschland unterliegt zahlreichen internationalen, europäischen und nationalen Verpflichtungen zur Reduzierung von Treibhausgasen und Luftschadstoffen. Dazu gehören diejenigen der Klimarahmenkonvention der Vereinten Nationen (UNFCCC), des Klimaabkommens von Paris in der Nachfolge des Kyoto-Protokolls und der Genfer Konvention über weiträumige, grenzüberschreitende Luftverschmutzung (CLRTAP 1979). Das Multikomponentenprotokoll der Wirtschaftskommission für Europa der Vereinten Nationen (UNECE) sowie die auf EU-Ebene gültige Richtlinie über nationale Emissionshöchstgrenzen für bestimmte Luftschadstoffe (NEC-Richtlinie) sehen ambitionierte Ziele für die Reduktion von Luftschadstoffen wie zum Beispiel für Ammoniak und Stickoxide vor.

Um Emissionen und Emissionsminderungsziele in der Land- und Forstwirtschaft zu ermitteln und zu quantifizieren, werden Quellen und Senken für Treibhausgase und Luftschadstoffe jährlich neu berechnet und veröffentlicht. Aufgrund unterschiedlicher Informationsquellen und Evaluierungsmethoden, sind die im Handbuch zur Erstellung nationaler Emissionsinventare (EMEP/EEA air pollutant emission inventory guidebook – 2016) enthaltenen Ammoniakemissionsfaktoren in den letzten Jahren mehrere Male geändert worden, was zu einer allgemeinen Unsicherheit über die Richtigkeit der ermittelten Ammoniakemissionen für synthetische Düngemittel geführt hat. Die Anwendung der neuen Emissionsfaktoren (EF) für Deutschland ab dem Jahr 2013 führte zu signifikanten Erhöhungen der Ammoniakemissionswerte und gleichzeitig zu massiven Überschreitungen der nationalen Emissionshöchstgrenzen. In der Folge entbrannte eine heftige Diskussion unter Experten aus den Bereichen Pflanzenernährung, Bodenkunde, Luftreinhaltung und Klimaschutz, aber auch im Industriesektor, in der die Richtigkeit der Emissionsfaktoren für Deutschland und die daraus berechneten Emissionswerte ernsthaft in Frage gestellt wurden.

Workshopziele und -methoden

Um die Problematik der Emissionsfaktoren und Emissionswerte einer Lösung zuzuführen, leitete das Umweltbundesamt eine Ausschreibung zur Durchführung eines internationalen Workshops ein, auf dem Experten aus Deutschland und Europa über ihre Erfahrungen bei der Messung von Stickstoffemissionen nach der Ausbringung von synthetischen Düngemitteln in der Landwirtschaft berichten sollten. Der Workshop sollte folgende Zielstellungen beinhalten:

- Ermittlung von Einfluss-Faktoren für die Emissionen von Ammoniak und Stickoxiden
- Bewertung der verfügbaren Messtechniken und ihre Eignung für den Aufbau von Datenbanken zur Ableitung von EF
- Aufdeckung von Wissenslücken
- Ermittlung und Empfehlung von Referenz- und Standardmessmethoden
- Entwicklung eines Fahrplans zur Einführung geeigneter Messmethoden.

Der **Internationale Expertenworkshop NIFLUM 2017** fand schließlich am 28. und 29. September in Berlin statt. Hauptziel war die Auseinandersetzung der mit der Aufstellung der Stickstoffemissionsfaktoren für das EMEP/EEA Handbuch verbundenen Probleme und Unsicherheiten. Mechanismen gasförmiger Stickstoffemissionen (NH_3, N_2O und NO_x) resultierend aus der Anwendung synthetischer Düngemittel sowie Methoden zur Messung von Stickstoff und Lachgas wurden diskutiert und evaluiert, um eine Basis für die Aufstellung einer Standardmessmethode für Deutschland und ggf. Europa zu schaffen mit dem Ziel der internationalen Anerkennung.

Der Workshop beinhaltete zunächst Übersichtsvorträge zu a) den Einflussfaktoren für gasförmige Stickstoffemissionen, ihren zugrundeliegenden Prozessen und den Minderungsoptionen und b) den Erfahrungen mit Messmethoden für Stickstoffemissionen einschließlich ihrer Stärken und Schwächen sowie den Anforderungen an das richtige und präzise Messen von Stickstoffemissionen. Nach jeder Lektion folgte eine intensive Diskussion im Rahmen der sog. World Café-Diskussionsmethode.

Schlüsselfragen des ersten World Cafés beinhalteten

- die Identifikation der wichtigsten Stickstofffreisetzungsprozesse
- Probleme bei der Erfassung von N-Emissionen
- Anforderungen an geeignete Messmethoden für Ammoniakemissionen
- Anforderungen an eine geeignete Messmethode für Stickstoffoxidemissionen.

Schlüsselfragen des zweiten World Cafés beschäftigten sich mit

- den Anforderungen an Ammoniakmessmethoden aus der Perspektive der Nutzer
- den Anforderungen an Messmethoden zur Erfassung von Lachgas aus der Perspektive der Nutzer
- Schlussfolgerungen für die Modellierung von gasförmigem Stickstoff
- der Bewertung der am besten geeigneten Methode zur Herleitung von EF.

Die Ergebnisse der World Cafés wurden in einer anschließenden Podiumsdiskussion mittels der sog. Fishbowl-Diskussionsmethode vorgestellt. Hierfür wurden die Informationen aus den beiden World Café-Diskussionsrunden vom jeweiligen World Café-Moderator zusammengefasst und von zunächst vier Debattierern diskutiert. Der Moderator dokumentierte und visualisierte die Kernpunkte. Das Abschlussgremium arbeitete erneut Stärken und Schwächen der Messmethoden heraus und machte Empfehlungen für eine Standardmessmethode sowie dafür geeignete Alternativen.

Ergebnisse, Schlussfolgerungen und Empfehlungen

Die Erstellung von nationalen N-Emissionsinventaren basiert unter anderem auf der Verwendung von empirischen und modellierten EF. Dabei ist die Datengrundlage zur Ableitung von Emissionsfaktoren für die N-Freisetzung bei Anwendung synthetischer N-Dünger unter Praxisbedingungen als unsicher einzuschätzen. Im Rahmen des internationalen NIFLUM Expertenworkshops wurden die vielfältigen, zur Ableitung dieser Daten eingesetzten Erfassungs- und Messmethoden sowie Modellansätze zur räumlichen und zeitlichen Auflösung von EF einer kritischen Bewertung unterzogen.

Für NH_3 ist die Datengrundlage zur Ableitung von EF besonders unsicher, mit der Folge, dass die 2013 revidierten EF bis zum Zweifachen über den bis dahin geltenden angehoben wurden, während gleichzeitig die auf Standorten in Deutschland bestimmten EF für mineralische N-Dünger, insbesondere für Harnstoff, i.d.R deutlich unter denen der derzeit geltenden EMEP Guidebook-Werte liegen. Die Unsicherheit resultiert einerseits aus einem Mangel an räumlich und zeitlich hinreichend aufgelösten Daten zur NH_3-Freisetzung bei der Düngerapplikation. So waren z.B. bei der Errechnung der NH_3-Emissionsfaktoren 2013, die europaweit Anwendung finden sollten, Daten regional nicht ausgewogen und es wurden NH_3-Emissionsergebnisse aus Untersuchungen einbezogen, die zu Zeitpunkten stattfanden, an denen in der landwirtschaftlichen Praxis nicht gedüngt wird (Experimente im Sommer bei hohen Temperaturen mit für die Praxis nicht relevanten hohen NH_3-Emissionen). Insbesondere zur Ableitung regional differenzierter Emissionsfaktoren, z.B. nach den für Deutschland differenziert vorliegenden zwölf Bodenregionen (mittels Modellen) reicht die verfügbare Datenbasis nicht aus.

Andererseits basieren die verfügbaren NH_3-Emissionsdaten auf Messmethoden mit z.T. sehr unterschiedlicher Richtigkeit (precision) und Genauigkeit bzw. Reproduzierbarkeit (accuracy). Grundsätzlich sind „offene“ Methoden, die die für die NH_3-Ausgasung relevanten Witterungsparameter nicht bzw. kaum beeinflussen, von den Kammermethoden (dynamische und geschlossene) zu unterscheiden. Zur erstgenannten Gruppe gehören die mikrometeorologischen Methoden, die generell als Referenzmethoden angesehen werden, obwohl auch für diese Methoden bisher keine empirischen Überprüfungen der Richtigkeit der Messergebnisse vorliegen. Zur zweiten Gruppe gehören die Windtunnel, die, wenn die Windgeschwindigkeit in den Tunneln der umgebenden Windgeschwindigkeit entsprechend angepasst wird, Ergebnisse liefern, die mit jenen aus mikrometeorologischen Messungen sehr gut vergleichbar sind. Allerdings ist auch bezüglich der publizierten Richtigkeitsüberprüfungen der Windtunnelmessungen einschränkend zu sagen, dass diese lediglich die Funktionalität der Windtunnels, nicht jedoch die Richtigkeit der Emissionsmessungen unter Umweltbedingungen zum Ziel hatten. Bei den übrigen diskutierten Methoden sind die Unsicherheiten noch größer. Als weitere wichtige Einschränkung beim Windtunnel ist zu bedenken, dass Niederschläge, die sich stark auf das NH_3-Ausgasungsgeschehen auswirken, nicht berücksichtigt werden.

Für N_2O liegen weitgehend abgestimmte Messprotokolle vor. Aufgrund des verglichen mit NH_3 geringen Einflusses des atmosphärischen N_2O-Partialdruckes auf die Ausgasung aus Böden ist die Erfassung mit Kammern (geschlossenen Hauben) über die Auswertung des Konzentrationsanstiegs des N_2O im Laufe kurzer Erfassungszeiten in den Hauben problemlos möglich, sodass die ebenfalls verfügbaren offenen, jedoch operativ sehr aufwendigen Methoden (Eddy-covariance) nicht zwingend eingesetzt werden müssen. Abstimmungsbedarf besteht hinsichtlich des Designs der Hauben und vor allem in Bezug auf die zeitliche Auflösung der Dynamik der Ausgasung.

Vor dem Hintergrund dieses Wissensstandes hält der internationale Workshop NIFLUM ein europaweit koordiniertes Programm zur Entwicklung, Vereinheitlichung und Abstimmung geeigneter Methoden zur Erfassung realistischer NH_3-Emissionen unter landwirtschaftlichen Praxisbedingungen für nötig.

Ziel muss es sein, eine international anerkannte, EU-weit vereinheitlichte Messmethode zu generieren, die die länderspezifischen, standörtlichen und agronomischen Besonderheiten berücksichtigt. Im Hinblick auf die Ansprüche an die zu vereinbarende Methodik ist zu bedenken, dass richtige (hohe Präzision) Emissionsmessungen mit ausreichender Reproduzierbarkeit (Genauigkeit, accuracy) unter ungestörten Witterungs- und Bodenverhältnissen (ambient conditions) nötig sind und gleichzeitig unterschiedliche Dünger und Applikationstechniken auf unterschiedlichen Standorten geprüft werden müssen. Dies verlangt die Entwicklung von robusten, preiswerten für Multiplot-Experimente geeigneten

Erfassungsmethoden. In Frage kommen dafür die einfachen, offenen Methoden (calibrated passive sampler method, standard comparison method), wobei die während des Workshops identifizierten Schwachstellen, die z.B. die Instrumentierung der Standardplots und die zur Vermeidung von Artefakten nötigen Abstände zwischen den einzelnen Versuchsplots betreffen, gelöst werden müssen. Für die Validierung müssen geeignete Methoden wie die IHF Methoden eingesetzt werden, die jedoch für sich weiter geprüft werden müssen. Im Zentrum steht dabei die Entwicklung von Ansätzen zur Bestimmung von Richtigkeit und Reproduzierbarkeit der Methoden. Vielversprechend dafür ist die auf der ^{15}N-Isothopie basierende Massenbilanzmethode.

Es wird empfohlen:

(1) Die Expertengruppe hält die Erarbeitung nationaler NH_3-EF für Deutschland für möglich und notwendig. Dazu sollte kurzfristig eine nationale Expertengruppe eingesetzt werden, die einerseits international erfassten Daten zur NH_3-Emission nach mineralischer N Düngung hinsichtlich ihrer Übertragbarkeit auf die Verhältnisse in Deutschland überprüft und andererseits auf der Grundlage der in Deutschland verfügbaren Daten bis Ende 2018 EF für NH_3-Emissionen aus Mineraldüngern erarbeitet. Diese Werte sollten Gültigkeit behalten, bis ein auf EU-Ebene abgestimmtes gemeinsames Vorgehen verabschiedet ist.

(2) Zur Vereinheitlichung der Methodiken auf EU-Ebene empfiehlt die Expertengruppe die Einrichtung einer COST Action (bzw. vergleichbare Aktivität), die neben den methodischen Arbeiten auch Messprogramme (einschließlich von Ringversuchen) zur Schließung der Datenlücken erarbeiten soll. Von besonderer Bedeutung ist hier die Entwicklung und Standardisierung von Methoden, die sich für NH_3-Emissionsmessungen in Parzellenversuchen eignen. Die Arbeiten dieser Expertengruppe sollten bezüglich der NH_3-Problematik neben den wissenschaftlichen Grundlagen auch die im entsprechenden VERA-Protokoll bereits niedergelegten Angaben berücksichtigen. Bezüglich der NO_x-Erfassung liegen abgestimmte Protokolle vor, die ebenfalls berücksichtigt werden sollten. Bei der Etablierung der internationalen Gruppe sollte dringend darauf geachtet werden, dass mindestens ein Mitglied der nationalen Expertengruppe vertreten ist.

(3) Um bestehende Kenntnislücken hinsichtlich der NH_3-Emissionen in Deutschland zu schließen, ist eine deutschlandweit konzipierte und abgestimmte Erfassung der NH_3-Emissionen aus synthetischen Düngemitteln sowie die Modellentwicklung für die Ableitung belastbarer nationaler und regionaler EF zwingend erforderlich. Dafür ist ein nationales Forschungsprogramm erforderlich, das sich sowohl mit der methodischen Entwicklung und Datenerfassung für NH_3-Emissionen aus der N-Mineraldüngeranwendung also auch mit Emissionsminderungsmaßnamen befasst.

1 Introduction

Nitrogen in Germany´s agriculture

Nitrogen is one of the building blocks of life, and its compounds occur in our soil, water and air. But anthropogenic overload and disturbance of the natural nitrogen cycle and of vulnerable systems can provoke health and environmental hazards. More than 50 per cent of Germany's reactive nitrogen compounds are released into the environment owing to farming activities. Other nitrogen inputs are attributable, in roughly equal amounts, to industrial activities, transportation and private households. Nitrogen is used as an agricultural fertilizer in order to achieve high yields of quality crops, provide sufficient plant nutrition and maintain soil fertility. The still unduly high nitrogen surpluses from Germany's farming sector result from more fertilizer being used than the crops actually need. Germany's national sustainability strategy target of limiting nitrogen surpluses to a three-year average of 80 kilograms of nitrogen (N) per hectare (ha) has yet to be reached. In 2010 Germany's aggregate nitrogen surplus was still 96 kg N ha^{-1} (Klinger et al., 2017). Ammonia and nitrogen oxide emissions are considerably contributing to the N-surplus, where livestock farming is playing the most important role.

Nevertheless the use of synthetic fertilizers is causing relevant emissions as well, due to uncertain datasets on emission rates during and after fertilization, this cannot precisely be quantified.

NH_3 emissions in Germany

Ammonia (NH_3) is mainly emitted by agriculture (about 95%). Main sources are animal husbandry, the storage and application of fermentation residues from biogas production in agriculture and the use of synthetic fertilizers. Less important are industrial processes (production of ammonia and nitrogenous fertilizers as well as calcined soda), firing processes, flue gas denitrification plants and catalytic converters in motor vehicles.

Since the mid-1990s, ammonia emissions from agriculture have dominated the summarized emissions of the acidifiers sulfur dioxide (SO_2), nitrogen oxides (NO_x) and ammonia (NH_3) calculated in acid equivalents. Calculating the acidification potential of these three pollutants, there is an increasing influence of NH_3 and thus of agriculture due to the much greater reduction of emissions of SO_2 and NO_x. From over 17% in 1990, the proportion of agricultural emissions of acidifiers rose to almost 56% in 2015. (UBA, 2014)

NOx emissions in Germany

Agriculture contributes to anthropogenic emissions of N_2O and NO_x. N_2O is a highly effective greenhouse gas and it contributes to ozone depletion in the stratosphere. In Germany about 80% of the total anthropogenic N_2O emission originate from agricultural production. These emissions include direct N_2O emission from soils, livestock houses and manure storage facilities, but also indirect N_2O emission induced by losses of reactive nitrogen from agriculture (mainly nitrate leaching and ammonia volatilization). Emission of NO_x in Germany decreased by about 56% since 1990, mainly due to reductions in the energy and transport sectors. Agriculture is responsible for about 10% of the current NO_x emissions in Germany. Emissions from agriculture are occurring as NO mainly during nitrification. (Flessa, H. see chapter 3.1).

International regulations and commitments for reducing harmful emissions and the role of emission inventories

Germany has agreed on various international, European and national commitments with differing objectives aimed at reducing emissions of greenhouse gas and air pollutant emissions. These include the United Nations Framework Convention on Climate Change (UNFCCC), the Kyoto Protocol and related Protocols, and the Geneva Convention on Long-range Transboundary Air Pollution (UNECE). Further, the EU NEC Directive is setting challenging targets for the reduction of air pollutants, i.g. ammonia.

In contrast to the other protocols of the Geneva Convention, which aim at individual pollutants, the Gothenburg Protocol focuses on the interaction of the pollutants. Due to the cross-sectoral approach, the protocol is called a multi-component protocol. The protocol consists of numerous regulations on emission reduction, monitoring, reporting, etc. and contains national emission ceilings (NECs for ammonia (and sulfur dioxide, nitrogen oxides, volatile organic compounds (VOC). With this approach, acidification, eutrophication and the formation of ground-level ozone shall be counteracted.

In order to identify and quantify emissions and emission-mitigation measures in agriculture and forestry, sources and sinks for greenhouse gases and air pollutants, emission inventories are calculated and published annually. Thus, key emission sources and critical hotspot regions are identified and underlying processes are analyzed. Emission inventories document further the time series of emissions. They allow controlling the effectiveness of mitigation measures of greenhouse gases and air pollutants and further serve as control of agreed emission reduction targets.

The compilation of the inventories must comply with the specifications of the corresponding conventions and the respective current regulations. The inventories should at the same time make data and findings available for policy advice, from which reduction potentials can be identified and the consequences of mitigation measures for emissions become transparent.

The EMEP/EEA air pollutant emission inventory guidebook provides guidance on estimating emissions from both anthropogenic and natural emission sources. It is designed to facilitate reporting of emission inventories by countries to the UNECE Convention on Long-range Transboundary Air Pollution and the EU National Emission Ceilings Directive. Member states and signatory parties are recommended to always refer to the methods documented in the latest guidebook version. The quantification of the emissions and stocks is calculated with models that describe emissions with sufficient temporal and spatial resolution in order to make emission reduction measures recognizable. This requires knowledge of the relevant activities and inventories in Germany as well as knowledge of suitable national emission factors or functions. The modeling of emissions and stocks (including stock changes) must comply with the scientific state of the art and must, according to the international guidelines, fulfill requirements on transparency, completeness, internal consistency, comparability and accuracy or uncertainty.

Impact of the EMEP emission factors for synthetic fertilizer to the national emissions inventory and the resulting uncertainties

Due to the various information sources and evaluation methods, the ammonia emission factors in the EMEP Guidebook have been changed several times within the last years, leading to general uncertainty regarding the credibility of the resulting ammonia emissions.

The revision of the EMEP Guidebook within the framework of the United Nations Task Force on Emission Inventories and Projections in 2013 led to drastic increases in the NH_3 emission factors for synthetic N fertilizers and consequently to the absolute N emissions in the German inventory. The emission factors for almost all the N containing fertilizers were increased by 76 to 606 % in the Guidebook 2013, solely the value for ammonium sulfate was revised downwards. The implementation of these emission factors in the German inventory resulted in significant changes in the emissions reported: While in the submission 2013 (using the 2009 factors) the requirements for the national emission ceilings of 550 kt for the year 2011 have been met, NH_3 emissions in the submission 2017 inventory were approximately 120 kt higher for the year 2011. Alongside to changes in the inventory methodology for the livestock sector, the new emission factors for synthetic fertilizers leading to an increase of the previous value of up to 80 kt NH_3, were mainly responsible for exceeding the German emission ceilings. (Döhler, 2015b)

In consequence, the results of the 2013 inventory a technical and scientific discussion arose among experts in the fields of plant nutrition, soil science, air pollution and climate protection as well as the industrial sectors. The correctness of the emission factors for Germany and involved inventory results were seriously called into question.

In particular, the following questions arose:

- Are EMEP emission factors for synthetic fertilizers plausible and precise for German conditions?
- Has the literature been adequately evaluated for the purpose of the inventories and are the statistical methods suitable for the derivation of emission factors?
- Are scientific publications in Germany sufficient for the derivation of national emission factors?
- Are the methods applied for recording the N emissions reflecting the reality of the N release from fertilized soils?

Consequences

The emissions factors for land application of synthetic N fertilizers, which can be used by operators of models dedicated for calculating NH_3 emission inventories must be based on reliable basic data. Recent experiences, expert evaluations and discussions suggest that these reliable data are not available. Differences due to applied monitoring methods are assumed to be a decisive reason. The available methods are highly different according to the purpose they have been developed for, not sufficiently approved and validated. Thus, although many data on emissions from synthetic fertilizers are available, the quality of data is supposed to be not precise, comparable and consistent. The use of these uncertain and inconsistent datasets led to several changes in emission factors during the recent years. Therefore, significant efforts are needed to improve the quality of data from NH_3 emission measurements in the future.

In order to overcome these challenges, the Federal Environment Agency has launched a call for tender for organizing an international workshop to be attended by experts from Germany and Europe, experienced in recording N species following the application of synthetic fertilizers under applied research conditions. The workshop should aim at an evaluation of

- the determining factors for ammonia and nitrogen emissions,
- the available measurement techniques and their suitability for generating datasets dedicated for the derivation of emission factors

and to identify resp. recommend

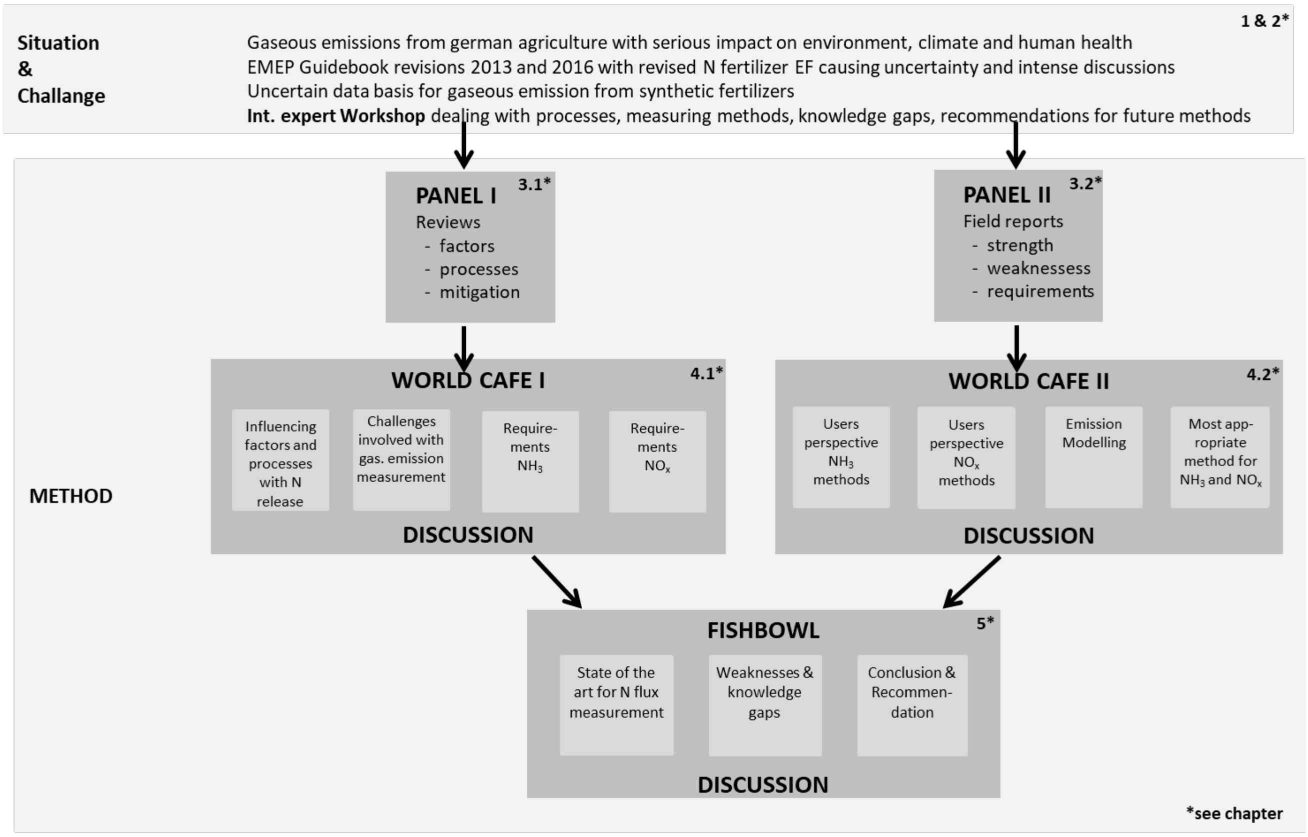
- knowledge gaps
- reference methods.
- standardized methods or
- develop a roadmap for achieving suitable methods

2 Workshop objectives and methods

The overall objective of the **NIFLUM International Expert Workshop 2017**, which took place on the 28th and 29th of September in Berlin, was to discuss challenges and uncertainties involved in generating the N fertilizer emission factors for the EMEP Guidebook. Mechanisms of gaseous nitrogen emissions (NH_3, N_2O and NO_x) from synthetic fertilizer application as well as methods for recording emissions of ammonia and nitrous oxide should be discussed and evaluated in order to provide the basis for the generation of a standardized recording method for Germany and, if appropriate, for European conditions, which should be internationally acknowledged. With unclear results, recommendations for a fast way to identify appropriate standard measurement approaches should be developed.

Basically, the workshop consisted of keynote lectures reviewing a) in **Panel 1** the influencing factors on gaseous nitrogen emissions, the underlying processes and the mitigation options, and keynote lectures reporting and reviewing b) in **Panel 2** the experiences with the recording methods for nitrogen gases, including the strengths, weaknesses and the requirements for a precise and correct N release monitoring. Each lecture section was followed by an intensive discussion using the **world café discussion method** (see Fig. 1)**.**

Figure 1: Objectives and structure of the NIFLUM Workshop



own illustration, DöhlerAgrar, 2017

This method is aiming at a fast information transfer, the collection of various arguments and rationales, the inclusion of all participants and the intensive dialog within large groups. Two world café discussion rounds were held, one dealing with the results from the review lectures on influencing factors, N release processes and mitigation options, the other with the practical experiences gathered from N emission recording campaigns. Each group was moderated by one of the introduction lecturers, who initialized the discussion, verbalized and visualized various rationales. During these sessions, each participant (except for the moderators) was free to switch between the groups. Further and finally, the moderators noted the key points of each world café group and visualized them on flip charts within the room of the conclusion panel, where all participants met for summarizing the world café results. Key questions to be dealt with in the world café session 1 according to the keynote speech Panel I included

- identifying of most relevant N release processes
- challenges involved with the recording of emissions
- requirements for a proper measurement of ammonia nitrogen fluxes and
- requirements for a proper measurement of nitrogen oxide fluxes.

Key questions of the world café session 2 according to the keynote speech Panel II involved

- requirements on ammonia nitrogen recording techniques from the user’s perspective
- requirements on nitrogen oxide recording techniques from the user’s perspective
- consequences for the modeling of gaseous nitrogen
- assessing the most appropriate recording method for the generation of emission factors.

The world café results (see chapters 4.1 and 4.2) were finally committed to the conclusion discussion panel, using the **fishbowl discussion method**.

Common panel or group discussions become ineffective in face of more than 10 participants due to long lists of speakers, less dialogues/long monologues and exclusion of speakers and arguments. The fishbowl method is used to reduce such problems. It is a „flying“ panel discussion. Debaters, who are not speaking or are not requested to answer, can be exchanged by the audience at any time.

The information gathered in the world café discussion panels I and II were summarized by the moderator and started with a group of 4 debaters. The moderator documented and visualized the key points. The conclusion panel worked out again strengths and weaknesses of recording methods and gave recommendations for a standardized measurement practice and recording method alternatives (see chapter 5).

3 Expert lectures

3.1 Reviews on mechanisms of NH_3 and NO_x emissions and mitigation options

Mechanisms of NH_3 formation and emission

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Ammonia (NH_3) emission is affected by climate, fertilizer composition, and a range of processes after the mineral fertilizer is applied to soil. Here is given a short introduction to three important soil fertilizer processes that influence NH_3 emission from fertilizers applied to soil. In this short review is presented NH_3 emission as affected by soil pH, cation exchange processes and solid phase processes.

Soil pH

Soil pH or soil exchangeable H^+ affects the potential for NH_3 emissions from applied mineral fertilizers significantly (Avnimelech and Laher, 1977; Sommer and Ersbøll 1996; Sommer et al. 2004). The emissions pH affected by the acidity of the dissolved fertilizers (Sommer et al., 2004a; Sommer et al., 2004b). The fertilizers may therefore be grouped as acidic with low NH_3 emission potential and alkaline with a high potential for NH_3 emissions (Table 1). Acid fertilizers are ammonium salts that in the soil cause a reduction in pH due to the emission of NH_3:

$$(NH_4)HSO_4(s) + H_2O(l) \rightleftharpoons NH_3(g)\uparrow + H_3O(aq) + HSO_4^-(aq) \qquad (1)$$

In contrast alkaline fertilizers, of which the most used are urea or ammonium bicarbonate (NH_4HCO_3) (Sommer et al., 2004a; Sommer et al., 2004b), increase pH due to emission of CO_2:

$$NH_4HCO_3(s) \rightleftharpoons HCO_3^-(aq) + NH_4^+(aq) \rightleftharpoons CO_2(g)\uparrow + H_2O(l) + NH_3(g)\uparrow \qquad (2)$$

The effect of mineral fertilizer acidity is modified by soil composition. In calcareous soils pH is affected by calcium crystal formation of the anion or in other words the solubility of the anions in an environment with high calcium ion (Ca^{2+}) concentration (Fenn and Hossner, 1985; Du Preez and Burger, 1988). Nitrate is soluble compared with SO_4^{2-} and HPO_4^{2-}. Sulphate and phosphate may precipitate with Ca^{2+} (Fenn and Hossner, 1985) in a process that causes dissolution of CO^{3-} and production of bicarbonate in soils, which due to a high content of lime mostly have a pH between 7 and 8:

$$NH_4^+(aq) + HSO_4^-(aq) + CaCO_3(s) \rightleftharpoons NH_4^+(aq) + HCO_3^-(aq) + CaSO_4(s) \qquad (3)$$

From this solution containing NH_4^+ and HCO_3^- the same reactions as presented in Eq. 2 may take place and thus the risk of losing large amounts of NH_3 due to emissions is high when adding ammonium sulphate and phosphate fertilizers to calcareous or newly limed soil (Larsen and Gunary, 1962; Fenn and Hossner, 1985). As a result of the pH of the fertilizers and effect of anion crystallisation, the general pattern of accumulated NH_3 emissions from fertilizers is in the following order: ammonium bicarbonate > urea > DAP > AS >CAN = MAP (Sommer and Jensen 1994; Sommer et al., 2004a; Sommer et al., 2004b).

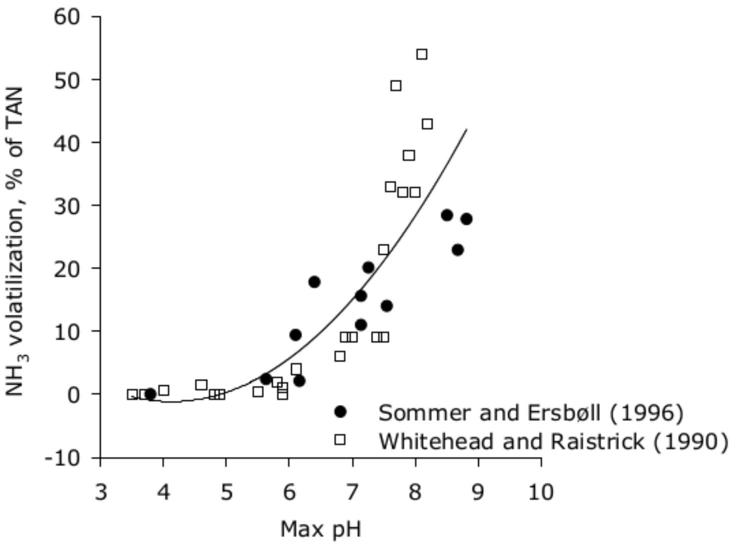
Table 1: Fertilizers grouped in relation to the acidity or alkalinity they produce when dissolved in soil water.

Acid	Moderate acid	Alkaline
$(NH_4)_2SO_4$	$(NH_4)H_2PO_4$	$(NH_4)HCO_3$
NH_4NO_3		$(NH_4)_2CO_3$
NH_4Cl		NH_3
$(NH_4)_2HPO_4$		$(NH_3)_2CO$

Sommer et al., 2004a; Sommer et al., 2004b

The soil pH buffering capacity (Avnimelech and Laher, 1977) will affect soil solution pH and influence the NH_3 emission potential of fertilizer mixed with soil. The pH buffering capacity is related to dissolved acids and bases and to organic matter functional groups. Therefore, NH_3 emissions from ammoniacal fertilizers are related to soil buffering capacity expressed as total acidity or titratable acidity (OH^- addition to increase pH to 9) (Izaurralde *et al.*, 1987; Stevens *et al.*, 1989; Sommer and Ersbøll 1996). However, the relationship is interacting with fertilizer pH buffering capacity and does not accurately depict the variations in NH_3 emissions as affected by soils (Sommer and Ersbøll, 1996). In consequence, it is seen that NH_3 emissions is exponential related measured maximum pH of the soil-fertilizer mixture (Fig. 2).

Figure 2: Cumulative NH_3 volatilisation from urea and mineral fertilizers related to maximum pH



after soil amendment

Whitehead and Raistrick, 1990; Sommer and Ersbøll, 1996

Hydrolysis of urea and dissolution ammonium salts are affected by the spatial distribution of the fertilizer in the soil, which interact with the physical form of the applied components. Around large pellets the concentration of solutes will be high and the pellets will significantly affect soil environment in contact with the pellets, whereas the concentration of H^+ and TAN in the environment of fine particles or droplets may be affected by soil characteristics. The larger pellets or particles will, therefore, be hotspots with very high TAN concentrations and pH different from that of the surrounding soil. Thus, this may be an environment where the activity of NH_3-ions should be included in the model calculations taking into account salting-out effects, because CO_3^{2-} or SO_4^{2-} concentrations may be high.

Soil CEC

TAN in soil will be partitioned between the three soil phases; liquid, solid, and gas phase. The NH_4^+ component in solution will be in equilibrium with NH_4^+ on the solid phase exchange site (Fleisher *et al.*, 1987). At pH <8, more than 95% of the TAN will be of NH_4^+ form and can be exchanged with exchangeable cations (*ex-C*). Most agricultural soil contains the divalent cations Ca^{2+} and Mg^{2+} with a high affinity for adsorption; the exchange of NH_4^+ on exchange sites therefore has to be defined with the activity ratio law (Russel, 1977):

$$NH_4^+ + ex{-}C \rightleftharpoons ex{-}NH_4 + C^+ \qquad (4)$$

$$NH_4^+ + ex - C \leftrightarrow ex - NH_4 + C^+$$

$$\frac{NH_4^+}{\sqrt{Ca^{2+} + Mg^{2+}}} = K\frac{Ex - NH_4}{Ex - Ca, Mg} \tag{5}$$

It can be seen from Eqs. (4) and (5) that increase in cation exchange capacity (CEC) will increase NH_4^+ adsorbed to the soil (Avnimelech and Laher, 1977; McGarry *et al*., 1987; Whitehead and Raistrick, 1990). At low cation exchange capacity, adsorption of NH_4^+ will not affect NH_3 emission, and at CEC below *ca.* 250 mmol kg^{-1} the effect of adsorption tends to be insignificant (O'Toole *et al*., 1985), whereas NH_3 volatilization is reduced at CEC above this level. Further, NH_4^+ does not exchange easily with Ca^{2+}, thus high Ca^{2+} concentrations in the soil may reduce the effect of a high soil CEC. This will be the case in calcareous soils, where high concentrations of exchangeable Ca^{2+} will reduce the fraction of NH_4^+ absorbed.

The consequence of the ratio law is that increasing soil water content due to rain will change the equilibrium and the divalent cations in solution will be exchanged with NH_4^+ (Chung and Zasoski, 1994). Conversely, if the solution is concentrated by water being removed due to drying, NH_4^+ will exchange with divalent cations on the CEC. Thus, during a drying event after fertilizer application, the concentration of NH_4^+ in solution will not increase linearly with evaporation of water, and in consequence the exchange process will reduce the rate of NH_3 emission expressed relative to initial TAN content; this effect is most pronounced in soil high in CEC, as can be deduced from the work of Fleisher *et al*. (1987). This retention to CEC during drying events may, in addition to the solid phase theory, contribute to an explanation of why NH_3 emission may be low from a soil that has been dried (Fenn and Kissel, 1976).

Solid phase processes

Ammonia losses from limed soils is lower after application of diammonoium phosphate (DAP) as compared to AS (Sommer and Ersbøll, 1996); the lower NH_3 emission from DAP in Ca-rich soil has been ascribed to precipitation of calcium ammonium phosphate or magnesium ammonium phosphate (struvite) (Larsen and Gunary, 1962; Whitehead and Raistrick, 1990).

The conditional stability constants for the solid phases of struvite may be calculated according to principles (Stumm and Morgan, 1970):

$$Mg^{2+} + NH_4^+ + PO_4^{-3} \rightleftharpoons MgNH_4PO_4(s) \tag{6}$$

In the microsites with fertilizers, precipitation of struvite is mainly controlled by Mg^{2+}, phosphate, and pH, as NH_4^+ is present in large amounts. Struvite precipitates and is stable at pH >6. and struvite can be formed after addition of urea and ammonium bicarbonate (ABC) to most soils and in some soils after addition of acid fertilizers; the amount of struvite precipitation will, as mentioned above, be related to Mg^{2+}, phosphate, and H^+ (Eq. 6). The precipitation of solid phases of ammonium will increase during a drying event, due to increasing concentrations of the ions in solution.

Salts with hydrated water may in absence of "free" water, i.e., in a dry soil, donate a proton to NH_3, transforming it into NH_4^+ (Evangelou, 1990). The loss of a proton produces a negative charge on the salt crystal, which facilitates the absorption of NH_4^+. This mechanism may in addition to the precipitation reactions explain the reduction in NH_3 emission from surface-applied ammoniacal fertilizers applied with Ca or Mg salts.

Options for the abatement of ammonia losses from synthetic nitrogen fertilizers

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Introduction

This article summarizes the results on ammonia emission mitigation options of field applied synthetic N fertilizers from a review on German applied research (Döhler, 2015a; Döhler, 2015b), from the UNECE expert group EPMAN (Bittman et al., 2014), and an Australian meta-analysis (Pan et al., 2016).

Ammonia emissions from synthetic fertilizer applications are dependent on fertilizer type, weather and soil conditions. Emissions from urea-based fertilizers are greater than from other fertilizer types, because hydrolysis of urea will cause localized rise in soil pH. Reported ammonia losses from urea fertilizers, which represent the most frequent synthetic N source globally, range from 1 to 60% of applied N. Losses on grassland from urea are considerably higher compared to arable land, due to higher urease activity.

Mitigation Options

Compared to urea fertilizers, the application of *non-urea based fertilizers and urea-containing mixed fertilizers* significantly decrease ammonia release by an overall reduction of 60%. Ammonium nitrate and ammonium sulphate are the two most effective non-urea fertilizers in reducing NH_3 volatilization by 75% relative to urea application.

Another and highly relevant technique is the *application timing management*. This represents a verified system to exploit the variation in ammonia emission potential based on environmental conditions, so as to use management of application timing to reduce overall emissions. Fertilizer applications under cooler conditions, cool and wet soils or prior to rainfall are associated with significantly lower ammonia emissions. In particular, the *timing management* is playing the most important role for the level of emissions for urea. Urea applied in early spring or late winter shows comparatively low losses of around 5% of applied N, when soils are wet and cold. Even if there is no rainfall following the urea application, low soil temperatures and “winter” moisture may keep losses fairly low.

Further, urea *granules* seem to lower ammonia losses significantly compared to *prills*. Band or slot incorporation of urea and other industrial fertilizers is potentially an option, but seems to be not always practicable in standing crops. Ammonia volatilization for all fertilizers tend to increase with N application rate.

Placement and rapid incorporation significantly decrease losses by more than 50% when compared to surface application, but seems to be not practicable in most cases. *Split applications* of N fertilizer, however, do not affect NH_3 volatilization, regardless of splitting frequency.

Urease inhibitors significantly decrease NH_3 volatilization. Urease inhibitors are blocking the urease activity, which decelerates urea hydrolysis, resulting for most active agents in a reduction of 50% of NH_3 volatilization (i.p. CHPT, NBPT, PPD, Ammonium Lignosulfonate). Combination of urease inhibitors may show positive or negative effects on NH_3 losses.

Controlled release fertilizers effectively mitigate NH_3 losses by more than 50%. These fertilizers extend the period during which the nutrients are available to the plant and, simultaneously, urea hydrolysis is minimized (in particular when urea granules are covered with impermeable membranes such as a sulphur coating). *Nitrification inhibitors,* however, tend to increase NH_3 volatilization.

Ammonia volatilization can be diminished by adding *NH_4^+-Ions binding amendments* like zeolite. Zeolites which show high cation exchange capacity turned out to be effective in reducing NH_3 volatilization in both acidic and alkaline soils. Ammonia loss may also be mitigated by the addition of pyrite to urea fertilizers. *Organic acid amendments* to fertilizers such as fulvic acid or humic acid reduce soil pH and subsequently NH_3 volatilization.

Irrigation significantly decreases NH_3 volatilization by one third, in contrary residue retention significantly increases losses by one forth.

Conclusion

Various strategies effectively decrease ammonia volatilization. Application timing management is one of the most effective measures in particular when fertilizers are applied at cold and wet soil conditions. Deep Placement, rapid incorporation, irrigation and coating of fertilizers as well reduce losses considerably. In particular for urea based fertilizers urease inhibitors mitigate losses by 40-50%. Split application does not effect losses, while residues may increase emissions.

Mechanisms of generation of N_2O and NO in agricultural soils

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The microbial processes nitrification and denitrification are the most important microbial sources of nitrous oxide (N_2O) and nitric oxide (NO) in soils (Firestone et al., 1989; Pilegaard, 2013).

Denitrifying bacteria produce N_2O under anaerobic conditions during the reduction of nitrate (NO_3^-) to dinitrogen (N_2), using available organic carbon (C) as energy source. During nitrification, N_2O is produced as a by-product of ammonium oxidation. This autotrophic nitrification process requires aerobic conditions and ammonium is used as energy source. Highest production of N_2O and NO during nitrification is found when nitrification is inhibited because of a low oxygen concentration. Besides these main sources, N_2O and NO are produced in other biotic and abiotic processes in soil, such as nitrifier denitrification (Wrage et al., 2001), coupled nitrification-denitrification, heterotrophic nitrification, and chemodenitrification (Heil et al., 2016).

Soil type and conditions, weather conditions, and nitrogen management have a large effect on N_2O and NO production in soils (Butterbach-Bahl et al., 2013; Pilegaard, 2013). Rapid changes in soil contents of mineral nitrogen (e.g. by application of fertilizers and manure), available C (e.g. by application of crop residues and manure), and oxygen (e.g. rainfall, groundwater fluctuations, and biological oxygen consumption) can result in strong increases in the production of N_2O and NO. Highest production is shown in fertilized soils during wet soil conditions, and especially in soils rich in organic matter (e.g. grassland soils, peat soils or soils to which organic matter is applied). The type of mineral or organic N fertilizer affects N_2O and NO emission in several ways, i.e. via the type of applied N (urea, NO_3^-, NH_4^+, and/or organic N), via the possible presence of easily available C (stimulates denitrification and oxygen consumption in the soil), and via the addition of other compounds (nutrients, metals, lime, water) affecting biological, chemical and physical soil processes.

Strategies to decrease N_2O and NO emission include improved nutrient management, in order to avoid accumulation of mineral N in the soil, and strategies aiming at decreasing the production of N_2O and NO in soil after N application, such as avoiding of N application during wet condition and the use of nitrification inhibitors.

Strategies for the abatement of N_2O and NO_x emissions

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Agriculture contributes to anthropogenic emissions of N_2O and NO_x. N_2O is a highly effective greenhouse gas and it contributes to ozone depletion in the stratosphere. In Germany about 80% of the total anthropogenic N_2O emission originates from agricultural production. These emissions include direct N_2O emission from soils, stables and manure storage but also indirect N_2O emission induced by losses of reactive nitrogen from agriculture (mainly nitrate leaching and ammonia volatilization). N_2O emission is closely linked to the input and microbial transformation of nitrogen in agriculture. In addition, large emissions of N_2O can occur during production of synthetic N fertilizers. N_2O emissions from production of ammonium nitrate can vary between about 4 t CO_2-equivalents per ton nitrogen (old production techniques) and about 1 t CO_2-equivalents per ton nitrogen (best available techniques). There is a large potential to reduce N_2O emission by using synthetic N fertilizers with a low CO_2-equivalent footprint. At the global scale population increase and human diet shifts are the main drivers of increasing N_2O emission from agriculture. In Germany area-related and yield-related N_2O emissions can be significantly reduced by improving efficiency of nitrogen use along the whole production chain. This includes the strict minimizing of nitrogen losses via nitrate leaching and ammonia emission. Nitrogen surplus strongly increases yield-scaled N_2O emission. The efficient recycling of nitrogen in animal slurries, manure and digestates in plant production is essential to improve total nitrogen use efficiency in agriculture and to reduce N_2O emission. Nitrification inhibitors may help to reduce nitrate leaching and N_2O emission. The current trend of increasing ammonia emissions from German agriculture has to be stopped and reversed. There are close links between emissions of NH_3 and N_2O.

Emission of NO_x in Germany decreased by about 56% since 1990, mainly due to reductions in the energy and transport sector. However, we are still far away from the national reduction target of the year 2020 (minus 39% compared to 2005). Emission of NO_x triggers ozone formation, nitrogen deposition, indirect N_2O emission, and respiratory diseases. Severe problems with high NO_x concentrations occur in particular in urban areas. Agriculture is responsible for about 10% of the current NO_x emission in Germany. Emissions from agriculture are occurring as NO mainly during nitrification. Measures to reduce N_2O emission from agriculture will also reduce emission of NO.

Mitigation of N_2O and NO_x emission should be an element of a more comprehensive nitrogen concept in agriculture that considers yield security but also resource efficiency and protection of soil, water, air and climate. There is no time to loose since it is obvious that Germany has severe problems to comply with binding international emission reduction targets.

The consumer has to be included in strategies to reduce emissions of greenhouse gases and air pollutants from agriculture since dietary habits have a strong influence on emission footprints of agricultural products.

3.2 Reviews on mechanisms of NH_3 and NO_x emissions and mitigation options

The VERA Test Protocol: Verification of emission reduction technologies in agriculture - General aims and current state of test protocol for land applied manure

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The objective of the Verification of Environmental Technologies for Agricultural Production (VERA) is to generate harmonized test procedures on the emission reduction performance of various technologies. VERA is a multinational cooperation initiated by Germany, Denmark and The Netherlands (VERA, 2017). Harmonizing test and verification procedures will result in a comparable test quality within Europe and simplify national approval processes by the application of common VERA results. For manufacturers this system reduces costs for the proof of functionality in the individual countries.

The verification of measurements is conducted by the VERA verification bodies. A verification is not to be confused with a certification: the verification focusses on the compliance of a test with the applicable VERA test protocol and the plausibility of data. It does not confirm the compliance of the technology with national or legal requirements which might differ from country to country.

The test protocols are developed by international experts. Currently, test protocols are available for land application of manure, manure storage, slurry separation, air cleaning and housing systems. A protocol for biogas is in preparation.

The protocol for land application of manure is currently under revision. Main aspect for discussions within the expert group are acceptable measurement techniques: apart from micrometeorological methods also wind tunnels have advantages as long as the aim is to determine reduction efficiencies compared to a reference technology. The revised version will not only describe the measurement techniques, but also define the reference technology, the mandatory test conditions and the measurement strategy including the number of adequate replicates.

For the time being the protocol on land applied manure will focus primarily on ammonia measurements. Even though odour is a politically very important aspect, it will not be considered as long as there are no appropriately validated methods for odour measurements in land application.

The idea to add emission measurements also from synthetic fertilizers to the scope of the test protocol was abandoned. Measurement strategies and techniques differ in some aspects too much. A separate test protocol will be developed later to be able to have harmonized procedures available for generating emission factors for synthetic fertilizers and mitigation efficiencies of application systems, inhibitors and coatings.

Estimating ammonia emissions from mineral fertilizers; a Tier 3 methodology

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Ammonia emission from mineral fertilizers will be a key source in most emission inventories, making a Tier 2 or higher methodology obligatory. The Guidebook version from 2007 (European Environment Agency, 2007) contained a methodology for ammonia emission from synthetic fertilizers that was last updated in February 2003. This was based on a review of the literature, including earlier reviews. It did not include the collation of data and statistical analysis. Separate emission factors were used for each of three climate zones, with the climate zones dependent upon air temperature in the spring. Thereafter, the sequence of events was as follows.

1. During the major revision of the Guidebook in 2008/2009, the three climate zones were replaced by equations linking emission to the air temperature in spring (European Environment Agency, 2009). The source of these equations is unclear but may have been linear interpolations between the midpoints of the previous three climate regions.
2. The Agriculture and Nature Expert Panel identified a review of ammonia emissions from fertilizers as a high priority in 2009.
3. In 2012, the EEA contracted another department in my university to undertake a revision of a limited number of Guidebook chapters, including ammonia emission from fertilizers. This review found scientific papers containing 364 empirical observations. With the exception of soil pH, no significant relationships were found between these observations and a range of management, climatic and soil variables, so it was agreed for the Guidebook 2013 version (European Environment Agency, 2013) to establish emission factors for each fertilizer type that were based only on soil pH. For Parties with cooler climates, this effectively increased emission factors for some fertilizers quite substantially.
4. Following detailed criticism at the 2014 TFEIP meeting, the Agriculture and Nature panel agreed that further work on the methodology was necessary. The EEA contracted Ricardo-AEA to do this in 2015/2016. It was agreed between the Agriculture and Nature Expert Panel that the work would be done in collaboration with the Department of Agrocecology, Aarhus University (using Danish funding in kind), with the contractors responsible for data collaction and Aarhus University responsible for data analysis. On the basis of 1209 observations from 109 separate studies, statistically significant empirical relationships between ammonia emission and a range of explanatory variables were developed. Taking into account the likely availability of input data, it was decided to generate Tier 2 emission factors based on fertilizer type, soil pH and air temperature. In the absence of survey data, the expected application periods for synthetic fertilizers were determined by expert judgement, and the Tier 2 emission factors generated on this basis. These appear in the 2016 version of the Guidebook (European Environment Agency, 2016).

The publication of (Pan et al., 2016) identified additional publications reporting studies in which ammonia emissions from synthetic fertilizers had been measured. Aarhus University obtained a copy of their database and identified a number of publications that had been missed in the earlier searches. The data from these studies has been incorporated in the Aarhus University dataset. Furthermore, it became clear that there were further data in non-English language scientific journals and reports. We are attempting to access these data.

The final objective is to develop a Tier 3 method that could be used by countries that have or could obtain activity data with a high spatial and temporal resolution. Tier 3 emission factor equations are currently being produced, based on approximately 1500 observations. However, the dataset used to develop the functional relationships is very unbalanced, meaning it is not possible to examine the interactions between explanatory variables (e.g. air temperature and rainfall) or whether significant rainfall immediately after application would be a better predictor of emission (as theory would predict). To do this would require additional, standardised measurements.

The management plan of the Guidebook includes periodic assessments of all methodologies in relation to developments in knowledge. However, we do not anticipate further adjustments of the Tier 2 emission factors for this source in the Guidebook in the near future.

Modeling ammonia emissions from urea and organic fertilizers – potentials and challenges

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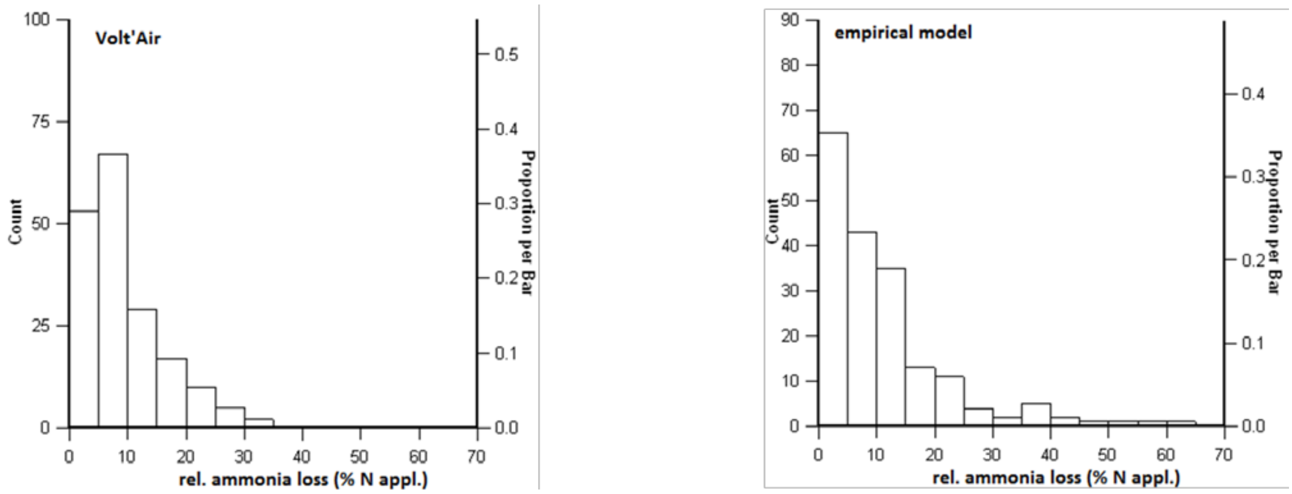
Ammonia emissions from field applied organic and urea fertilizers pose a high risk at agronomic efficiency and environmental safety. Modeling approaches were tested for both mineral and organic fertilizers to derive emission factors and to discriminate between ammonia emission characteristics of different organic fertilizer types.

The use of emission factors (EF) for ammonia (NH_3) after fertilizer application is a central tool for nitrogen management. Scenario modeling of emissions based on long-term weather data and variable application dates could provide a robust basis for the derivation of EFs. Two model approaches were used to quantify emissions of urea applied to winter wheat. The approaches comprised the dynamic model Volt'Air' and a statistical model. Scenarios were run for 15 years and 4 application dates in each year for 3 research sites. The empirical model performed better at predicting cumulative losses. Both models simulated more than half of relative NH_3 emissions (% urea N applied) in a range of 0-10%. The average and median EFs by both models over all application dates were 10.2% and 8.1%, respectively, and were substantially lower than the current European EFs for urea (15-16%). (Pacholski et al., 2017). Scenario modeling should be considered as a tool for the derivation of robust and representative EFs for NH_3 emissions for urea.

Figure 3: Frequency distribution of simulated relative ammonia emissions over 15 years (4 application dates per year) and 3 sites in Germany by an empirical and a deterministic model (Volt’Air) (n = 180 per plot)



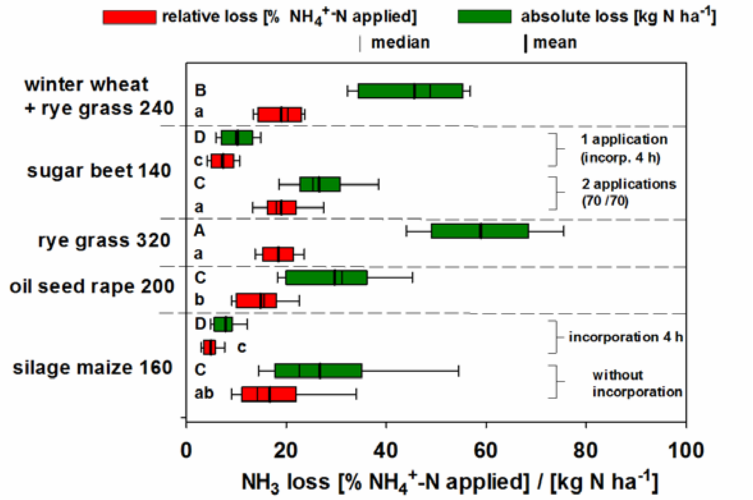
Pacholski et al., 2017

There is a need to quantify NH_3 emissions from biogas production systems. For scenario and regionalization simulations, model approaches for NH_3 emissions after biogas slurry application are of particular interest. Model development was carried out based on intensive field measurements carried out in the years 2007-2009 in biogas cropping systems grown in Northern Germany. Several new dynamic and empirical model approaches were tested (Gericke et al., 2012; Ni et al., 2012). In addition to the well-known principles for calculation of ammonia losses based on temperature, pH and soil water relationships new algorithms were implemented to account for the effects of slurry incorporation, crop type, canopy structure and precipitation on NH_3 emissions. Model results showed a good agreement with measured data with respect to both simulated ammonia loss dynamics as well absolute final losses. As compared to validation data the models show a quantitative accuracy of cumulated NH_3 losses in between 1-2 kg N ha^{-1}. Scenario calculations with the dynamic model (Table 2, Fig. 4) allowed differentiating between and evaluating slurry management options.

Table 2: Rotations, fertilization levels and application dates used in scenario calculation of ammonia emissions after application of biogas digestates in federal state of Schleswig-Holstein (1997–2008)

crop	kg N_{tot} ha^{-1}	application dates
maize	160 (a. incorp. 4H, b. without)	mid April
rye grass (4 cuts)	320 (120, 80, 60, 60)	mid March, mid May, begin July, begin August
winter wheat + intercrop (rye grass)	240 (80, 80 (wheat), 80 (rye grass))	mid March, mid April, begin August
sugar beet	a. 140 (incorp. after 4h) b. 140 (70 incorp. after 4h, 70)	a. mid April b. mid April, mid May
rapeseed	200 (120,80)	mid March, mid April

Figure 4: Median, mean and variation of ammonia emissions after application of biogas digestates to different biogas crops rotations affected by application method (trail hose vs incorporation; h = hours after application)



Pacholski et al., 2017

Modeling climate change impact on N2O emissions from agricultural soils based on long-term observations

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Introduction

Intensive agricultural land use is considered to be the major source of the anthropogenic contribution to the increase in atmospheric N_2O concentration during the last decades. A reduction of anthropogenic N_2O emissions therefore requires a change in agricultural management practices. Mathematical models help to understand the interaction between the determining processes of N_2O production and the dynamics of state variables affecting N_2O emissions. In particular, the impact of climate change on N_2O emissions can be better analyzed.

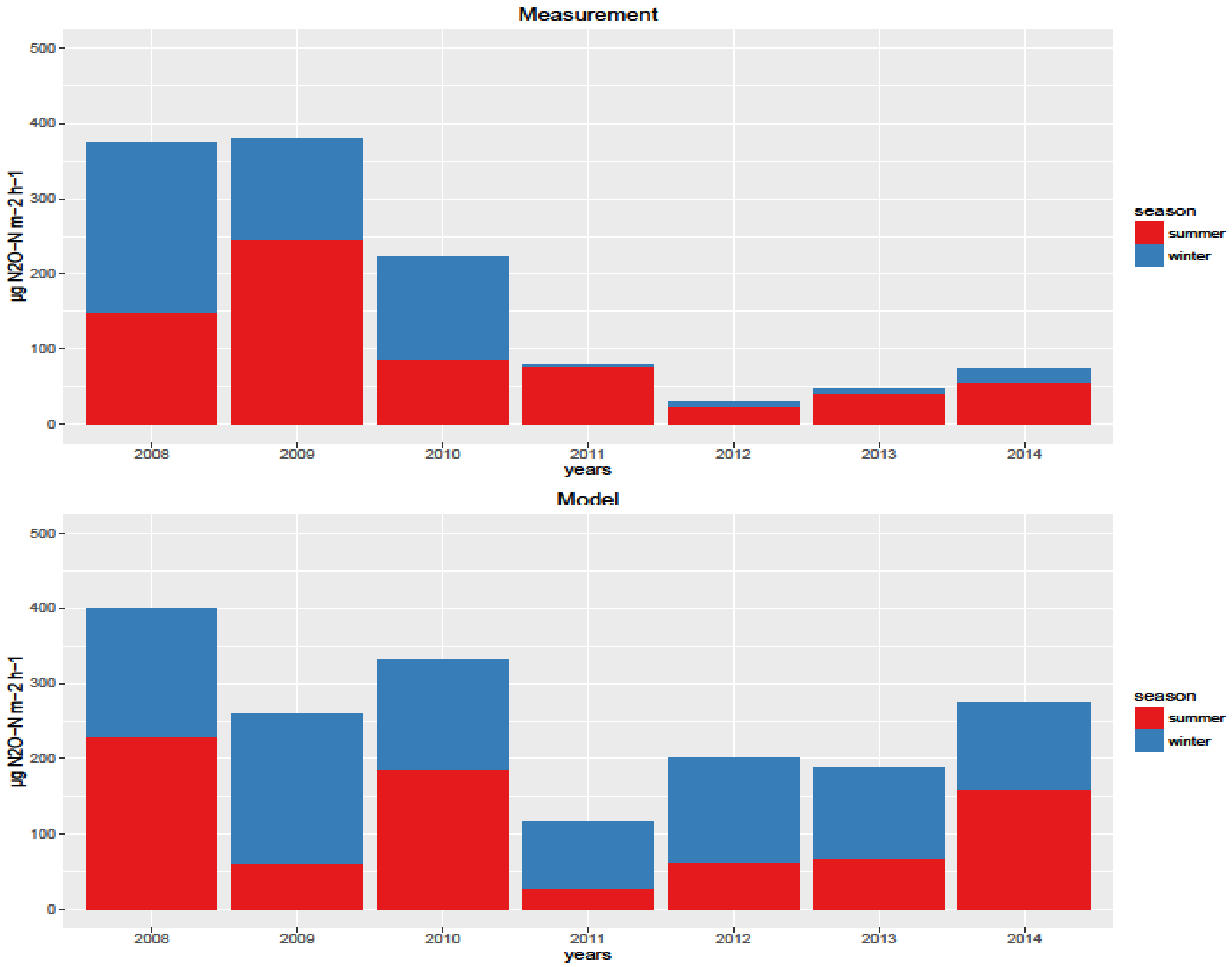
The aim of this study was to test a modeling approach for its ability to describe and quantify the long-term development of N_2O emissions from agricultural fields observed at the Research farm Scheyern situated 40 km north of Munich, Bavaria.

Data for model evaluation were obtained during 25 years (1992-2017) mainly by the closed chamber method. We applied a modeling approach, where a fixed N_2O/N_2 ratio for N_2O production is assumed and the transport of N_2O in the soil profile is neglected and further reduction of N_2O on the way to the soil surface is not considered.

Results

Generally, the modeling approach was able to describe the observed long-term and seasonal dynamics of N_2O emissions and events of high N_2O emissions due to increased denitrification activity after heavy precipitation, after N fertilization and during thawing after soil freezing. Only during the last seven years (2010-2016) winter emissions were overestimated.

Figure 5: Comparison of measured and simulated cumulative N_2O Emissions during summer (red) and winter (blue) half years from 2008-2014 at fields of the Research Farm Scheyern



Priesack et al., 2017

Conclusion

Estimation of N_2O emissions using mechanistic process-based models such as the model system Expert-N (Kaharabata et al., 2003; Priesack et al., 2006; Klier et al., 2011) is possible, if sufficient data for model parameterization and model tests are available. The overestimation of winter emissions during the last years 2010-2016 was caused by a too high assumed soil freezing rate and a neglect of the effect of the snow layer on the soil surface temperature. This lead to simulated soil freezing already during short frost periods being in contrast to the observation, where mainly due to snow fall during short periods of below zero air temperatures no soil freezing occurred. It is concluded that the decrease of frost thaw-events due to higher temperatures during the cold season is the main reason for the decrease of N_2O from the agricultural fields at the research farm Scheyern.

3.3 Recording of ambient NH_3 emissions and assessment of relevant methods

Considerations on methods for measurement of emissions from field applied mineral N fertilizers

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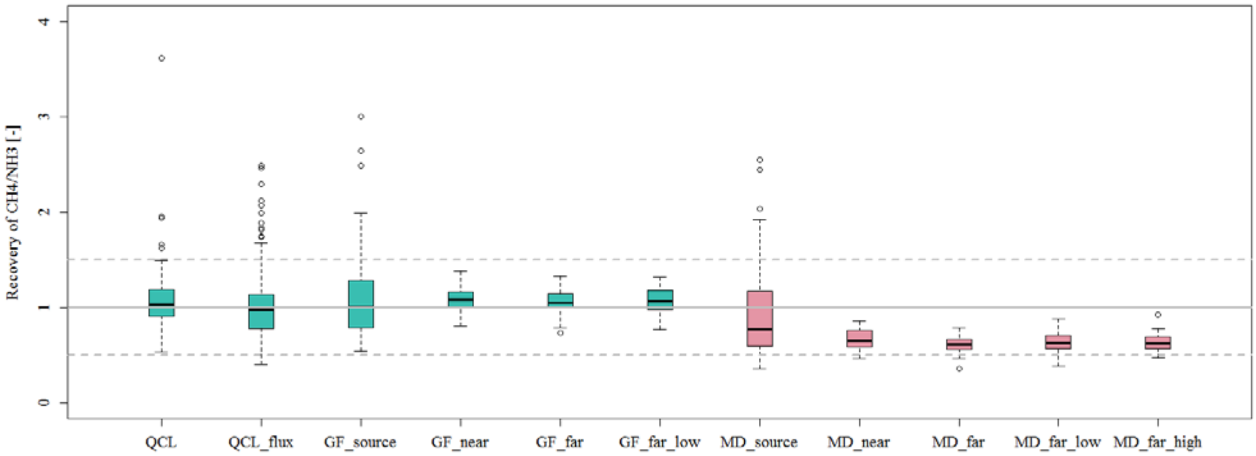
Emissions factors (e.g. for land application of mineral N fertilizers) which can be used by operators of models dedicated for building ammonia (NH_3) emission inventories must be based on reliable basic data. Recent experiences suggest that this is not always the case: e.g., Hafner et al. (submitted for publication) observed substantial deviations regarding NH_3 emissions from field application of slurry among research institutes within the ALFAM2 project (www.alfam.dk). Differences due to applied measurement methods were identified as one reason. We thus conclude that operators of emission inventory models are rather challenged by potentially invalid data than by a lack of data.

Therefore, significant efforts are needed to improve the quality of data from NH_3 emission measurements in the future. There is a potential for progress as can be demonstrated for the determination of NH_3 emissions from field applied slurry where substantial improvements have been achieved over the past years. Häni et al. (2016) performed experiments using automated impinger systems for the concentration measurement and a sonic anemometer for turbulence characteristics. The emission flux was determined with a bLS model (Flesch et al., 2004). This approach was improved by using line integrated measurement devices (i.e. miniDOAS; Sintermann et al., 2016). It was thoroughly evaluated based on experiments with an artificial source (Häni et al., 2017). The recovery rates of the inert tracer (CH_4) did not differ from 1. Recoveries for NH_3 were <1 which can be explained by deposition (Fig. 6). This experimental setup outweighs former limitations such as precision and time resolution of measurements and demand for labor. Still, the availability of instruments limits the number of measuring plots which might counteract the request for replicates in field studies.

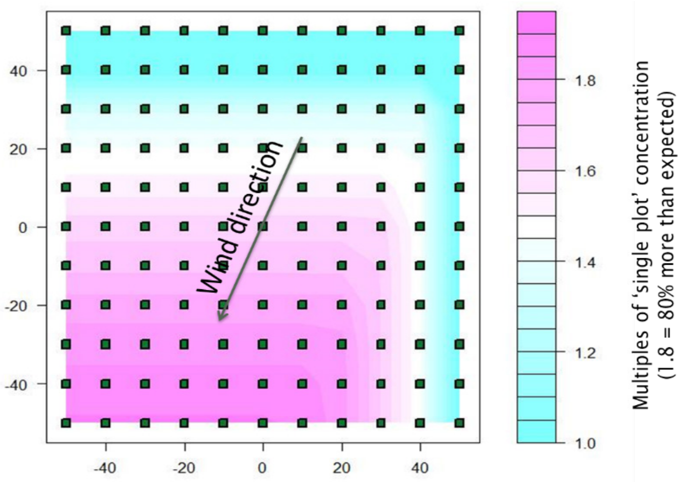
Figure 6: Scheyern Recovery rates of CH_4 (used as a tracer) (blue colored boxplots) and NH_3 (red colored boxplots) obtained in the experiments with an artificial source. Acronyms: systems measuring CH_4: QCL: Quantum Cascade Laser spectroscopy; GF: GasFinder, systems measuring NH_3: MD: miniDOAS. Source: concentration measurement at the center of the source, near and far denote a distance from the source center of the measurement downwind of approx. 15 m and 30 m, respectively; standard measurement height: 1.3 m, low and high denote measurement heights of 0.6 m and 2 m, respectively.



Häni et al., 2017

Multiplot approaches (e.g. Vandré and Kaupenjohann, 1998) are often chosen if emissions from various fertilizer types are investigated. The experiences derived from Häni et al. (2016, 2017) allow to scrutinize such methods. We identified the following challenges: i) point concentration measurements carried out for the reference system consisting of a grid of tubes releasing a defined amount of NH_3 gas in a 2 x 2 m plot very close (15 cm) to the grid most likely differ from a relatively homogeneous emitting fertilized plot depending on factors like the wind direction or the turbulence. ii) within the 2 x 2 m plot, deposition of NH_3 occurs. Häni et al. (2017) observed up to -15% in the net emission in the experiments on NH_3 recovery rates. Therefore, the precision of the scaling factor derived from the reference plot can hardly be assessed. iii) within a multiplot approach, concentration interference from adjacent experimental plots is likely to occur as shown in Fig. 7. The estimation of the interferences is challenging. Other multiplot approaches using chambers or wind tunnels must be critically examined due to the small size of covered surfaces and the influence of enclosures on the emissions.

Figure 7: Concentration interference from adjacent exper. plots within a multiplot approach with equal emission fluxes from all plots. Plot size: 2 x 2 m, distance between individual plots: 8 m; calculations based on bLS model of Flesch et al. (2004).



Kupper et al., 2017

We propose a possible alternative consisting of a combination of a multi-plot approach combined with the application of an up to date method, e.g. concentration or vertical flux measurement using QCL-TDLAS, miniDOAS or equivalent systems combined with dispersion modeling such as bLS or EC at practical size plots located nearby. A multi-plot approach as applied by Vandré and Kaupenjohann (1998) carried out without standard plots but with more background measurements between the plots would yield an improved assessment of the interferences between plots. It produces relative emissions between the various plots receiving different fertilizer types. For one or two of the most used fertilizer types, absolute emission factors are determined with the up to date method carried out in parallel. Absolute emission factors of all fertilizer types are generated by scaling the two approaches. Still, such an approach needs to be critically evaluated before it is applied for the generation of emission factors.

Measuring nitrous oxide ammonia and plant nitrogen uptake: experiences in Ireland

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Measurement of nitrous oxide and ammonia emissions from agricultural sources is receiving substantial attention in Ireland. Ireland has committed to reduce both ammonia and greenhouse gas emissions while continuing to grow agricultural output, particularly of dairy products.

Recently published research from Johnstown Castle presents the results of nitrous oxide measurements from dung and urine (Hyde et al., 2016; Krol et al. 2015; Krol et al. 2016), conventional and stabilised mineral fertilizers (Harty et al., 2016; Roche et al., 2016) using the static chamber approach. This work is being used to refine national inventories of nitrous oxide loss. Both multiple samplings per chamber over time and the use of ambient time (T) 0 air sample and a single sample at T40 or T45 have been used. The ambient plus T60 approach assumes a linear pattern of nitrous oxide accumulation during the chamber closure period. This assumption was tested using a subset of chambers from which multiple samples were collected. In the study of Harty et al. (2016) conducted at six site-years the percentage of non-linear fluxes ranged from 5 to 9%.

The method of urine patch simulation has been shown to influence nitrous oxide emissions (Forrestal et al., 2016). Integrated horizontal flux has also been used to measure ammonia loss from urea fertilizers with wind tunnels running for inter-comparison of several stabilised urea products. Ammonia emissions from dung, urine (Fischer et al., 2016) and a host of mineral fertilizers (Forrestal et al., 2016) have been measured using wind tunnels on grassland. The wind tunnels are very useful for assessing ammonia loss abatement potential of nitrogen stabilisers in a replicated setting and in a relatively small area. However, the absolute ammonia emissions measured by the wind tunnels, 28% on average from 10 applications (Forrestal et al., 2016), are significantly more than indicated by the difference in plant N recovery by urea compared to CAN or urea + urease inhibitor in adjoining plots. Plant N recovery differences between urea and urea protected with the urease inhibitor NBPT were <10% indicating an over-estimate of loss by the wind tunnel method (Forrestal et al., 2017a; Forrestal et al., 2017b).

The work continues with investigations of simple low cost passive systems using foam acid traps and Drager tubes.

Ammonia loss from Urea and CAN after application to winter wheat and winter oilseed rape – Results of Calibrated Passive Sampling (CPS)

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Introduction, Material & Methods

Since 2013, ammonia (NH_3) emission measurements after N fertilization in winterwheat (WW / 2013 & 2014) and winter oilseed rape (WOR / 2015 & 2016) have been conducted over 4 years. Analyses of NH_3 fluxes as well as calculation of related cumulative N losses were based on the Calibrated Passive Sampling method (CPS) as described in detail elsewhere (Pacholski et al., 2006; Gericke et al., 2011; Quakernack et al., 2012; Pacholski, 2016). The CPS approach was shown to deliver reliable results for broadcast application of mineral fertilizers in comparison to e.g. (i) passive flux sampling approaches with a backward Lagrangian stochastic dispersion flux model as well as (ii) the dynamic model Volt'Air' (Ni et al., 2015; Pacholski et al. 2017). Field experiments have been conducted at the Agricultural Experimental Station Cunnersdorf in Central Germany (51°22′N, 12°33′E; 130 m a.s.l.; ⌀ 9.1°C; ⌀ 620 mm; sandy loam, pH 6.5, C org 1.1%, N t 0.12%). NH_3 emissions were measured in randomized field plots (size 9 x 9 m with 9 x 9 m interspace; n=4) including unfertilized controls and fertilizers were compared by their relative NH_3 loss (% of applied N).

In total, five different N fertilizers were tested: calcium ammonium nitrate (CAN), granular urea (U), a formulation of granular urea with a urease inhibitor (U+UI), granular urea with a nitrification inhibitor (U+NI), and granular urea with a urease- and nitrification inhibitor (U+UI+NI). Here we focus only on U, U+UI+NI and CAN. In case of WW fertilizers were applied in three (CAN, UI) and two (U+UI+NI) split applications per year, respectively, while for WOR they were applied in two (CAN, UI) split applications per year and only once a year (U+UI+NI), respectively. The common number of applications is reduced by one when a nitrification inhibitor is added to the fertilizer (i.e. U+UI+NI). Total N input was 220 kg N ha yr^{-1} in WW and 180 kg N ha yr^{-1} in WOR.

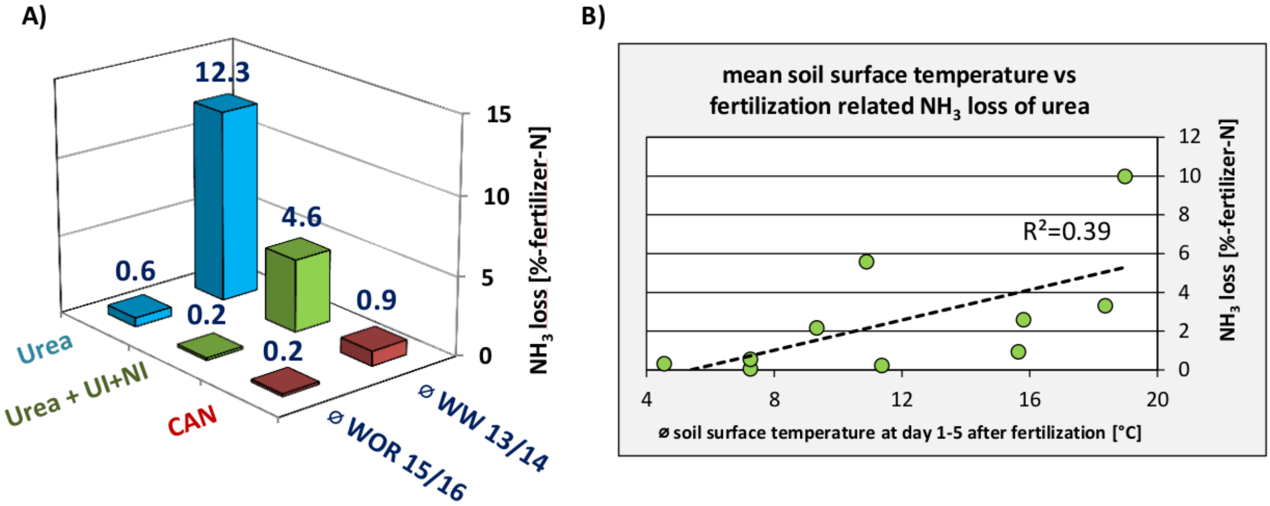
Results & Discussion

Over four years of practice-related fertilizer application to WW (2013 & 2014) and WOR (2015 & 2016) detected average total N loss via NH 3 was 7.0% for U, 2.6% for U+UI+NI and 0.6% for CAN, respectively. Consequently, the mean NH_3 loss was below the current European emission factor of urea for Germany (close to 15%; EMEP/EEA 2016) and moreover, was significantly further reduced by approx. 63% on average when an UI was applied concomitantly to urea. As principle expected, CAN was generally less susceptible to NH_3 loss (always < 1% of fertilized N), since no increase of soil pH takes place after its application to soil as in case of urea (Sommer et al., 2004a; Sommer et al., 2004b).

Significant differences have been found with respect to fertilized plant species and related NH_3 loss, in particular in case of urea application (Fig. 8A). While in WW NH_3 loss of U was on average 12.3% (2013: 13.1% / 2014; 11.5%) of fertilized N, in WOR only 0.6% (2015: 0.6% / 2016: 0.6%) of applied urea-N was emitted by NH_3 . A similar trend was also found for U+UI+NI, where in WW and WOR 4.6% (2013: 2.1% / 2014; 7.2%) and 0.2% (2015: 0.2% / 2016: 0.1%), respectively, has been emitted on average. Even if less pronounced, also CAN revealed a weak trend of higher NH_3 emissions when applied to WW (2013: 0.9% / 2014; 1.0%) in comparison to WOR (2015: 0.0% / 2016: 0.3%). As e.g. reported by Rogers and Aneja (1980) plants are differently suited to take up NH_3 directly from the surrounding atmosphere and thus, the plant species currently fertilized may have an impact on total NH_3 loss after a fertilization event. It remains, however, rather questionable if large differences as found here can be explained by different NH_3 uptake capacities of cropped plants.

Besides plant physiology effects as well as typical soil characteristics as pH and cation exchange capacity also the weather condition during as well as after fertilizer application is well known as a key driver of NH_3 loss (e.g. Sommer et al., 2004) and this mainly relates to temperature and moisture conditions (i.e. precipitation and soil water d namic). While the latter largely affects the distributionof a fertilizer within the soil, the former directly controls the equilibrium between NH_4^+ and NH_3 within the soil solution. As a main consequence NH_3 loss potential is significantly decreased if a fertilizer is washed into the soil soon after its application and otherwise is significantly increased by a rising soil temperature due to the resulting increase of NH_3 concentration in soil solution (to the detriment of NH_4^+) and thus, an increased NH_3 emission gradient towards the atmosphere.

Figure 8: (A) Average of total cumulative NH_3 loss after fertilization of U, U+UI+NI and CAN to winter wheat (WW 2013 & 2014) and winter oilseed rape (WOR 2015 & 2016), respectively, and (B) impact of seasonal weather conditions (visualized by the mean soil surface temperature of day 1 to 5 after fertilizer application) on NH_3 loss potential after a fertilization event (NH_3 loss represents the cum. NH_3 loss over 2 to 3 weeks following each single fertilization event of urea during the field campaign 2013 to 2016).



Spott et al., 2017

Considering that the practice-related fertilization strategy of WW differs clearly from that of WOR, it appears rather likely that observed NH_3 loss related to WW and WOR was in fact provoked by the prevailing weather conditions during fertilization. While WOR is fertilized during early spring under largely cold and wet conditions, WW is fertilized during middle to end of spring under progressively warmer and dryer conditions. Consequently, NH_3 loss potential could be assumed to generally increase in the course of season-related changes of temperature and/or moisture conditions from beginning to end of spring (March to June). It was found that at least a weak trend of an increasing NH_3 loss potential in relation to soil surface temperature after fertilization of urea did occur (Fig. 8B). Even if it is currently not provable as statistically significant due to the multifactorial complexity of NH_3 soil release as well as the limited number of annual data sets it underlines the fundamental impact of seasonal weather conditions during mineral fertilization of e.g. WW on the one hand and WOR on the other.

Conclusion & Outlook

Present results clearly demonstrate that an invariable NH 3 emission factor appears to be insufficient to represent NH_3 losses due to practice-related fertilization, in particular with respect to urea. Therefore, it is necessary to consider crop types and their related fertilization strategies to optimize the evaluation of soil NH_3 loss as induced by mineral fertilizer application. Moreover, the mean NH_3 loss of 7.0% fertilizer-N found for urea is lower than currently assumed and hence, challenges the latest European emission factor of approx. 15% as also recently reported by Pacholski et al. (2017). Despite the rather low NH_3 loss a concomitant application of an UI significantly reduced NH_3 release after urea fertilization by more than 50% independent from crop type and related fertilization strategy. In order to enhance present annual data sets of NH 3 loss after urea fertilization current field studies under practice-related conditions are continued within the national R&D network StaPlaRes (=N Stabilisation and Subsurface Placement as innovative Technologies to enhance Resource Efficiency of Urea Fertilization) partially funded by the Federal Ministry of Food and Agriculture.

Techniques for measuring ammonia emissions from land applications of fertilizers and manures

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Various techniques have been developed for the quantification of ammonia emissions following nitrogen amendments to soils, grassland or cropping systems. Different techniques are appropriate at different scales, with laboratory and small-scale field plots often being used for process understanding and comparative studies, while medium to large-scale field plots may be employed to estimate emissions under realistic ambient conditions. Measurement techniques also differ in the extent to which they influence the emission source, with static and dynamic chamber techniques strongly influencing conditions such as air flow and temperature at the emitting surface, while micrometeorological techniques provide a non-interfering means of estimating emissions. The choice of technique will therefore depend on the objectives of a given study, e.g. assessing the potential effectiveness of an emission reduction measure or developing an emission factor for use in farm-scale or national inventory models, and the resources available including equipment, consumables, labour and suitable land. Here I present a summary of three studies which were conducted to compare different measurement techniques and to assess the potential variability for different ammonia concentration samplers and flux measurement methods.

Samplers for measuring ammonia concentration or flux

Misselbrook et al. (2005) compared the performance of different ammonia concentration measurement methods using a large enclosed chamber with recirculating air into which a standard volume of ammonia was introduced. Concentration samplers included acid absorption flasks (with variation in acid strength, sample air flow rate and glass impinge end type – sintered to produce very small bubbles or open producing larger bubbles), filter badges and passive flux samplers ('shuttles', Leuning et al., 1985). The acid absorption flasks gave robust concentration measurements and there was no significant effect of acid strength, sample flow rate or end type. Shuttles gave very comparable concentration measurements to the acid flasks (accounting for air flow rate within the chamber) with a low coefficient of variation. Filter badges had a higher coefficient of variation and showed some bias in concentration measurement when compared against the acid absorption flasks.

Flux measurement techniques

Misselbrook et al. (2005) compared the integrated horizontal flux (IHF) mass balance technique, using shuttles for horizontal flux measurements, with wind tunnels and with the 'equilibrium concentration technique' (Misselbrook and Hansen, 2001) for four different manure types. They found the IHF and equilibrium concentration technique to give similar flux values, although some data were lost from the latter technique because of under- or over-exposure of filter badge samplers. The wind tunnel technique did not give consistently similar flux estimates, which is perhaps unsurprising as the fixed wind speed through the tunnels often differed greatly from ambient wind speed. Coefficient of variation for the measurement techniques were greatest for the wind tunnels and least for the IHF technique.

Misselbrook and Hansen (2001) compared the IHF technique with the equilibrium concentration technique over three experiments including urea fertilizer, cattle slurry and pig FYM. They reported that while flux estimates were similar for periods where there were sufficient data to compare techniques, several sampling periods were 'lost' for the equilibrium concentration technique because of under- or over-exposure of the filter badges.

Sanz et al. (2010) compared the IHF technique with a backward Lagrangian dispersion model (bLS, Flesch et al., 2007) employing the freely available WINDTRAX software (www.thunderbeachscientific.com) for flux estimation and found the two techniques to give very similar flux estimates.

In conclusion, the IHF technique employing passive flux samplers (shuttles) is recommended as the 'standard' technique for estimating fluxes under ambient conditions. The bLS technique is similarly robust and may be preferred where emission sources are not of regular shape and size. The wind tunnel technique is recommended for comparative measurements e.g. of different treatment effects, but is not recommended for derivation of absolute emission factors. The equilibrium concentration technique is not recommended because of the high probability of obtaining poor data for at least some of the sampling periods in any experimental campaign.

Referencing ammonia losses from fertilizer application

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Introduction

Agriculture contributes 94% of anthropogenic ammonia (NH_3) emissions. Twenty-three percent of these are attributed to mineral fertilizers. Due to its high loss potential and its world market share of 58%, urea plays a major role in mineral nitrogen fertilization.

Based on reported measurements and reviews of NH_3 losses from fertilizers, the EMEP/EEA air pollutant emission inventory guidebook – 2016 indicates that NH_3 emissions from urea are the most variable among mineral fertilizers, ranging from 6 to 47 % of the applied N. Emission factors have recently been modified. Besides direct incorporation of the fertilizer the use of urease inhibitors has the potential for substantially decreasing ammonia losses. However, large uncertainties prevail with regard to emission factors, being in part due to different methodologies used, the overall representativeness of the measurements reflecting various climatic/geographic conditions, inadequate representativeness of a given agronomical fertilizer management (time, dose, crop), and particularly also due to an unbalanced regional representativeness. It remains highly doubtful that semi-continental emission factors can be applied, most likely requiring to arrive at regional or even sub-regional inventories. However, the overall existing database is remaining meagre.

Various techniques including enclosure or chamber techniques, micrometeorological techniques, as well as N balance/difference methods have been used in the past to measure ammonia losses, with all having their pro´s and con´s. Some preferences have been given to either wind tunnel systems or micrometeorological methods such as the IHF method, however no method can be claimed to depict absolute ammonia losses.

In view of rather low emission values found in previous field studies in Southern Germany over multiple years assessing ammonia losses from urea and other mineral fertilizers and to further evaluate the results of different techniques used – semi-open dynamic chamber technique (Schraml et al., 2016) as well as a combination of passive flux sampler and calibrated closed chamber method (Pacholski et al., 2017) - we have worked on developing and evaluating a modified ^{15}N-balance method which might serve as a potential reference technique, fulfilling requirements of simplicity, cheapness, precision, being further applicable to small plot experimentation to evaluate multiple and replicated treatments (inorganic/organic fertilizers, liquid/granulated fertilizers, doses, timing) and being amenable to be used on multiple sites.

Materials & Methods

Field experiments with arable crops were conducted in Dürnast at the Research Station from TUM in Southern Germany, in the years 2002 to 2005, to determine NH_3 losses following the application of granulated urea to winter wheat and to bare soil. Ammonia emissions were continuously measured using a dynamic chamber system testing also the effect of urease inhibitors (UI).

In 2007 and 2008, field experiments were conducted on two intensive grassland sites in Dürnast to evaluate ammonia loss, using the dynamic chamber technique, and its potential reduction by UI´s.

Ammonia emissions from urea with and without UI applied to winter wheat were measured over three seasons in 2012-2013 by comparing the combined passive sampler/chamber method with a modified ^{15}N-field balance method.

Over five years, from 2011 to 2016, multiple experiments were conducted to further assess the potential of the newly developed improved ^{15}N-balance method to assess ammonia losses from mineral and organic fertilizers (Schmidhalter et al., 2017). Experiments were either conducted with winter wheat or with bare soils from various regions in Bavaria. A specific focus was on the assessment of incorporation vs. surface application besides specific aspects such as timing (daytime), type and dry matter content of slurry being relevant for organic slurries. The experimentation should further allow to delineate soil properties which affect ammonia losses.

Results

Generally, only low NH_3 emissions were detected varying between 0.1 and 2.7% of the urea N applied to winter wheat and between 2.6 and 16.3% of the N applied to bare soil following the cropping period. Urease inhibitors significantly reduced losses by 32 to 53% (Weber et al., 2001; Weber et al., 2004).

Even though climatic and soil conditions were chosen to ensure high NH_3 losses the sums of NH_3 emissions resulting from surface application of urea to grassland sites were comparatively low, averaging at 9.1% in 2007 and 7.2% in 2008. Urease inhibitors reduced ammonia losses by 60% (Schraml et al., 2016).

The ^{15}N-balance method delivered over three seasons in 2012, 2013 and 2016 urea losses from winter wheat of 6.4%. The combined passive sampler/chamber method showed lower losses and more variable results, indicating 0% as average of two applications in 2012 and 3.9% in 2013, resulting from three split applications with losses observed being 1.8%, 0%, 14.1% (Gassner and Schmidhalter, 2014, unpublished).

Ammonia losses determined with the same method in the season 2016 were <2,4% and 7.4% for calcium ammonium nitrate and for urea, respectively, applied to winter wheat (Parzefall and Schmidhalter, 2016, unpublished).

The new results obtained with the refined ^{15}N-balance method largely corroborate previous results obtained with the dynamic chamber method, but indicate some underestimations by the latter one.

The new technique allowed further evaluating ammonia losses from various soils originating from Bavaria. Ammonia losses from urea applied, e.g. on the bare soil in Dürnast were <1%, from 10 different soils from Bavaria were between 1-16% and averaged 7%. Another soil originating from Switzerland characterized by a very high pH and a very low buffer capacity/cation exchange capacity revealed a loss of up to 57%. Incorporation of urea on the Bavarian soils decreased losses from 7% to 2% (Frank, Buchhart and Schmidhalter, 2016, unpublished).

The relative efficiency of incorporation versus the use of UI´s was about 70% compared to 40% on arable sites. Urease inhibitors were more efficient on grassland sites.

The technique was also used for measuring ammonia losses from liquid organic slurries applied on bare soils confirming significantly higher losses from their application compared to mineral fertilizers.

Incorporation significantly decreased losses and timing and dry matter content revealed to be influential as well.

Harper (2005) stated that the IHF method is generally considered to be the most physically-correct technique and may be considered to be a standard for making comparisons where possible. He concluded that stable N isotopes, using short-term measurements also may be a good comparison in the absence of plant activity. We extend this that also in the presence of plant activity stable N isotopes using an improved protocol may serve as standard having even the potential to serve as absolute reference technique.

Conclusions

An improved ^{15}N field mass balance technique has been developed, which fulfills the requirements of simplicity, cheapness, precision, being further applicable to small plot experimentation and being able to handle multiple treatment-replication combinations. Following the suggested protocol the overall precision is estimated to be better than ±3% disregarding potential N_2 and N_20 losses, which are normally very low in relevant emission periods for organic slurries (1-3 days) or for urea (1-14 days). Overall the emission factors for urea determined by this method were considerably lower than suggested by the EMEP protocol (15.8%). Therefore emissions from urea can be markedly lower in South Germany (averaging about 7%) supporting the need for a better regional representation and for a critical re-evaluation of generalized emission factors.

NH_3 Flux – reference methods

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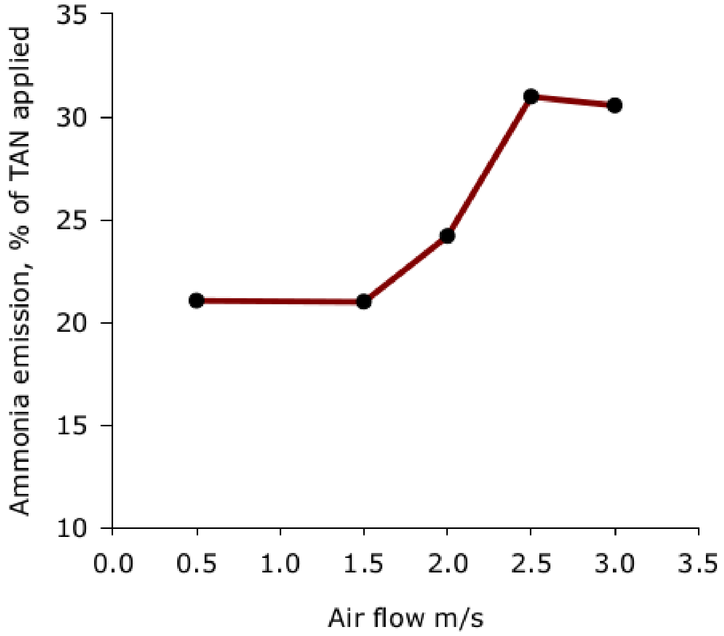
Agriculture is recognized as a major source of atmospheric ammonia (NH_3), contributing 55% of global NH_3 emissions (Bouwman et al., 1997), with other sources including both woody biomass and fossil fuel combustion (Sutton et al., 2001). Globally, synthetic fertilizers contribute 11 Tg NH_3 yr^{-1} (Beusen et al., 2008).

A large variety of methods have been used to quantitatively and qualitatively measure NH_3 emission. Micrometeorological techniques and dynamic chambers/wind tunnels are the most widely used methods that give emissions estimates. The micrometeorological methods are thought to be unbiased while the management of wind tunnels controlling the environment will affect emissions, mainly through the effect on air flow in the wind tunnels, which may have a significant influence on NH_3 emission (Fig. 9).

Figure 9: Cumulative NH_3 emission measured using wind tunnels for 0-5 h following cattle slurry application to grassland

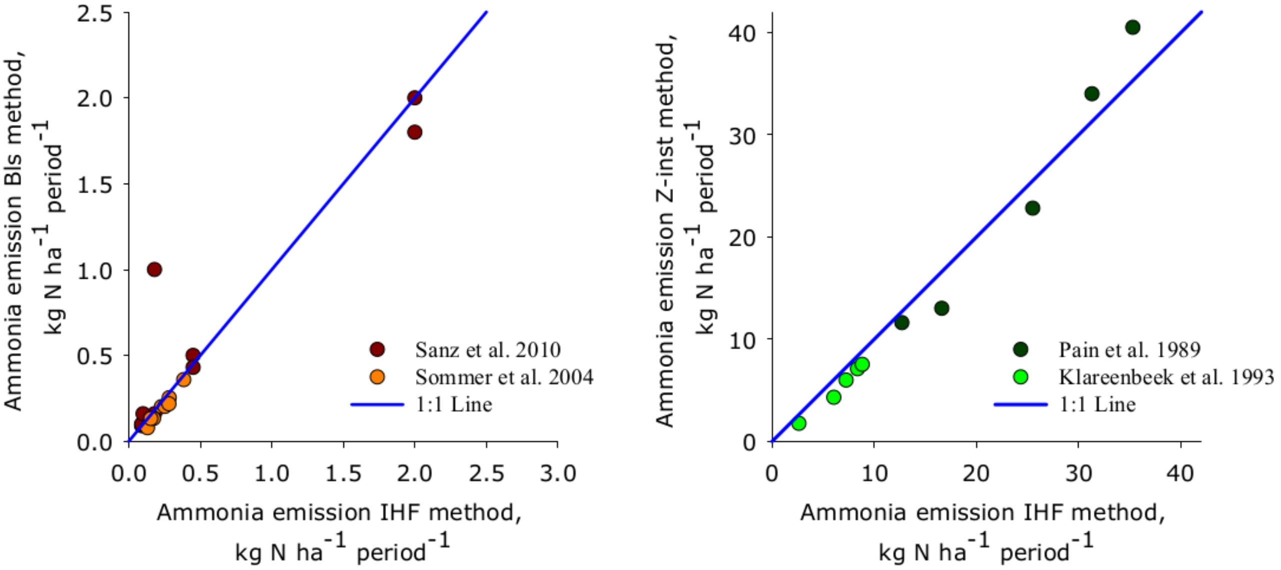


Thomson et al., 1990

The integrated horizontal flux (IHF) is a widely used technique for measuring NH_3 emission and generally accepted as being non-intrusive regarding the source (Fig. 10). Therefore, the full profile IHF technique has been used in inter-calibration studies testing different methods (Schjørring et al., 1992; Sherlock et al., 2002; Sintermann et al., 2011).

N mass balance methods and ^{15}N recovery can't be recommended for measuring NH_3 emission. A significant amount of the ^{15}N applied to soil will within few days be transformed to organic N on a fallow soil (Chantigny et al., 2004), or be transformed and taken up by plants in a field with crops and transformed and thus be accounted for as NH_3 emission, consequently these mass balance and ^{15}N recovery methods overestimate NH_3 emission (Black et al., 1985).

Figure 10: Ammonia emission measured with the bLS method (left) and the ZINST method (Right) versus emission measured with the integrated horizontal flux method (IHF)

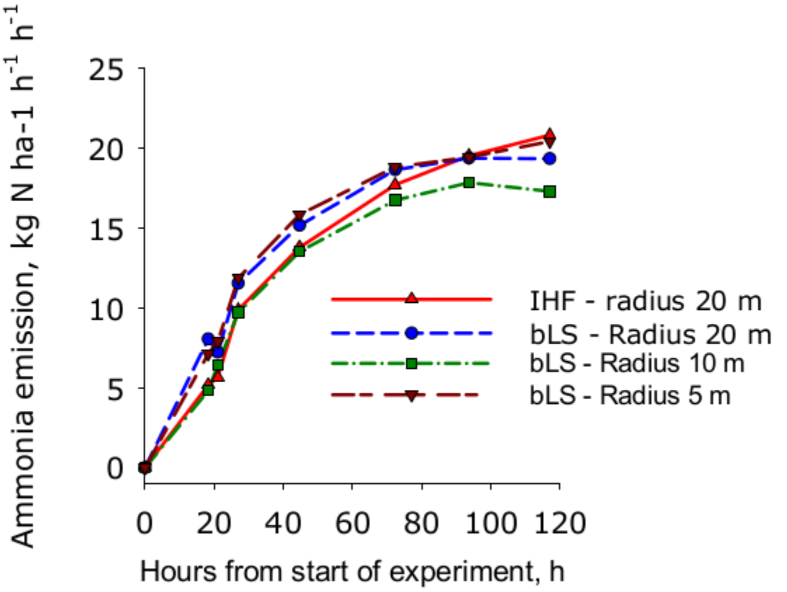


Sommer, 2017

Dynamic chambers / wind tunnels

In a recent review it was concluded that NH_3 emission measured with wind tunnels adjusted to an air flow of 1 m/s deviate from the emission measured using the IHF methods (Sommer and Misselbrook, 2016). Many studies using wind tunnels are carried out at a constant airflow of 1 m/s. In contrast, measured emissions are not significantly different from those measured with IHF method in studies where airflow in wind tunnel is adjusted to the ambient wind speed. Wind tunnels influence the air flow pattern and cause turbulent convection in the air layers above the emitting surface, but the similarity in measured emissions for the two measuring techniques may be because the soil surface resistance to NH_3 transport is often the most important rate regulating variable. The review (Sommer and Misselbrook, 2016) concluded that the wind tunnels are well suited to test the emission reduction efficiency of new technologies, and that a recovery of 100% of released NH_3 can be obtained if wind tunnels are designed to avoid pulses of wind into the tunnel through the canopy opening and leaks from the tunnels.

Figure 11: Ammonia emission from small plots with a diameter of 5, 10 and 20 m measured using the bLS method and emission measured using the integrated horizontal flux method



adapted from Pedersen et al., 2017

Reducing plot size used for the micrometeorological methods

A recent study (Pedersen et al., 2017) showed that there is no significant difference in NH_3 emission from small plots (radius 5, 10 and 15 m) measured with micrometeorological methods and emission calculations based on a backward Lagrangian Stochastical dispersion (bLS) model compared to those obtained by standard integrated horizontal flux method (IHF, radius 20m). Further, costs of the micrometeorological tests may be reduced by use of a cheap versatile method combining passive diffusion NH_3 samplers (ALPHA samplers) and battery-powered anemometers, ALPHA samplers should be exposed for a sufficiently long period. The cost for one study over one week, which included equipment for 4 plots and 8 measurement intervals and using the ZINST or bLS methodology was $2800 if horizontal fluxes was measured using the ALPHA samplers compared to $12000 using the Leuning samplers, and $14000 using gas washing bottles. The study also showed that using wind tunnels on small rectangular plots (length 2 m and width 0.5 m) is as costly as measuring emissions with the Leuning samplers or gas washing bottles using the bLS methodology.

3.4 Recording of ambient N_2O emissions and assessment of relevant methods

Measurement of actual and potential N_2O and N_2 flux rates on soil samples by the helium incubation approach

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The largest global nitrogen pool is dinitrogen (N_2) in the atmosphere. Main sources of N_2 formation are microbial mediated processes like denitrification. However, N_2 fluxes are highly uncertain due to the difficulty in detecting newly formed N_2 against the high atmospheric background N_2 concentration (78% vol.). As a result, the N_2:N_2O ratio of denitrification end-products is not well characterized, and the controls on the ratio are poorly understood. But the ability to quantify the relationship between N_2O and N_2 fluxes is an essential prerequisite for better understanding of the human impact on terrestrial N dynamics, especially the gaseous N-loss of cultivated soils.

At present, the incubation of soil cores into an artificial, N_2-free atmosphere is the only approach which prevents artefacts in N_2O and N_2 production and consumption processes and unintentional changes in substrate availability for the present microbial community.

In this case, soil samples were placed in special gas-tight incubation vessels at a climate box. To substitute ambient N_2 from the vessels, sequences with moderate evacuation followed by flushing the vessels with an artificial He/O_2/trace gas mixture were conducted to the system. Subsequently, for 48 h a continuous gas flow rate was adjusted to the vessel headspaces to remove the remaining “atmospheric” N_2 and to establish stable emission rates. After that, from each vessel, N_2O, CH_4, CO_2, and N_2 headspace concentrations were continuously measured in order to get information about the actual flux dynamics. Finally, the current N_2O and N_2 flux potential were measured by replacing the He/O_2 gas mixture with pure He.

In a second helium incubation study the N_2O and N_2 fluxes were quantified for a drained fen grassland site that has been fertilized differently with synthetic nitrogen fertilizer (calcium ammonium nitrate, 0 kg N ha^{-1} yr^{-1} vs. 480 ha^{-1} yr^{-1}) for more than 50 years. Parallel to this, we also analyzed the microbial community involved in the N_2O and N_2 production.

From N_2O measurements to N_2O emission factors

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Emission factors are the model used most by greenhouse gas inventories. An emission factor represents the (linear) relationship of an activity, such as a fertilizer input, to an emission, such as an N_2O emission. Derivation of emission factors makes high demands on experimental setup and measurements. The Intergovernmental Panel on Climate Change (IPCC) only recognizes emission factors based on whole-year measurements and typically measurements at multiple sites in multiple years are required. For fertilizer emission factors experimental setups need to include multiple fertilization intensities and preferably a treatment without fertilization.

The primary basis for current IPCC (direct) N_2O emission factors are measurements using manual chambers. For these a closed chamber is applied on a field plot and air samples are taken over the closure time. These samples are analyzed by gas chromatography and the N_2O flux is calculated from the gradient of a concentration – time model.

Figure 12: Greenhouse gas measurements using automated chambers

Fuß, 2017

Automatic chambers (Fig. 12) improve this method by allowing more frequent measurements. Recent developments of fast and precise online N_2O analyzers allow further improvements such as shorter closure times, use of field robots or even field-scale auto-samplers. Even more representative measurements can be achieved by use of the eddy-covariance technique, but this requires suitable topographic and meteorological conditions and cannot be used in field experiments with randomized block designs.

Example: Nitrous oxide emissions from oilseed rape cropping

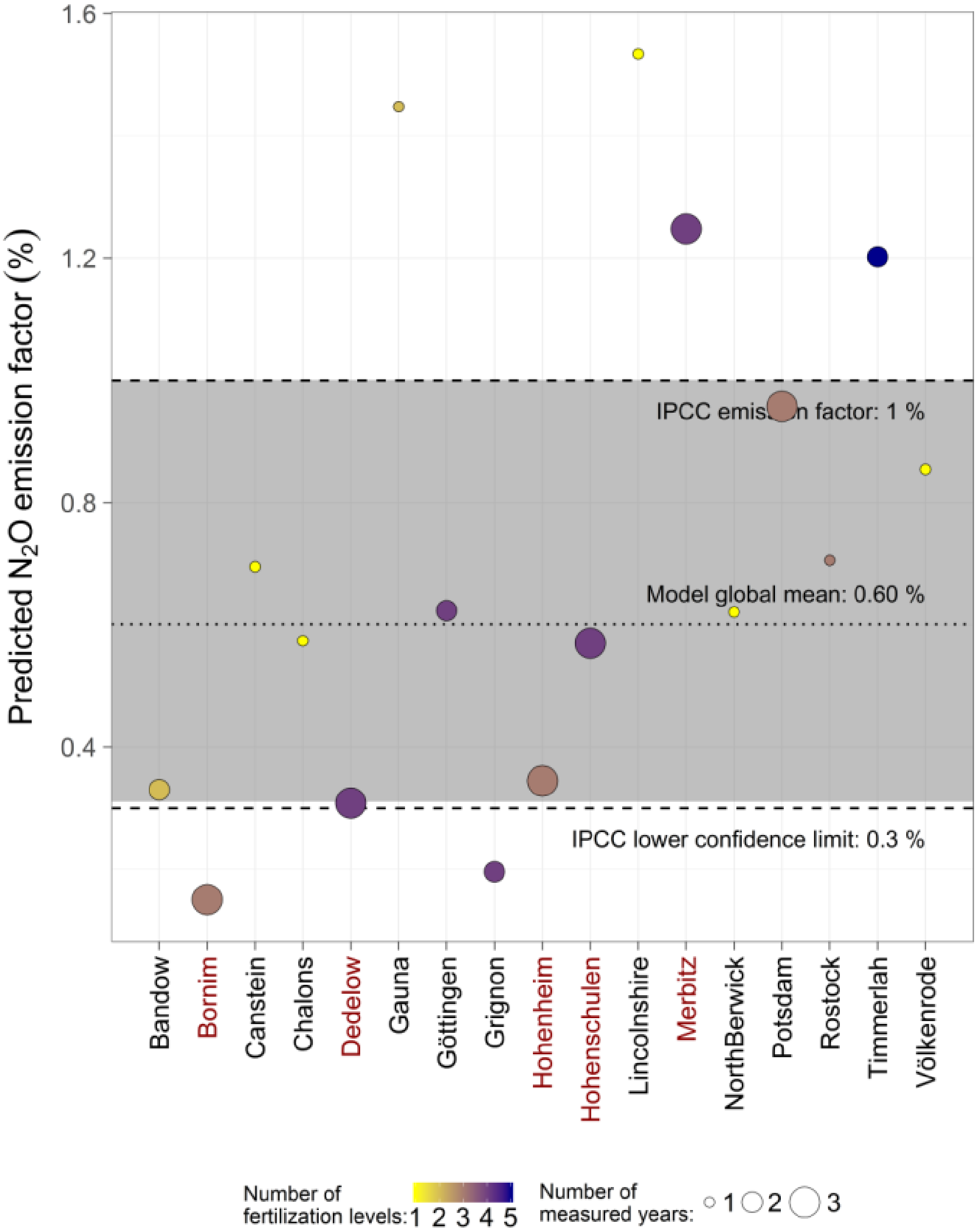
A recent example of an approach for deriving a crop-specific N_2O emission factor is the project “Mitigation of GHG emissions from rapeseed cultivation with a special focus on fertilization”. As a first step, this project collected 43 data points of annual N_2O emissions from oilseed rape cropping measured at 12 research sites. This data was evaluated according with a mixed effects model (of log-transformed N_2O fluxes) according to methodology of Stehfest and Bouwman (2006). Because literature studies had not been conducted with the goal of deriving an emission factor, they often studied only very few or even single fertilization intensities which resulted in large uncertainty of the derived emission factor. Thus, the project measured N_2O emissions from oilseed rape cultivation with fertilization intensities from zero to 240 kg N ha^{-1} a^{-1} at five research sites in three years (Fig. 13).

Figure 13: Position of field sites in Germany (left) ,; randomized plot experiment at site Hohenschulen with whole oilseed rape – winter wheat – winter barley crop rotation and different fertilization intensities (right)

left: TI 2018; right: Räbiger, 2013

A mixed effects model combining the new measurements with the literature data resulted in an emission factor at 200 kg N ha-1 a-1 fertilization of 0.6 % (CI: 0.3 % - 1.0 %) (Ruser et al., 2017). However, annual and spatial variation was still large (Fig. 14) as is typical for N2O emissions.

Figure 14: Estimated direct N_2O emission factors for oilseed rape cropping at 200 kg N fertilization at all research sites included in the model.



Fuß, 2017

Static and ventilated chamber methods for the measurement of ammonia and N_2O emission: pros, cons and applications

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The agricultural sector (namely animal husbandry and nitrogen fertilizers application) is responsible of up to 94% of global ammonia (NH_3) and approximately 5% nitrous oxide (N_2O) EU-28 emission (Eurostat, 2010). Thus, the sector poses serious risks to the environment. The range of approaches to the problem of measuring emission rates of nitrogen (ammonia and nitrous oxide) either from livestock sector and chemical fertilizers is wide, whereas the range of available techniques for measuring ammonia concentrations and/or ammonia flux rates in air is even wider. Due to the necessity to measure emission with a good level of accuracy it's necessary to use *robust* methods, defined as methods which are able to measure emission fluxes to within acceptable levels of accuracy and precision, using techniques which do not require a high level of operator skill and are *sufficiently portable* that can be shown to function acceptably in real farm situation (Phillips et al., 2000). Moreover, the methods to be used shall allow emission measurements over time-periods from 1h upwards to 24+ hours. Nitrogen emission are influenced by several environmental and managing factors (e.g. temperature, wind speed, soil humidity, application methods), thus measuring systems shall not alter climatic conditions or shall allow to reproduce them. According to international literature when different measurement systems are used of quantify nitrogen fluxes from the same emitting source, very often final results differ significantly. Hence, standard methods for measuring emission are needed to guide research on abatement strategies and to produce international inventories.

Static and ventilated chambers are widely used to quantify nitrogen emission, nevertheless their field of application is related to the type of nitrogen flux (either ammonia or nitrous oxide) that has to be measured and to the final goal of the measurement (e.g. the need to get relative or absolute emission values). The presentation provides an overview of the possible fields of application of both systems and of their points of weakness and strength.

The Automated Cavity Ring Down Spectroscopy Usage for Nitrous Oxide and Ammonia Emissions from Synthetic Fertilizer Application

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Introduction

The reduction of gaseous nitrogen emissions is one of prioritised aim of Latvia environmental policy. The aim of this research was to evaluate synthetic fertilizer such as urea and ammonia nitrate application dose impact on ammonia and nitrous oxide emissions.

The experiment of gaseous nitrogen emission measurements using cavity ring down spectroscopy (CRDS) were designed in laboratory and field. The field experiment were designed with following synthetic fertilizer application rate 0; 120; 150; 180 and 240 kg N^{-1} ha^{-1}. There were used transparent and no transparent chambers with diameter 23 cm and volume 3 litres. The connection of chambers with CRDS device Picarro G2508 were made with 9 m long Teflon tube with diameter of 0.125 inches. The CRDS device Picarro G2508 were used to measure concentrations of nitrous oxide and ammonia. The soil flux rate were calculated using Soil Flux Processor (SFP) (Fleck et al., 2013). The measurements were made one day before synthetic fertilizer application and five days after. As well as nitrous oxide and ammonia emissions were measured twice month on regularly base.

The Multivariate Analysis of Variance (MANOVA) procedure was used for data analysis. The most important purpose to use MANOVA was to explore how independent variables (application rate of N fertilizers) and timing of applications influence patterning of response on the dependent variables – emissions of N_2O and NH_3.

Results

The results of nitrous oxide emissions field measurements show low emissions however there are significant differences between fertilizer application rates. The emission rate for N additions from mineral fertilizers is 0,01 with uncertainty range from 0,003 till 0,03 (IPCC, 2006). The measured emission rate for N additions from mineral fertilizers is in range from 0.004 till 0.006 which is very close to lower bound of uncertainty.

The results of ammonia emissions did not pass verification and are not included in results.

Conclusions

The CRDS device Picarro G2508 is relatively new equipment and there is need to evaluate and calibrate measurement time for appropriate N_2O and NH_3 emission calculations.

The measurements have to be done in field and in laboratory, to test different soil type's reaction on fertilizer application.

The modeling tool have to be developed for N_2O and NH_3 emission calculations at Latvia national level.

4 World Café Discussions

Introductory remarks and recommendations by the workshop experts

It was agreed that the discussion groups should focus in particular on NH_3 emissions and to a lesser extent on N_2O emissions, because of the dominant role of agriculture for the emission of the gas NH_3 having several negative effects on environment, climate, and health.

Furthermore, it was agreed that the discussion groups should focus on the field scale (e.g. the hectare scale) for analyzing the factors determining emissions of NH_3 and NO_x. It was pointed out that emissions occur not only from agricultural soils but also from stables and manure storage. The groups decided to focus on emissions from agricultural soils.

4.1 Requirements for the recording methods resulting from physical, chemical and biological processes (World Café Session I)

A) Factors and processes determining NH_3 and NO_x emissions from agricultural soils

NH3:

- **Amount and type of nitrogen fertilizer applied:** Amount and type of fertilizer, application technique, total amount of TAN applied, TAN content, dry matter content and structure of the fertilizer, fertilizer pH and specific pH effects of fertilizers, addition of urease inhibitor, addition of acid
- **Soil properties:** Soil pH and pH buffer capacity, cation exchange capacity, soil texture, soil moisture
- **Vegetation characteristics:** Vegetation type, height of vegetation
- **Weather conditions:** Wind speed, air temperature, precipitation after application, radiation

NO_x:

- **Amount of nitrogen fertilizer applied:** Amount of fertilizer, N surplus, soil nitrate availability, addition of nitrification inhibitors, application technique (e.g. slurry injection)
- **Soil properties:** Soil moisture, soil organic carbon availability, soil texture, probably soil pH
- **Vegetation:** Crop type, crop rotation system, crop residue management
- **Weather conditions:** Precipitation pattern, air temperature, freeze-thaw cycles

B) Primary challenges with the measurement of gaseous N emissions from soils

NH_3:

For ammonia (NH_3) emissions the following crucial points were identified:

- we have to deal with a sticky gas, which may be kept by metals, plastics etc.
- additionally it is highly reactive and may interact with the measuring equipment
- ammonia fluxes show a high temporal variability, but mainly follow a diurnal pattern
- a high variability of background concentrations can be observed as well
- various measurement methodologies for the determination of fluxes are available, but we do not exactly know, which is reflecting the reality best

NO_x:

For nitrous oxide (N_2O) and nitrogen oxides (NO_x) the following crucial points were identified:

- the release of N_2 is not or almost not measurable, therefore plausibility checking is difficult
- many factors are influencing the N_2O and NO_x emissions
- anaerobic soil conditions as a major influencing factor are not measurable
- N_2O and NO_x fluxes show a high temporal variability
- a high variability of background concentrations of nitrogen oxides can be observed as well
- the measured results allow only a limited statement of the representativeness of the emissions

C) Requirements for the recording method resulting from the natural processes of NH_3 volatilization

Ammonia emissions are most influenced by micrometeorological conditions. Therefore recording emissions aiming at high precision should be performed under undisturbed ambient conditions. Thus, proper monitoring with high precision and reproduceable results can only be achieved by methods, which do not disturb or affect natural processes in and above soils. These requirements are most met by "open recording methods" (standard comparison method) rather than by "enclosure" methods (see Table 3).

Table 3: Evaluation of Ammonia flux recording methods – ambient conditions

Factor	Micro-meteo-rological method	Wind tunnel	Dynamic chamber	Standard comparison method	Calibrated passive sampler method	Static chamber & acid traps	^{15}N recovery	Relevance for emission recording
Temperature	+	+	-	+	+	0	+	3
Rain	+	-	-	+	0	-	+	3
Wind	+	0	-	+	-	-	+	3
Soil humidity	+	-	-	+	0	-	+	2
Air humidity	+	+	+	+	0	-	+	2
Soil characteristics	+	+	+	+	+	+	+	0
Crop canopy (LAI, height)	+	-	-	+	+	+	-	3

The relevance of the factors for NH_3 emission recording has been rated on a scale from 0 to 3, by "0" being least and "3" most relevant for emission recording. The suitability of the available recording methods to internalize these factors has been rated from "not suitable" (-), over "restrictedly suitable" (0), to "suitable" (+).

D) Requirements for the recording method resulting from the natural processes of N_2O and NO_x volatilization

Measurements

- For N_2O and NO measurements different measurement equipment is needed, but the emissions can be measured in the same experimental set-up (e.g. a field experiment with treatments in replicates)

- N_2O and NO are produced during the same processes (nitrification and denitrification). The ratio of N_2O/NO is affected by environmental factors. Is it possible to derive an average N_2O/NO ratio (based on field experiments and lab studies)? In that case it is sufficient to measure only one of the gases (probably N_2O) and estimate the emission of the other gas using the ratio.

Temporal variability

The temporal variability of fluxes is high. Therefore, there is a need to measure as often as possible (continuously), but at least once per week with more measurements during events, such as nitrogen application, rain, and soil tillage.

For setting up the measurement strategy, one should be aware of diurnal variability. Avoid measuring always at a time of the day with high emissions, because this leads to bias estimates.

Because of annual variations in climate and crops (rotations) there is a need for measurements during several years.

Quantification

- Emission factors should be based on field experiments with a sound statistical set-up, a reference fertilizer and an unfertilized control.
- Quantification of mitigation options can be based on emission factors for mitigation options, using the same set-up as for the reference, or on specific experiments comparing the reference with the mitigation option. From these experiments, reduction factors can be derived. These reduction factors can be applied on the emission factors for the reference fertilizer. The accuracy of experiments in which a reduction factor for mitigation options is derived can be less than that with which emission factors of the reference fertilizer is derived.

Modeling

- For the development, calibration, and validation of models, additional measurements of the parameters required for the model(s) should be obtained, including nitrogen application, soil properties, weather conditions and crop.
- It was questioned, if the quality of process-based models is sufficient. This should be verified to avoid a huge effort to collect the data for the parameters for inaccurate models.

Innovations

- Laser techniques are available for rapid and accurate measurement of N_2O concentrations in the field.
- Dynamic chambers capable of opening and closing automatically are available, so semi-continuous measurements can be made.

Collaboration

- A study should be carried out to combine emission data and emission factors from different regions and countries. From this study, emission factors can be derived for countries that don’t have country-specific emission factors. In addition, conditions (soil-crop-climate combinations) for which no emission factors are available can be distinguished. Future research may focus on filling the gaps in knowledge.

4.2 Most suitable recording methods for gaseous N emissions (World Café Session II)

A) User’s perspective: Requirements for an NH_3 emission measurement method

The discussions were wide ranging but covered the following issues:

Who are the users?

- Policy makers: require robust EF and mitigation reduction factors for the use in scenario models for policy development
- Government inventory compilers: need robust EF and mitigation reduction factors for accurate inventory compilation that can be used with national statistical activity data; need uncertainty estimates
- Modelers: for development/improvement of field-, farm-, and regional-scale models
- Farmers/consultants/industry: robust parameters for farm-scale decision support tools that will reflect on-farm environment and practices
- Researchers: need practical, reliable, low-cost techniques for developing EF and assessing mitigation options

Representativeness of derived EF

It is important that the developed EF reflect actual practices of and are representative for the conditions under which emissions would normally occur. Users of the data must be able to have confidence in those data which may have been derived from various sources (different experiments, research groups). Data must therefore be reliable and reproducible, and reflect confidence in that experiments have been properly conducted and instrumentation well maintained and used. The consistency of the chosen approach is important and guidelines (e.g. VERA) can help with this. What statistical data are available with which EF will be combined – this may influence the resolution at which EF might be disaggregated.

Practical considerations

Users of the recording method (rather than the subsequent data) are generally looking for low cost, simple, and portable techniques that don't require large land areas, great time input or highly skilled technicians to run. In this way, many measurements across different sites, soils, conditions and practices can be made to develop robust EF.

Required information

The developed emission estimates (or EF) must be placed in context so that the important driving factors of emission can be understood and represented in subsequent algorithms for EF development. Therefore, additional metadata needs to include soil, weather, practices, etc.; again, use of common guidelines and protocols (e.g. VERA) can help with this.

Additional data on other N pathways can be very useful (particularly for modellers), e.g. nitrous oxide emissions, nitrate leaching, subsequent yield impacts. There is value in multiple measurements from a single plot treatment.

Quantification of uncertainties is important; what is the variability in the data; what statistical methods are appropriate for combining data from different experiments/sources; what level of precision is required in development of mitigation reduction factors.

B) User's perspective: Requirements for an N_2O and NO_x emission measurement method

Who is the end user?

A. Ultimately those defending emission inventories to IPCC

- Should be less biased than Tier 1 approach
- Size of the dataset – some country specific data is better than none?
- Reliable data – verified by peer reviewed publication of data – activity data should be collected and the publications should facilitate meta-analysis which could further improve regional estimation of loses.
- Desirable to have a database of response and controlling factors

B. Those measuring:

- Cost, ability to take many measurements, precision, frequency, robustness of system, defining season boundary, meet modeler requirements.

C) Requirements for models to establish emission inventories

The participants focused on the type of models that would provide emission estimates with a high spatial resolution. This was partly because it was felt that a high spatial resolution was necessary to capture the geographic variations in climate, soil characteristics and fertilizer management. However, it also necessary to enable reporting of emissions at the scale of the EMEP grid.

The main factors considered desirable to take into account were:

- The type of fertilizer (chemical composition)
- The weather conditions in the days after it was applied (particularly rainfall and temperature).
- The method of application
- The soil characteristics (pH and possibly CEC)
- The type of crop cover
- The timing (when during the year it was applied)

There was a lot of discussion concerning how feasible it is to obtain these activity data. Information on the type of fertilizer may be available at the national level, although fertilizer tourism appears to be important for some countries (i.e. significant amounts of fertilizer purchased in country A are exported and used in country B). It appears that soil data is likely to be available (either nationally or via the European Soils Database) and cropping data would be recorded in connection with the EU single farm payment (but there was uncertainty whether these data would be accessible, for reasons of confidentiality. Data concerning the method of application would be available in some countries but not in others.

A great challenge is to tie all this information together. In order to be able to develop a model that takes all the above mentioned factors into account, it is necessary to know which type of fertilizer is applied to which soil, how it is applied, and when and where the application is made (so that the link to the weather conditions can be made), which crop (if any) is present. Two methods were discussed. One would be to use a mixture of existing data and the knowledge of local agricultural experts. This would be the cheapest but could be challenged as biased (e.g. if farm advisors only work for the better farmers). The second option would be to collect the data using a farm survey. This would be expensive and would also have to be carefully planned to avoid bias but might be usefully combined with questions concerning other aspects of farm management that would be useful for reporting under CLRTAP or UNFCCC (e.g. timing and application method for manure spreading).

D) Identifying the most appropriate method for recording NH_3 und NO_x emissions

Summary of expert concluding comments (see Table 4):

- For achieving reliable data in order to a) generate emission factors and b) modeling datasets the “open methods” shall be used, since they enable emission recording under natural conditions.
- Micrometeorological methods are assumed to be preferable, when few variants are to be assessed.
- Comparative studies e.g. various treatments may be performed by using wind tunnel (dynamic chamber), standard comparison methods, calibrated passive sampler method, or even static chambers.
- Multiplot experiments may be performed by using standard comparison methods rather than wind tunnels or dynamic chambers. Micromet methods are not suitable for that purpose, but should be used for validation of the outcomes.
- Nevertheless a verification testing of the methods is necessary, since accuracy actually has not been approved (see world café discussion 4.1 B)

Table 4: Evaluation of Ammonia flux recording methods – suitability

Factor	Micro-meteo-rological method	Wind tunnel	Dynamic chamber	Stan-dard compa-rison method	Cali-brated passive sampler method	Static chamber & acid traps	^{15}N re-covery	Rele-vance for emissi-on re-cording
Disturbance ambient conditions	+	0	-	+	0	-	+	3
Fertilizer type	+	+	+	+	+	+	+	0
Application technique	+	+	0	+	0	0	0	2
Suitability for multiplot recording	-	0	+	+	+	+	+	3
Avoidance of artefacts	+	0	0	?	+	+	-	3

The relevance of the factors for NH_3 emission recording has been rated on a scale from 0 to 3, by “0” being least and “3” most relevant for emission recording. The suitability of the available recording methods to internalize these factors has been rated from “not suitable” (-), over “restrictedly suitable” (0), to “suitable” (+) and (?) “not rateable”.

Summary of expert concluding comments (see Table 5)

- For many sites or treatments manual chambers have to be used
- Choice of GC or laser approach for measurement. Potential for laser movement issues but may be able to be overcome
- The high time resolution approaches are also needed to understand temporal and diurnal flux variation as well as to validate the manual chamber output.

Table 5: Evaluation of N_2O flux recording methods – suitability

Factor considered by experts	*Manual chamber & *Gas chromatography* analysis of N_2O	Manual chamber & laser analysis	Auto chambers	Eddy covariance
Suitability for emission factor generation	0	0	0	0
Cost	0	0	-	-
Labour (amount)	0	+	+	+
Skill needed	0	-	-	--
Precision	0	++	0/+	++
Replication	0	-/0	-	--
Temporal resolution	0	0	++	+++
Spatial resolution	0	0	-	-
Potential for artefacts	0	+	0/+	+++
Suitability for plot scale measurement	0	0	+	-
Spatial representation	0	0	-	++

*Manual chamber + *Gas chromatography (MCGC)* analysis of N_2O was considered to be the standard approach and given a rating of 0 by the experts with all other approaches rated –, 0 or + (negative, equal to standard or positive, respectively) relative to MCGC for the factors considered by the experts. For example, additional skill requirement is considered a negative and decreased artefacts is considered a positive i.e. the – or + does not indicate the direction of change rather the perception of the experts regarding desirability.

5 Conclusions and Recommendations

5.1 State of the art for N flux measurement

Ammonia emission measuring methods (for details see Shah et al., 2006; Misselbrock et al., 2005; Sommer and Misselbrock, 2016)

Enclosure/Chamber Methods. In the enclosure method, ammonia concentration in the airstream or mass released from a covered, treated surface is determined. In closed-static or semi open chambers, flux is determined based on ammonia mass recovered on a trapping medium and the chamber area. Ammonia flux can be calculated in real time or on a time-averaged basis depending on how ammonia concentration is detected. A wind tunnel is one type of enclosure that is open at one end, through which ambient air is pulled across the treated surface by a fan at the other end.

Because the enclosure affects both convective heat transfer and counter radiation, design as well as dimensions of the chambers and airflow rate can all affect the enclosure temperature response and thereby reduce or enhance flux (compared to ambient conditions). Removing the enclosure between samplings can reduce the artifacts caused by chambers. Enclosures left on-site during rainfall will overestimate the emission of NH_3. An additional problem is, that enclosure application is limited in tall crops.

Since ammonia losses are mainly due to convective flux, closed-dynamic chambers and wind tunnels better mimic wind conditions and are preferable over the closed static or semi open chambers. Because of their small footprints and high spatial variability of the flux, enclosures are assumed to be unsuitable for developing ammonia emission factors. However, enclosures can be used to compare relative emissions due to different treatments when the ammonia sources are applied uniformly on the surface. For testing ammonia volatilization models, wind tunnels are more suitable than chambers because they modify internal conditions to a lesser degree and better mimic natural airflow. Further, wind tunnels with logarithmic velocity profiles would better represent ambient conditions.

Micrometeorological Methods. Three micrometeorological methods, namely, integrated horizontal flux method (IHF), eddy covariance, and backward Lagrangian Stochastic (bLS) model, were discussed during the workshop.

In the **IHF method**, surface flux from a treated plot transported upwind horizontally by the eddying wind movement is captured in a vertical plane of the same width downwind. Vertical ammonia flux, adjusted for background emissions, is calculated as the integrated product of the ammonia concentration and the wind speed recorded in multiple heights above the soil surface. The advantage of the IHF method is its simple yet robust theoretical basis that requires only very few assumptions.

The **ZINST method** is a special case of IHF wherein a single measurement of ammonia concentration and windspeed is sufficient. It is that height (over bare ground or short crop) at which the normalized horizontal flux remained virtually unchanged, irrespective of stability conditions. ZINST is a function of surface roughness and plot radius, increasing more or less linearly. Because ZINST requires a well-developed normalized flux profile over flat and uniform areas, unacceptable errors may result when applied to disturbed and heterogeneous conditions, as well as over taller crops which cause increasing surface roughness.

The **eddy covariance method** is a direct micrometeorological measurement method to quantify turbulent gas exchange, where the average air passing through a measurement point is measured in terms of vertical wind speed, direction of motion, and gas concentration or density over a given measurement interval. This makes it possible to spatially integrate N fluxes into the atmosphere at the landscape level. The result, which is usually adjusted by a correction factor, is called the Eddy Flux. The correction of the raw data obtained is carried out due to the unavoidable inability of the measuring system to detect all flow-relevant air turbulences (eddies). The eddy-covariance equation is consisting of the flux density of a scalar, and the vertical wind speed, and the concentration of the scalar. While the gas measurement according to the eddy-covariance method, the eddy flux or the gas measurement takes place by means of a measuring tower directly in the open system of the atmosphere, usually in a sensor height of several meters. In addition to N fluxes carbon dioxide, methane and water vapor can also be measured. For the application of the eddy-covariance equation, measurements of the fluctuation of the trace gas concentration and the vertical wind speed are necessary.

In the **bLS Model method**, also called the “inversion dispersion modeling,” the first step is to prerun the bLS model from a tower within or downwind of the source to develop a catalog of touchdowns of particles on the source, specifically, their vertical velocities. Next, wind speed, ammonia concentration and wind direction are measured at the tower. Finally, a constant based on the number of trajectories touching down within the source boundary, is calculated. The constant is a function of the mast height, the surface roughness, stability length, depth of mixed layer and source characteristics. The flux can, thus, be calculated as the product of ammonia concentration and wind speed divided by the constant.

The **“standard comparison” method (SC)** can be considered as a kind of micrometeorological method, because it is applicable to unconfined plots. Ammonia is trapped in semi open acid traps placed above the soil surface in the center of the plot. First, a transfer factor determined in a “standard” plot (by relating the ammonia mass recovered in the acid traps to the known mass released at the soil surface by a diffuser connected to a NH_3 gas source) is corroborated in “control” plots by sampling the N content of the slurry applied to plastic gutters. Ammonia recovery in the acid trap in the fertilized plot is multiplied by the transfer factor to obtain flux. Whereas no meteorological measurements is required, all of the plots require a homogeneous wind field and uniformity in extent and orientation. The transfer factor fluctuates because of shifting wind directions. The method is suitable for multiplot experiments, however, as advised by the workshop adjustments of standard plots and distances between differently treated experimental plots are needed.

The “calibrated passive sampler” method (CPS) is linking a simple semi-quantitative measuring method used in all plots, with a quantitative method by simultaneous measurements using both methods on selected plots. As a semi-quantitative measurement method passive samplers are used like in the SCM. However, instead of a “standard” plot a dynamic chamber method (Dynamic Tube Method) is used to obtain a transfer factor, which converts the semi-quantitative measures of the passive samplers into quantitative NH_3 emission data (kg nitrogen ha^{-1}). The principle underlying this approach is that passive samplers placed in a homogeneous experimental field have the same NH_3 absorption behavior under identical environmental conditions. Therefore, a transfer co-efficient obtained from single passive samplers can be used to scale the values of all passive samplers used in the same field trial. The method can be used under conditions with bare soil or small canopies (<0.3 m) and is applicable to multi plot studies.

The **N recovery method (balance)** involves a complete N balance for all of the N addition and loss pathways, except the gaseous N loss. Thus, the balance of inputs and outputs yields the sum of the gaseous N losses. Ammonia volatilization and denitrification could happen simultaneously, particularly under wet conditions, resulting in simultaneous evolution of NH_3 and other gaseous N species. Depending on soil, crop, and weather conditions, ammonia flux may only be a fraction of the total gaseous N emissions. However, since the transformation of applied ammonia-N requires longer time than the emission of NH_3 after addition of reduced N fertilizers, the method is assumed to be suitable for derivating ammonia losses during a few day experimental period, and has thus the potential to serve as (probably the only) method for real prove of precision of NH_3 emission measurements.

Nitrogen oxide emission measuring methods (for details see Rapson and Dacres, 2014)

Enclosures/Chambers are the most common approach to measuring gas fluxes from the soil surface, enabling the accumulation of gases of interest in a known volume. The size of the chamber can vary greatly, from less than 1 m^3 to greater than 150 m^3. The chamber is placed over the soil surface and closed for a short period of time, during which, samples are collected and analyzed to determine the change in concentration of N_2O.

The advantage of chambers is that they are easily deployed and do not require the use of extremely accurate or rapid analytical techniques. Both manual chambers (where the chamber is closed and opened by an operator) and automated chambers (where the chambers are opened and closed through a pneumatic system) have been used. Manual chambers are highly labor intensive, limiting the number of readings that can be collected but, because they are cheap, more spatial locations can be sampled. The use of automatic chambers allows many more readings over a longer study period, but their operating requirements and their cost mean that this method is suited to small areas only (<25 m^2). It is important to bear in mind that the use of chambers causes soil disturbance and disrupts the soil microclimate, so chambers should be deployed only briefly. The time for which chambers need to be closed is determined by the limit of detection (LOD) and the precision of the technique used to measure N_2O concentration.

Eddy covariance is the most direct method for measuring a flux over a surface. In eddy covariance, the aim is to make direct measurements of the rate of vertical transport of nitrogen oxides. The instantaneous vertical flux density at a point in the atmosphere is the product of the vertical wind speed (measured with a 3D anemometer) and gas concentration at the same point (determined with a gas analyzer). The instantaneous fluxes are averaged over sampling periods, generally between 15 min and 1 h to include all the effective transporting eddy sizes. Eddy covariance is the preferred micrometeorological method, as it provides a direct measurement of vertical flux that is independent of atmospheric stability and does not require some of the simplifying assumptions made in other micrometeorological techniques. However, eddy covariance requires fast-response instrumentation operating at frequencies of 10 Hz or higher. The need for fast, sensitive gas analyzers is a limiting factor in the use of Eddy covariance measurements.

Innovations for emission rate measuring techniques

In the last decade there was no significant development, providing neither new measuring principles nor improved accuracy or preciseness of emission rate recording. Significant progress can be observed in the automatization of sampling procedures and the detection preciseness of NH_3 and N_2O gas concentrations via laser techniques. However, these improvements do not significantly contribute to a better overall recording of the emission rates in principle, because the weaknesses, which are responsible for lacking of accuracy and preciseness lie in the mass flow recording.

Conclusions

Ammonia emission rates can be directly estimated using enclosures, micrometeorological methods, standard comparison methods, calibrated passive sampler method or indirectly by nitrogen (^{15}N) recovery methods. Although low cost and replicable, chambers modify environmental conditions and are suitable only for comparing treatments.

Wind tunnels do not modify environmental conditions as much as chambers, but they may not be appropriate for determining accurately ammonia fluxes; however, they can be used to compare emissions and test models. Larger wind tunnels that also simulate natural wind profiles may be more useful for comparing treatments than micrometeorological methods because the latter require larger plots and are, thus, difficult to replicate. Further, one of the main constraints of wind tunnels is, that rainfall, which largely affects NH_3 emissions cannot be taken into account.

For determining absolute ammonia flux, the micrometeorological methods are the most suitable because they are nonintrusive, however a final prove of precision is still missing.

All three methods, IHF, Eddy-covariance and bLS require relatively large areas for accurate estimations. Thus, the methods are not suitable for multi plot experiments.

With its simpler theoretical basis and fewer restrictions, the integrated horizontal flux (IHF) method is preferable over other micrometeorological methods. With uniform wind flow, the ZINST method requiring measurement at one predetermined height may perform comparably to the IHF method but at a lower cost. The Eddy covariance method requires large fetch lengths (>100 m) with uniform surface attributes that preclude their use over plots <1 ha. Whereas the bLS method can be used on smaller plots, its accuracy is reduced under certain stability conditions.

The simple theoretical and operating basis of the SCM (and CPS) indicates, this method to be most suitable for multiplot and multivariant experimental designs. However, the extent of mutual influence between differently treated experimental plots is not finally clarified.

The ^{15}N recovery method may in short experimental periods serve as a reference method and help to assess the accuracy and preciseness of other methods.

All methods are not finally proved for their accuracy. Numerous experiments have been performed for the comparison of results and the suitability for certain purposes. However, it is not known, which method is reflecting the real emission rates best and accurate.

Nitrogen oxide emission rates namely N_2O can be directly estimated using chambers and micrometeorological methods. For determining absolute N_2O flux, the eddy covariance method is assumed the most suitable because it is nonintrusive, however a final prove of precision is still missing. Eddy-covariance require relatively large areas for accurate estimations. Thus, the method is not suitable for multiplot experiments. Although being inexpensive and enabling replications, chambers modify environmental conditions. Since influences on N_2O partial pressure are comparatively low, there is currently no alternative for determining fluxes from experimental fields and field plots.

5.2 Weaknesses & knowledge gaps

Various techniques including enclosure or chamber techniques, micrometeorological techniques, as well as N balance/difference methods have been used in the past to measure ammonia losses, all of which having their pro´s and con´s. Some preferences have been given to either wind tunnel systems or micrometeorological methods such as the IHF method; however, no method can be claimed to depict absolute ammonia losses. Therefore, the quantification of NH_3 emissions from bare and vegetation-covered soil surfaces is still challenging.

Since the emission of NH_3 is largely affected by the prevailing weather conditions, any method which alters the ambient conditions e.g. wind, precipitation or air and soil temperature, must in principle cause bias. The IHF methods "are generally considered to give reliable emission estimates for ambient conditions" (Sommer and Misselbrook 2016). However, independent assessments of precision and accuracy of these methods are still missing. For this reason, widely accepted methods require further verification. Sommer and Misselbrook (2016) compared NH_3 emission rates using IHF methods and wind tunnels. The authors showed that emission levels measured with both methods were not significantly different, if the air flow in the wind tunnels was adjusted to the ambient wind speed. This could be accepted as a proof for the precise performance of the IHF methods, if the performing quality of wind tunnels would have been ensured. Eight experiments on the recoveries of NH_3 emitted from various sources with known emission rates, cited in the paper of Sommer and Misselbrook (2016), show a recovery rate range from 66 to 122%. However, all experiments except for one are exclusively testing the performance of the wind tunnels, since the source of emitted NH_3 was induced into the wind tunnels. Thus, the effects of ambient weather conditions on the acquisition of emitted NH_3 were not considered. In conclusion, this means that a final scientifically sound proof of the performance of both of these sophisticated methods is still missing.

In a recent paper Pacholski et al. (2017) analyzed NH_3 emission data gathered over a three year period caused by urea application at three different sites across Germany. They applied developed models and showed that scenario modeling might be considered as a powerful tool for the derivation of EF. However, the authors concluded that both is needed, a much more expanded data set and further development of the models.

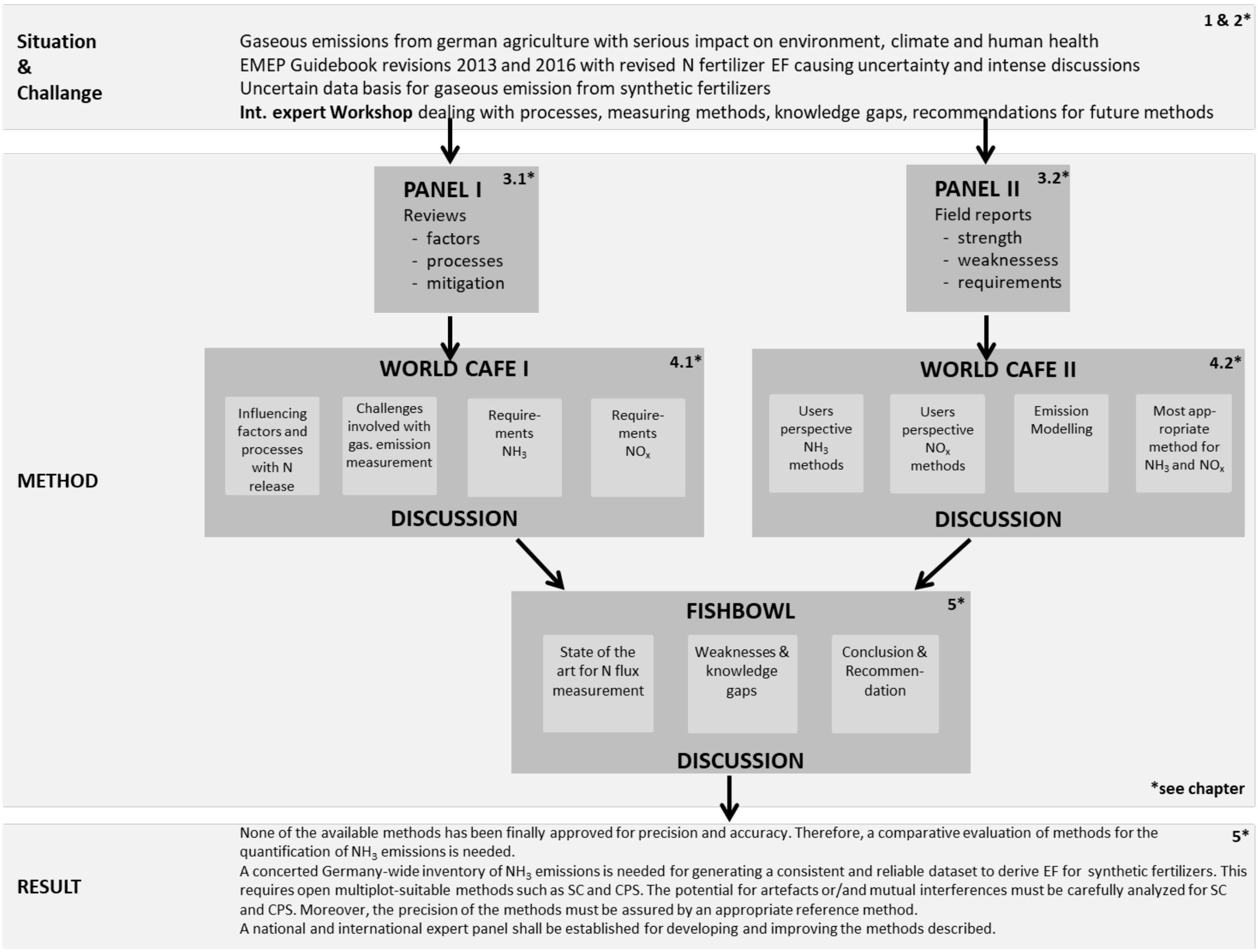
In order to generate the urgently needed data set multi plot experiments have to be conducted at different sites across Germany to generate regional EF. Since different synthetic fertilizers, the effects of urease- and nitrification-inhibitors as well as other mitigation strategies like the incorporation of the fertilizers in the soil have to be tested, numerous testplots are required. To this end, appropriate methods for multi plot measurement of NH_3 emissions have to be applied. Eddy-covariance and IHF methods are not suitable, because they require large areas. Wind tunnels are not appropriate as well since they yield acceptable results only, if the wind inside the tunnel is adjusted to the outside wind requiring elaborate and costly techniques, which is not affordable for large multi plot experiments. The SCM was originally developed for multi plot studies and is thus, in principle, most suitable for the needed research. However, as outlined in the workshop, some improvement concerning the standard plot is required, which can be solved in pilot studies on the method. In general, when it comes to multiplot experiments, it has to be ensured by the design that interferences between the differently treated plots are avoided. At the workshop it was noted that the distances between plots are crucial. Further, the precision of the method has to be ensured by comparison with reference methods like IHF and in particular the ^{15}N balance method.

With respect to N_2O and NO_x the expert group generally agreed that the chamber methods yield reliable emission data, although the final prove for this statement is also missing. Open questions arise with respect to timing and frequency of data collection. Further, a harmonized and generally accepted protocol should be developed.

5.3 Recommendations

The establishment of national N emission inventories is based on the utilization of modeled emission factors (EF). It has to be considered, however, that the empirical data base for the deduction of EF for emissions of gaseous N along with the application of synthetic N fertilizers under practical conditions has to be regarded as weak. In the course of the international NIFLUM expert workshop both various available recording and measurement methods for collecting these data and respective modeling approaches have been critically assessed.

Figure 15: Objectives and recommendations of the NIFLUM Workshop



Gaseous emissions from german agriculture with serious impact on environment, climate and human health
EMEP Guidebook revisions 2013 and 2016 with revised N fertilizer EF causing uncertainty and intense discussions
Uncertain data basis for gaseous emission from synthetic fertilizers
Int. expert Workshop dealing with processes, measuring methods, knowledge gaps, recommendations for future methods

None of the available methods has been finally approved for precision and accuracy. Therefore, a comparative evaluation of methods for the quantification of NH_3 emissions is needed.
A concerted Germany-wide inventory of NH_3 emissions is needed for generating a consistent and reliable dataset to derive EF for synthetic fertilizers. This requires open multiplot-suitable methods such as SC and CPS. The potential for artefacts or/and mutual interferences must be carefully analyzed for SC and CPS. Moreover, the precision of the methods must be assured by an appropriate reference method.
A national and international expert panel shall be established for developing and improving the methods described.

own illustration, DöhlerAgrar, 2017

For NH_3 the data base for the deduction of EF is especially uncertain, which resulted in up to two times larger EF in the current EMEP guidebook, compared to those in the previous version, while at the same time the EF for mineral nitrogen fertilizers, in particular urea, determined at German sites are significantly below the ones currently in force for the EU. On the one hand, the uncertainty is resulting from a lack of sufficient spatially and temporally explicit data on NH_3 volatilization resulting from mineral fertilizer application. For the calculation of NH_3-EF 2012, for example, which were intended to be applied European-wide, data from the UK were heavily overrepresented, and NH_3 emission data from measurements at times when no fertilization took place in agricultural practice (experiments in summer at high temperatures with high NH_3 emissions not relevant in practice) were used. In particular, the available data base is not sufficient for the derivation of regionally differentiated EF, e.g. according to the twelve soil regions established in Germany (using modeling techniques).

On the other hand, the available NH_3 emission data are based on recording methods with differing precision and accuracy. Generally, a distinction is made between "open" methods which do not or hardly impact the weather parameters, and chamber methods. The first group mentioned includes micrometeorological methods which are generally regarded as reference methods although to date no empirical assessments on the precision and accuracy of these methods exist. The second group includes wind tunnels which deliver results comparable to those of micrometeorological measurements, if the wind speed inside the tunnels is controlled in accordance with the ambient wind speed. However, it can be said restrictively, that the published accuracy controls of the wind tunnel recordings tested only the functionality of the wind tunnels themselves and not the precision of the emission recordings under ambient environmental conditions. For the other methods discussed the uncertainties are even larger.

For N_2O largely consistent measurement protocols exist. Due to the - compared to NH_3 - small influence of atmospheric N_2O partial pressure on the emissions from soils, estimates, relaying on a short-term linear increase of N_2O concentrations, can be conducted in closed chambers. Thus, the also proven but more elaborative open techniques (e.g. Eddy-covariance) do not necessarily have to be deployed. However, there is a need for coordination with respect to the design of the chambers, and in particular with regard to the temporal resolution of the measurements.

Against the background of this state of the art, the international NIFLUM expert workshop encourages the establishment of a EU-wide, coordinated research program to develop standardized methods for the precise quantification of NH_3 emissions under ambient agricultural-practice conditions.

The central goal must be to generate a broadly agreed method which considers the country specific climatic and soil properties, as well as differences in agricultural management practices. With respect to the final target (reliable, generally accepted EFs for the whole of Europe) it has to be assured that the method must be proven according to both precise and accurate measurements under ambient weather and soil condition. At the same time it has to be considered that multi plot experiments are needed to study the effects of different fertilizer types under different site conditions on the emission of NH_3. Thus, the methods to be developed have to be robust as well as cheap and must be applicable in multi plot research experiments. Both the calibrated passive sampler method and the standard comparison method may come into consideration for this purpose. However, the weaknesses of these methods, which were identified at the workshop, such as the instrumentation of the standard plots or the required distances between the differently treated experimental plots in order to avoid artifacts, have to be overcome. IHF methods may be used for the validation of these methods; however, the IHF methods themselves need to be further tested. A central point of that matter is the development of scientifically sound approaches for testing the precision of the methods. In this regard, the ^{15}N based mass balance method might be promising.

In summary, the following is recommended to the German authorities:

(1) The expert group agrees that country-specific EF could be developed and are needed for Germany. To this end, a short-term national expert group should be nominated proposing provisional EF for synthetic N fertilizers on the basis of all available data in Germany until the end of 2018. These EF should be valid until an EU-wide procedure is agreed upon.

(2) The expert group recommends to establish an international expert group (e.g. in the frame of a COST action) which could set up standardized emission recording methods at the level of the European Union. This group should, besides the methodical work, also develop EU-wide balanced data acquisition programs in order to cover missing information (including ring trial tests). Besides considering the scientific basis, the expert group should also take into account the profound preliminary work of VERA. With respect to NO_x, generally agreed protocols are available, which should be considered as well. When establishing the international group, it should be assured that members of the national expert groups are represented.

(3) In order to cover existing knowledge gaps with respect to NH_3 emissions in Germany, a Germany-wide well designed complementary inventory of NH_3 emissions from synthetic fertilizers along with model development is mandatory for the derivation of regional EF. This national research program should address both the methodical development as well as the data acquisition for NH_3 emissions resulting from N mineral fertilizer application.

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