



Les échanges de polluants gazeux et particulaires entre la surface et l'atmosphère à l'échelle locale

Benjamin Loubet

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**LES ECHANGES DE POLLUANTS GAZEUX ET
PARTICULAIRES ENTRE LA SURFACE ET
L'ATMOSPHERE A L'ECHELLE LOCALE**

-

**SURFACE-ATMOSPHERE EXCHANGE OF
PARTICULATE AND GASEOUS POLLUTANTS AT
THE LOCAL SCALE**

-

Mémoire de HDR présenté à l'école doctorale des sciences de
l'environnement d'Ile de France

par

Benjamin Loubet

Le 29 Novembre 2011

-

Devant le jury composé de :

Philippe Bousquet (rapporteur)

Gilles Bergametti (rapporteur)

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RESUME

L'agriculture joue un rôle clé dans la pollution de l'air et le changement climatique : elle est responsable de 10% des émissions de gaz à effet de serre d'origine anthropique et elle est la première source anthropique d'azote réactif et de pesticides émis dans l'environnement. L'agriculture contribue aussi à l'émission et la formation de particules dans l'atmosphère et à la dissémination d'organismes génétiquement modifiés dans l'environnement. Mais dans le même temps, l'étendue des surfaces agricoles contribue fortement au dépôt de polluants atmosphériques, notamment ozone et composés azotés. Par ailleurs, des écosystèmes agricoles bien gérés peuvent constituer un puits efficace de gaz à effet de serre. Mieux quantifier le rôle de l'agriculture dans les échanges de gaz à effet de serre et de polluants (et en particulier l'azote) entre les surfaces terrestres et l'atmosphère est donc une étape clé pour développer une agriculture durable.

L'échelle locale, allant de la parcelle à l'exploitation agricole, est essentielle dans l'étude des transferts d'azote et de particules entre l'agriculture et l'atmosphère car c'est l'échelle à laquelle les flux vers l'environnement sont les plus forts (azote, pollens). Les recherches résumées dans ce rapport contribuent à la compréhension et la quantification des *émissions et du devenir des polluants et des pollens à cette échelle locale* et à l'identification des *sources et puits de polluants et de gaz à effet de serre dans les écosystèmes agricoles*, avec un intérêt particulier sur l'ammoniac, l'ozone et le pollen. Ces recherches ont mis en évidence le rôle central des conditions environnementales (températures et humidité de surface, vent) et du contrôle biologique (structure du couvert, échanges stomatiques, point de compensation) dans les échanges des composés étudiés entre la surface et l'atmosphère.

Les perspectives de ce travail sont d'améliorer la quantification des flux de carbone, d'azote, de gaz à effet de serre et de composés réactifs (composés organiques volatiles, aérosols et composés acides) entre les surfaces cultivées et l'atmosphère et de comprendre les interactions entre ces flux à long terme. Le couplage de modèles d'écosystèmes avec des modèles d'échanges de polluants réactifs et de gaz traces est vue comme un jalon important dans l'accomplissement de cet objectif. En parallèle la quantification des flux de ces composés avec des techniques de pointe dans des systèmes agronomiques actuels et innovants devrait permettre de valider ces modèles et analyser les évolutions à long terme.

ABSTRACT

Agriculture plays a key role in climate change and air pollution: It is accounting for around 10% of the total anthropogenic greenhouse gas emissions, and represents the main entry of anthropogenic reactive nitrogen and pesticides to the environment. It is recognised as a large contributor of atmospheric particulate matter and contributes to the dissemination of genetically modified organism in the environment. But agricultural lands represent a large fraction of the terrestrial surfaces and as such contribute a great deal to pollutant recapture, like ozone and nitrogen compounds. If well managed, agricultural ecosystems may also be a sink of greenhouse gases. Quantifying the role of agriculture in the exchange of greenhouse gases and pollutants (and especially nitrogen) between terrestrial surface and the atmosphere is therefore an essential step towards developing environmentally sustainable agriculture.

A key issue when dealing with exchange between agriculture and the atmosphere is to account for the local scale, from the field to the farm, which is also the scale at which the fluxes to the environment are the largest (nitrogen, pollen). The researches reported here contribute in understanding the *emissions and fate of pollutants and pollens at this local scale* and in identifying the *sources and sinks of pollutants and greenhouse gases within agricultural ecosystems*, focussing on ammonia, ozone and pollen in particular. These researches showed the central role of environmental conditions (surface temperatures and humidity, wind) and biological control (plant growth and structure, stomatal aperture, compensation point) in the surface-atmosphere exchange of these compounds

The perspectives of these researches are to improve the quantification of the fluxes of carbon, nitrogen, greenhouse gases and reactive compounds (volatile organic compounds, aerosols and acid compounds) between managed land and the atmosphere and understand the interactions between these fluxes over the long term. The coupling of ecosystem models with pollutant and greenhouse gases exchange models including chemistry within the canopy is viewed as a major milestone in achieving this objective. In parallel, long term measurements of fluxes of greenhouse and reactive gases with up to date methods, in current and innovative agronomical systems will be undertaken to validate these models and give long term trends.

REMERCIEMENTS

Le travail qui est résumé dans ce rapport est le fruit de collaborations multiples. C'est un travail collectif en somme, issu des relations de travail que j'ai pu entretenir avec mes collègues de l'INRA : ceux qui m'ont transmis leur expérience et leur goût pour la recherche, et qui m'ont fait confiance pour encadrer des étudiants en thèse, Bernard Itier, Pierre Cellier, Laurent Huber ; ceux avec qui m'ont permis d'aborder avec enthousiasme et persévérance de nouveaux thèmes de recherches, Christophe Fléchar, Eric Lamaud ; ceux qui m'ont fait découvrir de nouvelles thématiques de recherche, Sophie Générmon, Carole Bedos, Patricia Laville ; ceux avec qui j'ai partagé un bout de chemin avec des échanges toujours fructueux, Sylvain Dupont, Sébastien Saint-Jean, Romain Roche, Jean-François Castell ; ceux avec qui nous avons mené, ensemble, dans la durée et la bonne humeur un travail de recherche commun, Eric Larmanou, Erwan Personne, Céline Decuq, Olivier Fanucci, Brigitte Durand, Dominique Flura, Sylvie Masson, Olivier Zurfluh, Nicolas Mascher, Jean-Christophe Gueudet ; mais aussi tous les autres collègues de l'équipe Biosphère Atmosphère qui m'ont à leur manière apporté leur aide et leur soutien, Benoît Gabrielle, Nathalie Gagnaire, Andrée Tuzet, Nader Katerji, Michel Lauransot ; et enfin tous le personnel de l'unité et en particulier des services communs sans qui je n'aurais pas pu accomplir ce travail.

Des collègues d'autres instituts et universités ont grandement participé à l'élaboration dans la durée de ce travail, et en premier lieu les collègues du CEH-Edinburgh (UK), Mark Sutton, Eiko Nemitz, Celia Milford, Mark Theobald, Paul Hill, Ute Skiba, Christine Braban, Daniela Famulari, mon collègue de l'ECN (NL), Arjan Hensen, mes collègues de l'AgroScope (SW), Christoff Ammann, Albrecht Neftel, Christoph Spirig, mon collègue du CRA(IT), Gianfranco Rana, mon collègue de l'université d'Alberta (CA), John Wilson, mon collègue du CSIRO (AU), Ray Leuning.

Ce travail collectif est avant tout le fruit du travail des étudiants en thèse que j'ai eu l'opportunité et le plaisir de co-encadrer. Je les remercie tous vivement pour leur travail dont ce document s'est beaucoup nourri : Nathalie Jarosz, Rea Massad, Alexis Marceaux, Patrick Stella, Thomas Bouvet, Rossana Ferrara. Je remercie également les post-doctorants avec qui j'ai eu l'occasion de travailler au cours de ces années, Otmane Souhar, Amir Feiz, Juliette Faburé, ainsi que les nombreux étudiants de master, licence, BTS, Vincent Debost, Matthieu Mouton, Afroun Abdenor, Pascal Martelli-Garon, Ivanka Panic, Julien Louchard, Julien Martin, Ouaffa Saber, Estelle Compagnon, Matthieu Mutel, Gaetan Laurent, Malya Abdelouahab, Marine Millet, Khaled Tamazirt, Francis Vermot de Boisrolin.

Enfin je remercie Sabine, Charlotte, Anaïs et Valentin, qui m'ont apporté, ..., le bonheur tout simplement (nécessaire à toute activité professionnelle sereine...) ; mes parents, Michel pour m'avoir donné envie de faire ce métier, et Elisabeth pour m'avoir donné des clés essentielles dans le monde du travail.

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1. CV DÉTAILLÉ

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PROFESSIONAL EXPERIENCE

2000 – 2011 **Senior researcher at Institut National de la Recherche Agronomique (INRA, FR).**
Grignon
« Atmospheric dispersion of gaseous pollutant and particulate matter at the local scale ».
« Exchange of pollutant and GHG between the atmosphere and agricultural ecosystems ».

1997 – 1998 **Temporary exchange of staff with ITE (Institute of Terrestrial Ecology)**
Edinburgh **(UK).**
Seasonal changes of the ammonia stomatal compensation point in grassland and maize.

1996 – 2000 **PhD thesis at INRA Grignon (FR):**
Grignon
"Modelling NH₃ dry deposition in the vicinity of sources".

1995 **Master training at INRA Grignon (FR):**
Grignon
"Evaluation of the wind-tunnel technique for measuring NH₃ emissions"

1994 **License training at the „Institut für Kernenergie und Energiesystem (IKE,**
Stuttgart **DE):**
"Numerical study of a passive protection against nuclear core fusion ".

DIPLOMS

1995-2000 **PhD at Université Paul Sabatier (Toulouse, FR):**
Grignon
http://tel.ccsd.cnrs.fr/documents/archives0/00/00/32/50/index_fr.html

1995 **Research Master in fluid mechanics at Université Aix-Marseille II**
Marseille **(Marseille, FR).**
Master (ingénieur) at « École Centrale de Marseille » in fluid mechanics.

LANGUAGES

FRENCH: mother tongue.	GERMAN: Good understanding.
ENGLISH: fluent.	SPANISH: Some notions.
	ITALIAN: Good understanding,

COMPUTERS AND SOFTWARES

Programming languages:	Basic, Pascal, Visual Basic, C, C++, Campbell.
Data analysis and treatment:	R, Matlab, Labview, ImageJ.
basics:	UNIX, DOS, Windows / Word, Excel, PowerPoint.

EXTRA-PROFESSIONAL ACTIVITIES

Associative:	Responsible of salaries in an associative kinder garden (2001-2006)
Music:	Guitar and bass-guitar. Played in professional and amateur bands.
Sports:	Football / Volleyball / Swimming / skiing.

PHD THESIS STUDENTS (CO-ENCADREMENTS)

- 2009 – 2011: Stella, Patrick. Modélisation des flux d'ozone sur les couverts agricoles. Partition du dépôt entre les voies stomatique, cuticulaire et sol.
- 2008 – 2011: Marceau, Alexis. Pollinisation inter-parcellaire chez le maïs: analyse et couplage des processus conditionnant la présence du pollen viable en fonction de la distance à la source
- 2005 – 2008: Massad, Rea S. Mechanistic modelling of the stomatal compensation point for ammonia.
- 2001 – 2003: Jarosz, N. Modelling maize pollen dispersal. Contribution to cross-pollinisation.

SCIENTIFIC COORDINATION OF LOCAL AND NATIONAL RESEARCH PROGRAMS

- 2011- 2016** PI INRA du projet EU-FP7 ECLAIRE (Effect of Climate Change on Air Pollution Impacts and Response Strategies for European Ecosystems)
- 2011- 2016** PI INRA du projet EU-FP7 INGOS (Integrated non-CO₂ Greenhouse gas Observation System)
- 2010- ...** Animateur de l'axe thématique « Fonctionnement de l'agro-écosystème et échanges avec l'atmosphère » de l'équipe Biosphère-Atmosphère (directeur : Benoît Gabrielle).
- 2009- 2012** Représentant Français de l'action COST804
- 2009- 2012** Projet R2DS de la région Ile de France (coordinateur principal) : Interactions entre l'ozone et les oxydes d'azote dans les couverts végétaux.
- 2008- 2010** Projet SAMBA (NERC, UK) (responsable d'un work-package) : Evaluation de l'efficacité d'une zone tampon boisée pour réduire les émissions d'ammoniac par les bâtiments d'élevages.
- 2008- 2009** Pollutions de Proximité, Transport et Agriculture (PPTA) (Projet PRIMEQUAL) (Coordinateur principal en collaboration avec C. AUBRY du SAD). Evaluation des dépôts issus des transports sur l'agriculture francilienne.
- 2006- 2011** NITROEUROPE : Responsabilité dans le suivi des flux de surface et le développement de méthodes de mesure de flux innovantes.
- 2002- 2006** BIOPOLLATM (Coord. P. Cellier) - (Animation scientifique de l'axe 5) Paramétrisation des échanges de polluants (O₃, NO_x, NH₃) entre la végétation et l'atmosphère.
- 2002- 2004** POLLEN (Appel d'offre CNRS-INSU) - (Coordinateur principal) Etude Mécaniste du Transport et du Dépôt de Pollen de Maïs dans un Paysage Hétérogène.
- 1998-2001** GRAMINAE (Projet CEE 4^{ème} PCRD) – (Animation d'un « Work Package ») Modélisation du dépôt d'ammoniac (NH₃) à courte distance des sources.

TEACHING

Between 12 and 17 hours teaching per year in master. “Heat balance”. “Exchange of pollutants and particulate matter between the surface and the atmosphere”. “Short-range dispersion”.

PUBLICATIONS

52 publications in peer-review journals. 45 communications in congress. 16 research reports, 21 student reports.

2. PUBLICATIONS

Publications dans des revues internationales à comité de lecture et dans des chapitres d'ouvrages.

Par ailleurs une extraction des articles dans « Web of Science » donne les indications suivantes : **Nombre d'articles : 51, nombre de citations : 505, Nombre d'articles qui citent ces travaux : 274, nombre de citation moyenne par article : 10.31, h-index : 14.**

Les autres publications (congrès, rapports, etc.) ne sont pas présentées ici. Au total cela fait 194 publications.

- [1] Bedos, C., Rousseau-Djabri, M.F., **Loubet, B.**, Durand, B., Flura, D., Briand, O. & Barriuso, E. 2010. Fungicide volatilization measured and estimated by inverse modelling: the role of vapour pressure and the nature of foliar residue. *Environmental Science Technology*, **44**, 2522–2528.
- [2] Bouvet, T., **Loubet, B.**, Wilson, J.D. & Tuzet, A. 2007. Filtering of windborne particles by a natural windbreak. *Boundary-Layer Meteorology*, **123**, 481-509.
- [3] Cellier, P., Theobald, M.R., Asman, W., Bealey, W., Bittman, S., Dragosits, U., Fudala, J., Jones, M., Lofstrom, P., **Loubet, B.**, Misselbrook, T., Rihm, B., Smith, K., Strizik, M., van der Hoek, K., van Jaarsveld, H., Walker, J. & Zelinger, Z. 2009. *Assessment Methods for Ammonia Hot-Spots*. Springer, Dordrecht.
- [4] David, M., **Loubet, B.**, Cellier, P., Mattsson, M., Schjoerring, J.K., Nemitz, E., Roche, R., Riedo, M. & Sutton, M.A. 2009. Ammonia sources and sinks in an intensively managed grassland canopy. *Biogeosciences*, **6**, 1903-1915.
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3. ENCADREMENT DE THESES ET DE STAGES

J'ai co-encadré trois thèses, et suis actuellement en train d'en encadrer une. J'ai également participé activement à l'encadrement d'une autre thèse. Par ailleurs j'ai encadré de multiples stages à différents niveaux (BTS, L, M1, M2), ainsi que quatre post-doctorats.

Les travaux de thèse co-encadrés ont conduits à la publication conjointe de 12 articles de rang A (Bouvet et al., 2007; David et al., 2009; Jarosz et al., 2005 ; Jarosz et al., 2003a; Jarosz et al., 2004; Marceau et al., 2011a; Massad et al., 2009; Massad et al., 2008; Massad et al., 2010b; Stella et al., 2011a; Stella et al., 2011b; Stella et al., 2011c) et 1 article soumis.

3.1. Thèses co-encadrées

- 2001 – 2003 : Jarosz, N. : Modélisation de la dispersion atmosphérique des semences de maïs. Contribution à la maîtrise des risques de pollinisation croisée. **Thèse de doctorat**, Institut National Agronomique Paris-Grignon, Paris, 125 pp. (co-encadrement avec L. Huber).
- 2005 – 2008 : Massad, Rea S. : Modélisation mécaniste du point de compensation stomatique pour l'ammoniac. **Thèse de doctorat**, co-encadrement avec A. Tuzet et P. Cellier.
- 2008 – 2010 : Alexis Marceau : Pollinisation inter-parcellaire chez le maïs : Analyse et couplage des processus conditionnant la présence du pollen viable en fonction de la distance à la source. **Thèse de doctorat**. Co-encadrement avec Laurent Huber.
- 2009 – 2011 : Patrick Stella : Modélisation des flux d'ozone sur les couverts agricoles. Partition du dépôt entre les voies stomatique, cuticulaire et sol. **Thèse de doctorat**. co-

encadrement avec P. Cellier.

J'ai également participé activement à l'encadrement de la thèse de Thomas Bouvet entre 2005 et 2007 (apport méthodologique sur le terrain, aide à l'interprétation des données de terrain), sans toutefois être encadrant officiellement.

2005 – 2007 : Thomas Bouvet : Heavy particle dispersion over level terrain and in windbreak flow. University of Alberta. **Thèse de doctorat.**

3.2. Encadrement de stages

Année	Niveau	Sujet du stage	Participation
2010	M2	Modélisation du dépôt des pesticides gazeux sur des plans d'eau.	Co-encadrant
2009	L x 2	Suivi au champ des concentrations en azote dans le sol et la plante et des émissions de gaz à effet de serre (binôme).	Co-encadrant
2008	M1	Modélisation biophysique des échanges d'ozone (O ₃) entre le sol, la plante et l'atmosphère.	Co-encadrant
2007	M1	Mise au point d'un système de mesure de flux de NO _x et d'O ₃ par gradient.	Encadrant
-	BTS	Programmation d'un automate pour la mesure des flux d'NH ₃ (binôme).	Co-encadrant
2006	M2	Etude de l'influence de la rosée sur la conductance non-stomatique de l'O ₃ .	Encadrant
-	BTS	Acquisition de données de flux par la méthode des corrélations.	Co-encadrant
-	M2	Estimation des dépôts de polluants à proximité des axes de transport.	Co-encadrant
2005	IUP-1	Vitesse de sédimentation du pollen.	Encadrant
-	M2	Modélisation des flux d'O ₃ et de NO _x dans un couvert de maïs.	Co-encadrant
-	M1	Evaluation de systèmes de mesure de la durée d'humectation.	Co-encadrant
2004	IUP-1	Vitesse de sédimentation du pollen.	Encadrant
-	Maîtrise	Vitesse de sédimentation du pollen.	Co-encadrant
-	DEA	Estimation des sources et puits de polluants dans un couvert de maïs.	Encadrant
-	DESS	Acquisition de données de turbulence.	Encadrant
2003	DESS	Dispersion et dépôt de pesticides.	Co-encadrant
2002	DUT	Vitesse de sédimentation du pollen.	Encadrant
-	DEA	Chambre de fumigation à l'ozone.	Encadrant
2001	DESS	Dispersion et dépôt d'ammoniac atmosphérique.	Encadrant
1999	License	Vitesse sédimentation et modélisation de la dispersion du pollen.	Co-encadrant

4. ENSEIGNEMENT

Après avoir enseigné en IUP à l'UPMC pendant 3 ans 30 heures de cours/TD par an entre 2002 et 2005, je suis actuellement engagé dans des cours à l'université de Marne la vallée où je donne 6 heures de cours par an ainsi qu'à l'UPMC/AgroParisTech où je donne 3 heures de cours par an.

5. ANIMATION / ENGAGEMENT DANS DES PROJETS

Mon engagement dans des programmes nationaux et internationaux s'est fait soit en soutien à des travaux de recherche déjà engagés soit en appui à des travaux de recherche émergents :

Période	Coordination de programmes de recherche - Animation scientifique
2010- ...	Animateur de l'axe thématique « Fonctionnement des agro-écosystèmes et échanges avec l'atmosphère » de l'équipe Biosphère-Atmosphère (directeur : Benoît Gabrielle).
2011- 2016	PI INRA du projet EU-FP7 ECLAIRE (Effect of Climate Change on Air Pollution Impacts and Response Strategies for European Ecosystems)
2011- 2016	PI INRA du projet EU-FP7 INGOS (Integrated non-CO ₂ Greenhouse gas Observation System)
2009 - 2012	<u>Représentant Français</u> de l'action COST804
2009 - 2012	Projet R2DS de la région Ile de France (<u>coordinateur principal</u>) : Interactions entre l'ozone et les d'oxydes d'azote dans les couverts végétaux.
2008 - 2010	Projet SAMBA (NERC, UK) (<u>responsable d'un work-package</u>) : Evaluation de l'efficacité d'une zone tampon boisée pour réduire les émissions d'ammoniac par les bâtiments d'élevages.
2008 - 2009	Pollutions de Proximité, Transport et Agriculture (PPTA) (Projet PRIMEQUAL). (<u>Coordinateur principal</u> en collaboration avec C. AUBRY du SAD). Evaluation des dépôts issus des transports sur l'agriculture francilienne.
2006 - 2011	NITROEUROPE : <u>responsabilité</u> dans le suivi des flux de surface et le développement de méthodes de mesure de flux innovants.
2002 – 2006	BIOPOLLATM (Coord. P. Cellier) - (<u>Animation scientifique</u> de l'axe 5) Paramétrisation des échanges de polluants (O ₃ , NO _x , NH ₃) entre la végétation et l'atmosphère
2002 - 2004	POLLEN (Appel d'offre CNRS-INSU) - (<u>Coordinateur principal</u>) Etude Mécanisme du Transport et du Dépôt de Pollen de Maïs
1998 - 2001	GRAMINAE (Projet CEE 4 ^{ème} PCRD) – (<u>Animation d'un</u> « Work Package ») Modélisation du dépôt d'ammoniac (NH ₃) à courte distance des sources

6. SYNTHÈSE DES TRAVAUX / SYNTHESIS OF WORK

6.1. Introduction

This introduction briefly gives the context of my research. The scientific objectives of my work are then described, and the methodologies developed to achieve these objectives are summarised. The rest of the document is then structured in three parts, the first treating of “*Emissions and fate of pollutants and pollens over the short-range*”, the second dealing with “*Sources and sinks of pollutants and GHG within canopies*”, and the third part which gives a short synthesis of the main outcomes. Finally my future research priorities are summarised.

6.1.1. Context and issues

My researches were undertaken in the general context of how *agriculture impacts its environment*. This is why my researches were focussed on (i) ammonia, which originates from agricultural activity by more than 90%, (ii) pollens in the context of increasing cultivation of genetically modified organisms (GMO), and more recently, (iii) the greenhouse gas budgets of arable lands, which may be a major lever for diminishing anthropogenic GHG emissions, and (iv) the evaluation of short range deposition of pesticides. Although my researches were conducted in this general context, they were focussed on *potential* impacts, which were mainly evaluated as the net fluxes entering or leaving a given compartment, like ammonia, ozone or pesticides deposition to semi-natural ecosystems, pollen deposition to non-GMO crops, or NH_3 , CO_2 , N_2O and NO emissions to the atmosphere. In this global context, three major issues were identified as structuring my researches and are summarised in the following.

6.1.1.1 Reduced nitrogen: a local issue but a global threat to the environment

Due to the decrease of sulphur and nitrogen oxides emissions under a series of UNECE protocols, reduced nitrogen (NH_x) has become the dominant pollutant in Western Europe contributing to acidification of ecosystems (e.g. Vestring and Storing, 2000). At the global scale ammonium (NH_x) and nitrogen oxides (NO_x) emissions are comparable, although large uncertainties exist on NH_x emissions (Bouwman et al., 1997; Dentener and Crutzen, 1994). Moreover, NH_x deposition, with other reactive nitrogen compounds deposition (NO_x , HNO_3), leads to eutrophication and changes in the biodiversity of semi-natural ecosystems (Fangmeier et al., 1994; Krupa, 2003). Although atmospheric ammonia (NH_3) is not a greenhouse gas (GHG), deposition of NH_x may lead to increased GHG emissions (such as nitrous oxide N_2O) (Melillo et al., 1989) or reduced consumption of methane (CH_4) (MacDonald et al., 1997). Additionally, ammonium sulphate aerosols, $(\text{NH}_4)_2\text{SO}_4$, contribute to half of the negative radiative forcing of the atmosphere due to aerosols (Adams et al., 2001; Houghton et al., 2001), as well as contributing to impacts of secondary aerosol on human health.

At the global scale the use of synthetic fertiliser has dramatically increased over the past century since the discovery of the so called Haber-Bosch process which is used to synthesise NH_3 from atmospheric N_2 and H_2 by iron catalysis at high temperature (700 K) and pressure (500 atm) (Howard and Rees, 1996). This trend is expected to increase in the

future with increasing demand for food consumption and biofuel (Erisman and Sutton, 2008; Galloway et al., 2008). The increase in fertiliser synthesis, biological fixation with legumes and combustion processes lead to an increasing pool of reactive nitrogen being released to the environment, which we unfortunately lack to recycle efficiently for food production; an effect the so-called Nitrogen cascade (Galloway et al., 2008). If there is no drastic changes in the current consumption and environmental policy, it is expected that the impacts of reduced nitrogen to the environment will become a major issue in the coming decades (Sutton et al., 2011).

As it is known since the end of the 19th century (Eriksson, 1952; Sutton et al., 2008), ammonia mainly originates from livestock (Bouwman et al., 1997; Dammgen et al., 2005; Misselbrook et al., 2000). The main NH_x sources are housing and waste storage (Bussink and Oenema, 1998), and land spread manure (Génermont and Cellier, 1997; Sommer et al., 2003). Hence the main NH_x emissions are “hot spots” sources in the sense that they are intense and either spatially small (point sources, such as animal houses and manure storage) or temporally short (application of manure) (Loubet et al., 2009a).

The fact that NH_x is mainly emitted by “hot spots” leads to potentially large local impacts. Indeed, as a very soluble and reactive gas, NH_3 is readily deposited to the plants and the soil surfaces as well as absorbed by the plants (Fowler et al., 2009; Loubet, 2000). The large NH_3 concentrations encountered near “hot-spots” therefore lead to large deposition rates at the local scale (Asman, 1998; Asman and van Jaarsveld, 1992; Theobald et al., 2009). Local scale deposition of NH_3 also contributes to lower net emission of NH_x to the atmosphere and therefore contributes to decrease the long range transport of NH_x (Asman, 2001; Asman and Janssen, 1987; Asman and van Jaarsveld, 1992).

Although the main identified sources of NH_x are “hot spots”, NH_3 is also emitted by plants for which NH_3 is a major component of their internal N cycling (Massad et al., 2008). There is an ongoing issue as to whether the emission of NH_3 by plants may explain part of the gap between observed and modelled NH_3 concentrations (“the ammonia gap”). The exchange of NH_3 between the atmosphere and the plant communities are linked with the concept of stomatal compensation point (Farquhar et al., 1980; Sutton et al., 1995) which involves complex processes (Massad et al., 2010b). Due to this complexity, empirical approaches are essential to produce estimates of these compensation points. Recently (Massad et al., 2010a) parameterised the compensation point for a range of ecosystems based on the amount of nitrogen received. The plant ammonia compensation point may also be viewed as a parameter controlling the NH_3 atmospheric concentration.

Understanding and predicting the role of the biosphere in the reduced nitrogen cycle from the local to the global scale, and trying to identify and minimise the leaks in the nitrogen cascade will be certainly a major issue in the coming decades.

6.1.1.2 Maize GMO contamination and breeding quality

Since many years plant breeders have been interested in controlling maize pollen spreading to control the quality of their seeds. More recently, the introduction of genetically modified organisms (GMO) have raised new issues on gene transport to the environment. For maize in Europe, since wild relatives do not exist, the main concern is therefore to control the “contamination” of conventional maize fields with GMOs. Such a control is necessary to

allow the co-existence of conventional and GMOs crops. The question in central-America is however different since GMO introduction was shown to contaminate wild relatives (Quist and Chapela, 2001). Maize is essentially cross-pollinated by wind (Aylor et al., 2003). The dispersion therefore depends mainly on the geometric configuration of the emitting and target fields, the turbulent conditions (Dupont et al., 2006; Jarosz et al., 2005), the emission dynamics (Marceau et al., 2011a), and the pollen physical characteristics (size, weight) (Jarosz, 2003). The pollination of surrounding fields further depends on the pollen and silks viability (Marceau, 2010). The main way to avoid contamination is therefore to promote time shifts in flowering of neighbouring fields. Another way is by arranging the source-targets geometry and especially designing the area between two fields (windbreaks, bare soils). There is however a contamination risk even at large distances (up to 1 km and even at tens of kilometres) (Loubet et al., 2004).

The first studies on pollen dispersal were conducted with statistical approaches based on quasi-mechanistic models fitted to measured out-crossing rates (Klein et al., 2003). These empirical approaches, although readily applicable, could hardly be extrapolated to different pollen characteristics, geometrical and environmental conditions. The question especially arose in the early 2000 years as to whether different corn crops and physical barrier could limit the out-crossing rates. With the progress in physical modelling of maize pollen dispersal, using Lagrangian Stochastic dispersion models, a great range of environmental, geometrical and pollen characteristics could be studied (Aylor et al., 2003; Jarosz et al., 2004; Loubet et al., 2003b). The use of turbulence k - ϵ model further extended the range of geometrical configuration that could be studied, and especially the role of vegetative barriers onto pollen dispersal (Dupont and Brunet, 2006; Dupont et al., 2006). All these models rely on a good description of the settling velocity distribution of the pollens. The development of a simple method to measure pollen settling velocity (Loubet et al., 2007) have given us all the tools to allow a better understanding of maize pollen dispersal mechanisms in the last 5 years.

However, if the pollen dispersal is essential in the out-crossing process, the timing between the source and the target field is even further important, such as is the pollen viability. The dynamics of pollen emission and viability was therefore essential to study to get the full range of processes involved in out-crossing. Bio-statistical approaches were used to study and model maize pollen emission and viability dynamics (Marceau, 2010; Marceau et al., 2011a).

6.1.1.3 Can arable ecosystems be environmentally sustainable?

At the global scale, agriculture is accounting for 10 to 12% of the total anthropogenic greenhouse gas (GHG) emissions. The dominant GHG component is nitrous oxide (N_2O) which accounts for 54% of the anthropogenic GHG emissions, then comes methane (CH_4), but carbon dioxide (CO_2) is only evaluated to contribute 1% (Smith et al., 2007). However recent syntheses suggest that most arable lands should have a larger CO_2 contribution to the GHG atmospheric budget: indeed, although they all show a positive balance in CO_2 flux (net absorption of CO_2 , also called net ecosystem production NEP), if the exports and imports are taken into account (which gives the net biome productivity, NBP), the balance becomes most often negative (Beziat et al., 2009; Ceschia et al., 2010; Kutsch et al., 2010; Loubet et al., 2011b; West and Marland, 2002). Examples of croplands acting as systematic

sinks of carbon (Aubinet et al., 2009) however highlight the potential for mitigating GHG emissions from croplands. For example, the conversion of croplands into grasslands is known to effectively sequester carbon, even over the short scale, provided there is sufficient nitrogen input to counterbalance carbon losses through increased mineralization (Ammann et al., 2007). Reduced tillage may also increase C and N storage in topsoil (Angers et al., 1997). But (Baker et al., 2007) stresses out that long-term experiments showed no storage. Incorporation of carbon-containing organic fertilizers in croplands might also reduce the net carbon losses (Freibauer et al., 2004; Smith, 2004), but should increase N₂O emissions in the mean time and even might increase carbon losses through priming effect (Angers et al., 2010). Nitrous oxide emissions result from nitrification and denitrification processes in the soil. These emissions increase with nitrogen supply. These biological processes critically depend on soil nitrate content, temperature, moisture, and density (Flechard et al., 2007; Henault et al., 2005; Laville et al., 2011; Skiba et al., 2009). Optimizing the management of arable land in the prospect of their long term sustainability in carbon and greenhouse gas emissions is challenging, and requires at first a deeper understanding of the underlying processes of carbon and nitrogen cycling and their interactions, which are still not clear.

Apart from their role in the GHG emission balance, arable lands are also playing a central role in atmospheric pollution. Indeed, they significantly contribute to pollutant emissions: pesticides (Bedos et al., 2002; van Pul et al., 1999) and NH₃ (Sommer et al., 2003) originate almost exclusively from agriculture. Similarly, nitrogen oxide (NO) emissions from agricultural soils are significant (6% global emissions, IPCC, 2007), and primary particle emissions through harvest and tillage may also be significant although these emissions are scarcely studied (Faburé et al., 2011). Some of these emissions are known to affect greatly the tropospheric chemistry, especially NH₃ through aerosol formation (Adams et al., 2001), and NO through O₃ formation (Rolland et al., 2010; Wild, 2007). However, agricultural lands cover a large fraction of the terrestrial surface (50% in France, 47% in Germany, in 2008, Eurostat). As such, they could contribute as great deal to the recapture of atmospheric pollutants by dry and wet deposition (Erisman et al., 2005; Flechard et al., 2011; Fowler et al., 2009), and they should be able to accumulate these compounds “safely”. In particular, ozone (O₃) and ammonia (NH₃) are very effectively deposited to the biosphere through stomatal and non-stomatal pathways (Flechard et al., 2011; Lamaud et al., 2009; Stella, 2011 #5360; Stella et al., 2011c). It was estimated that 40% of the atmospheric O₃ depletion in Europe was due to deposition (Memmesheimer et al., 1997). At the global scale, O₃ deposition is estimated as 1.5 times larger as the stratosphere-troposphere exchange (Wild, 2007).

Although these surface-atmosphere exchange processes are essential they are still not very well understood, which causes a great variability in both emission (Bedos et al., 2010; Sutton et al., 2009a) and dry deposition estimations (Flechard et al., 2011; Wild, 2007). Especially, non-stomatal deposition and the biological control of the exchanges need further research (Grontoft, 2004; Lamaud et al., 2009; Massad et al., 2009; Massad et al., 2008; Massad et al., 2010a; Massad et al., 2010b; Stella et al., 2011a; Tuzet et al., 2011).

Improving our understanding in pollutant and GHG exchanges, as well as the C/N cycling of agricultural surfaces seems therefore critical for evaluating the environmental burden as well as the potential “services” of agriculture ecosystems and therefore for contributing to build a sustainable agriculture.

6.1.2. Objectives of the undertaken researches

Within this context, my researches were organised in order to answer specific questions within these three larger issues mentioned, focusing on the largest gap in knowledge and linking up these issues with common tools (modelling, experimental designs). These researches can be separated in three areas which are causally and spatially connected each other: (1) emissions from hot spots, (2) short-range dispersion and deposition, and (3) atmosphere-cropland exchanges of trace gases (Figure 1). Each area was followed by a set of objectives which are given here:

(1) Emissions from hot spots

- to **quantify** ammonia emissions from hot-spots;
- to **identify the key parameters** controlling maize pollen emissions;

(2) Short-range dispersion and deposition

- to **identify the key parameters** driving ammonia short-range deposition;
- to **evaluate** potential ammonia recapture by tree belts;
- to **quantify** maize pollen dispersion and deposition over short-range;
- to **identify and quantify the key parameters** driving maize pollen dispersion over the short-range;

(3) Atmosphere-cropland exchanges of trace gases

- to **identify** the sources and sinks of ammonia in the canopy;
- to **quantify** the ammonia stomatal compensation point and its response to nitrogen supply;
- to **identify and quantify the key parameters** driving non-stomatal ozone deposition;
- to **quantify** the nitrogen, carbon and GHG fluxes of a full crop rotation;

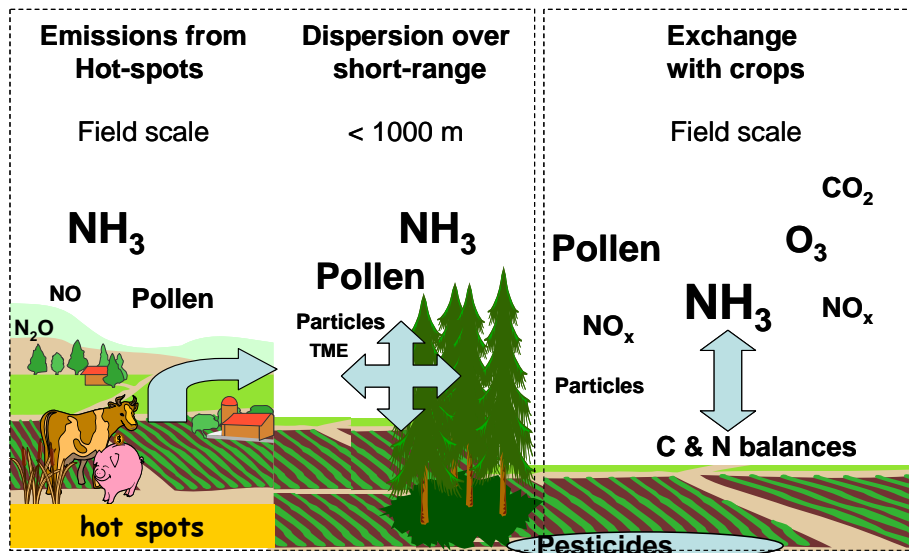


Figure 1. Scheme of the researches undertaken, together with the objects studied. The size of the font is roughly proportional to the intensity of research.

The researches undertaken on pollen, although seemingly disconnected to the work on pollutants and GHG, were however tightly linked to the work on NH_3 : they were both based on a common modelling framework which will be detailed in the following. Similarly the

experimental and modelling work on NH_3 , O_3 , NO_x and GHG were based on common methodologies (flux measurements) and concepts (resistance analogy). Most of the efforts were put on research on ammonia in terms of object studied and on measurements in terms of methodology.

6.1.3. Methodologies

The methodology used in the different studies reported here is given in detail in each chapter. A wider picture of the concepts, models, and experimental approaches is however summarized here.

6.1.3.1 *Experiments*

In terms of **experimental approaches**, the experiments were set up either to provide the basis to validate process models, or to investigate these processes under controlled or real conditions. This has led to two kinds of experimental work with the following motivations:

- Quantifying the sources and sinks of trace gases and pollens based on **micrometeorological measurements** in either **homogeneous** or **inhomogeneous conditions**.
- Investigating the processes underlying trace gases and pollen exchange between the biosphere and the atmosphere mainly based on experiments under **controlled conditions**.

A number of experiments was set up in these three axes and is summarized in Table 1. The major investments were however performed in:

- Developing a range of methods to measure NH_3 concentration including analytical techniques: development of dry denuders, wet denuders, membrane gaseous separation and conductivity analysis, and development of an automated ammonia gas analyser (ROSAA), for which a patent is pending.
- Evaluating and developing dynamic flux chambers for NH_3 and O_3 exchanges in controlled conditions.
- Developing methods to measure deposition and settling velocity of pollens.
- Using the Eddy Covariance (EC) method to measure trace gases in the field, and developing high frequency loss correction methods.
- Using mass balance methods for both NH_3 and maize pollen to evaluate short-range deposition under advective conditions.

Table 1. Experimental setup in which I had a significant input.

Setup	Short description	Publications (peer reviewed and PhDs)
CarboEurope-IP (EU, FP6) 2004-2009	Long term measurement of net ecosystem exchange of carbon dioxide and carbon balance of a crop rotation. I set up the eddy-covariance mast and the flux calculations in Grignon.	(Bedos et al., 2009; Loubet et al., 2011b; Moors et al., 2010; Tuzet et al., 2011; Yi and et al., 2010)
NitroEurope-IP (EU, FP7) 2006-2011	Long term measurement of carbon, nitrogen and GHG fluxes over a crop rotation. I coordinated and analysing measurements on the site.	(Laville et al., 2009; Laville et al., 2011; Lehuger et al., 2010; Skiba et al., 2009)
ROSAA 2005-2011	Development of a robust and sensitive ammonia analyser (ROSAA) coupling three wet effluent denuders with a flow injection analyser by conductimetry and membrane separation. I coordinated the development of the analyser and programming the automation.	(Loubet et al., 2010) A patent has been posted in 2010
Biopollatm (FR) 2002-2005	Quantifying and modelling the ozone impact plant functioning. Separating ozone stomatal and non-stomatal fluxes. I set up an ozone eddy-covariance mast in Grignon.	(Lamaud et al., 2009) (Loubet et al., 2011b)
Pollen settling tower 2004-2007	I developed a simple set up to measure pollen settling velocity based on a fast camera, a simple light and a Matlab® program.	(Loubet et al., 2007) thesis A. Marceau thesis N. Jarosz
Pollen dispersion and deposition 2003-2006	Three field experiments were set up where pollen concentration (rotorods), pollen horizontal fluxes (mass balance) and pollen deposition (cups and Coulter counter) were measured, together with turbulence measurements with ultrasonic anemometers. I coordinated the setup and analysing the data.	(Jarosz et al., 2005; Jarosz et al., 2003a; Jarosz et al., 2004) Thesis N. Jarosz
Ozone flux chamber 2002-2005 (2011)	A fumigation flux chamber for ozone was developed, with CO ₂ and water vapour control and flux measurements. I coordinated the development and programmed the automations.	Thesis S. Lebard
Ammonia flux chamber 2007-2009	A fumigation flux chamber was developed for ammonia, with CO ₂ and water vapour control and flux measurements. I coordinated the development and programmed the automations.	Thesis R.S. Massad (Massad et al., 2009) (Massad et al., 2010b)
O ₃ , NO and NO ₂ fluxes (2002 and 2008-2011)	Fluxes of O ₃ , NO and NO ₂ by the aerodynamic gradient and the eddy covariance method was set up in Grignon. I coordinated the development, programmed the automations and coordinated the data analysis.	Thesis Patrick Stella (Stella et al., 2011a; Stella et al., 2011b; Stella et al., 2011c)

6.1.3.2 *Modelling*

In terms of modelling, my main modelling work has focussed on developing short-range dispersion and surface-atmosphere exchanges of trace-gases and particles (Table 2). This work has led to two sorts of dispersion and deposition models for both trace-gases and particles:

- Lagrangian Stochastic models of dispersion and exchange of either gases (MODDAAS-2D) or pollens (SMOP-2D), to investigate the deposition of these compounds in the very short range taking into account the spatial variability of the sources and sinks within the canopy. These models are based on the simulation of the particles (real or air parcels) trajectories to reconstruct a concentration field. The main limitation of these models is that they require the turbulence field as an input.

They have however been recently coupled to a k-epsilon model (Aquilon / Thetis) which allows to investigate complex canopy structures.

- Dispersion models based on semi-analytic solutions of the advection-diffusion equation coupled with surface exchange models (FIDES-2D and FIDES-3D), for either gases or particles. These models were used to investigate advection errors, short-range deposition and source estimation by inverse modelling. They are based on the hypothesis of dynamically homogeneous surface (z_0 , z/L and u^* constant) and can not deal with transfer through the canopy as opposed to the LS based models. They are however much faster to run and are as such complementary to the LS models.

Additionally, I have contributed to the development and parameterisation of a range of surface-atmosphere-exchange models for ammonia, ozone, and maize pollen:

- The Surfalm-NH₃ model which combines a surface energy balance and a two-layer gaseous exchange model (Personne et al., 2009). This combination was made in order to account for the essential role of the surface temperatures (both soil and plant surfaces) and relative humidity on ammonia exchange. This model has recently been adapted to O₃ exchange with success, owing to the same sensitivity of O₃ surface-exchange parameterisation to both surface relative humidity and temperature (Stella et al., 2011a).
- A mechanistic ammonia compensation point model was proposed by (Massad et al., 2010b) for leaving leaves of crops based on a thorough review of the underlying processes (Massad et al., 2008). This model explicitly accounts for the passive and active transfers of ammonia and ammonium between the leaf compartments and for the sources and sinks of NH_x in the leaf cells.
- Regarding pollen exchange, (Marceau et al., 2011a) proposed a biophysical framework for modelling maize pollen release to the atmosphere which accounts for environmental factors such as wind, temperature and humidity.

Table 2. Models developed and models to which I have contributed.

Model	short description	Publications (peer reviewed and PhDs)
FIDES-2D (2001-2011)	FIDES-2D (Flux Interpretation by Dispersion and Exchange over the Short-range) is a dispersion-deposition model based on the coupling of a semi-analytical solution of the advection-diffusion equation in the atmospheric surface boundary layer, first derived by (Godson, 1958) and developed by (Huang, 1979), with a resistance analogue surface layer model including a compensation point for NH_3 . The model has been adapted for pesticides and has also been either used in a forward or an inverse mode. The model as initially developed in only two dimensions (along-wind and vertical) assumes homogeneity in sources and sinks along the direction transversal to the wind-direction.	(Loubet and Cellier, 2001) (Loubet et al., 2009b) (Sutton et al., 2009a) (Loubet et al., 2009a) (Hensen et al., 2009) (Bedos et al., 2009) (Loubet et al., 2010)
FIDES-3D (2002-2010)	The same as FIDES-2D but in three dimensions.	(Loubet et al., 2010)
MODDAAS-2D (1999-2006)	MODDAS-2D (MODElling Dispersion and Deposition of Atmospheric Ammonia over the Short-range) is a Lagrangian Stochastic (LS) dispersion model based on the theoretical work of (Thomson, 1987). The turbulence has been parameterised for the surface-layer and in-canopy transfer, and the dispersion model have been coupled to a bi-directional exchange model including a stomatal and a cuticular pathways.	(Loubet et al., 2006) (Sutton et al., 2009b) (Loubet et al., 2009a) (Cellier et al., 2009)
SMOP-2D (2003-2005)	SMOP-2D (Stochastic Mechanistic model for Pollen dispersion and deposition) is an extension of MODDAAS-2D to large pollens and more generally to particles larger than a few microns and smaller than 300 μm . Basically, a settling speed is included in the displacement equation of the LS model, the Lagrangian time scale is corrected to account for cross-trajectory effects (inertial effect and a rebound algorithm is included to account for non-sticky surfaces. The model has further been adapted to parameterise the turbulence in a simple manner over a succession of canopies. The model is limited to non-Brownian particles (no Brownian diffusion included) and particles smaller than 300 μm in aerodynamic diameter) (limit above which the momentum conservation equation should be used).	(Jarosz et al., 2005) (Jarosz et al., 2004)
MODDAS-2D / SMOP-2D coupled with Thetis-2D (2009-2010)	The main limitation in the MODDAS-2D and SMOP-2D models was that the turbulence was parameterised. Although this was well adapted for a homogeneous surface, it did not allow investigating complex geometries such as tree-belts and hedges that are options for mitigating pollen cross-contamination or ammonia deposition to sensitive ecosystems near farm buildings. In that prospect the LS models have been coupled to the Thetis k - ϵ model (Dupont et al., 2006; Foudhil et al., 2005)	No publications yet, except reports.
Surfatm- NH_3 (2001-2009)	The Surfatm- NH_3 model is a two-layer three-pathway NH_3 -soil-plant-atmosphere exchange model based on (Nemitz et al., 2000b) coupled with a surface balance model (Choudhury and Monteith, 1988), developed by (Personne et al., 2009). The model has been successfully compared to NH_3 fluxes measured over a grassland field during a cut-fertilisation event (Sutton et al., 2009a).	(Personne et al., 2009) (Sutton et al., 2009a) (Fowler et al., 2009)
Leaf- NH_3 compensation point mode (2007-2009)	The mechanistic leaf- NH_3 compensation point model developed by (Massad et al., 2010b) is based on four compartments, the atmosphere, the apoplast, the cytoplasm and the vacuole, which exchange NH_x and NO_3^- and are fed by the xylem. The cytoplasm is the location where sources and sinks of NH_x and NO_3^- occur, with nitrate reduction and photorespiration both generating NH_x , while the Glutamine Synthase-Glutamate Synthetase cycle (GS/GOGAT) being the main sink of NH_x through assimilation to amino acids. The latter was considered to be limited by the availability of substrates (ammonium and organic carbon) as well as by accumulation of its products (Amino acids). The	(Massad et al., 2009; Massad et al., 2008; Massad et al., 2010b)

	main difficulty in this modelling approach was the sensitivity to the parameterisation of photosynthesis and photorespiration and the organic carbon content, as well as the exchange parameters.	
Contribution to parameterisation of O ₃ deposition (2002-2011)	Ozone deposition to the ground and plant surface is known to occur through the stomata but also at the soil and plant surfaces. A residual deposition term called non-stomatal deposition has also been shown to be dependent on the relative humidity (Lamaud et al., 2009). However, since this residual term is experimentally determined using the magnitude of the other terms, it is essential to study precisely the stomatal and soil sinks. In (Lamaud et al., 2009) the stomatal and non-stomatal pathways were parameterised. In the parameterisation of (Stella et al., 2011a), a unique parameterisation of the soil resistance to ozone deposition was found as a decreasing function of relative humidity at the surface roughness height.	(Stella et al., 2011a) (Lamaud et al., 2009)

Following this brief introduction, the report is structured as followed: In a first part, the researches undertaken on the *“emissions and fate of pollutants and pollens over the short-range”* are summarised and divided in three parts: *“ammonia emissions by hot-spots”*, *“ammonia deposition near hot-spots”*, and *“maize pollen dispersal”*. Then the researches dealing with the *“sources and sinks of pollutants and GHG within canopies”* are summarised emphasising three topics, *“sources and sinks of ammonia within a canopy and the compensation point”*, *“ozone deposition and interaction with NO in agricultural fields”*, and the *“carbon and nitrogen cycles of a crop rotation”*. In each of these chapters, the issues are introduced, the main methods developed are exposed and the major results are given. A synthesis then summarises the researches undertaken.

6.2. Emissions and fate of ammonia and pollens over the short-range

This first chapter will recall the research undertaken on NH_3 and maize pollen emissions from hot-spots (farm buildings and fields) and their subsequent dispersion and turbulent exchange with the canopy and the ground surface, over the short-range (typically a few hundreds of meters).

6.2.1. Ammonia emissions from hot-spots (farms and agricultural fields)

6.2.1.1 Introduction

Ammonia is mainly emitted from animal housings, manure storage, and land-spread manure, and to a smaller extent from mineral fertiliser application and grazing (Bouwman et al., 1997; Misselbrook et al., 2000). Hence, in intensive agricultural areas, most NH_3 sources are concentrated in small areas surrounding the farms, which may be defined as a *hot-spot*. It is well known that NH_3 concentration above NH_4^+ solution doubles every 5°C and also increases with the solution pH (Genermont and Cellier, 1997). These features, together with the surface layer turbulent exchange rate, and the soil processes, lead to the observed variability of NH_3 emissions.

Emissions of NH_3 from housings depend mainly on the number of animals (which defines also somehow the renewal flow-rate), and the feeding quantity, but also on the conception of the building, and the type of management (Sommer et al., 2006), as well as the litter pH. The ventilation rate (Seedorf et al., 1998a) and the temperature inside the stables (Seedorf et al., 1998b; Wathes et al., 1998) are also essential factors regulating the emissions. In naturally ventilated stables, the rate of ventilation results from a combination of free and forced convection and hence depends on wind and outdoor and indoor temperatures (Hensen et al., 2009). However, the emissions from animal housings do not only depend on the number of animals, but also partly on the manure handling system (liquid manure/solid manure, slatted floor, partially slatted floor, deep litter etc.) and storage system (open tanks, tanks with a crust, tanks with a cover) (Faburé et al., 2011; Hutchings et al., 2001).

Emission of NH_3 after fertilisation depends on the nature of the fertiliser (liquid or solid manure, mineral fertilizer, urea), on the application method and the farming practices, on the soil properties (pH, humidity, buffer capacity), as well as on the meteorological conditions (temperature, radiation, wind speed). The time-lap between the application and the incorporation as well as the precipitations also play a critical role (Faburé et al., 2011; Genermont and Cellier, 1997). Emissions of NH_3 from storage facilities mainly depend on pH, temperature, wind speed and the presence of crust (Faburé et al., 2011).

Although there is a large number of studies reporting measurements of NH_3 emissions from farm buildings, land spread manure and to a fewer extent mineral fertiliser application, there is still a need for good measurements, either because the methods used to derive the standard emission factors can be questioned (wind-tunnels may not be representative of real conditions; mass balance method may overestimate emissions) or because the practices are continuously changing under the pressure of environmental policies and mineral fertiliser suppliers. There is therefore a need to quantify these emissions with simple and reliable methods, under varying management practices, either from buildings or agricultural fields.

There is moreover a need to further investigate the emissions from plants over longer terms (compensation point emissions) in order to better understand the potential role of these emissions onto the overall ammonia atmospheric balance (Massad et al., 2010a; Sutton et al., 2009a).

In the following we present the results of several studies where NH_3 emissions from fields and farm building were estimated with three methods: (1) The inverse modelling method using some of the dispersion models of Table 2 in combination with NH_3 concentration measured with a range of techniques with different integration times; (2) the aerodynamic gradient method using mini wet effluent denuders combined with a flow injection conductivity analyser: the ROSAA analyser developed in our lab for that purpose; and (3) the eddy covariance method using a Quantum Cascade Laser analyser.

6.2.1.2 *Methods and models*

In this section only the models and methods which were specifically developed are detailed. Other standard methods are not given and can be found in reference books such as (Kaimal and Finnigan, 1994; Lee et al., 2004; Seinfeld and Pandis, 1998).

Emissions estimate by inverse modelling

The dispersion model FIDES-3D

The model is based on (Godson, 1958) and (Philip, 1959) solution of the advection-diffusion equation, which assumes power-law profiles for the wind speed $U(z)$ and the vertical diffusivity $K_z(z)$. This approach also assumes no chemical reactions in the atmosphere and a homogeneous surface in terms of dynamics (roughness, U , K). The dispersion model is detailed in (Huang, 1979). In our approach, based on the general superimposition principle (Raupach, 1989; Thomson, 1987), we consider the dispersion function $D(x, y, z/x_s, y_s, z_s)$ (in s m^{-3}) which relates the concentration χ at a location (x, y, z) , to the source strength S at location (x_s, y_s, z_s) :

$$\chi(x, y, z) = \chi_{bgd} + \int_{\text{all } x_s \text{ and } y_s} S(x_s, y_s, z_s) D(x, y, z | x_s, y_s, z_s) dx_s \quad (1)$$

Where χ_{bgd} is the background concentration, assumed to be constant with height, and fixed to the concentration measured in the surrounding, and x , y and z denote direction towards North, towards West and along the vertical, respectively. Following (Godson, 1958; Huang, 1979; Philip, 1959), D is evaluated as:

$$\begin{aligned} U(z) &= az^p \\ K_z(z) &= bz^n \\ D(X, Y, z) &= \frac{1}{\sigma_y \sqrt{2\pi}} \exp\left(-\frac{(Y)^2}{2\sigma_y^2}\right) \times \frac{(zz_s)^{(1-n)/2}}{b\alpha X} \times \exp\left(-\frac{a(z^\alpha + z_s^\alpha)}{b\alpha^2 X}\right) \times I_{-v}\left(\frac{2a(zz_s)^{\alpha/2}}{b\alpha^2 X}\right) \\ \sigma_y &= \frac{1}{\sqrt{2}} C_y x^{\frac{2-m}{2}} \end{aligned} \quad (2)$$

where $\alpha = 2 + p + n$, $v = (1 - n) / \alpha$, I_v is the modified Bessel function of the first kind of order $-v$, and C_y and m were taken parameters from (Sutton, 1932). Here,

$X = (x - x_s) \sin(WD) - (y - y_s) \cos(WD)$, and $Y = (x - x_s) \cos(WD) - (y - y_s) \sin(WD)$, where WD is the wind direction. The values of a , b , p and n are inferred by linear regression between $\ln(U)$, $\ln(K_z)$ and $\ln(z)$, over the height range $2 \times z_0$ to 20 m, using $U(z)$ and $K_z(z)$ estimated from the Monin-Obukhov similarity theory (see, *e.g.*, (Kaimal and Finnigan, 1994)). Following (Loubet et al., 2001), to ensure that equation (2) can be solved, the source height is taken as $z_s = 1.01 z_0 + d$, where d and z_0 are the displacement and roughness heights, respectively. In FIDES-3D, the source strength $S(x_s, y_s, z_s)$ is considered homogeneous over each source patch. The model is described in details in (Loubet et al., 2010).

The dispersion model FIDES-2D

The two-dimensional dispersion model (FIDES-2D), derived from integration of equation (2) over y , was also used. The source strength can either be considered as a homogeneous flux source type or a homogeneous concentration type. In the later case, the canopy compensation point χ_{can} is introduced. The source in the homogenous surface concentration case is modelled as described in (Loubet et al., 2001):

$$S(x) = - \frac{\chi(x, d + z_0) - \chi_c}{R_b} \quad (3)$$

Where R_b is the pseudo-boundary layer resistance modelled as $R_b = (Bu_*)^{-1}$, with B the sub-layer Stanton number, and u_* the surface layer friction velocity. The model is described in details in (Loubet et al., 2001) and (Loubet et al., 2009b).

The inversion methods

If the source is of “homogeneous flux” type, the concentration χ_{model} is estimated based on Eq. (1) with a unit source strength and then S is evaluated as $S = \chi_{meas} / \chi_{model}$ at the measurement location (x_m, y_m, z_m) . If the source is of “homogeneous concentration” type, χ_c is evaluated by minimising the difference between χ_{meas} and χ_{model} using a Newton-Raphson method. S is then evaluated at the mast location using Eq. (3).

Measurement methods for NH_3 concentrations and fluxes

Alpha samplers average NH_3 concentration measurements

In addition to the gradient and the EC flux measurements, aAlpha badges were widely used as simple and reliable measurement method for long term monitoring (Sutton et al., 2001b). Three set of badges are usually were put at the location of interest for a time usually longer than 4 hours and usually of a week or a month. The filters were extracted in 3 ml double deionised water and analysed with a the an NH_3 specific analyser, like the FLORRIA analyser (Mechatronics, NL).

Wind tunnel measurements

The wind-tunnel technique is widely used for estimating NH_3 emissions following slurry or fertiliser applications. Wind-tunnels are a special form of large dynamic chambers (Lockyer, 1984), in which a fan is used to draw air through the wind-tunnel formed by an almost transparent polyethylene roof covering a small area of about 1 m^2 . However wind-tunnels are criticised, as semi-controlled systems, as they produce unrealistic emissions due to oasis effect and perturbed turbulent conditions (and therefore perturbed micrometeorological conditions). These discrepancies may also lead to wrong dynamics in

NH₃ volatilisation due, for instance, to over-evaporation of the slurry in the first hours. Additionally, the wind wind-tunnels were not properly calibrated. We therefore did a study on both the calibration of the wind tunnel technique with a prescribed CO₂ source (Loubet et al., 1999a) and the evaluation of the turbulent transfer conditions within the tunnel (Loubet et al., 1999b).

Aerodynamic gradient method (AGM)

The aerodynamic gradient method (AG) is a reference method for measuring NH₃ fluxes and the most commonly used nowadays (Flechard and Fowler, 1998; Sutton et al., 1993). It is based on the evaluation of the flux from the vertical concentration gradient and the turbulent diffusivity. The main limitation of this method is the requirement of high resolution, multi-channel, high temporal NH₃ analysers such as wet annular denuders like AMANDA (see (Milford et al., 2009) for a comparison between analysers), or GRAHAM (Kruit et al., 2007), as well as the photoacoustic analysers (Devries et al., 1995), or mini wet effluent denuders (Loubet et al., 2010; Milford et al., 2009). The uncertainty of the AG method depends on the precision of the analyser. (Milford et al., 2009) found, for AMANDA analysers, that the CV of the flux ranged from 20 to 30% for large fluxes and was larger than 76% for small fluxes (10 ng NH₃ m⁻² s⁻¹). Following the approach described by (Sutton et al., 1993), the flux is calculated from the friction velocity (u_*) and concentration scaling parameter (χ_*):

$$F_x = -u_* \chi_* \quad (4)$$

$$\chi_* = k \frac{\partial \chi}{\partial [\ln(z-d) - \Psi_H]} \quad (5)$$

where k is von Karman's constant ($k = 0.41$), z is height above the surface, d is zero plane displacement height, χ is NH₃ concentration and Ψ_H is the integrated stability correction functions for scalar properties, calculated from the Monin-Obukhov length (L) according to the description of (Sutton et al., 1993). The friction velocity u_* and the Monin-Obukhov length L are usually obtained from ultrasonic anemometer using the eddy covariance method.

The ROSAA analyser

The ROSAA (RObust and Sensitive Ammonia Analyser) developed by INRA is a three-channel mini-wet effluent denuder, online analyser with a small airflow rate to measure simultaneously NH₃ concentrations at 3 locations on a 30 min basis. The ammonia is trapped in an acid stripping solution and stored in flasks before being analysed sequentially by conductimetry coupled with semi-permeable membrane gaseous separation. The small air flow rate is designed to allow in-canopy and small flux chamber measurements and the advantage of the denuder lies in the separation of the gaseous from the aerosol phase. A patent has been posted for the ROSAA analyser (patent registration 10 55253, UCPI, France). The Figure 2 gives a simplified scheme of the ROSAA analyser.

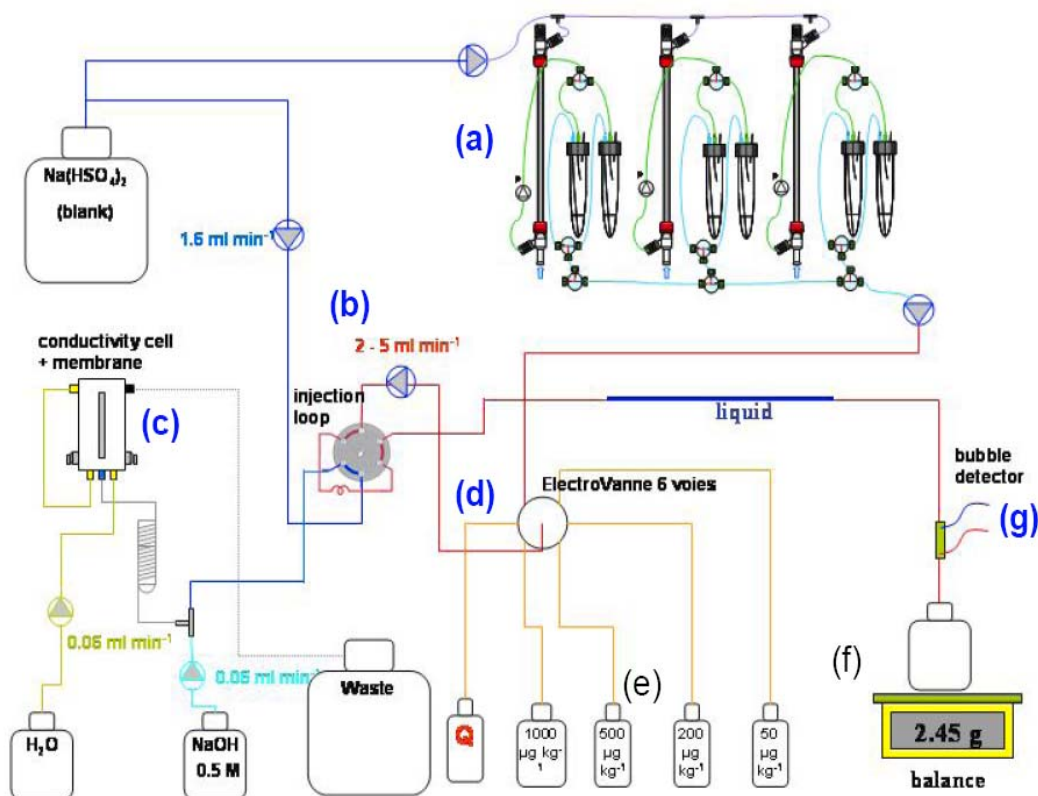


Figure 2. Scheme of the ROSAA analyser. (a) The three denuders to sample the air and two reservoirs per denuder to store the liquid while analysing. (b) The injection valve to analyse successively the reservoirs and the standards. (c) The ammonium analyser by conductivity and membrane separation. (d) Electro-valves to sample either from the denuder or the standards. (e) The four standards which are sampled every 2 hours. (f) The precision balance to measure the mass of liquid in each reservoir. (g) The bubble detector to control the injection of liquid.

The eddy covariance method (EC)

The eddy covariance method (EC) is well known and used extensively for heat, water vapour and carbon dioxide fluxes (among others). It has recently been possible to expand the EC method for NH_3 with the use of Tunable Diode Lasers (TDL) and Quantum Cascade Lasers (QCL) (Brodeur et al., 2009; Whitehead et al., 2008). The uncertainty of the EC technique itself has been estimated for latent heat as around 18% by (Nemitz et al., 2009b). However, the main limitation for NH_3 resides in the high frequency losses due to the stickiness of NH_3 on the walls of the inlet lines and the required analyser resolution. Whitehead et al. (2008) have found around 60% underestimation of the flux when compared to AG methods, of which the major part can not be corrected for not explained, while Brodeur et al. (2009) found that the current QCL would only allow measurement of fluxes larger than $200 \text{ ng NH}_3 \text{ m}^{-2} \text{ s}^{-1}$. However recent studies have shown that proton transfer reaction-mass spectroscopy could overpass these problems and be suitable for measuring NH_3 fluxes with EC. By heating the line up to 180°C , (Sintermann et al., 2011b) managed to reduce the high-frequency loss issue.

In the EC method, the flux (F_χ) of a scalar χ , at a given height, is directly estimated as the covariance between the instantaneous deviations of vertical wind speed (w') and scalar concentration (χ'). In the results presented here, the QCL-TILDAS (Aerodyne) was used. It is a quantum cascade laser absorption spectrometer which estimates the NH_3 concentration






by measuring the differential absorption of a laser at a very precise wavelength of 963 nm, between the sample cell and the reference cell. High-frequency loss corrections were estimated using the ogive approach of (Ammann et al., 2006). An average correction factor of around 10 was found.

6.2.1.3 *Results and discussion*

Improving the wind-tunnel methodology

The wind-tunnel is a dynamic chamber which requires measuring the outflow of trace-gas. This is performed by measuring the concentration and the wind speed in the cylindrical outflow section. We found that within this section, the vertical profiles of wind speed and concentration were non-uniform showing that the flow was far from being mixed, and leading to an underestimation of the actual flux ranging from 77% to 87%, mainly due to the unmixed trace-gas. The turbulent component of the horizontal flux was found to be less than 0.5% of the mean component. This study further suggested that an optimal sampling system could decrease the error due to sampling to a small percentage (less than 10%, Table 3), while a flow modifier could halve the error due to the wind profile (Loubet et al., 1999a). (Loubet et al., 1999b) further showed that the tunnels tend to overestimate fluxes due to both an oasis effect, and a larger friction velocity inside the tunnel than outside due to an increased wind speed gradient close to the surface.

Table 3. Recovery efficiency of several sampling systems placed in the output section of the wind-tunnel system estimated by numerical integration of the measured concentration and wind speed profiles. From (Loubet et al., 1999a).

Sampling point spacing	Recovery efficiency, %				
	Duct configuration and number of tappings				
	 C1 1 point	 C2 10 points	 C3d 15 points	 C3u 15 points	 C4 20 points
(i) Linearly spaced sampling points	61	114	93	89	89
(ii) Quadratically spaced sampling points	—	134	104	99	100.4

Ammonia volatilisation following slurry and fertiliser application

The inverse modelling method, the AGM, the REA and the EC methods have all been used to estimate emissions from field following slurry, ammonium-nitrate fertiliser and urea application (Loubet et al., 2010; Loubet et al., 2009b) (Table 4). The estimated losses were ranging from a few kg N ha⁻¹ up to almost 60 kg N ha⁻¹. When turned into emissions factors these losses ranged from 1.3% for the urea pellets in Rutigliano (a very dry site in southern Italy which was only partly followed) to 56% TAN for cattle slurry broadcasted in Grignon in August 2009. The overall results of Table 4 are mostly coherent: The broadcasted cattle slurry applications gave the larger emissions factors while ammonium nitrate application over grassland leads to a 7.6% TAN losses. The estimated emissions factors for the cattle slurry in northern Italy is however very low. It may be explained by the very low wind speed occurring when the slurry was spread (0.05 m s⁻¹ in CAR2010 and 0.1 m s⁻¹ in COR2009). For comparison, u_* in Grignon and Rennes were larger than 0.2 m s⁻¹.

Table 4. NH₃ emissions from the fields measured by AGM, EC or inferred by inverse modelling.

Datasets	Ecosystem	Measurement method	Concentration measurement	Fertiliser type	N supply	N-NH ₄ ⁺ supply kg N ha ⁻¹	NH ₃ loss	Emission factor %TAN*
RE1994	Bare soil	MB AGM FIDES	Chemiluminescence NH30m	cattle slurry	232	114	57	50%
BS2000	Grassland Sandy soil	AGM REA FIDES	AMANDA mini-WEDD	Calcium ammonium nitrate pellets	108	54	4.1	7.6%
GR2008	Bare soil Loamy soil	AGM FIDES	ROSAA Chemiluminescence-17C	cattle slurry incorporated (48h)	76	56	22	39%
GR2009	Bare soil Loamy soil	FIDES	Chemiluminescence-17C Alpha-badges	cattle slurry incorporated (48h)	78	57	32	56%
RU2008	Growing Sorghum	EC FIDES/WindTrax AGM AGM-badges	QCL-TILDAS (Aerodyne) Alpha badges ROSAA	Urea pellets	240	240*	15	6.2%
COR2009	Bare soil sandy loam	FIDES WindTrax	Alpha badges	cattle slurry incorporated (24h)	203	148	4.0	2.7%
CAR2010	Bare soil Silty-clay	FIDES WindTrax	Alpha badges	cattle slurry incorporated (24h)	190	139	3.5	2.5%

* Here all the urea is supposed to be converted to ammonium

The measured NH₃ emissions, apart from giving an overall picture of the NH₃ emission factors, also give insights into the underlying emissions processes. This is well illustrated by the NH₃ flux measured in Rutigliano (Italy) following urea application as estimated with the FIDES model and compared with the QCL Eddy Covariance measurement corrected for high-frequency losses (Figure 3). During this experiment, in the summer 2008 in this region of southern Italy, the soil was very dry and the urea pellets could not decompose to ammonium unless some water was applied. This led to an NH₃ flux which peaked after irrigation and rain events and gradually decreased afterwards. Moreover a clear diurnal pattern can be seen which did not follow the radiation and the temperature patterns. This pattern did not either reflect the carbon fluxes, suggesting that this was not a stomatal flux, but rather a soil flux, which was limited by the availability of soil humidity to allow urease activity.

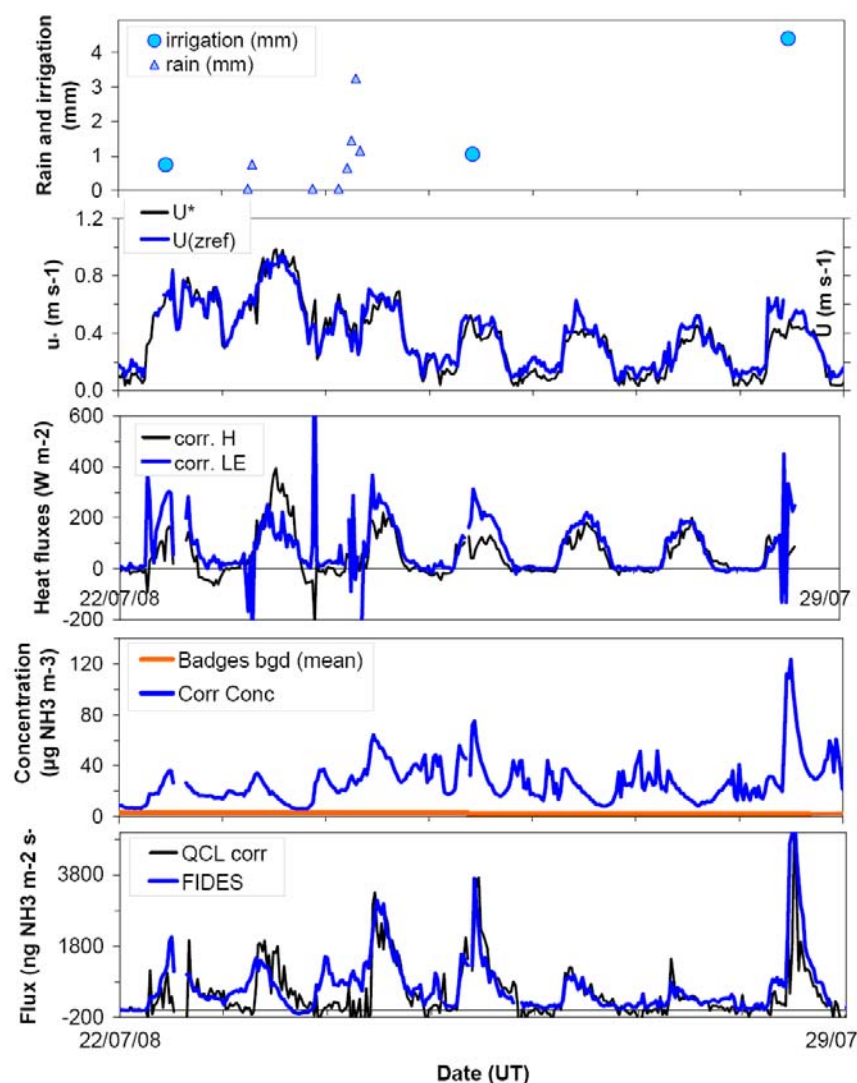


Figure 3. Ammonia fluxes and concentrations together with the friction velocity u^* , the sensible H , and latent LE heat fluxes, over the most emitting period following application of 240 kg N ha^{-1} urea to a sorghum field in Rutigliano in July 2008. The fluxes estimated with the FIDES model (blue line) based on the concentration in the field (measured with the QCL) and the background concentration (measured with badges) are compared with the fluxes estimated by the Eddy Covariance method with the QCL and corrected for high frequency losses (black line).

Ammonia emissions from farm buildings

Ammonia emissions from a farm with 380 cows and 170 pigs was estimated with the FIDES-2D and -3D models and compared to a Gaussian dispersion model (Hensen et al., 2009). The estimations made were based on 30 min NH_3 concentrations measured with AMANDA analysers. The emissions estimated with the three models ranged from 5.7 to $9.2 \pm 0.7 \text{ kg N-NH}_3 \text{ day}^{-1}$ for the whole farm. The FIDES models hence gave around 30% smaller estimates than Gaussian model which was itself lower than what was estimated from the national emission factors. However, we also showed in this study that accounting for the dry deposition near the farm in these inversion modelling estimations would lead to roughly 40% larger emissions estimates.

One of the outcomes of this study was the estimation of the daily dynamics of the farm source (Figure 4). The source-strength exhibited a clear diurnal cycle with a maximum in the morning (07:00– 08:00 GMT) and a minimum at night. This variability can be fully explained by changes in the indoor temperature and the ventilation rate.

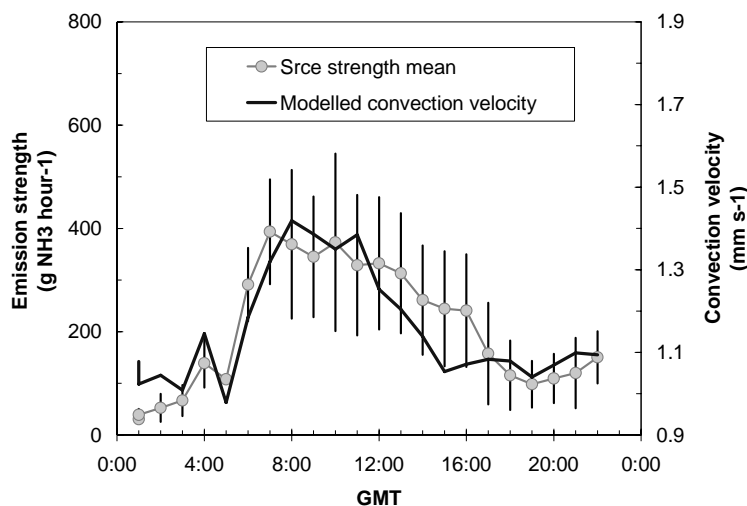


Figure 4. Diurnal variation of NH₃ emissions from naturally ventilated farm buildings containing 550 animals (2/3 cattle and 1/3 pigs) in Braunschweig, Germany. The estimate was obtained by an inversion method, using measured NH₃ concentration at 230 m downwind from the farm and a local dispersion model (FIDES-2D, Loubet et al., 2001). Also shown is an equivalent “convection velocity” representing the building ventilation rate, which was estimated as the sum of a free and forced convection terms. The error-bars are \pm standard deviation. From (Loubet et al., 2009a).

Indeed, a free and a forced convection velocity were calculated by adapting (Monteith and Unsworth, 1990) and (Murphy and Knoerr, 1977) approaches. These velocities were computed as the inverse of the transfer resistance R_b , using u_* as a velocity scale, the difference between indoor and outdoor temperatures, and a characteristic size of the building of 10 m taken. Although the expressions from Murphy et al. (1977) are not adapted to free and forced convection in buildings, they can give a good qualitative information

on the daily variability of the ventilation rate. It can be seen in that the daily variability was well reproduced. Moreover the emission strength was directly correlated to the indoor temperature of the stable (Source $[g\ h^{-1}\ NH_3] = 2.03 \exp^{0.2342 \times T\ [^{\circ}C]}$, $R^2=0.771$), as is expected from the thermodynamical equilibrium between the gas and the liquid phase.

6.2.1.4 Conclusions

- The contribution of my work in this research area was concentrated on developing and evaluating methods to estimate NH₃ emissions from hot spots.
- The inverse modelling approach to estimate field emissions was proved to be in very good agreement with the other flux measurement methods over a wide range of methods and conditions (within a few percents) (Loubet et al., 2010). This conclusion is supported by the work of Flesch, Wilson and Crenna using backward Lagrangian Stochastic modelling (bLS), which have led to the WindTrax software. They also found a good agreement between inferred and prescribed sources (within 20%), even when the flow field was perturbed (Flesch et al., 2005a; Flesch et al., 2005b; Flesch et al., 2004; Flesch et al., 1995). Furthermore, we have showed that the “flux driven” hypothesis is valid when using the inverse modelling method for NH₃ as long as the fetch of the field is larger than around 20 m (the error is then smaller than 5-10%) (Loubet et al., 2010). Finally, we have also pointed out that it should be possible to use inverse modelling methods to retrieve NH₃ emissions using NH₃ concentrations integrated over long periods (up to four weeks) (Loubet et al., 2010). This specific issue will be studied further in order to try to get a simplified method based on using diffusive samplers (badges) and a dispersion model to estimate NH₃ emissions from small sized fields (Loubet et al., 2011a).

- If the previous point was showing that the inverse modelling method was reliable, the argument can also be reverted, to deduce that the ROSAA analyser was also a reliable method, the two methods validating each other. The ROSAA analyser developed in the lab to measure NH_3 fluxes was indeed proved to be reliable for measuring NH_3 fluxes with the AGM after slurry spreading, when compared to inverse modelling (Loubet et al., 2010). This good behaviour of the ROSAA analyser is confirmed by a direct comparison of the concentration measured with diffusive samplers (badges) which shows a good agreement over a two weeks period (Figure 5). If the ROSAA was performing well, the QCL (as used here) was severely underestimating the

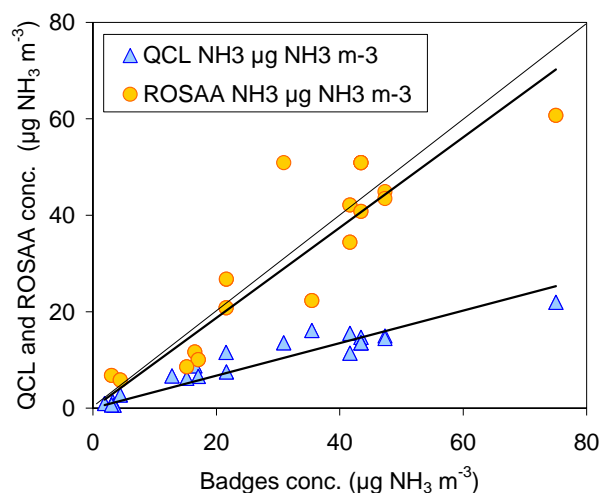


Figure 5. Concentration of NH_3 measured with the ROSAA analyser and the QCL-TILDAS versus the diffusive samplers (badges). Data were obtained in the Rutigliano (IT) experiment, at 1.4 m height in a sorghum field, following urea application. Each point corresponds to an integration period of 6 to 18 hours. ROSAA: $y = 0.94x$, $R^2 = 0.83$. QCL: $y = 0.34x$, $R^2 = 0.88$.

- This was also observed by (Whitehead et al., 2008), with however a less severe underestimation ($\chi_{(\text{QCL})} = 0.6\chi_{(\text{AMANDA})}$). If the concentration is underestimated with a QCL, the NH_3 fluxes measured with a QCL is also largely underestimated. Whitehead et al. (2008) found a flux 47% smaller with the EC-QCL method which they can't correct for nor explain. Following the work of Sintermann et al. (2011) it seems that EC NH_3 flux measurements can be achieved using a heated inlet line up to 150°C . This heated line hence becomes a problem under smaller NH_3 fluxes where volatilised NH_4^+ aerosols may contribute significantly to the measurements. It also poses some practical problems (condensation) for using such heated lines with QCLs since the cell itself is at a lower temperature.
- Ammonia emissions from farm buildings and field operations have been intensively studied for 20 years. The mechanisms leading to NH_3 emissions are now reasonably known and sound mitigation options have been proposed to reduce these emissions: these may be bravely summarised as follows: decreasing the source of NH_3 by adjusting the diet, increasing the grazing time when possible, covering properly the storages units, and using injection or incorporation methods for applying the slurry on a non-desiccated soil (Faburé et al., 2011). However, although there is a large number of studies on NH_3 emissions, recent advances in methods (Inverse modelling, QCL, electron transfer reaction mass spectroscopy, GRAHAM, ROSAA, diffusive samplers, photoacoustic analysers) make direct and reliable NH_3 estimations at the field scale plausible now or in the near future (Flesch et al., 2009; Kruit et al., 2007; Loubet et al., 2010; Sintermann et al.; von Bobrutzki et al.). As pointed out by (Sintermann et al., 2011a), there may be a need to revise some of the emission factors currently used for broadcasting emissions as these may be based on biased emissions estimates. There is also a need to regularly measure NH_3 emissions from new application techniques, diet changes, as well as new

wastes from digesters or waste treatment plants. Reminding the threat that reduced nitrogen represents for the environment and the urgent need to better recycle this both precious and threatening compound(s) (Sutton et al., 2011), all this points toward a renewed interest in direct measurements of NH_3 emissions from all agricultural sectors.

6.2.2. Ammonia deposition near hot-spots

6.2.2.1 Introduction

The NH_x emitted by hot-spots is either (i) dry-deposited as gaseous NH_3 by stomatal absorption and non-stomatal adsorption to canopy surfaces (Sutton et al., 1993; Sutton et al., 1995), (ii) dry-deposited as particulate ammonium (NH_4^+) essentially by Brownian diffusion (particle size $< 1 \mu\text{m}$), (iii) wet-deposited as ion NH_4^+ , or (iv) transformed by chemical reactions with other gases or aerosols (Dlugi et al., 1997; Nemitz and Sutton, 2004; Nemitz et al., 2004a; Nemitz et al., 2004b). But NH_3 can also be emitted by the plants themselves, which can either act as sinks or sources of NH_3 depending on their nitrogen (N) nutrition status and the atmospheric NH_3 concentration (Flechard et al., 2010; Loubet et al., 2002; Massad et al., 2009; Massad et al., 2008; Massad et al., 2010b; Mattsson et al., 2009; Schjoerring and Mattsson, 2001; Schjørring, 1997). Moreover, non-stomatal adsorption of NH_3 is influenced by the load of acidic pollutants to the surface (Burkhardt et al., 2009; Fléhard et al., 1999; Flechard et al., 2011; Massad et al., 2010a).

The combination of hot-spot sources and effective deposition processes leads to sources and sinks of NH_x being spatially heterogeneous at a scale smaller than the kilometre, with quite large deposition rates to expect on the very short scale (Dragosits et al., 1998; Dragosits et al., 2006; Dragosits et al., 2002). Direct measurement of NH_x deposition near hot-spots is however challenging due to local advection (Hensen et al., 2009; Loubet and Cellier, 2001; Loubet et al., 2003a; Loubet et al., 2009b). Indirect estimates using mass balance, ^{15}N labelling, SF_6 to NH_3 ratio methods, as well as modelling studies, have estimated that the fraction recaptured within 2 km downwind from the source of NH_3 emitted ranges between 2% and 60% (Asman, 1998; Loubet and Cellier, 2001; Loubet et al., 2003a; Loubet et al., 2006; Sommer and Jensen, 1991; Theobald et al., 2001). The large variability of NH_x deposition near sources critically depends on the canopy structure surrounding the source (roughness, side fluxes) (De Jong and Klaassen, 1997; Draaijers et al., 1994; Klaassen, 1991; Klaassen et al., 2002; Loubet et al., 2006; Theobald et al., 2001), the emissions from the active vegetation through the NH_3 compensation point (Massad et al., 2010a; Riedo et al., 2002; Schjørring and Mattsson, 2001), from the litter (Nemitz et al., 2000a), or from the soil (Genermont and Cellier, 1997), as well as non-stomatal NH_3 fluxes (Burkhardt et al., 2009; Erisman and Wyers, 1993; Fléhard et al., 1999; Loubet and Cellier, 2001; Sutton et al., 1995; van Hove et al., 1989). Less known, are wet deposition fluxes and chemical transformations of NH_x near intensive sources, as well as direct emissions of particulate NH_4^+ (McCulloch et al., 1998; Nemitz et al., 2009a; Nemitz and Sutton, 2004). Despite this knowledge on local deposition, its quantitative assessment within regional atmospheric models is still challenging at European scale, and probably in all regions having large livestock populations. As a result, options related to spatial interactions in hot-spots have until now been little considered within mitigation strategies to reduce trans-boundary NH_x pollution.

The complexity of the processes involved and the variability of the deposition fluxes near hot-spots have led to the use of models and monitoring techniques to evaluate the fraction of NH_x re-deposited locally. In this section, we present two models developed to quantify NH_3 deposition at the local scale, we then present and discuss the main effects influencing NH_3 short-range deposition and finally we present an example of mitigation option to recapture ammonia using tree-belts.

6.2.2.2 *Models developed*

Two models were developed in this research to study NH_3 (and other pollutant) short-range deposition: the FIDES and the MODDAAS models. They are both based on the same superimposition principle given in Eq. (1) (Thomson, 1987). These models are further based on another essential concept regarding the bi-directional exchange of NH_3 , which was first developed in my PhD where it is showed that a bi-directional model is equivalent to a “sum” of two unidirectional models, in the sense that the flux is the sum of the fluxes in each pathway (

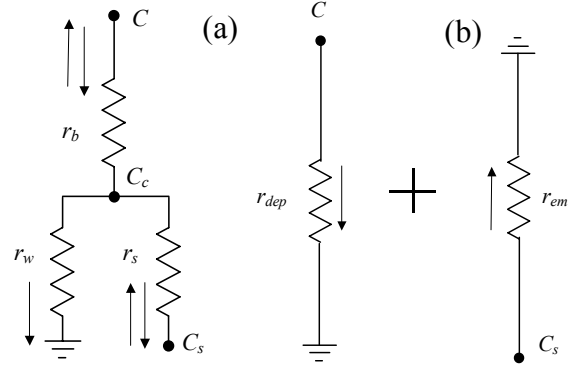


Figure 6. Resistive scheme model for NH_3 exchange at the leaf scale. **(a)** Standard representation of the model, and **(b)** representation of the model with two additive pathways. Here r_b , r_w and r_s are the boundary layer, cuticular and stomatal resistances, and r_{dep} and r_{em} are virtual deposition and emission resistances respectively. χ and χ_s are the air concentration and the stomatal compensation point. Taken from (Loubet et al., 2006).

Figure 6). This concept is advantageous in that it separates a surface model which is completely explicit (C_s and r_{em} are known) with one which is implicitly (C is unknown) used to couple the dispersion models with the plant-atmosphere exchange model in FIDES and MODDAAS:

$$\chi_i = \chi_i^{\text{ref}} - \sum_{j=1}^{N_{\text{can}}} D_{ij}^{\text{dep}} \left(\frac{\chi_i}{r_j^{\text{dep}}} \right) \quad i = 1..N \quad (6)$$

where χ^{ref} is the sum of the background concentration, the concentration generated by all known sources and the compensation points, assuming no deposition is occurring, r_{dep} is the virtual deposition resistance and D is the dispersion matrix, while i, j are numberings indexes and N_{can} is the number of canopy cells. If the resistances are independent of the atmospheric concentration, the coupling results in a linear system which is solved with common methods (Loubet et al., 2006). The limits of this approach are that no chemical reactions can be taken into account in the gas-phase (because of the superimposition principle) and that the resistances are not dependent upon the concentration (which excludes some ways accounting for saturation of the surfaces)

This approach has been used in both the FIDES and the MODDAAS models which are shortly described thereafter.

FIDES

The FIDES model couples a dispersion model over a homogeneous surface which has already been described in the previous chapter (0.0.0.0 and Eq. (2)), and the one layer bi-directional surface exchange model of

Figure 6. The coupling is performed by solving Eq. (6), in which the dispersion matrix is given by Eq. (2). Equation (6) is then explicitly solved in the 2D model by replacing N_{can} by i , which is possible since there is no backward dispersion in the dispersion model. In the 3D model, the Eq. (6) is solved by a matrix inversion method. The advantage of the 2D model is that (since it is explicit) it is very fast and can therefore be easily used for sensitivity analysis or long term studies. The FIDES model is described in (Bedos et al., 2010; Hensen et al., 2009; Loubet et al., 2009a; Loubet et al., 2010).

MODDAAS-2D

The MODDAAS-2D model is a two-dimensional Lagrangian Stochastic (LS) dispersion model coupled with a multi layer resistance analogue model. In each layer the resistance model is that of

Figure 6. The coupling is made through Eq. (6) which is solved by a matrix inversion method. A refinement in the resistance approach has been introduced in MODDAAS: the boundary leaf layer resistance was parameterised as resulting from a free and forced convection flow, which tends to limit this resistance in low wind speeds (Loubet et al., 2006).

The LS dispersion model is based on the theoretical description of (Thomson, 1987). Basically, the location (x, y) and velocity (u, w) of a fluid parcel is modelled as a joint stochastic process satisfying the following stochastic differential equations (Loubet, 2000; Loubet et al., 2006):

$$\begin{aligned} du &= a_u dt + b_u d\xi_u & dx &= (u + U)dt \\ dw &= a_w dt + b_w d\xi_w & dz &= (w + W)dt \end{aligned} \tag{7}$$

where t is the time, $d\xi_u$ and $d\xi_w$ are Wiener increments, and a_u and a_w , being the drift terms and b_u and b_w the acceleration terms, and U and W are the Eulerian mean wind velocity components. These terms are parameters of the LS model which are determined based on two major hypotheses:

- (1) The Kolmogorov theory of inertial cascade which, together with an isotropic turbulence hypothesis, defines the local acceleration $b_u = b_w = \sqrt{(C_0 \varepsilon)}$, where C_0 is a universal constant, which was chosen as $C_0 = 3.12$ to ensure the coherence between the LS model and the turbulent Schmidt number in the surface layer ($Sc = 0.64$) (Flesch et al., 2002). See (Loubet, 2000) for details on the determination of b and (Loubet et al., 2006) for a discussion on C_0 .
- (2) The entropy principle (or third principle of the thermodynamics), which stipulates that the fluid parcels should keep homogeneously distributed if they were initially homogeneously distributed. This principle is translated in the language of stochastic processes as: the probability density function (pdf) of all the existing particles $P(x, z, u, w)$ should be equal to the Eulerian pdf P_a , which in turns, means that P_a satisfies the Fokker-Planck equation associated with Eq. (7). Since P_a is known and

b_u and b_w are also known, a_u and a_w , can be deduced by solving the Fokker-Planck equation using $P=P_a$ (See (Thomson, 1987) or (Loubet, 2000) for details).

- (3) There is however a third hypothesis which should not be forgotten. Indeed, since in two and three dimensions the previous hypothesis does not lead to a unique solution, there is a subjective choice to be made which leads to different models. (Wilson and Flesch, 1997) proposed to select non-spinning trajectory models, while (Reynolds, 1998) argued the opposite. In MODDAAS, the approach of Wilson et al. (1997) was taken. This later hypothesis can be viewed as a closing hypothesis just as in Eulerian models.

With these three hypotheses, a and b can be derived. Originally, in MODDAAS-2D, the turbulence statistics (P_a) are parameterised based on the Monin Obukhov similarity theory in the surface layer and based on a literature review in the canopy layer (Loubet et al., 2006). This is one important limit of the model which was therefore not adapted to study the transfer of ammonia in complex geometries such as tree edges or hedges, which are of interest to mitigate NH_3 emissions or at least reduce NH_3 concentrations in natural area (Dragosits et al., 2006). In the pollen dispersion model (SMOP), which is an extension of MODDAAS (Jarosz et al., 2004), the roughness change has been parameterised, but rather too simplistically, especially in terms of mean shear stress and ε . To overpass this limitation, MODDAAS has been coupled with a k - ε model, as explained in the next chapter. Finally, a Random Walk model has been implemented in MODDAAS in order to allow direct comparison with Eulerian models. In a Random Walk model, only the stochastic joint process is only the location of the fluid parcel (x, z), and the Stochastic differential equation simply becomes:

$$\begin{aligned} dx &= U dt + (2 K_x)^{1/2} d\zeta_u \\ dz &= W dt + (2 K_z)^{1/2} d\zeta_w \end{aligned} \tag{8}$$

where K_x and K_z are the x and z components of the eddy diffusivity.

The coupled MODDAAS-Thetis model

MODDAAS has been coupled to Thetis, a k - ε turbulence model parameterised for canopy flow, hence including a wake production and a wake dissipation terms in the turbulent kinetic energy k budget, and a modified budget for the dissipation term ε (Foudhil et al., 2005). Thetis (previously called Aquilon) has been successfully tested against two wind-tunnel experiments: the homogeneous wheat canopy flow of (Brunet et al., 1994) and the clearing-edge flow of (Raupach et al., 1987). From these comparisons it can be concluded that Thetis reproduces very well the velocity statistics up to the second order but may fail to reproduce well the dissipation rate ε near the top of the canopy, because of intrinsic limitations of the k - ε approach in a canopy flow.

Nevertheless, the coupling of the two models consisted in using the output of the Thetis as the turbulence input of the MODDAS model, namely: U and W , the horizontal and vertical components of the wind velocity, σ_u and σ_w , the standard deviation of the horizontal and vertical components of the wind velocity, $\overline{u'w'}$, the mean shear stress, and ε the dissipation rate of the turbulent kinetic energy. However, Thetis does not output directly σ_u and σ_w , but rather k . The coupling between the two models hence required partitioning k

into its horizontal lateral and vertical contributions, where k is $k = 0.5 (\sigma_u^2 + \sigma_w^2 + \sigma_v^2)$. This was done by seeking the constants α_u , α_v and α_w (α_i) coefficients so that $\sigma_i = \alpha_i (2k)^{0.5}$. Following Taylor (1921), we stipulated that the vertical diffusivities in the Lagrangian (K_z^L) and Eulerian (K_z^E) approaches should converged at long travel times (t larger than the Lagrangian time scale T_L) (namely $K_z^L \rightarrow K_z^E$, when $t / T_L \rightarrow \infty$). Based on the definitions of $K_z^L = \sigma_w^2 T_L$ and of $K_z^E = C_\mu k^2 / (Sc \varepsilon)$, where Sc is the Schmidt number and C_μ is a constant of the k - ε model. This hypothesis an expression for α_w :

$$\alpha_w = (C_\mu C_0 / 8 Sc)^{0.25} \quad (9)$$

with $C_\mu = 0.03$, $C_0 = 3.12$ and $Sc = 0.64$, one gets $\alpha_w = 0.3677$. By further assuming a constant ratio $\sigma_u / \sigma_v = \alpha_{uv} = 1.25$, which corresponds to an average over a range of measurements made in the planetary boundary layer (Loubet et al., 2006), one gets $\alpha_u = 0.7262$ and $\alpha_v = 0.5809$. This gives roughly $\sigma_u / u_* = 2.6$ and $\sigma_v / u_* = 2$, which is coherent with the literature (see e.g. Loubet, 2000). This coupling has been implemented to test several mitigation options in poultry farming, whereby either the farms are surrounded by a tree-belt or even the chickens are freely walking below the canopy. The model has been compared to wind-tunnel measurements of turbulence, ammonia and methane release in a pine canopy. The profiles of σ_w and methane concentration compared favourably well (data not shown here, nor published yet).

6.2.2.3 *Results and discussion*

Drivers of ammonia short-range deposition

In my PhD work I showed using MODDAAS and measurements that short-range deposition of NH_3 was influenced by (1) the turbulence and especially σ_w which determines the rate of dispersion and ε which determines the initial dispersion, but more importantly by (2) the surface resistances (cuticular r_w and stomatal r_s) and the stomatal compensation point (χ_s). It was also showed that the location of the source relative to the canopy was essential and the model was very sensitive to this parameterisation. Other features highlighted were the fact that under dry climate NH_3 deposition was limited by the stomatal aperture while under humid climate, the cuticular deposition was the driving process.

Building up on these results, the FIDES model was used in a review study to evaluate the effects of a range of environmental variables on NH_x deposition, including the possibility of particulate mater deposition downwind of a farm building (Loubet et al., 2009a). Using the FIDES model means that no canopy transfer is modelled and the surface is homogeneous, which is a simplification that does not affect the qualitative impact of each factor on short-range deposition. Some of the results of (Loubet et al., 2009a) are shown in Figure 7.

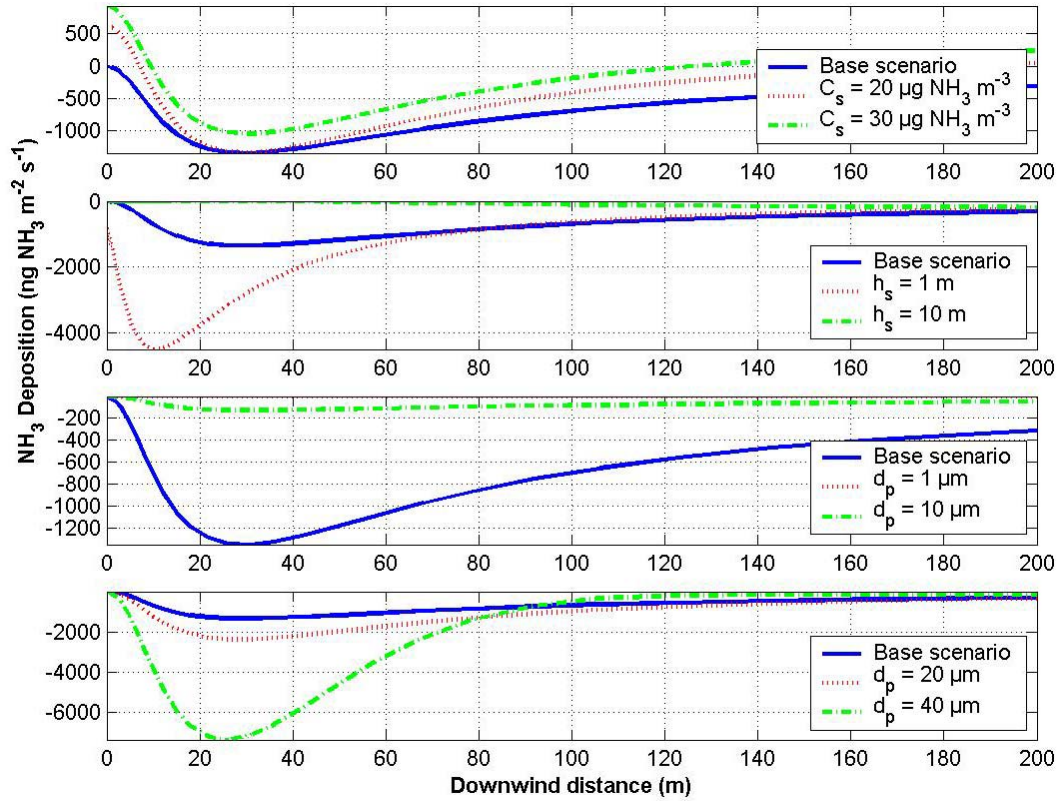


Figure 7. Ammonia and ammonium deposition downwind from a $800 \text{ kg NH}_3 \text{ y}^{-1}$ farm building of $5 \text{ m} \times 50 \text{ m}$ surface with an exhaust located at a height of 2 m , as a function of downwind distance, as estimated with the FIDES-2D model. The base scenario corresponds to ammonia, a wind speed of 3 m s^{-1} at the source height, a roughness length (z_0) of 10 mm , a displacement height (d) of 0 m , a neutrally stratified boundary layer, a stomatal resistance $R_s = 80 \text{ s m}^{-1}$, a cuticular resistance $R_w = 20 \text{ s m}^{-1}$, and a compensation point $C_s = 0 \text{ } \mu\text{g NH}_3 \text{ m}^{-3}$. Several effects are considered: canopy compensation point (canopy receiving large amount of nitrogen $C_s = 20 \text{ } \mu\text{g NH}_3 \text{ m}^{-3}$, canopy saturated with nitrogen $C_s = 30 \text{ } \mu\text{g NH}_3 \text{ m}^{-3}$); source height (source very close to the ground $h_s = 1 \text{ m}$, source at the roof of a building $h_s = 10 \text{ m}$); particles of $1 \text{ } \mu\text{m}$ or $10 \text{ } \mu\text{m}$ and dust of $20 \text{ } \mu\text{m}$ and $40 \text{ } \mu\text{m}$.

Figure 7 shows that:

- (1) an increase of the stomatal compensation point C_s decreases local deposition of NH_3 and can even lead to emissions of NH_3 at distances larger than 100 m downwind from hot spots, which was also shown by Loubet et al. (2006);
- (2) An increase in source height decreases local deposition of NH_3 and inversely. However, emissions at lower heights lead to larger deposition near the source, but also lead to smaller deposition at further distances, due to increased depletion of NH_3 from the plume at lower distances. The distance where the deposition peaks is also increasing with increasing source height, which is expected by an increase of the time needed for the plume to reach the ground;
- (3) Particles lower than $10 \text{ } \mu\text{m}$ are not depositing efficiently, whereas particles of $20 \text{ } \mu\text{m}$ and $40 \text{ } \mu\text{m}$ show larger deposition than the base scenario. This suggests on the one hand that only large particles of dust may redeposit locally and hence if these particles are avoided the local effects should be minimal. On the other hand it indicates that PM10 and lower particles emitted from farm buildings are really contributing to the atmospheric burden and are not locally deposited.

The fraction of NH_3 emitted that is recaptured at 200 m and 2000 m from a source allows to quantitatively comparing the effect of each scenario (Figure 8). Up to 30% of NH_3 is recaptured at 200 m downwind from the source in the base scenario and this amount varies between 12% and 55% depending on the environmental conditions (not considering particles). Apart from stability and wind speed, which are influential but can not be easily modified by abatement techniques (though wind-speed at the source height might be by sheltering with trees), the most influential parameters are (1) the source height, (2) the surface roughness, (3) the surface resistance, and (4) the stomatal compensation points. Hence, abatement techniques should preferentially focus on one of those parameters.

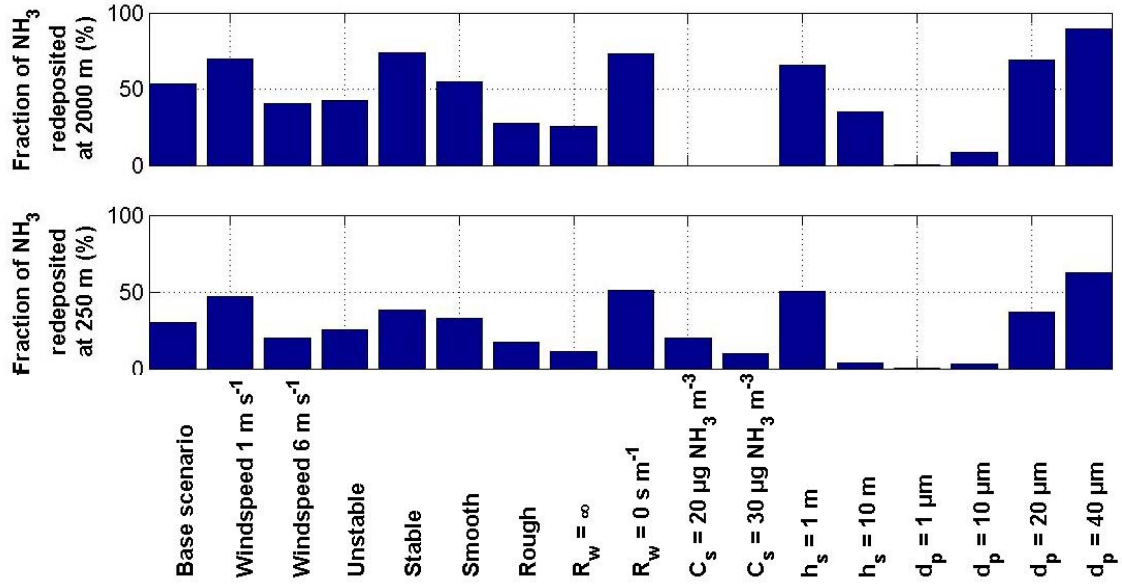


Figure 8. Fraction of NH_3 re-deposited at 2000 m and 200 m* downwind from a $800 \text{ kg NH}_3 \text{ y}^{-1}$ farm building of $5 \text{ m} \times 50 \text{ m}$ surface with an exhaust located at a height of 2 m, estimated with the FIDES-2D model. The base scenario is described in Figure 7. Several effects are considered: wind speed at the source height (1 or 6 m s^{-1}); boundary layer thermal stratification (unstable $L = -20 \text{ m}$, stable $L = 20 \text{ m}$, where L is the Monin-Obukov length); surface roughness (Smooth $z_0 = 1 \text{ mm}$, Rough $z_0 = 1000 \text{ mm}$); surface resistance (only stomatal absorption $R_w = \infty$, surface completely absorbing $R_c = R_b$, where R_b is the boundary layer resistance of the canopy); canopy compensation point (canopy receiving large amount of nitrogen $C_p = 20 \mu\text{g NH}_3 \text{ m}^{-3}$, canopy saturated with nitrogen $C_p = 30 \mu\text{g NH}_3 \text{ m}^{-3}$); source height (source very close to the ground $h_s = 1 \text{ m}$, source at the roof of a building $h_s = 10 \text{ m}$); particles of $1 \mu\text{m}$ or $10 \mu\text{m}$ and dust of $20 \mu\text{m}$ and $40 \mu\text{m}$. At 2000 m, the fraction re-deposited for the scenarios $C_s = 20$ and $30 \mu\text{g NH}_3 \text{ m}^{-3}$ are not shown for clarity: the cumulated emission at 2000 m downwind amount 65% and 125% of the emission from the farm, respectively. * in the figure legend 250 m should read 200 m.,

In a simplified view, abatement techniques should try to maximise deposition very close to the source. Figure 8 suggests that this could be achieved by sheltering the emission from wind (both by setting the source at the lowest possible height, or having trees around), and by ensuring an effective sink in the surrounding (well watered canopy, with well evaporating vegetation on the ground). One practical way to recycle nitrogen in such a system might be to have tall trees with small LAI and a well watered under-storey arable crop (which hence can utilise the excess nitrogen and recycle it through the food chain).

Such a mitigation option might however loose its benefit over the long term, due to possible drawbacks. First of all, recurrent NH_x deposition to the tree belt will lead to increasing ammonia compensation point. The model of (Massad et al., 2010a) suggests a

very large increase of the compensation point in the first tens of meters and an increase of a few $\mu\text{g NH}_3 \text{ m}^{-3}$ at 200 m for the source given in this study. Secondly, the reactive nitrogen deposited near the farm, if not used by the vegetation, will enter the so-called nitrogen cascade and may lead to increased environmental burden, such as nitrate loads in the water reservoirs, indirect N_2O emissions, eutrophication (Galloway et al., 2008; Sutton et al., 2011). Of course, such a “fertilisation” may also be viewed beneficial, as it may lead to increased carbon sequestration by grasslands under elevated CO_2 (Reich et al., 2006) and trees under actual conditions (Magnani et al., 2007). However the results of Magnani et al. (2007) is debated because of likely N saturation in the sites selected (De Schrijver et al., 2008) and implausible C:N sequestration ratios (more than 700 kg C per kg N whereas current experimental evidence points towards a range 30-70 kg C per kg N) (de Vries et al., 2008). Therefore such a beneficial effect is still unclear on unmanaged ecosystems.

Nevertheless, NH_3 recaptured by tree belts also involves complex turbulence and lateral fluxes of NH_3 which are beyond the physical capabilities of a model like FIDES and requires the use of a turbulence model couples with a multilayer deposition model. The MODDAAS-Thetis model was used in this prospects as discussed in the next paragraphs.

Example of a local mitigation option: ammonia recaptured by tree-belts

There is a rising interest in tree-belts as potential mitigation option to limit NH_3 and odours emissions of farms and especially poultry farms. There is also an interest in the benefits that may be gained with silvopastoral systems where the animals are grazing freely within woodland. There may be benefits in terms of NH_3 but also odours emissions as well as animal welfare, and public image of agriculture. In order to quantify the potential interest for ammonia recapture, the MODDAAS-Thetis model was used over a range of realistic scenarios for UK agriculture, in the framework of the SAMBA project. Each scenario was based on a single sketch: a set of five canopy types were considered, which covers an extent around the source Q_s which itself can stand in a canopy, and has its own geometry (Figure 9).

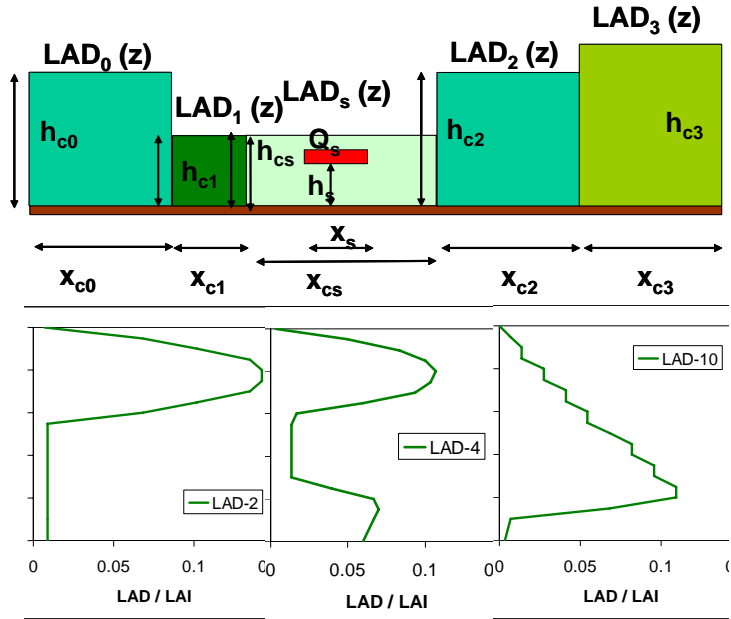


Figure 9. General scheme of the woodland and source geometry that were tested in the scenarios (upper panel), and examples $LAD(z)$ profiles of the canopies 0-4 used (lower panel).

Each canopy is defined by its height and Leaf Area Density profile $LAD(z)$, and its stomatal compensation point. The canopies were chosen to represent several kinds of trees (Figure 9) and grassland with homogeneous $LAD(z)$ was also considered. The deposition parameters used were such as to reproduce a maximum deposition and the compensation point was set to zero. Three kinds of scenarios were considered: (1) a “housing” scenario with a source at 2 m height, (2) a “lagoon” scenario with a source located at the ground, and (3)

an “understorey” scenario, where the source reproduces the emissions from chickens freely walking under a quite open canopy. For these three scenario types, the *main canopy* was considered to be the canopy surrounding or above the source while the *backstop canopy* was the canopy placed further away from the source which was supposed to capture NH_3 .

An example output of the model is given for a farm housing surrounded by a 30 m-long woodland with constant LAD, and an LAI of 6 and without *backstops* (Figure 10). It shows typical features of such a geometrical setup: the source is slightly shielded with a wind speed below 2 m s^{-1} at the source height and a very low wind speed in the downwind canopy, while the turbulent kinetic energy (and hence σ_w and σ_u) is much larger due to wake production on the plant elements, hence increasing the dispersion efficiency near the source and leading to quite an efficient backward diffusion as seen on the concentration map. However σ_w is yet smaller in the downwind part of the tree belt and the “quieter” part of the domain stands in the wake of the tree belt. The concentration map exhibits a classical dispersion pattern however perturbed by the presence of the canopy: quickly decreasing concentration in the tree belt, and slightly increasing concentration in the tree belt wake region. The resulting deposition was estimated as quite a large fraction (16%).

The maximum recapture simulated was 28%, 19% and 60% for the housing, the lagoon and the understorey systems, respectively. The lower recapture in the case of the lagoon is explained by the fact that the plume remains very close to the ground (because the source is there, where the canopy density is generally low for trees. The larger recapture in the understorey case is due to the effective sheltering of the source leading to much larger concentration in the canopy and therefore large deposition fluxes.

These simulations showed that in the case

of the *farm housing* the deposition is almost proportional to the LAI of the canopy if the tree belt is homogeneous (only one canopy type); while if a backstop canopy is present the deposition is not proportional to its size. They also showed that the pine trees (LAD-10 in Figure 9) are the most efficient for NH_3 recapture in the *main canopy* when there is a backstop, and that increasing the size of the tree belt is marginally beneficial above a certain size when a large backstop is present (around 25 m) because most of what can be recaptured is already recaptured.

This study also showed that the deposition rate increased roughly proportionally with the LAI if the LAI and the LAD are identical in the main and the backstop canopies. The increase of the width of the main canopy does not proportionally increase the deposition rates since in this case the deposition to the backstop decreases. The canopy with a dense and homogeneous LAD favors deposition, while canopy with a dense crown and an open trunk space disfavors recapture. When the source is close to the ground (lagoon and understorey setups), a dense canopy near the ground should be favored rather than a canopy with a dense crown. Taller canopies with identical LAI lead to smaller deposition rates

6.2.2.4 Conclusions

- Deposition of NH_x within one kilometre from hot-spots ranges from 2% to 60% of emitted NH_x , and is mainly due to dry deposition of NH_3 , since wet deposition, in a temperate climate, is evaluated as less than 5% recapture of the emitted NH_x . Moreover,

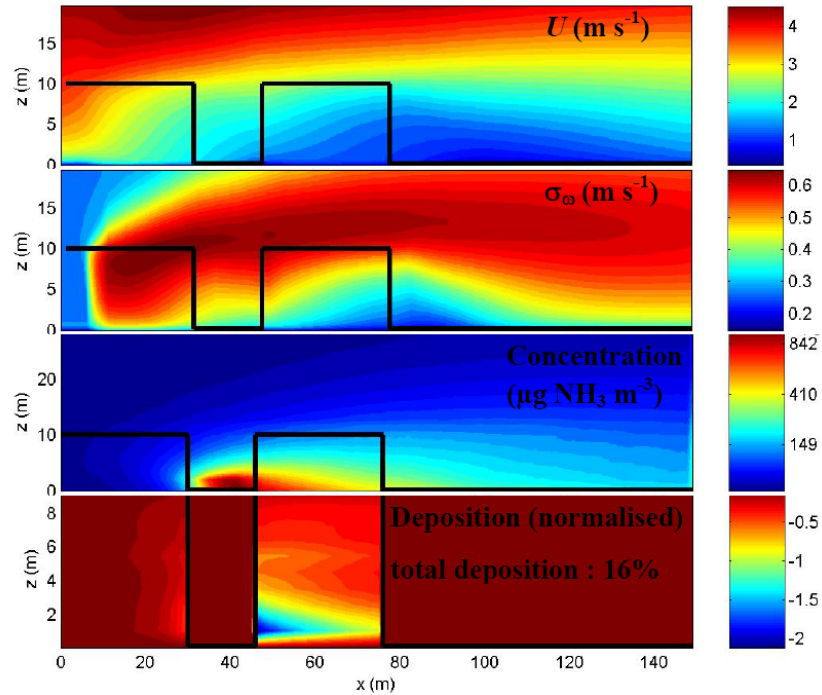


Figure 10. Example of output of the MODDAS-Thetis coupled model with the wind speed U , the standard deviation of the vertical velocity σ_w , the NH_3 concentration and the NH_3 deposition flux. The run corresponds to a canopy of 30 m long (materialised by the black lines) with a LAI of $6 \text{ m}^2 \text{ m}^{-2}$ and a constant LAD profile and no backstop canopy. The source is located between 2 and 2.5 m in z , and between 33 and 43 m in x . 16% of the emitted NH_3 is redeposited in the 30 m canopy. The MODDAS model was used in a RW mode (equivalent to Eulerian diffusion model).

photochemical reactions and chemical reactions with gaseous acids are unlikely to greatly affect local dispersion and deposition of NH_x near hot spots, although (Loubet et al., 2011b) recently challenged this idea. Dry deposition of NH_3 near hot-spots results from a combination of turbulent dispersion, stomatal absorption, and non-stomatal deposition. (1) Turbulent dispersion depends upon the topography of the site, the shape of the farm buildings, the structures of the surrounding canopies, the height at which NH_x is released into the atmosphere, the wind speed and atmospheric stability. Dry deposition is sensitive to all of these parameters. The height of release, or more generally the wind speed at the source height, is probably one of the most important parameter. However, little has been studied on the detailed turbulence surrounding the source and hence no definitive conclusions can be drawn onto which parameter is the most influential on dispersion in the case of farm buildings. In the case of emission from fields, there is less unknowns. (2) Deposition due to stomatal absorption is large, and hence the “green” LAI of vegetation surrounding hot-spots, as well as the vegetation water stress, are major parameters influencing NH_x deposition. (3) Deposition of NH_3 to external surfaces of plants is a major influential process, which is also dependent upon the leaf surface and their wetness. Non-stomatal deposition can increase local NH_x deposition by a factor of two or three.

- The tree belt as a mitigation method to reduce NH_3 emissions from farms could capture at most 30% of the emitted NH_3 within a hundred meter of a farm building. Shetlering lagoons with trees may lead to around 20% recapture. Silvopastoral systems may be seen as a good alternative which leads to higher recapture efficiency due to a better sheltering of the source. In any case, increasing the canopy LAI will lead to a better recapture, but the horizontal geometry of the canopy density should be studied cautiously as the localization and density of the *main* and the *backstops* canopies can affect the deposition in each of these compartments. Indeed, It should however be stressed here that in reality, the deposition should be smaller due to larger resistances and compensation points. Additionally, the predicted deposition is large and therefore, the canopy and the ground are likely to “saturate” and therefore the cuticular resistance is likely to increase, especially under dry conditions. Moreover, the soil and canopy compensation point may also increase with time leading to decrease in the recapture efficiency.
- All these studies on short-range deposition are difficult to validate, since measuring NH_3 fluxes under advective conditions or with complex geometries remains a challenge which is still to be faced (Loubet et al., 2009b). Of course the atmospheric NH_3 concentration is used as a proxy to “validate” the dispersion modules, but the surface exchange modules can hardly be validated in real conditions (Theobald et al., 2001). We have to rely on surface exchange models which are studied under homogeneous field conditions or in laboratories (Massad et al., 2010a; Personne et al., 2009; Sutton et al., 2009a).
- Finally the benefits in terms of NH_3 recapture on the local scale should be balanced with the potential threats to the environment that this additional reactive nitrogen load may cause, like indirect N_2O emissions, acidification, or nitrate leaching.

6.2.3. *Maize pollen dispersal*

6.2.3.1 *Introduction*

The last centuries have seen the extension of hybrid crops, while the last decade has led to the extension of genetically modified plants throughout the world at a pace of 10 millions hectares per year to reach 120 millions hectares in 2008 (James, 2008). Cross pollinations between conventional and genetically modified (GM) or hybrid crops may lead to durable introgression of alien genes into wild species. Such “contamination” of natural ecosystems is causing ecological or financial prejudice (Coleno et al., 2009; Quist and Chapela, 2001).

In the prospect of both evaluating the risk of cross-pollination and the possible management options to reduce it, a range of pollen dispersal models have been developed for several plant species (Di-Giovanni and Beckett, 1990; Dupont et al., 2006; Jarosz et al., 2004; Kawashima et al., 2004; Klein et al., 2003; Lavigne et al., 1996). Both modelling and experimental data have shown that, apart from the meteorological conditions, the geometry and the density of the pollen grain (which induces modifications in the aerodynamics properties) explain a large part of the differences in dispersal between species or varieties (Di-Giovanni et al., 1995; McCartney, 1997), the geometry of the source and the target canopies being the other major driver of the differences (Dupont et al., 2006; Jarosz et al., 2003c; McCartney, 1994). A useful parameter that combines the effects of both geometry and density on pollen dispersal is the so called settling velocity (V_s) (Aylor, 2002; Di-Giovanni et al., 1995; Loubet et al., 2007). The dispersed pollen also requires to be viable to fecundate the target fields, and this viability evolves with environmental factors (Aylor, 2003; Aylor, 2004; Bohrerova et al., 2009; Brunet et al., 2003). Hence, the geometries of the sources and targets canopies (as well as the geometry of the surface in-between them), the settling velocity and the viability or pollen form a key set of parameters for understanding and quantifying the spread of anemophilous pollens and their potential impacts on plant biodiversity, agricultural production or even human health.

In this chapter we review the work undertaken to better quantify and predict the pollen emission and its subsequent dispersion and deposition, as well as the potential effects of wind-barriers to limit their spreading. The experimental and modelling tools developed are briefly reviewed prior to discuss the main results from this work.

6.2.3.2 *Methods and models*

Lagrangian Stochastic model of pollen dispersal SMOP-2D

The dispersion of maize pollen by the wind was modeled with the SMOP-2D, which was developed based on the MODDAAS-2D model. SMOP-2D is a therefore a Lagrangian stochastic (LS) model that simulates the dispersion of pollen grains in a very similar manner as the spore dispersal model of (Aylor and Flesch, 2001). Pollen can be treated as a passive scalar, with a settling velocity V_s adding up to the vertical velocity component, provided that the size is in the range $1\ \mu\text{m} \leq \text{diameter} \leq 300\ \mu\text{m}$ which are limits for which Brownian diffusion affects deposition and inertia becomes a dominant process and the full equation of motion must be solved (Wilson, 2000). An essential metrics of the particles motion is the Stokes number St , which is a measure of the particle response to the flow motions and is the ratio of the particle response time τ_p to the fluid characteristic time τ_k . The particle response

time τ_p can be computed as the time for a particle to reach its settling velocity V_s in still air under the acceleration of gravity: $\tau_p = V_s / g$. When the Stokes law is applicable τ_p is a function of particle density ρ_p , particle diameter d_p and the air dynamic viscosity μ (Seinfeld and Pandis, 1998):

$$\tau_p = \frac{\rho_p d_p^2}{18\mu} \quad (10)$$

The time scale τ_k can either be the characteristic time scale of the fluid structure of the size of vegetation elements if the studied process is the deposition by impaction, or the size of the turbulent structures at the dissipation-range scale (Dupont et al., 2006).

In SMOP-2D, Eq. (7) of MODDAAS-2D simply becomes:

$$\begin{aligned} du &= a_u dt + b_u d\xi_u & dx_p &= (u + U)dt \\ dw &= a_w dt + b_w d\xi_w & dz_p &= (w + W - V_s)dt \end{aligned} \quad (11)$$

Due to gravitational forces and inertia, heavy particles do not follow the fluid trajectories exactly (Sawford & Guest, 1991). This effect, called “cross-trajectory” is taken into account by reducing the *fluid velocity time scale along a particle trajectory*, T_L^P , compared to that for a *fluid trajectory*, T_L (Sawford & Guest, 1991):

$$T_L^P = \frac{T_L}{\sqrt{1 + \left(\frac{\beta \cdot V_s}{\sigma_w} \right)^2}} \quad (12)$$

Where β is an empirical dimensionless constant. In this study β was taken to be 3 (Snyder and Lumley, 1971). But, the value of β for particle dispersion is still subject to debate and can vary from 1 to 5 depending on the turbulence characteristics and the experimental setup (see e.g. (Wilson, 2000)).

The other major change from MODDAAS is the way deposition is accounted for. In MODDAAS, NH_3 exchange is modeled with a resistance analogue model, and the coupling is performed by solving a linear system since the deposition flux depends on the concentration and *vice-versa*. However, in SMOP, the deposition was chosen to be modeled using a probabilistic approach: at each time step: a uniform random number is calculated and the trajectory is stopped (deposition occurs) if this random number is larger than the deposition probability. The deposition probability is the probability that on the trajectory segment, the particle “encounters” a plant or a ground element, multiplied by a capture efficiency which accounts for possible rebounds. The deposition was expressed as the sum of the gravitational settling and the inertial impaction contributions (Bouvet et al., 2007). Hence the deposition probability is expressed as:

$$P = (u_p A_{yz} E_{l,yz} + w_p A_{xy} E_{l,xy}) dt \quad (13)$$

Where A is the projected leaf area densities and E_l the capture efficiency. The capture efficiency of settling was assumed to be maximum, while the impaction capture efficiency was set to $0.86 / (1 + 0.442 St^{1.967})$, following the work of (McCartney and Aylor, 1987), where St is the Stokes number ($St = U V_s / (g l)$, g being the earth gravitational acceleration

and l being the typical size of plant elements). This later efficiency can never reach one, which means that at least 14% of the particles that impact on leaves experience a rebound. The particles rebound were also modeled as in (Aylor and Ferrandino, 1985).

The settling velocity distribution of the pollen was assumed Gaussian with the average and standard deviation being input parameters of the model. The SMOP-2D model was further expanded from MODDAASS-2D to account for simple change in canopy types (maize, bare soil, forest) by adding a fully empirical parameterization of the turbulence in the transition zone, based on a simple 3rd degree polynomial interpolation (Jarosz et al., 2004). In (Bouvet et al., 2007), the same model was used but was coupled with the Reynolds-averaged Navier–Stokes wind model of (Wilson et al., 2001) based on the second-order turbulent closure of (Rao et al., 1974). The rebound algorithm was also refined in (Bouvet et al., 2007).

Adaptation of FIDES for particle dispersion

The FIDES model was also modified to simulate particles dispersion and deposition. For that purpose, two modifications were made in FIDES: (1) the vertical diffusion was diminished to account for the “cross-trajectory effect”, which simply reflects the diminution of the particle Lagrangian time scale τ_p (Eq. (11); (Bouvet and Wilson, 2006), and (2) the deposition was modelled with a standard deposition velocity model for particles taken from (Seinfeld and Pandis, 1998):

$$K_p(z) = \frac{K_{gas}(z)}{\sqrt{1 + \left(\frac{1.6 \cdot V_s}{u_*} \right)^2}} \quad (14)$$

$$V_d(z) = \frac{1}{R_a(z) + R_{bp} + R_a(z)R_{bp}V_s} + V_s \quad (15)$$

Where $R_a(z)$ is the aerodynamic resistance (for gases and particles), and R_{bp} is the boundary layer resistance for particles. The main limit in the approach taken in FIDES-particle is that it does not account for the gravitational settling of the particles in the dispersion scheme which leads to the plume settling.

Pollen fluxes, concentrations and viability

The validation of SMOP-2D model required datasets of pollen or particle dispersion which were very scarce at the time we started to study pollen dispersal and which were inexistent for maize pollen. Indeed, the validation of the model required a description of the input variables (meteorology, turbulence characteristics, source pattern) and parameters (canopy structure, pollen settling velocity) as well as measurements of the main output variables, concentration and deposition fluxes. We also needed to get experimental evidences of local dispersion and deposition, starting by measuring the pollen emission and its deposition, but also estimating the pollen viability, the pollen settling velocity and size distributions and its humidity. We therefore designed a range of experiments to both get experimental references and validate the LS dispersion model (Jarosz et al., 2005; Jarosz et al., 2003a; Jarosz et al., 2004; Marceau, 2010; Marceau et al., 2011a). In Bouvet et al. (2007) the specific question of filtering particles has been studied, which can be useful in answering the specific question of how to mitigate crop contamination via anemophilous pollen transfer.

Details descriptions of the methods can be found in (Jarosz et al., 2005), (Marceau, 2010) and (Bouvet et al., 2007). Briefly, the pollen concentration in the atmosphere was measured with Burkard traps (suction and subsequent impaction on a grease roll) for a continuous recording of the source strength, and with Rotorods (rapidly rotating arms impacting the pollen), while pollen deposition was measured with cups filled with an isotonic solution to avoid the pollen to explode in water, and subsequently analysed with a Coulter counter (resistivity method). The turbulence was characterised with ultrasonic anemometers placed above and within the canopy as well as at several distances from the canopy centre. The standard meteorological variables (air temperature and humidity, wind speed, wind direction, precipitation, wetness sensors) were also recorded. To measure the pollen emission dynamics about 25 maize tassels were placed in bags every day for 24 hours periods and then the number of pollen grains was counted. Additionally, mass balance masts were placed at 3 and 10 m downwind of the emitting fields in two experiments to evaluate the pollen flow out of the emitting field and its subsequent deposition. In these masts the integrated horizontal flux was estimated as the integral of the product of the mean concentration times the mean horizontal wind speed measured at 5 heights. The pollen viability was either measured as the percentage of pollen germinating in a germination media (but this method was found to be difficult to standardise; (Marceau, 2010)), or by exposing castrated individual maize plants downwind from a maize field (Loubet et al., 2004). The pollen humidity content was measured by measuring fresh and dry weight.

Pollen settling velocities distribution

As a key parameter in dispersion models, which had a great effect on short-range deposition (Dupont et al., 2006; Jarosz et al., 2004) measurements of V_s distribution was required. Furthermore, the viability measurements and (Aylor, 2002) suggested that there may be two distributions of maize pollen size and therefore of V_s . A specific setup has therefore been designed to measure the V_s distributions of pollen (Loubet et al., 2007), which is briefly described here. The settling velocity distribution was measured by video-recording the fall of pollen grains illuminated by lights in a dark room situated below a settling tube. Particles were released from a 0.95 m tube with 0.15 m diameter. The bottom end of the tube was sealed in a black photographic chamber (230x230 cm), with dimension chosen to avoid aerodynamic wall effects. Two sealed fences on the side were used to light pollens by the mean two fiber-optic lights (150 W in total). On the front of the chamber a window enables to film with a camera (XCD-X700, Sony, Japan) equipped with a zoom (ICA30, 12.5-75 mm, macro, 1:1.8) that provided a 5cmx5cm field of view. To prevent heating and thermal convection within the chamber, the black chamber was surrounded with 5cm width insulating polystyrene box. Temperature was measured with a thermometer and remained below 30°C and stable in time. The camera CCD shutter was set to $\tau=42.67 \pm 0.005$ ms of integration time to record pollen trajectories with a frequency of 15 images per second. An image analysis program was then set-up in Matlab to retrieve the length (L) of the pollen trajectories on each image. The settling velocity was then computed by the means of the equation $V_s=L / (\alpha \times \tau)$, with α (pixel/m) estimated by image calibration. The setup was validated with standard polystyrene beads and *Lycopodium* spores which diameter was precisely determined with a Coulter counter. The setup was therefore proved to be very precise (less 2% error on the mean V_s for large particles and less 12% error for lycopodium spores) as well as robust (Loubet et al., 2007).

In the following, two major outputs of these researches are highlighted.

6.2.3.3 *Results and discussion*

Emission, viability and settling speed of maize pollen

Overall, the seasonal maize pollen emission pattern is well represented by a Gaussian curve, lasts between 5 and 10 days, and depends on the average vapour pressure deficit (VPD) during the period. A massive amount of pollen is released (between 8 and 800 10^9 pollen grains per ha). The diurnal cycle of the pollen release is either mono-Gaussian if the mean temperature during the morning is smaller than 21.6°C or bi-Gaussian otherwise (Marceau et al., 2011a). This is explained by the capability of the pollen to mature during the morning under high temperatures. The diurnal pattern of pollen shed was further found to be quite well determined by the VPD by (Jarosz et al., 2005) as well as by (Viner et al., 2010), while (Marceau et al., 2011a) found a better relationship with the mean wind speed during the early morning and relative humidity. However, the model of Marceau et al. (2011), although much more empirical than the model of Viner et al. (2010), was successful in predicting the secondary peak of pollen shed unlike the Viner et al. (2010) model. The two approaches may however be reconciled in the future if one considers not only the VPD or wind speed and humidity but rather integrated variables.

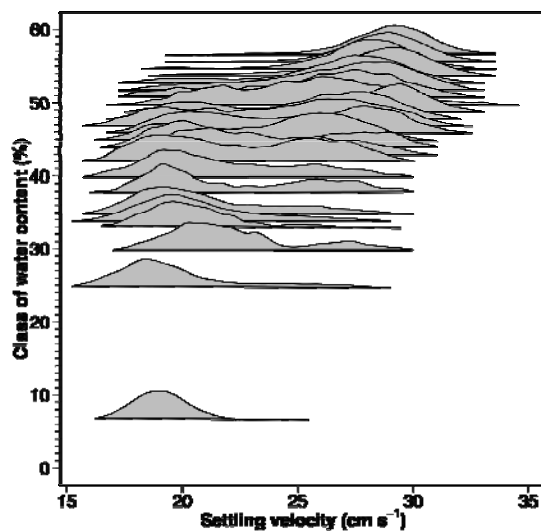


Figure 11. Empirical settling velocity distributions versus classes of water content. Settling velocity distributions are normalized by their maximal value to ensure that all distributions are visible, thus areas under the curves are not proportional. From Marceau (2010).

Once the pollen is shed from the anther, its successful pollination first relies on the pollen viability. (Jarosz, 2003) found a striking relationship between V_s and the average humidity content of the pollen: The V_s distribution is bi-Gaussian (also seen by (Loubet et al., 2007)) with a first peak between 15 and 20 cm s^{-1} and a second one at around 30 cm s^{-1} . Marceau (2010) generalised the study of Jarosz et al. (2003) and found indeed a bi-Gaussian distribution (Figure 11). Marceau (2010) also found that the area under the curve of the second mode was very clearly linearly related to the water content of the pollen, starting from a water

content of around 20-30% below which the second mode disappears. Moreover, building up on these results, (Marceau et al., 2011b), have further hypothesised that the viable pollen was the spherical pollen corresponding to the second mode of V_s (Figure 11). Based on this hypothesis and making use of the linear relationship between mean water content and viability of pollen reported by (Fonseca and Westgate, 2005) Marceau et al. (2011) have proposed a new relationship between the mean settling velocity and the viability rate of maize pollen. This demonstrated relationship between the pollen water content, its viability and its settling speed velocity which is promising as it may give a simple method to

measure the mean water content and viability of maize pollen based on the settling tower methodology of (Loubet et al., 2007).

This would indeed be an important aspect to further study as the measurements of pollen viability performed in the field as a function of downwind distance from the emitting field (by means of fecundation of castrated plants) showed a gradual decrease of the fecundation (Figure 12) which is not reproduced by our models. This decrease of pollen viability could not be explained by a drying effect during the time of the pollen travels

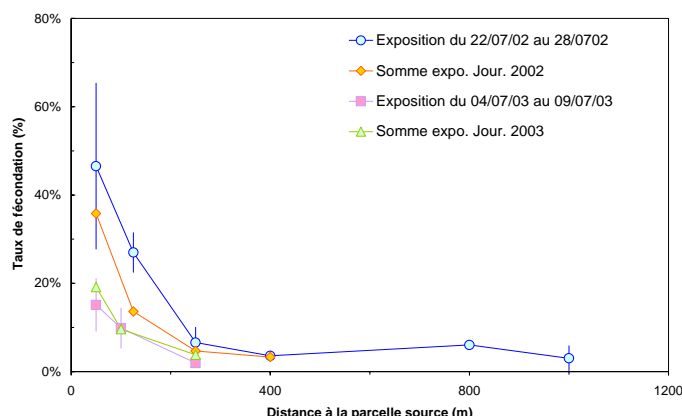


Figure 12. Fecundation rate of castrated maize plants as a function of downwind distance from the emitting field for several runs. From (Loubet et al., 2004).

as this would be much too short a time. It may well be explained by the link found between the viability and the settling velocity by Marceau et al. (2011b), through their correlation with the wind velocity under certain type of climate. Indeed, although they showed that for a given meteorological situation, the decrease of pollen viability with distance occurs over a very short distance (10 to 20 m). Since viability is correlated with VPD which itself is correlated with the wind speed, the resulting fecundation which integrates over a day or even several days may well explain this pattern: when the VPD is large the pollen is less viable but it goes further away, while when the VPD is smaller, the pollen is more viable but it travels over a shorter distance (mainly due to wind-speed). (Marceau, 2010) have explored this hypothesis but the meteorological conditions chosen are not those of the Figure 12 which showed very calm conditions even in the early morning when the pollen was already shed from the anthers. This should be further studied.

Short-range deposition of maize pollen

The short-range deposition of maize pollen was studied with experimental approaches, in order to provide references (Jarosz et al., 2003b), as well as with modelling studies (Jarosz et al., 2005; Jarosz et al., 2004), to investigate scenarios. An essential part of the modelling work has been devoted to validating the modelling approach.

The experimental campaigns showed that pollen concentrations and deposition rates decreased rapidly with distance from the crop: concentrations decreased by about a factor of 3 between 3 m and 10 m downwind of the source while deposition rates at 30 m were less than 10% of those at 1 m. Given all the data obtained, it appeared that the deposition pattern follows a power law (Figure 13) over intermediate distance downwind from the source (up to 150 m). The dispersal distance appeared to increase with the source canopy height, and the roughness length of the downwind canopy. However at longer distances (1000 m) the pollen deposition rate was substantially less than would have been found by extrapolating the power law function found at intermediate distances.

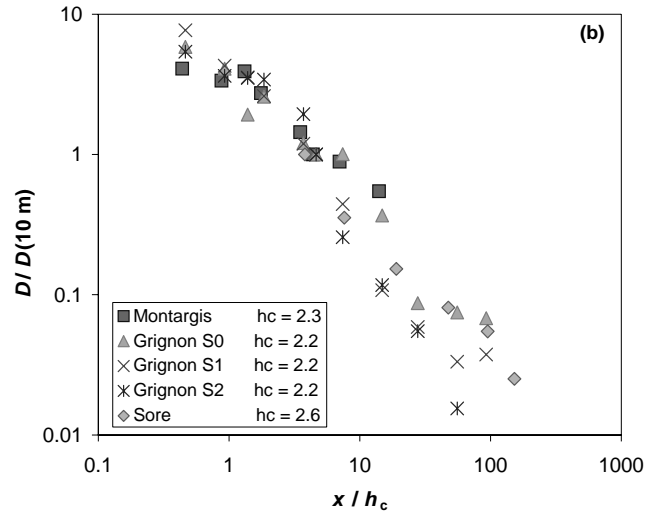


Figure 13. Relative deposition normalised by deposition at $x = 10$ m as a function of relative downwind distance normalised by the canopy height, h_c for all experiments. From (Jarosz et al., 2004).

However at longer distances (1000 m) the pollen deposition rate was substantially less than would have been found by extrapolating the power law function found at intermediate distances.

The horizontal flux of pollen estimated from mass balance approaches, ranged from 0 to $240 \text{ grains m}^{-2} \text{ s}^{-1}$ at 3 m from the source. The comparison of deposition rates estimated by difference between the mass balances at 3 and 10 m downwind from the source and direct deposition measurement with cups showed a good agreement provided the wind direction was aligned with the masts within 30° .

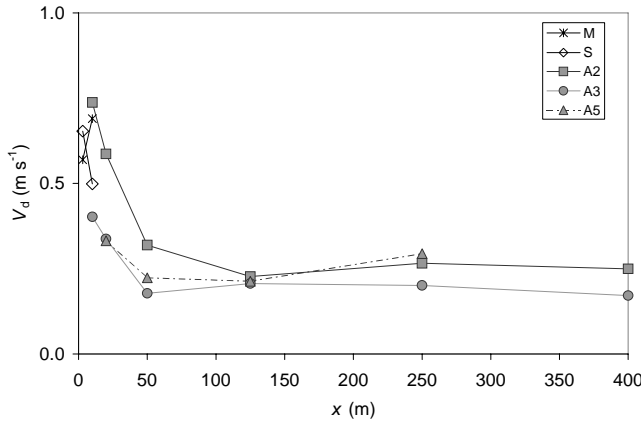


Figure 14. Deposition velocity as a function of the downwind distance at Montargis (M), Grignon (S) and Sore (A2, A3 and A5). Results at Montargis and Grignon were averages of all runs. From (Jarosz et al., 2004).

The deposition velocity determined as the ratio of the deposition rate to the airborne concentration ranged from 0.2 to 0.7 m s^{-1} , which is 1 to 3 times greater than the mean settling velocity V_s measured by (Jarosz, 2003) or (Marceau et al., 2011b) or published (ranging from 0.2 m s^{-1} to 0.3 m s^{-1}). Moreover there is a clear increase of V_d above V_s close to the source ($x < 50$ m) (Figure 14). Overall, accounting for the larger V_d in the lee of the canopy improved the performance of the SMOP and AQUILON models in simulating the

deposition (Figure 15) (Dupont et al., 2006; Jarosz et al., 2004). However AQUILON showed a better agreement between the modelled and measured concentration with large V_d near the source, because of a much larger vertical dispersion in AQUILON. The assumption that V_d is identical to V_s is applicable for zero inertia particles, for which the particles follow the fluid parcels and for large inertia particles for which the flow has a negligible effect on

the particle trajectory (Elperin et al., 2007; Scott et al., 2009; Zaichik and Alipchenkov, 2009). It was indeed observed by (Maxey, 1987) and (Aliseda et al., 2002) that particles with Stokes numbers around one show higher settling speed in turbulent flows than in still air. This effect results from two mechanisms: (1) the preferential sweeping by turbulence, where particles are expelled from vortices due to centrifugal forces and are then preferentially swept (they leave the eddy) on the downward side of eddies (Aliseda et al., 2002; van Aartsijk and Clercx, 2010). This mechanism leads to an increased deposition velocity in turbulent structures. The second mechanism (2) is the clustering of particles (Zaichik and Alipchenkov, 2009) which results from the same mechanism of sweeping by turbulence, and leads to the particles therefore accumulated in a region with a high strain rate (van Aartsijk and Clercx, 2010). These particles which are then clustered affect the turbulence locally and may in turn settle faster. These particular effects occur for Stokes number of ~ 1 . (Dupont et al., 2006) have shown based on the trials of (Jarosz et al., 2003a) that the Stokes number would indeed be close to 1 lee of a maize canopy favouring such an effect. This would not be the case for smaller particles such as lycopodium.

Finally, we could also mention that the observed V_d enhancement could not be explained by the negative vertical air velocity found downwind from a rough-to-smooth change which was correctly accounted for in AQUILON (Dupont et al., 2006).

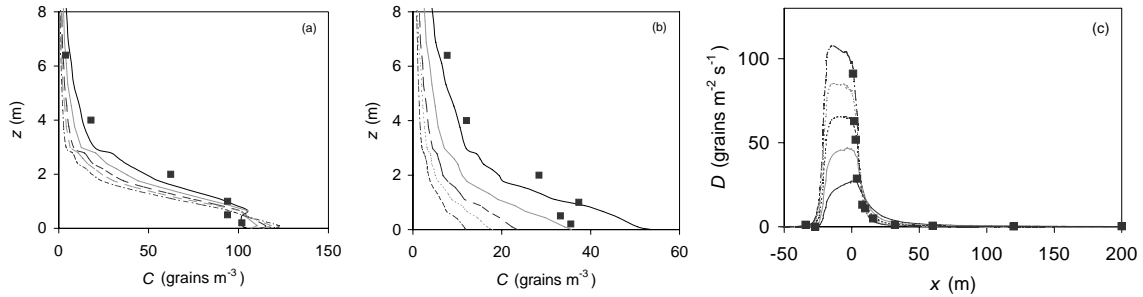


Figure 15. Modelled and measured concentration profiles at (a) $x = 3$ m and (b) $x = 10$ m downwind from the source and (c) the deposition flux as a function of x . Simulations are from Grignon S₁₃ with $V_s = 0.26$ m s^{-1} for single grains (black thin line), 0.37 m s^{-1} for doublets (grey thin line), 0.45 m s^{-1} for triplets (black dotted line), 0.52 m s^{-1} for quadruplets (grey dotted line) and 0.58 m s^{-1} for quintuplets (black dotted dash line).

The SMOP-2D maize pollen dispersion model was compared to a large number of data (Jarosz et al., 2004). SMOP-2D correctly simulated the airborne pollen concentration pattern downwind from a small-sized maize crop but generally underestimated the deposition rates in the first 10 m downwind from the crop. Factors that could account for the discrepancy between modeled and measured deposition rates were evaluated by sensitivity analysis. The same simulations with the Eulerian model Aquilon (now Thetis) by (Dupont et al., 2006) gave similar discrepancies, which indicates that these were not due to a wrong parameterization of the turbulent field in SMOP-2D. As discussed previously, our current analysis points toward a wrong parameterization of the settling velocity under turbulent conditions, when the Stokes number is close to unity (Wang and Maxey, 1993). The turbophoresis effect may also be involved in the model underestimation of the deposition (Reynolds, 1999b). Studying a way to include such parameterizations in SMOP as well as an updated deposition model would be a major improvement of SMOP in the future.

6.2.3.4 *Conclusions*

- Three main findings can be retained: (1) the settling velocity distribution of maize was found to be bi-modal, with one mode corresponding to the light, dry and non-viable pollen and the other one to the heavy, viable pollen; (2) the measured deposition pattern was found to follow a power law function of x / h_c over distances lower than 150 m and a smaller deposition at further distances; (3) the deposition velocity in the lee of the emitting canopy was significantly higher than the settling velocity, an effect that could be explained by an increased V_s by turbulent sweeping and particle clustering under the specific conditions of a Stokes number close to 1.
- The main limitation in the LS approach for modelling heavy particles dispersion is to account correctly for the differences between the fluid tracer and heavy particles statistics of motion. Indeed, heavy particles experience inertia and gravity, which are not experienced by fluid parcels (Reynolds, 1999b). In SMOP-2D (Jarosz et al., 2004) as in (Bouvet et al., 2007) we have chosen the approach of (Wilson, 2000) consisting in simulating the particle parcel dispersion with the same LS model as a fluid parcel and only modifying the particle Lagrangian time scale (as well as the vertical displacement). This choice was justified by the fact that the maize pollen particles were in the right size range so that the inertial time scale τ_p was small when compared to the Lagrangian time scale, except close to the ground (Bouvet et al., 2007; Wilson, 2000). However, this approach may be limited for larger particles mainly driven by inertia, or conditions with smaller turbulence, like in the downwind edge of a maize field (turbophoresis). The SMOP model is also not adapted for small particles experiencing Brownian diffusion (Reynolds, 1999a). Moreover the coupling with the k - ϵ model may not be fully satisfying since components of k are not known. A coupling with a Large Eddy Simulation model (LES) may be interesting in that it would give the three components of k . The model should therefore be modified in the future if one would like to treat more general questions.
- The second limitation in the current approach is the parameterisation of the settling velocity V_s under turbulent conditions, when the Stokes number is close to unity. Under such circumstances, the settling velocity would be increased by turbulent sweeping and particle clustering (Wang and Maxey, 1993; Zaichik and Alipchenkov, 2009). It is very likely that our observations of increased deposition velocity in the lee of the maize canopy would be due to such an effect. Trying to work out a parameterisation of V_s under non-homogeneous turbulent flow from existing work (Wang and Maxey, 1993; Zaichik and Alipchenkov, 2009) would be a substantial improvement of our modelling approach.
- Finally, most parts of the pollen emission dispersion and deposition has been studied and modelled (Jarosz, 2003; Marceau, 2010). If not fully satisfying in some parts (dispersion in the lee of the canopy, validation of the pollen viability), taken together, all these studies have substantially improved our understanding of local contamination of maize field with exogenous pollen. This work has also pointed toward one major parameter for the dispersion (the settling velocity, V_s), which is also suggested as an interesting proxy to account for the pollen water content and therefore for the pollen viability.

6.3. Sources and sinks of pollutants and GHG within canopies

In this chapter we will report the studies undertaken to better understand, parameterise and model the exchanges of pollutants between the surface and the atmosphere: ammonia (NH_3), ozone (O_3), and nitrogen oxides (NO and NO_2). The studies on the role of the agro ecosystems in the exchange of greenhouse gases (carbon dioxide, CO_2 and nitrous oxide N_2O) will then be reported. This chapter is organised as follows:

- In a first part, the role of the vegetation in regulating the surface exchanges will be the focus, with ammonia taken as an example, and a discussion on the sources and sinks of ammonia in a canopy integrating the concept of stomatal compensation point.
- In a second part, the work undertaken on emissions and deposition of chemically reactive species (O_3 and NO_x) will be presented and discussed.
- In the third part, the question of integrating the fluxes over crop rotations to estimate balances of carbon, nitrogen and greenhouse gases at the field scale will be the focus point of the discussion.

6.3.1. *The sources and sinks of ammonia in a canopy and the compensation point*

6.3.1.1 *Introduction*

There are several pathways for the exchange of trace-gases between the terrestrial ecosystem and the atmosphere: the soil, the external surfaces of the leaves and stems, the stomatal exchange and the chemical interactions within the canopy space. Moreover, in fertilised crops, ammonia can be volatilised from the canopy, whereas deposition is more likely on semi-natural ecosystems (Fowler et al., 2009). However as a result of the complex interactions between the sources and sinks within a canopy, and especially the turbulent transfers between the canopy compartments (Figure 17), as well as the atmospheric concentration which are highly influenced by the distance to hotspots, a fertilised crop may behave as a sink for NH_3 . In particular there was still a controversy in the early 2000s as to where the NH_3 source was located in the canopy (Sutton et al., 2001a; Sutton et al., 2007; Sutton et al., 2009b): were the stomates the main sources or was the litter or the soil driving the emission. This question was especially critical in grassland canopies (Sutton et al., 2001a). Put in another way, the question is turned into a classification of the potential emission of each compartment of the canopy, whether it is emitting or depositing then depends upon the location of this compartment and the transfer resistance between the compartments and with the atmosphere. To answer this critical question, it is necessary to understand each exchange process separately and to combine them into a model to compare to integrated measurements.

Stomatal exchange is limited by molecular diffusion, and therefore dependent upon the molecular weight of the gas (Farquhar et al., 1983). The diffusive exchange is proportional to the concentration difference between the atmosphere close to the leaf boundary layer (χ_{z0}) and inside the substomatal cavity (χ_s). It is limited by the boundary layer resistance r_b and the stomatal resistance r_s . The stomatal compensation point is the gas concentration in thermodynamic equilibrium with the liquid phase $[\text{NH}_3]_l$ in the stomatal cavity. For NH_3 ,

the Henry constant K_H of this equilibrium is strongly dependent on temperature: for a given ammonium concentration in the apoplastic solution, χ_s will double every 5 °C (Husted and Schjørring, 1996). In the liquid phase, $[\text{NH}_3]_l$ is in equilibrium with its coupled acid NH_4^+ . This chemical equilibrium is strongly dependent on pH, its pKa is 9.25 at 25°C (Flechard and Fowler, 1998). The pH of the apoplast is determined by the concentration of acid and base species. However, numbers of elements in the apoplast has not been measured yet, and measurement of apoplastic pH is subject to large uncertainties. Apoplastic NH_4^+ is dynamically exchanged with the leaf cells, the xylem and the phloem. In the cell, NH_4^+ is created and consumed in the photorespiratory cycle and especially the GS/GOGAT cycle (Glutamine Synthetase, GS, and Glutamate Synthase, GOGAT), but it is also an intermediate in the nitrogen assimilation process and can be reduced from NO_3^- in the leaf itself (Farquhar et al., 1983).

The cuticle is a highly dynamic compartment for NH_3 . Indeed, as a very soluble gas, NH_3 is readily adsorbed to any wet surface, which is expressed in the cuticular resistance dependency on relative humidity (Van Hove et al., 1988). However, ammonia is also alkaline and its deposition therefore also depends on the water pH. The composition of the water film on the leaves, and the deposition of acidic gases or aerosols, are therefore of critical importance in NH_3 cuticular exchange (van Hove et al., 1989). Moreover, depending on the NH_3 concentration difference between the leaf surface and the atmosphere NH_3 can either be adsorbed or released. Finally, water evaporation, rain, or condensation on the leaves may themselves induce NH_3 transfers by changing water concentrations or by mass transfer (Fléhard et al., 1999; Flechard et al., 2011).

The litter is a known source of NH_3 to the atmosphere due to decomposition of proteins in the leaves (Mattsson and Schjoerring, 2003; Nemitz et al., 2000a). This process is also linked to water content of the leaves, since in dry leaves all biological processes are diminished, while with water the biological decomposition of proteins should be activated. However, the senescence process is a largely unknown process, which should not lead to large losses of nitrogen as most plants actively transport the nitrogen from senescing leaves to grains and active leaves. Other plants like oilseed rapes are known to release large amounts of nitrogen from the litter leaves, of which a part is recaptured by the siliques in the gas phase (Nemitz et al., 2000a).

The soil may also be a potential source of NH_3 , just as the apoplast, depending on the NH_4^+ concentration and the pH of the liquid phase. The NH_3 potential is therefore mainly dependent on the availability of NH_x in the soil. Ammonium mainly comes from application of slurry and ammonium containing (or releasing) fertiliser (ammonium based or urea). But NH_4^+ can also be released from soil processes, mainly denitrification which leads to the production of NH_4^+ from NO_3^- or organic matter mineralization, or be consumed in the soil firstly by plant absorption, organisation, oxidation, nitrification, and of course it can also be trapped onto the electronegative ions in the soil (Génermont and Cellier, 1997). However, most of the studies on NH_3 emissions from soils have focussed on short term emissions (few weeks) following application of either slurry or fertiliser (a large number were not even on bare soil (Sintermann et al., 2011a)). Although this was perfectly justified since the canopy grew rapidly again, as well as since it became difficult to measure and model the

small fluxes, there is yet a lack of knowledge of NH₃ emissions from soils underneath canopies.

Finally, one essential feature of NH₃ exchanges is that it is an equilibrium process, which depends on the NH₃ concentration difference between compartments (soil, leaves, apoplast and atmosphere). The magnitude of the flux therefore depends on both the magnitude of the concentration in the gas phase in each compartment and the transfer resistances between each compartment. But additionally, the temperature and wetness of each compartment is also essential. Therefore a good characterisation of the microclimate of each compartment and the transfer resistances between each compartment are essential in studying NH₃ transfer.

This chapter summarises the main methods and models developed to try to identify and quantify the NH₃ sources and sinks within agricultural canopies, and the main results achieved. A new modelling approach is then discussed.

6.3.1.2 *Methods and models*

I have used mainly three methods to study the NH₃ sources and sinks within canopies, which progressively go down from field to plot, to leaf scales: (i) The micrometeorological flux measurements, (ii) the dynamic flux chambers or *cuvette* measurements, and (iii) the apoplastic extraction methods. The first method has already been presented in chapter 0.0.0.0 and will not be presented here, while the two other methods are presented here. Moreover, SVAT models have been used to help interpreting the fluxes and understanding the behaviour of the sources and sinks within the canopy. Finally, a process model has been proposed to study the stomatal compensation response to nitrogen supply, transpiration and photosynthesis.

Apoplastic compensation point determined by apoplastic extraction

The leaf stomatal compensation point χ_s can be determined from the apoplastic NH₄⁺ concentration and pH, by means of extraction with successive infiltration and centrifugation of leaf segments (Husted and Schjørring, 1995a; Schjørring, 1997). This technique has been successfully applied to several plants in the field (Massad et al., 2009; Mattsson et al., 2009; Schjørring et al., 2001). However, the extraction technique is subject to uncertainties, regarding potential regulation of the apoplastic pH and NH₄⁺ by the plant during the extraction, and buffer effects (Schjørring, 1997). Moreover, the technique has been found to give lower estimates as those retrieved from micrometeorological methods (Hill et al., 2001), which may be due to spatial variability at the microscopic scale of pH or NH₄⁺ in the apoplast. The compensation point χ_s (μg NH₃ m⁻³) is often expressed as a function of the ratio of ammonium to proton molar ratios [NH₄⁺] / [H⁺] in the solution. This ratio is temperature and pH independent:

$$\chi_s = M_{NH_3} \times K_H(T) \times K_D(T) \times \frac{[NH_4^+]_{ap}}{[H^+]_{ap}} \times 10^9 \quad (16)$$

where M_{NH_3} is the molecular mass of NH₃ in g mol⁻¹, K_H and K_a are the dimensionless Henry and acidity dissociation constants. $K_H(T)$ is highly temperature dependent as it roughly doubles every 5 °C.

Canopy compensation point derived from fluxes

The canopy NH_3 compensation point (χ_c) can be inferred from simultaneous measurement of fluxes and concentrations of NH_3 , either from micrometeorological methods over large fields (Milford et al., 2009; Sutton et al., 2009a), or from dynamic chamber methods (Husted and Schjørring, 1995b). The method then is based on finding at which concentration the flux is zero (Husted and Schjørring, 1995b). Some studies have shown the effectiveness of these methods to assess the ammonia compensation point for different species, environmental conditions, and its response to environmental parameters, and plant nutrition (Kruit et al., 2007; Massad et al., 2009; Mattsson and Schjørring, 1996).

Flux chambers

In order to study NH_3 exchange processes, the flux chamber shows the advantage of being controlled or at least partially controlled. A flux chamber was developed for O_3 and NH_3 which was designed to get a controlled concentration of NH_3 (or O_3) and water vapour in

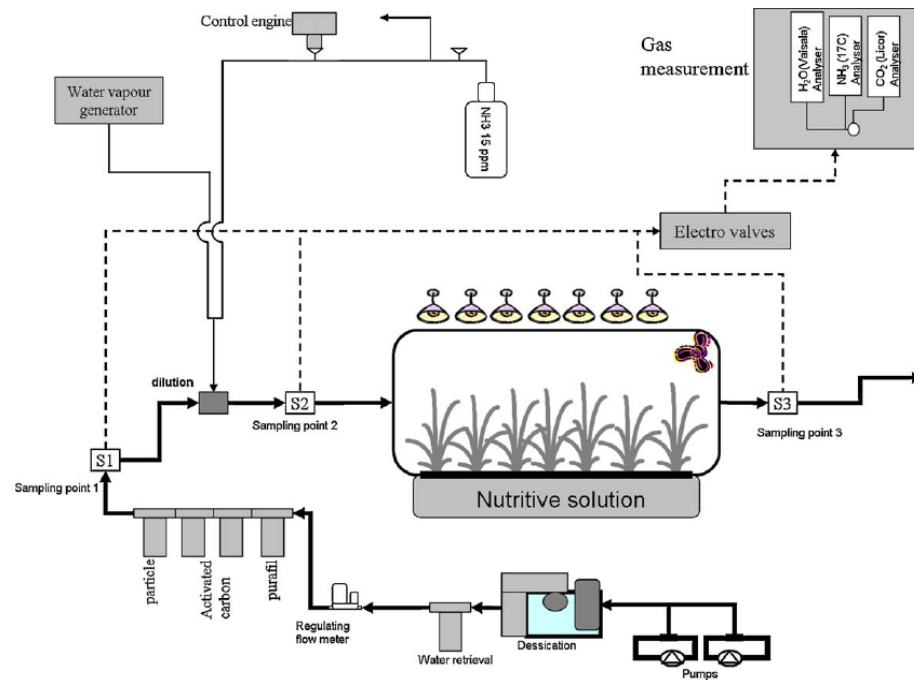


Figure 16. Schematics of the NH_3 flux chamber as described by (Massad et al., 2009).

the inlet line and to measure incoming and outgoing concentrations from the chamber (Figure 16). The chamber was design to expose only the leaves of the plants which roots could be maintained in a nutritive solution. The light was provided by halide lamps providing $350 \mu\text{mol m}^{-2} \text{s}^{-1}$. The chamber material was either Teflon PFE (walls: $50\mu\text{m}$ film) or Teflon PTFE (bottom). A Teflon coated fan was added in the chamber to increase the mixing. A chemiluminescence analyser was used to measure NH_3 concentrations (ThermoEnvironment, 17C). The compensation point was determined by changing the input concentration and determining at which concentration the flux was zero. One of the main difficulties of the flux chamber method is to find the compromise between a small flow rate to increase the sensitivity of the flux and a large mixing in the chamber to decrease the aerodynamic resistance and diminish wall interactions.

SVAT models

The exchange of NH_3 between the surface and the atmosphere requires considering at least three compartments: (1) the ground surface (which can either be a litter or soil), (2) the plant surfaces (cuticles) and (3) the stomatal cavity. Moreover, NH_3 exchange (actually O_3 as well) is highly dependent on the temperature and humidity of these compartments. It is

therefore critical to get these parameters when modelling surface-atmosphere exchange of NH_3 . This is what is done in Surf atm- NH_3 (Personne et al., 2009), a model combining NH_3 , heat and water vapour transfer at the soil-canopy-atmosphere interface (Figure 17). Briefly, this model combines a modified energy balance model of (Shuttleworth and Wallace, 1985) with the two layer NH_3 exchange model of (Nemitz et al., 2000b).

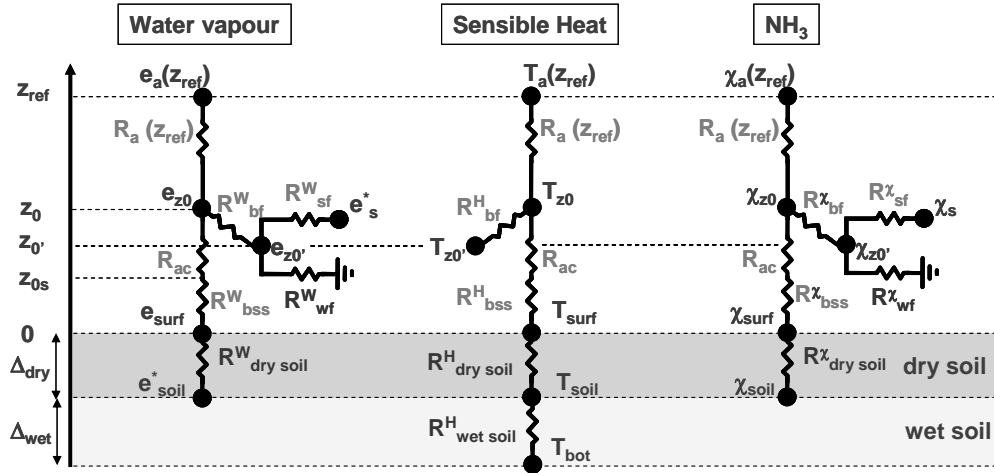


Figure 17. Resistance scheme for water vapour, heat, and NH_3 exchange models as in the Surf atm- NH_3 model. (Personne et al., 2009).

6.3.1.3 Results and discussion: Sources and sinks of ammonia in a plant canopy

The stomatal compensation point and its drivers

Based on apoplastic extractions, (Loubet et al., 2002) found that the ammonia compensation point at 20°C of *Lolium perenne* grass varied drastically from 0.02 to more than 10 $\mu\text{g NH}_3 \text{ m}^{-3}$ following a cut and fertilisation (65 kg N ha^{-1} of N-PK pellets) event in a Scottish grazed grassland. The corresponding emission potential (Γ) varied from about 20 to around 1000. This Γ peaked following fertilisation and came back slowly to its low value within 20 to 30 days. The observed dynamics of Γ resulted from a combination of a short and sharp increase (up to 20 times) in the NH_4^+ content of the apoplast which started just following fertilisation and lasted 10 days and a subsequent increase in the pH of the apoplast (from 6.5 to 7.8) which started around 10 days following fertilisation and lasted for around 20 days.

Compensation point and pH

The dynamics of the pH increase suggests that the increased apoplastic pH following cut-fertilisation was due to an increased uptake of NO_3^- and a decreased uptake of NH_4^+ . Indeed, although the effect of N nutrition on the apoplastic pH is still unclear, plants relying on NO_3^- nutrition tend to have a higher apoplastic pH, due to nitrogen assimilation in the shoots, while NH_4^+ fed of mixed $\text{NH}_4^+/\text{NO}_3^-$ fed plants would tend to have a lower apoplastic pH (Massad et al., 2008). The change in mineral uptake observed in (Loubet et al., 2002) was believed to be due to an increased availability of NO_3^- and a decreased availability of NH_4^+ in the soil 10 to 15 days following cutting/fertilisation, combined with an increased uptake of NO_3^- and a decreased uptake of NH_4^+ by the plant during the re-growth process (Louahlia et al., 2000). This study, despite quantifying the changes in apoplastic compensation point in *Lolium perenne* L. also highlighted the crucial role played by the pH and hence the ratio of NH_4^+ to NO_3^- uptake in determining NH_3 exchange between the surface the atmosphere. This finding was supported by (Mattsson et al., 2009)

who did not find a significant change in the apoplastic pH of *Lolium perenne* L. following fertilisation, which is coherent with the fact that in their study of the soil $\text{NO}_3^-/\text{NH}_4^+$ ratio did not change following fertilisation. This change in pH with NO_3^- to NH_4^+ nutrition was however not supported by the results of (Massad et al., 2009) on oilseed rape leaves who found a constant pH with highly variable $\text{NO}_3^-/\text{NH}_4^+$ nutrition ratios.

Compensation point and nitrogen supply

The NH_3 stomatal compensation point, which is determined by the apoplast NH_4^+ and pH, is therefore closely related to the nitrogen form transported by the Xylem sap from the roots (Massad et al., 2008). Although it is usually admitted that NH_4^+ is assimilated in the roots prior to its transport to the shoots, there are several evidences that NH_4^+ may be at least partly transported to the shoot. Several authors have shown that χ_s increased with increasing N supply, and preferentially with NH_4^+ (Massad et al., 2010a; Mattsson and Schjørring, 1996). Apoplastic extractions made on maize (Loubet et al., 2009a) showed indeed a linear increase of Γ (or χ_s) as a function of nitrogen supplied as ammonium nitrate. A similar increase was observed by (Mattsson et al., 2009) for *Lolium perenne* L. and by (Massad et al., 2009) for oilseed rape leaves, although they found lower Γ than for maize. A review by (Massad et al., 2010a) confirms this general behaviour where Γ is related to the nitrogen supplied to the field (both from atmospheric deposition and nitrogen supply), with a slope ranging from 2 to 20 (supply in $\text{kg N ha}^{-1} \text{ y}^{-1}$) on annual basis. The daily dynamics of the apoplastic compensation point should be related to the xylem water flux (and hence the stomatal opening) (Massad et al., 2008; Massad et al., 2010b). In *Lolium perenne* L. (Herrmann et al., 2009) have measured a daily course of the apoplastic NH_4^+ concentration showing a maximum around noon and a minimum at night, and the opposite cycle for the pH. These measurements would be in agreement with the assumption of water transported NH_4^+ from the roots to the apoplast.

Litter, soil, and stomatal contribution to the NH_3 exchanges

Although the stomatal compensation point is a driver of the NH_3 exchange between the surface and the atmosphere, it also results from the combination of soil, litter cuticle and stomatal exchange and the turbulent transfer between these compartments. (Loubet et al., 2002) found that the stomatal compensation point increased following fertilisation, but the magnitude of χ_s could not explain the NH_3 fluxes measured above. The GRAMINAE experiment performed in Braunschweig allowed us a far better understanding of the mechanisms leading to NH_3 emissions following cut and fertilisation, through a set combination of measurements and modelling (Sutton et al., 2009b). Indeed, the apoplast, soil and litter extractions showed that the emission potential (Γ) of the stomatal compartment was more than two order of magnitude lower than the soil Γ which was itself up to one order of magnitude lower than the litter Γ following cutting and fertilisation (Mattsson et al., 2009; Sutton et al., 2009a). The flux chamber method (cuvette) used in the field agreed with the apoplastic extractions in ranking the NH_3 emission potentials from each compartment (David et al., 2009). These cuvette measurements further showed that the litter emission potential decreased drastically when the litter was dried, and that the soil itself was a strong source immediately following cutting (David et al., 2009).

The cuvette and extraction techniques allowed ranking the emission potentials of each compartment. The modelling approach (Personne et al., 2009) allowed us to quantify the

contribution of each compartment to the net NH_3 flux and also to understand how the changes in the micrometeorological conditions following cutting contributed to the NH_3 fluxes. It was found that in tall grassland, the litter was a source of NH_3 but that the whole canopy was a weak sink overall. This result was further confirmed by an in-canopy inverse modelling approach indicating that the bottom 10 cm of the canopy was a strong source, but that NH_3 was recaptured at the top of the canopy (Nemitz et al., 2009c).

The NH_3 emissions observed after the grass was cut were explained by a combination of three factors: (1) the stomatal and cuticular sink were removed, (2) the transfer resistance between the litter and the soil to the upper layers was reduced, and (3) the litter temperature was increased by 5°C inducing an increase by a factor of two of the litter compensation point (Personne et al., 2009; Sutton et al., 2009b). Additionally, the larger day-to-night variations in temperature and the exposure of litter to radiative cooling at night would have exposed directly the litter to dew-fall, increasing mineralization and providing a larger potential for ammonia emission from this compartment (David et al., 2009).

The emissions following fertilisation are mainly explained by the emission potential from the ground surface. The litter surface was found to be the most likely source of NH_3 rather than the soil, based on resistance modelling (Personne et al., 2009) and cuvette measurements (David et al., 2009). Indeed, the additional transfer resistance through the litter would not reproduce the night time emissions measured following fertilisation (Personne et al., 2009). Moreover, the wet litter surface would have been efficient in moisturising the fertiliser pellets leading to emissions from the litter surface (David et al., 2009).

Towards a mechanistic model of ammonia stomatal compensation point

The NH_3 compensation point has been studied on a variety of plants from semi-natural, grasslands, forest or arable land, with the variety of techniques presented here (Massad et al., 2010a). Although these measurements allow to reach a good level of understanding of the response of stomatal Γ to environmental conditions (and especially nitrogen supply), there is still very little work done on modelling the stomatal compensation point in relation to plant metabolism. (Riedo et al., 2002) have proposed such a model (PASIM) for grasslands, based on a whole plant budget of apoplastic and symplastic nitrogen and a varying fraction of this ammonium in the apoplastic nitrogen pool. However PASIM tend to give too large stomatal compensation points but does not include litter emissions which are essential, as shown by the comparison with the GRAMINAE experimental results (Sutton et al., 2009a).

Based on this lack of modelling, (Massad et al., 2008) have reviewed the links between plant N metabolism and NH_3 stomatal compensation point χ_s in arable plants. The root uptake and xylem transport is of primary importance since it brings directly to the apoplast NH_4^+ and NO_3^- and also since it may affect the apoplastic pH. The phloem transport should be of smaller importance since it carries elaborated organic molecules such as sugars, amino acids and hormones. It however influences the photosynthesis cycle and as such may influence χ_s . Moreover, the phloem may play a large role in senescing leaves. The ammonium content in the apoplast then largely depends on its transport (active or diffusive) through the cell membranes. Passive transport is due to differences in concentrations or electrochemical gradients across the membranes, while active transport implies energetic

consumption in the form of Adenosine TriPhosphate (ATP) to transfer NH_4^+ against an electrochemical gradient. In the cell NH_x is produced by nitrate reduction but mostly by photorespiration, which is a source 10 times or more larger than nitrate reduction. However the Glutamate synthesis, which produces amino acids from carbon skeletons, based on the enzymes Glutamine Synthetase (GS) and Glutamate Synthase (GOGAT), is every efficient in assimilating the NH_x produced, which regulates the NH_x content in the cells. This later process however requires organic carbon as a substrate (which is produced by photosynthesis) and is inhibited by the accumulation of the amino acids produced. Finally the vacuole may be considered as a passive reservoir for NH_x and an active one for NO_3^- (Massad et al., 2008).

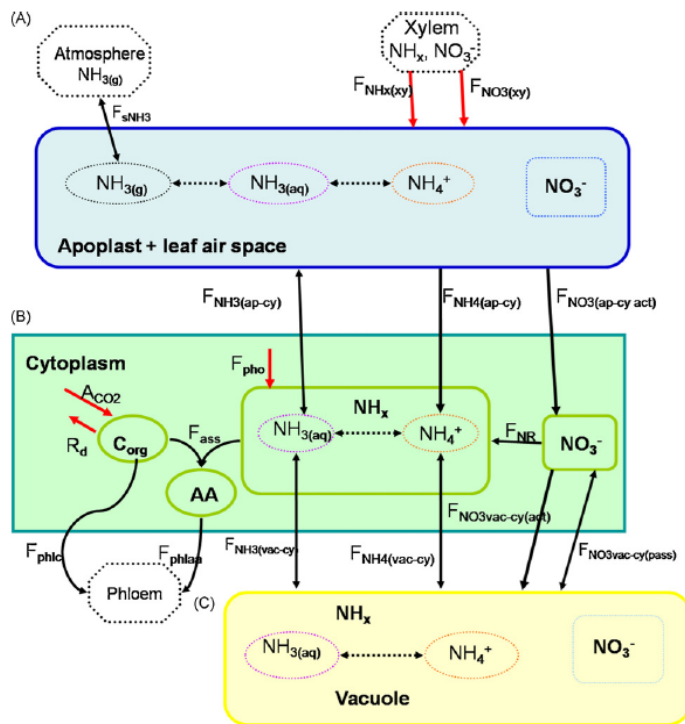


Figure 18. Scheme of the ammonia stomatal compensation point model, showing the compartments and the flows. Taken from (Massad et al., 2010b).

These processes have been implemented into the STAMP model by (Massad et al., 2010b) (Figure 18). The results of the STAMP model showed that the main driver of χ_s was the temperature and the xylem flux of ammonium to the leaves, and that the cytoplasmic and apoplastic compartments were relatively isolated from each other because of a small active transport. The photosynthetic and photorespiratory activities therefore also did not affect greatly χ_s . The model was further shown to be very sensitive to the NH_4^+ active

transport rate from the apoplast to the cytoplasm, which is a highly uncertain parameter. After tuning this active transport rate, a good agreement could be found between measured and modelled χ_s (Massad et al., 2010b).

6.3.1.4 Conclusions

- A range of methods and models have been developed to study the sources and sinks of NH_3 within plant canopies. These methods have proven to be useful when used together as they are complementary: extraction techniques and cuvette methods are useful in identifying the compartments contributing to NH_3 exchange and ranking their emission potentials (Γ). In turn, soil-plant-atmosphere resistance modelling was essential for quantifying the role of aerodynamic resistances, temperature and humidity effects on NH_3 exchange. Finally process based modelling allowed to identify the most essential processes that drives NH_3 stomatal compensation point, and gives new research directions.

- The studies conducted on grassland showed that the litter and the soil had the largest emission potential, while the growing leaves had always a lower emission potential. However, the litter and soil did not contribute to the total flux in a tall canopy because of both a large in-canopy aerodynamic resistance and recapture from the upper layer. Following a cut, NH_3 emissions occurred because of a combination of many factors, among which the exposure of the litter to the atmosphere and its increased temperature was dominant. In addition the increased daily dynamics in moisture at the litter interface (due to dew fall and drying) may also contribute to an efficient mineralization of the organic matter in the litter.
- A process model for the stomatal compensation point has been proposed, which shows, using the available parameterisation of the transfer rates between cell compartments, that the apoplastic and cytoplasmic compartments were quite isolated from each other. As a consequence, the modelled χ_s was found to be primarily dependent on NH_4^+ nutrition fluxes and not dependent on photosynthesis/photorespiration. These findings indicate that research on this topic should focus on transfer rates between the cell and the apoplast as well as on the apoplastic pH.

6.3.2. Ozone deposition and interaction with NO in agricultural fields

6.3.2.1 Introduction

Tropospheric ozone (O_3) is a major pollutant both affecting human health (Hubbell et al., 2005; Lippmann, 1993; Weschler, 2006), and ecosystems either agricultural or natural (Karnosky et al., 2007; Ren et al., 2007). Moreover, at the global scale, background O_3 concentrations have increased by a factor of two in the last century (Anfossi and Sandroni, 1997; Vingarzan, 2004), and model predictions suggests that it should continue rising by a factor 2 to 4 in the coming century (Vingarzan, 2004), due to increased of ozone precursor emissions by fuel consumption at the global scale (World Energy Outlook, 2007, International Energy Agency) and increased temperature (IPCC, 2007). In Europe, this increased background O_3 concentration should however be coupled with a decrease in the peaks magnitude because of a diminishing local pollution (NEG-TAP, 2001). Recent studies suggests that O_3 impacts on plants may reduce CO_2 absorption and therefore provide a positive feedback to the GHG budget (Felzer et al., 2007). Modelling O_3 exchange between the atmosphere and the biosphere and partitioning this O_3 deposition between stomatal and non-stomatal pathways is therefore becoming a challenge in terms of pollution and global warming issues.

Great progress has been made in the last 30 years on the understanding of the O_3 cycle in the troposphere (e.g. (Crutzen et al., 1999)). There are however still uncertainties in the processes controlling O_3 deposition to vegetal surfaces (Ashmore et al., 2007; Fowler et al., 2009). Ozone deposition has been studied for a range of vegetations. Some experiments have also been performed on O_3 deposition onto building materials (Grontoft, 2002; Usher et al., 2003). In the 1970s, (Bennett and Hill, 1973) and (Galbally and Roy, 1980) have provided a synthesis on O_3 deposition to vegetative canopy, and parameterised deposition velocities, which are still used in current models. Throughout the years, the deposition models have however evolved, by improved non-stomatal deposition (Altimir et al., 2004; Grantz et al., 1995; Lamaud et al., 2009; Zhang et al., 2002; Zhang et al., 2003; Zhang et al., 2006), or by inclusion of multi-layered deposition scheme (Walton et al., 1997), and chemical interactions within the canopy or above (Kohlmaier et al., 1997; Kramm et al., 1996; Kramm et al., 1995; Kulmala et al., 1999; Tuovien et al., 2001)(Brönnimann et al., 2001; Emberson et al., 2001). A review of modelling approaches is given in (Wesely and Hicks, 2000) and (Fowler et al., 2009).

These researches have brought the community to a consensus on the O_3 deposition process, which is represented as a sum of four pathways: stomatal absorption, soil deposition, cuticular deposition, and eventually chemical depletion in the air column. In this chapter we present some results of the researches undertaken to improve the understanding and parameterisation of these pathways. These researches mainly focussed on real conditions measurement of O_3 deposition velocities over crops, and its interaction with NO concentrations and fluxes.

6.3.2.2 Methods and concepts

This section presents the methods and modelling tools used in theses studies. The main methods used were the eddy covariance (EC) and the aerodynamic gradient (AG) methods

for O_3 , NO and NO_2 flux measurements. The principles of these methods have been presented in previous chapters; therefore we will focus here on specificities for O_3 and NO.

Eddy Covariance O_3 fluxes and NO fluxes

Ideally, the EC method consists in estimating the flux as average of the product of the concentration times the vertical component of the wind velocity, measured in an infinitely small volume at a frequency higher than the Kolmogorov frequency. However, in practice, the instrument used sample a large volume (ultrasonic anemometers, open-path instruments), and sample at a frequency below 50 Hz and most often below 10 Hz. Moreover, close-path instruments use a tubing to carry the sampled gas to the analyser, which lead to a mixing of the turbulent signal equivalent to a low-pass frequency filter. This is especially true for the ozone and NO analysers used here. The ozone analyser is a chemiluminescent close-path analyser (reaction with a cumarin dye fixed on a target) with a sampling line of around 2 m and sampling at around 10 Hz. The NO analyser is a chemiluminescent analyser (reaction with O_3) with a longer sampling line (3 to 7 m) and sampling at around 1 Hz.

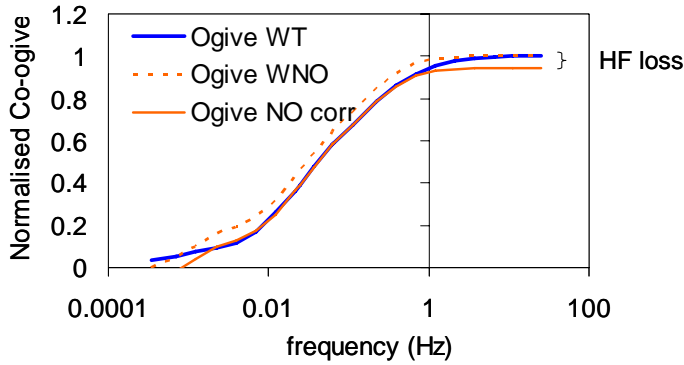


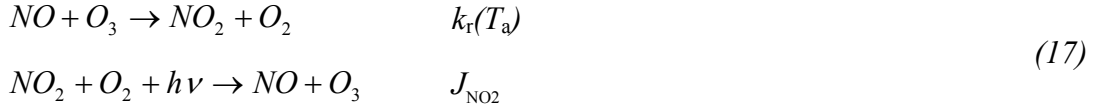
Figure 19. Example of the high frequency loss correction method based on ogive similarity between heat (WT) and NO (WNO). NO Corr is the corrected ogive (fitted to the WT ogive in the middle frequency range). The flux loss is the difference between the blue and the orange lines at the highest frequency.

which the points being too far away from the regression line were eliminated progressively (*robustfit* function under Matlab®). The high-frequency damping correction was simply evaluated as the value of the fitted NO (or O_3) co-ogive (Og_{wNO}) at the highest frequency. A novelty have been introduced whereby the frequency band over which the linear regression is performed is determined as the frequency for which Og_{wT} larger than 0.01 and Og_{wNO} is smaller than 0.8. The co-ogives were calculated using detrended signals. Figure 19 shows an example of the correction method with NO and T_a co-ogive as well as the fitted NO co-ogive and the corresponding estimation of the high-frequency attenuation. It shows a typical correction for NO and O_3 of less than 10%.

Due to the analysers' specificity, a high frequency loss correction method was adapted from (Ammann et al., 2006). Starting from the hypothesis of similarity between all scalars cross-spectra, the method consists in fitting the co-ogive for NO (or O_3) Og_{wNO} (the co-ogive is the integrated cross-spectra from low to high frequencies) against the co-ogive of air temperature Og_{wTa} . The fitting was made with an iterative linear least square method in

Turbulent and chemical time scales

The NO- NO_2 - O_3 triad is subject to chemical reactions in the air column, of which the following two are the most important to account for in the surface layer because of their quite small time scales.



where k_r ($= 44.4 \exp(-1370/(T_a + 273))$) in $\text{ppm}^{-1} \text{ s}^{-1}$ (Walton et al., 1997) and J_{NO_2} are the reaction rate and the photolysis frequency for the two reactions. These reactions may lead to a chemical source or sink for these compounds within the canopy but also in the air column above the canopy. The strength of these reactions will mainly depend on the time available during the travel of the air parcels in their pathways between the ground and a given height above the canopy. This travel time is called the turbulent transport time (τ_{trans} in s) between the ground and given height (z). It can be expressed as the transfer resistance through each layer multiplied by the layer height (Garland, 1977). If one considers the resistance scheme of Figure 17, the turbulent transport time would be:

$$\tau_{trans} \approx R_a(z) \times (z - d - z_0) + R_{ac} \times d \tag{18}$$

where $R_a(z)$ and R_{ac} are the aerodynamic resistances above and within the canopy, d and z_0 are the displacement height and roughness length. Following Lenschow (1982), the chemical time scale τ_{chem} can be estimated as a function of the reaction rate constants and the average concentrations within the pathway:

$$\tau_{chem} = \left[j_{NO_2}^2 + k_r^{*2} ([O_3] - [NO])^2 + 2j_{NO_2} k_r^* ([O_3] + [NO] + 2[NO_2]) \right]^{0.5} \tag{19}$$

This equation leads to asymptotic limits when NO, O_3 or NO_2 becomes the dominant specie. The chemical depletion time for O_3 then simply becomes $\tau_{chem} = 1 / (k_r^* [NO])$. Here k_r^* has been introduced. It is an average reaction constant accounting for the fact that O_3 and NO concentrations are fluctuating: $k_r^* = k_r \overline{[O_3]} \cdot \overline{[NO]} / (\overline{[O_3][NO]})$. Within the canopy, J_{NO_2} is decreasing due to shading and the reaction between NO and O_3 becomes the dominant reaction.

Aerodynamic Gradient Methods for O_3 and NO

In order to evaluate the fluxes and the chemical reactions between O_3 and NO_x above the ground surface, it is necessary to measure the concentration gradient and the fluxes together. A fast switching AG method was therefore developed for such measurements with chemiluminescent O_3 , NO and NO_2 analysers. The main issue for this method was to ensure a constant and large flow in the sampling lines and a fast switching between the levels in order to avoid chemical depletion in the tubes and non-stationary issues. The latter being a specific issue in the Grignon field site located close to large traffic roads (Stella et al., 2011b).

6.3.2.3 Results and discussion: Ozone non-stomatal deposition

Ozone fluxes have been measured in the Grignon field site since 2004 on maize, wheat, barley, mustard rotation. NO emissions were measured with automatic chamber methods from 2006 to 2010, and were also measured with the EC method in the summer 2008 and together with NO_2 fluxes with the AG method during experimental campaigns 2009 and 2010. The measured O_3 deposition velocity was used to parameterise O_3 exchange between the surface and the atmosphere. We will focus here on some results on the exchange with bare soil, with the cuticle and on the NO- O_3 interaction within and above the canopy.

Ozone deposition onto bare soil

Modelling correctly O_3 deposition onto bare soil is a prerequisite to correctly estimate the cuticular and stomatal deposition. It is as such an important pathway. Unfortunately, there are not many datasets reporting measured O_3 deposition onto bare soil and often deposition to the soil is modelled with a constant resistance, while a few studies report dependency of O_3 deposition to soil wetness (Massman, 2004) (Bassin et al., 2004).

In order to parameterise O_3 deposition onto bare soil, (Stella et al., 2011a) used three datasets from the Grignon field site. A correlation analysis showed that the main factor influencing the soil resistance for O_3 ($R_{soil}(O_3)$) was the relative humidity of the air in contact with the ground, estimated as the relative humidity at z_0 (Figure 20). Although $R_{soil}(O_3)$

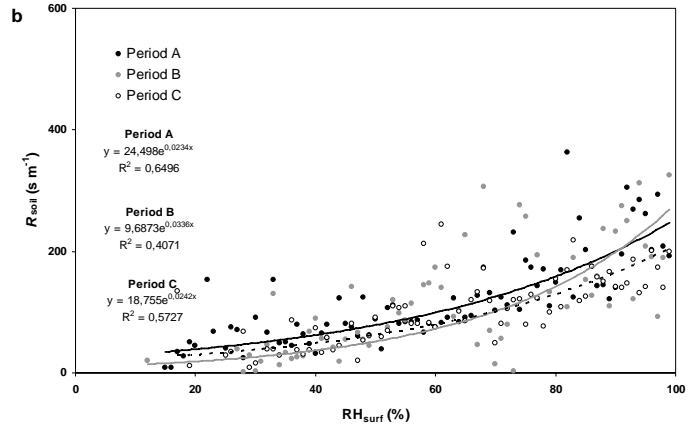


Figure 20. Relationship between soil intrinsic resistance and relative humidity at z_0 . From (Stella et al., 2011a)

was found to vary with surface temperature and air relative humidity, the surface relative humidity was found to be the parameter working on the largest dataset. The soil resistance was found to increase with increasing surface relative humidity which is contrary to what was found for cuticular resistance (Lamaud et al., 2009). (Stella et al., 2011a) found that $R_{soil}(O_3) = (21 \pm 1) \exp[(0.024 \pm 0.001) RH(z_0'_{soil})]$. This relationship can be explained by a decreasing ratio of dry soil surface to wet soil surface with increasing relative humidity. Since O_3 is not soluble, its deposition may be decreased. In a theoretical approach, (Tuzet et al., 2011) found a similar explanation, where the soil resistance is increasing with the increasing soil dry layer thickness. The parameterisation of (Stella et al., 2011a) has improved significantly the agreement between modelled and measured deposition velocity over bare soil in Grignon when compared to the parameterisation proposed by (Bassin et al., 2004). However, this parameterisation was found to fail when soil NO fluxes were large although a simple NO - O_3 chemical reaction scheme could not explained the enhanced deposition rate. Moreover, this parameterisation would need to be further tested on different soil textures as it should be expected that the response to surface relative humidity would be different.

Ozone and NO interactions in and above the canopy

The reaction between NO , NO_2 and O_3 is expected to play a role in air-surface exchange of NO_x and O_3 . Two main issues are of interest: (1) the NO emitted from the ground reacts with O_3 to form NO_2 while it is travelling upwards, leading to flux divergences; and (2) the advected NO - NO_2 - O_3 react within the canopy space. The first issue is well known and has been studied by several authors (Duyzer et al. 1995), while the second has been less studied.

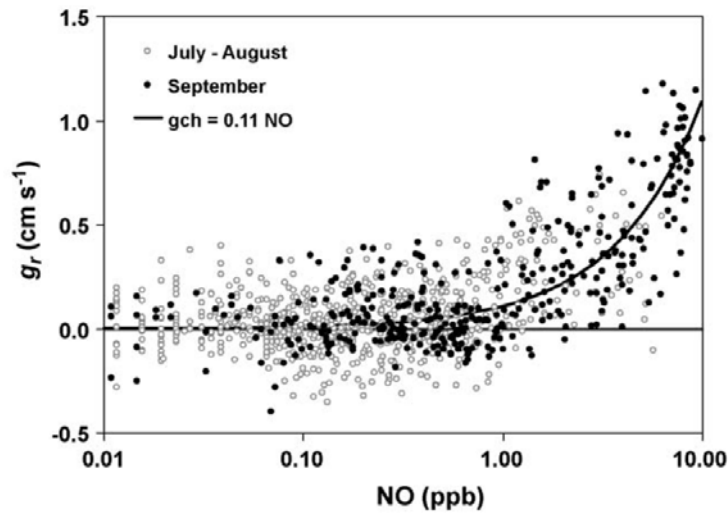


Figure 21. Residual conductance for ozone as a function of the NO concentration in a maize canopy. From (Lamaud et al., 2009). The residual conductance is estimated as the difference between the measured conductance and the sum of cuticular, soil and stomatal conductances.

found that this linear correlation could be explained by the reaction of O_3 with NO within the canopy. Indeed, developing upon the approach of (Dearellano and Vanweele, 1993), we could stipulate that the equivalent conductance due to chemical depletion of O_3 would be equal to the length of the pathway divided by the chemical time scale. Applied to the canopy pathway, one gets.

$$g_{chem} = h_c / \tau_{chem} = k_r \times [NO] \times h_c \quad (20)$$

In (Lamaud et al., 2009) we interpreted this chemical reaction as the reaction above the canopy, but since we had $(z_m - d - z_0) = 2.75 \sim h_c$, both interpretation could be real. Equation (20) (which gave a numerical application of $g_{chem} = 0.11[NO]$) was found to fit very well the residual conductance (Figure 21), suggesting that chemical depletion of O_3 would be a powerful pathway for O_3 deposition (g_r up to 1 cm s^{-1}) in polluted areas, where NO concentrations would be larger than 0.5 to 1 ppb.

In (Stella et al., 2011b), the effect of chemical reactions of the NO- O_3 -NO₂ triad on the NO, O_3 and NO₂ fluxes has been studied over a bare soil following slurry application. The very dry conditions encountered in this study led to quite small and very short in time NO emissions: two days emissions following a rainfall event, with maximum fluxes of $7 \text{ nmol m}^{-2} \text{ s}^{-1}$. The chemical reaction between NO and O_3 was found to generate a divergence of up to 10% for the NO and NO₂ fluxes but affected the O_3 fluxes by less than 1% on average owing the magnitude of each flux (the O_3 flux was around ten times stronger than NO and NO₂ fluxes). Moreover, when the chemical time

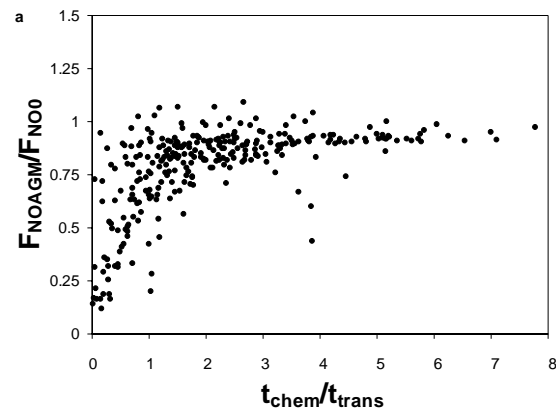


Figure 22. Ratio of NO flux at 1.5 m to the ground NO flux as a function of the ratio of the chemical to turbulent transport time scales. From (Stella et al., 2011b)

scale was of the same order as the transport time scale the NO and NO₂ flux divergence could reach up to 80% of the flux.

6.3.2.4 Summary and conclusions

- Ozone deposition onto bare soil was found to decrease with relative humidity of the air at the ground surface. This relationship is currently explained by the diminution of the effective surface available for O₃ deposition with increasing wetness. Whether this relationship found in Grignon would hold onto other soils however remains to be checked. The effect of litter or mulch should also be studied for completeness.
- The chemical reaction between NO and O₃ was found to play a significant role in a tall canopy like maize for NO concentrations larger than 1 ppb. In such a case, it can either be the advected NO that reacts with O₃ therefore adding a chemical deposition pathway which can simply be expressed as the pathway length divide by the chemical time scale. This simple framework should be tested to check under which conditions this chemical depletion would be a significant sink for O₃.
- Ozone in turns affects NO fluxes from the ground by transforming NO into NO₂ while it is transported away from the ground surface. This process was found to represent up to 10% of the NO and NO₂ fluxes above a bare soil. On the contrary NO fluxes have very little impact on the O₃ flux (less than 1% divergence).

6.3.3. Carbon and nitrogen cycles of a crop rotation

6.3.3.1 *Introduction*

Agriculture has been estimated to account for 10–12% of the total anthropogenic greenhouse gas (GHG) emissions in 2005. GHG emissions from agriculture are dominated by fluxes of nitrous oxide (N₂O: 54%) and methane (CH₄: 46%) with carbon dioxide representing a minor contribution (CO₂: 1%) (Smith et al., 2007). Among agricultural lands, croplands seem to be mostly sources of carbon for the atmosphere with a very variable net biome productivity (NBP) ranging from $-40 \text{ g C m}^{-2} \text{ y}^{-1}$ to more than $-300 \text{ g C m}^{-2} \text{ y}^{-1}$ (Beziat et al., 2009). Examples of croplands acting as systematic sinks of carbon (Aubinet et al., 2009) highlight the potential of agricultural management for mitigating GHG emissions from croplands. Among potential management options, the conversion of cropland into grassland would be most effective. Abandoning or reducing the intensity of tillage is also recommended to reduce net emissions from croplands at least transiently by increasing storage of C and N in topsoil layers, although the efficiency of these measures are still a subject of debate (Angers et al., 1997). (Baker et al., 2007) even pointed out that most of the experimental evidence of reported benefits may have been biased and that long-term experiments have shown no beneficial effect at all. In addition to reduced tillage, re-incorporating carbon-containing organic fertilizers back onto croplands has been advocated as another option to reduce net carbon losses of agricultural land (Freibauer et al., 2004; Smith, 2004). Application of organic fertilizers is, however, known to increase emissions of other greenhouse gases, particularly nitrous oxide (N₂O). The very stable gas N₂O is thought to contribute 6% to the combined radiative forcing, and arable soils are responsible for 60% of the global anthropogenic N₂O emissions (Smith et al., 2007). Emissions of N₂O result mainly from nitrification and denitrification in soil, increase with increasing nitrogen supply, and critically depend on soil temperature, soil moisture, and soil density (Flechard et al., 2007; Henault et al., 2005; Skiba et al., 2009).

Beyond the GHG balance, other environmental effects of increasing manure supply (as a mitigation option) should be considered, such as ammonia (NH₃) and nitrogen oxides (NO_x) emissions to the atmosphere, which contribute to atmospheric pollution and are considered as an environmental threat to (semi-) natural ecosystems (Fowler et al., 2009). Another issue is the potential effect of increasing fresh organic carbon supply to the soil (plant exudates and residues, organic amendment) on the mineralization of “old” soil organic carbon, the so-called “priming effect” (Fontaine et al., 2007). While solid manure has been observed to promote carbon sequestration in soils, liquid manure, which contains highly decomposable carbon, may lead to a large priming effect at intermediate application rates (Angers et al., 2010). In addition, questions rise on the link between organic carbon and nitrogen in soils and the effect of either carbon or nitrogen loss or gain on the coupled system. Long-term experiments suggest that the C:N ratio may increase with fertilization and especially with farmyard manure supply, but never to reach the levels of C:N observed in grassland and forest soils (Blair et al., 2006).

These issues point towards the need to measure carbon, nitrogen and GHG fluxes above croplands and in the long term in order to (1) evaluate and compare the components of the nitrogen and carbon fluxes over the years and crop rotations, (2) estimate the uncertainty in

the different components of the carbon and nitrogen fluxes and discuss them, and (3) estimate the carbon, nitrogen and GHG balances of these ecosystems, where N₂O may be a large contributor. In this chapter, we present measurements and estimations of the components of the carbon and nitrogen fluxes over a maize-winter wheat-winter barley-mustard crop rotation in the north of France between 2006 and 2009.

6.3.3.2 Methods

The methods used to measure the N and C flux components were described in (Loubet et al., 2007; Loubet et al., 2011b; Skiba et al., 2009; Sutton et al., 2007) and are therefore not detailed here, apart from a short description of the field site, the CO₂ fluxes and the N₂O flux measurements.

The Grignon field Site

The Grignon site (48.9 N, 1.95 E) is located at around 40 km west of Paris, France. It consisted in a 20 ha field located on a plateau with a gentle slope towards the north-east and surrounded by gentle valleys. The instrument fetches ranged from 100 m to more than 400 m. The farm is substantial with 200 cattle, 500 sheep and a production of 900 lambs per year on average. The field was managed with the following crop rotation: maize, winter wheat, winter barley, mustard, and with reduced tillage since 2000. The field received a variable amount of nitrogen ranging between 150 and 300 kg N ha⁻¹ y⁻¹ mainly as nitrogen solution and cattle manure (usually once every three years). The soil is a silt loam with 18.9% clay and 71.3% silt in the top 15 cm, organic carbon content was around 20 g C kg⁻¹ and pH (water) was 7.6, while the bulk density was 1.3 g m⁻³. The soil was much deeper to the south-west where it reached more than 1 m while to the north-east where its depth was less than 0.6 m.

The CO₂ fluxes

The sensible heat, CO₂ and water fluxes were measured by the eddy covariance method, with an infrared gas analyser (7500, Licor, USA) coupled with a sonic anemometer (R3, Gill, UK) sampling at 50 Hz. The Net Ecosystem Exchange (NEE) was computed according to the CEU methodology (Aubinet et al., 2000). The NEE was then gap filled and partitioned with the method of (Reichstein et al., 2005), to obtain the Gross Primary Production (GPP) and the ecosystem Respiration (Reco), which are linked together by the following relationship: $NEE = GPP - Reco$.

The CO₂/N₂O/NO chambers

The CO₂, N₂O and NO_x fluxes were measured using 5 to 6 automatic chambers which are described in details by (Laville et al., 2009; Laville et al., 2011). Each chamber (0.7×0.7 m²) was sampled sequentially for 15 minutes for N₂O, CO₂ and NO_x. The CO₂ and N₂O fluxes were estimated from gas accumulation in the chamber during the 15 minutes period, while NO fluxes were estimated during the first 15 s and corrected for reaction with ozone as detailed in (Laville et al., 2011). The spatial variability between the chambers was around 30% for CO₂ and NO_x and around 70% for N₂O. The protocol is detailed in (Loubet et al., 2011b).

6.3.3.3 *Results and discussion*

Respiration, assimilation and net carbon fluxes

The crop rotation was a net sink of CO₂ of NEP of $+4.4 \pm 0.7 \text{ Mg C ha}^{-1} \text{ y}^{-1}$. The inter-annual variability of the carbon fluxes was mainly due to changes in TER ($-8.2 \text{ Mg C ha}^{-1} \text{ y}^{-1}$ and 22% CV over 5 years), while the GPP was remarkably stable ($12.3 \text{ Mg C ha}^{-1} \text{ y}^{-1}$ and 2% CV over 5 years). The comparison between the automatic chamber CO₂ fluxes and the TER showed a very good agreement when the chamber enclosed the canopy (during wheat, barley, and mustard periods). This congruence supports the plausibility of the results of both methods for characterizing ecosystem respiration. These latter results suggested that measuring only TER by chambers could be an alternative to estimating NEP by Eddy Covariance systems since GPP was almost constant. The mustard catch-crop limited the C losses over winter, with an average carbon balance of zero. These estimations were based upon long term integration of fluxes of carbon and nitrogen compounds measured with the Eddy Covariance and the chamber method, together with estimated exports and imports. This study shows this method to be highly uncertain. The uncertainty on carbon fluxes linked with the energy balance deficit need to be further investigated as this is a general feature in many sites as shown by Franssen et al. (2011). A special attention should also be taken to estimate the exported biomass.

Nitrogen fluxes

Ammonia volatilization of $-28 \pm 7.3 \text{ kg N ha}^{-1}$ following slurry spreading was the largest observed N flux. However, since slurry was only spread every three years on average, it would represent only around $-9 \text{ kg N ha}^{-1} \text{ y}^{-1}$ loss every year. Nevertheless, incorporation of manure following its application may have a great potential for reducing N losses from the crop rotation provided that higher leaching losses of nitrate could be avoided. The time intervals of three years between applications of slurry hamper the definition of starting and end points for the calculation of mass balances. Longer observation periods, e.g. at least nine years, would smooth “edge” effects related to the choice of starting and end points leading to improved average balances of the crop rotation. Nitrate leaching was the most significant yearly contribution to the N fluxes at the site constituting a loss of $-11.7 \pm 1.0 \text{ kg N ha}^{-1} \text{ y}^{-1}$. Dry and wet deposition added 6.7 ± 3.0 and $5.9 \pm 0.1 \text{ kg N ha}^{-1} \text{ y}^{-1}$, respectively, to the field. However the estimated N dry deposition was very uncertain with a standard deviation between the four models of $3.30 \text{ kg N ha}^{-1} \text{ y}^{-1}$, an uncertainty mainly due to the discrepancy in NH₃ deposition estimates. Moreover soluble organic nitrogen deposition was not taken into account and it may well contribute significantly to the N deposition in the Paris area. The N₂O and NO fluxes did not contribute significantly to the N budget (N₂O flux: $-1.8 \pm 0.04 \text{ kg N ha}^{-1} \text{ y}^{-1}$ NO flux: $-0.7 \pm 0.04 \text{ kg N ha}^{-1} \text{ y}^{-1}$). The inter-annual variability of the N₂O fluxes was high, and most likely related to the soil water content during the spring (which is also during the nitrogen fertilization period) and the mineral nitrogen content of the soil during the autumn (which corresponds to the period when crop residues are decomposed). Nitrogen losses via denitrification and N-fixation were both neglected in our study, despite their potential relevance for the overall nitrogen balance. The improvement of field methods for estimating denitrification and nitrogen fixation should help estimating this component in the future.

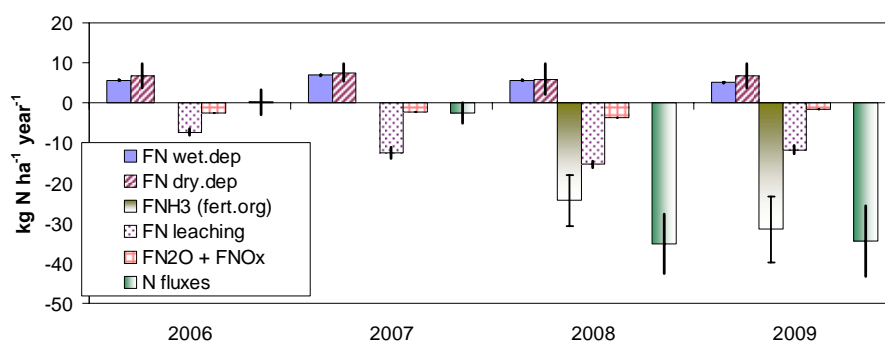


Fig. 10. Details of the N fluxes estimated over the period 2006-2010. “FN wet. dep.” stands for nitrogen wet deposition (ammonium and nitrate); “FN dry. dep” stands for nitrogen dry deposition (NH_3 , NO_2 , HNO_3 , aerosols NH_4^+ , NO_3^-); “FNH3 (fert. org)” stands for NH_3 volatilization following organic fertilization; “FN leaching” stands for nitrogen leaching (nitrate); “FN2O + FNOx” stands for N_2O and NO_x emissions; and “N fluxes” is the sum of the previous nitrogen fluxes. Negative fluxes denote a loss from the system and vice versa. The error-bars show the uncertainty on the measurements.

The C, N and GHG budget of the rotation

Despite a NEP of $+4.4 \pm 0.7 \text{ Mg C ha}^{-1} \text{ y}^{-1}$, the investigated crop rotation was a net source of carbon with a NBP of $-1.3 \pm 1.1 \text{ Mg C ha}^{-1} \text{ y}^{-1}$ when imports of carbon with organic fertilizers and exports with harvested biomass and leached water were included in the balance. This carbon loss would represent a loss of 1.1% of the soil organic carbon stock per year. Carbon imports of $0.4 \text{ Mg C ha}^{-1} \text{ y}^{-1}$ with organic fertilizers would have to be multiplied by four to compensate the observed net loss of carbon. The nitrogen balance was slightly negative, with a loss of $-38 \pm 28 \text{ kg N ha}^{-1} \text{ year}^{-1}$ over the four year period studied. The crop rotation was a net source of GHG with an equivalent loss of $-1.5 \pm 1.1 \text{ Mg C-eq ha}^{-1} \text{ y}^{-1}$. Although N_2O fluxes were small, they contributed up to 16% of the GHG budget. Since the soil respiration represented approximately 50% of TER and variations in TER largely determined annual carbon budgets, any practice reducing soil respiration should increase the net carbon uptake of the crop rotation. Indeed, our data suggest an increasing trend of NEP and NBP. Because largest carbon losses through respiration were observed under maize, improving the management of the catch crop between barley and maize seems essential for decreasing the overall carbon losses.

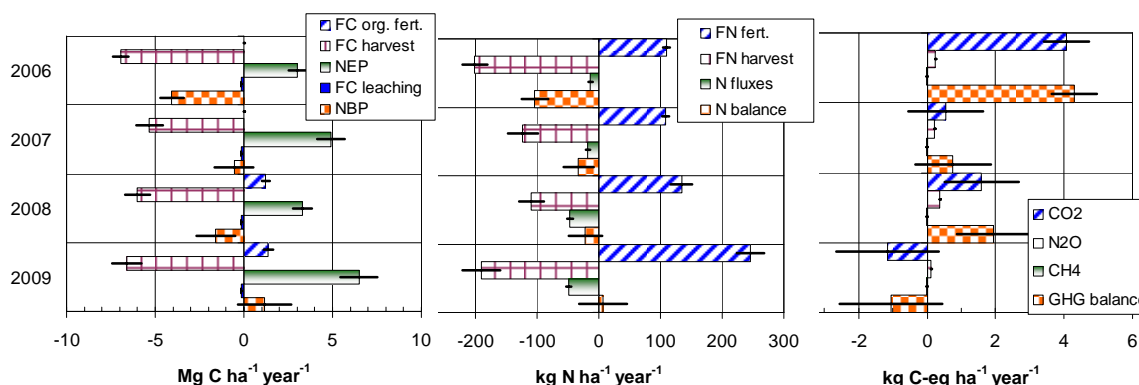


Fig. 8. Carbon, nitrogen and greenhouse gas balances of the field over the period 2006-2009. “N fluxes” is the sum of dry and wet de position, N leaching, N_2O and NO_x fluxes and NH_3 volatilization. For the C and N balances, positive numbers denote a gain for the field while negative ones denote a loss, while for the GHG it is the opposite.

6.3.3.4 *Conclusions*

- Croplands mainly act as net sources of the greenhouse gases carbon dioxide (CO₂) and nitrous oxide (N₂O), as well as nitrogen oxide (NO), a precursor of tropospheric ozone. We determined the carbon (C) and nitrogen (N) balance of a four-year crop rotation, including maize, wheat, barley and mustard, to provide a base for exploring mitigation options of net emissions.
- The crop rotation had a positive net ecosystem production (NEP) of $4.4 \pm 0.7 \text{ Mg C ha}^{-1} \text{ y}^{-1}$ but represented a net source of carbon for the atmosphere with a net biome production (NBP) of $-1.3 \pm 1.1 \text{ Mg C ha}^{-1} \text{ y}^{-1}$. The nitrogen balance of the rotation increased with the carbon balance and resulted in net losses of $-38 \pm 28 \text{ kg N ha}^{-1} \text{ y}^{-1}$.
- The main nitrogen losses were nitrate leaching ($-11.7 \pm 1.0 \text{ kg N ha}^{-1} \text{ y}^{-1}$) and ammonia volatilization ($-9 \text{ kg N ha}^{-1} \text{ y}^{-1}$). Dry and wet depositions were 6.7 ± 3.0 and $5.9 \pm 0.1 \text{ kg N ha}^{-1} \text{ y}^{-1}$, respectively. Fluxes of nitrous (N₂O) and nitric (NO) oxides did not contribute significantly to the N budget (N₂O: -1.8 ± 0.04 ; NO: $-0.7 \pm 0.04 \text{ kg N ha}^{-1} \text{ y}^{-1}$) but N₂O fluxes equaled 16% of the total greenhouse gas balance.
- Longer term experiments would be necessary to capture the trends in the carbon and nitrogen budgets within the variability of agricultural ecosystems.

6.4. Summary

NH₃ emissions from hot-spots. The contribution of my research on NH₃ emissions from hot-spots mainly focussed on developing, evaluating and improving methods to estimate NH₃ emissions from hot-spots. A multi-level NH₃ wet-chemistry analyser (ROSAA) was developed and proved to be reliable when compared to reference methods such as the passive diffusion samplers. The ROSAA analyser was also positively compared to inverse modelling methods to estimate NH₃ volatilisation following slurry spreading. A simple Eulerian dispersion and deposition model (FIDES) was developed and used to retrieve NH₃ emissions from fields and farm buildings by inverse modelling and also to evaluate local advection errors. The inverse modelling approach with FIDES was proven to be valid to estimate NH₃ emissions from field sources, and the hypothesis of “surface concentration-driven” source (which is equivalent to a compensation point hypothesis) was proven to be necessary only for very small fields (smaller than around 20 m). The inverse modelling methodology was suggested to work with time-integrated concentration up to monthly periods, with however a systematic error which can be up to 30% for 100 m large fields. Although NH₃ emission is a known mechanism, there is a lack of measurements in real conditions, and especially in France. Moreover, recent measurements suggest that the current emission factors of NH₃ volatilisation should be revised. Moreover, new application methods, diet changes, or application of new residual organic matter (like residues of digesters) points toward a renewed necessity to directly measure NH₃ emissions from all agricultural sectors.

NH₃ deposition near hot-spots. The ammonia emitted from these hot-spots is dispersed in the atmosphere. However, in the short-range, the high concentrations lead to large deposition rates which can reach 60% of the emissions within 1 km. Two models were developed to study NH₃ deposition near hot-spots, an Eulerian model (FIDES) and a Stochastic Lagrangian model (MODDAAS). Dry deposition of NH₃ near hot-spots is essentially sensitive to the wind speed at the source height, the deposition resistances, and hence the LAI, and the soil and stomatal compensation points. It was further shown that non-stomatal deposition can increase local NH_x deposition by a factor of two or three. Using MODDAAS coupled with the Thetis *k*- ϵ model, mitigation options were studied to reduce NH₃ emission to the environment by placing the source within a tree-belt. This method was found to recapture at most 30% of the NH₃ emitted by a farm building within a hundred meter. However silvopastoral systems may be seen as a good alternative which leads to higher recapture efficiency due to a better sheltering of the source. It was however stressed out that these studies on short-range deposition are difficult to validate, since measuring NH₃ fluxes under advective conditions or with complex geometries remains a challenge which is still to be faced and we have to rely on surface exchange models which are studied under homogeneous field conditions or in laboratories. Finally the benefits in terms of NH₃ recapture on the local scale should be balanced with the potential threats to the environment that this additional reactive nitrogen load may cause, like indirect NH₃ and N₂O emissions, acidification, or nitrate leaching.

Maize pollen short-range deposition. The case of pollen dispersal is different from NH₃ in terms of topic but it is actually very close in terms of methodology (models, measurements). Indeed, the MODDAAS Lagrangian stochastic dispersion model was adapted to account for

gravity and inertia. Additionally to this modelling work, measurements of pollen concentrations, fluxes and pollen viability were developed. Especially, a novel method to measure the distribution of settling velocity V_s was set up, after V_s was identified as one of the main parameter driving the local dispersion. Taken together, all these studies have substantially improved our understanding of local contamination of maize field with exogenous pollen. Three main findings can be retained: (1) the settling velocity distribution of maize was found to be bi-modal, with one mode corresponding to the light, dry and non-viable pollen and the other one to the heavy, viable pollen; (2) the measured deposition pattern was found to follow a power law function of x / h_c over distances lower than 150 m and a smaller deposition at further distances; (3) the deposition velocity in the lee of the emitting canopy was significantly higher than the settling velocity, an effect that could be explained by an increased V_s by turbulent sweeping and particle clustering when the particle response time is of the order of the fluid characteristic time. Finally, this work has also pointed toward one major parameter for the dispersion (the settling velocity, V_s), which may also be an interesting proxy to account for the pollen water content and therefore for the pollen viability.

Sources and sinks of NH_3 in a canopy and the stomatal compensation point. A range of methods and models have been developed to study the sources and sinks of NH_3 within plant canopies. These methods have proven to be complementary: extraction and cuvette methods can be used to identify and rank the compartments contributing to NH_3 , while resistance modelling was essential in quantifying the environmental control on NH_3 exchange, and process based modelling allowed to identify the most essential processes driving NH_3 stomatal compensation point. The studies conducted on grassland showed that the litter and the soil had the largest sources, while the growing leaves were mainly a sink. However, due to efficient recapture by green leaves and low turbulence within the dense canopy, the soil and the litter did not contribute to the total flux in a tall canopy. Following a cut, NH_3 emissions occurred because of a combination of exposure of the litter to the atmosphere, and increased temperature and an increased wetness variability of the litter promoting biological activity. A process model for the stomatal compensation point has been proposed, which shows, using the available parameterisation of the transfer rates between cell compartments, that the apoplastic and cytoplasmic compartments were quite isolated from each other. As a consequence, the modelled χ_s was found to be primarily dependent on NH_4^+ nutrition fluxes and not dependent on photosynthesis/photorespiration. These findings indicate that research on sources and sinks of NH_3 in a canopy should focus on litter emissions, cell-apoplast NH_3 transfer rates as well as the pH in the litter, cuticle, soil and apoplastic compartments.

Ozone deposition and interaction with NO in agricultural fields. Ozone deposition onto bare soil was found to decrease with relative humidity of the air at the ground surface. This is explained by the diminution of the dry soil surface available for O_3 deposition with increasing wetness. It is likely that this empirical relationship found in Grignon would not hold as such in other soils, but may require including soil structural parameters such as the soil porosity. The chemical reaction between NO and O_3 was found to play a significant role on O_3 deposition velocity in a tall canopy like maize for NO concentrations larger than 1 ppb. In such a case, it can either be the advected NO that reacts with O_3 therefore adding a chemical deposition pathway which can simply be expressed as the pathway length divide

by the chemical time scale; a simple approach that should be checked against measurements. Ozone also affects NO fluxes from the ground by transforming NO into NO₂ while it is transported away from the ground surface. This process was found to represent up to 10% of the NO and NO₂ fluxes above a bare soil. On the contrary NO fluxes have very little impact on the O₃ flux (less than 1% divergence).

Carbon and nitrogen cycles of a crop rotation. The fluxes of the major C and N compounds were followed in a maize, wheat, barley mustard rotation in Grignon. From these measurements, it was found that the rotation was an efficient CO₂ sink with a net ecosystem production (NEP) of 4.4 Mg C ha⁻¹ y⁻¹. However, if it is assumed that the exported carbon is quickly transferred back to the atmosphere, the rotation became a source of CO₂ to the atmosphere of -1.3 Mg C ha⁻¹ y⁻¹. The nitrogen balance of the rotation increased with the carbon balance and resulted in net losses of -38 kg N ha⁻¹ y⁻¹. The main nitrogen losses were found to be nitrate leaching and ammonia volatilization, while dry and wet depositions also significant. Fluxes of N₂O and nitric NO did not contribute significantly to the N budget but N₂O fluxes equaled 16% of the total greenhouse gas balance. Finally the very large uncertainties in the flux method, and the very large year-to-year variability in the budgets claims for longer term experiments to capture the trends in the carbon and nitrogen budgets within the variability of agricultural ecosystems.

6.5. Conclusions

6.5.1. *Environmental control of pollutant, GHG and particle exchanges between managed ecosystems and the atmosphere*

These researches showed the *central role of the environmental conditions on NH₃ and O₃ exchange between terrestrial ecosystems and the atmosphere*. Indeed, for these pollutants, which exchange depends primarily on the thermodynamic equilibrium between the surfaces (liquid for NH₃, solid for O₃) and the atmosphere, the *turbulent transfer* is an essential process. This was demonstrated in the grassland study where the NH₃ emission potential of the litter was shed by the transfer through the leaves, but also in the short-range dispersal studies where the wind speed was found to be one of the main parameter driving the short-range deposition. It was also shown in the study on O₃ where it was found that the non-stomatal pathway represented the largest deposition pathway, and was primarily driven by u^* . The turbulent transfer is also the primary factor affecting particle transfer over the short-range, and special attention should be paid to the turbulent structures with characteristic times of the same order of the particle response time. Turbulent transfer is however not the primary factor for biogenic sources like N₂O, NO and CO₂ respiration.

For the same reasons of thermodynamic equilibrium, the *surfaces temperatures* are also essential, and their roles were also clear in increasing the litter NH₃ emissions. The *humidity* also plays an essential role in affecting the cuticular deposition of both NH₃ and O₃. However, if the adsorption process on water films has been clearly demonstrated for NH₃, the underlying process leading to an increased cuticular deposition of O₃ with relative humidity remains unclear. But it is clear that the humidity affects the exchange of O₃ and NH₃ with the surface. Indeed, it was shown that water, as a key compound for biological processes, plays an essential role in litter NH₃ emissions or NO soil emission and in turn O₃

deposition. Moreover, the presence of water at the soil surface changes the surface of dry soil available for O₃ deposition.

6.5.2. Major compartments of the ecosystems involved in these exchanges

In terms of ecosystems compartments, it appears that the *dry layer of soil and the litter layer* are key compartments to study pollutant exchange between the surface and the atmosphere. Indeed, the thickness of the dry layer of soil was suggested to control the O₃ exchange at the soil surface, but also clearly changed the NH₃ emission potential measured in cuvettes. As already mentioned, the litter plays a major role in controlling NH₃ emissions. Ozone deposition to litter leaves has never been studied but it may affect the turbulent transfer to the ground and may also be impacted by volatile organic compounds emissions. The soil and litter compartment are also essential for other pollutant emissions like NO, pesticides, or greenhouse gas emissions (N₂O, CO₂ through respiration). It is also the place of poorly quantified processes like biological fixation and denitrification (N₂O, N₂).

The *cuticle* is also an essential compartment of O₃ and NH₃ exchanges, which remains poorly understood for O₃ and not well quantified for NH₃. The difficulty in studying cuticle exchange processes is that it is difficult to isolate this pathways from the soil and stomatal pathways. It therefore requires having a very robust parameterisation of the soil and stomatal pathways to allow estimating the cuticular pathways. This was clear in the study of O₃ deposition to maize, where a new approach for estimating the stomatal conductance (a modified Penman Monteith approach using the GPP) had to be developed prior to estimating the non-stomatal deposition. The cuticle was also identified as an essential pathway for pesticides emissions following application onto a canopy.

The *stomatal*, and more generally, the leaf is also an essential compartment when studying both O₃ and NH₃ exchange between the atmosphere and the biosphere. For O₃, the question mainly resides in the potential impact of O₃ on the leaf functioning, the detoxication potential of the leaf and the reaction with ascorbate in the apoplast, while for NH₃, the main question resides in the exchange rates of NH₃ between the cells and the apoplast and the pH of the apoplast. It is striking to note that the apoplastic pH is a key factor in both O₃ and NH₃ exchange processes since ascorbate is one of the major constituent affecting the pH of the apoplast.

The *within-canopy air layer* should also be considered, especially for dense and tall canopies favouring long transfer timescales, and fast reacting chemical species. The chemical source-sink term for O₃ was found to be significant for advected NO conditions with concentrations larger than 1 ppb in a tall maize canopy, while NO fluxes may be affected by ambient O₃ concentration even over bare soils.

6.5.3. Biological versus anthropogenic control of pollutant, GHG and particle exchanges between managed ecosystems and the atmosphere

At the plant level, the canopy development can be considered as the major biological process controlling the surface exchange of pollutants and pollens. Indeed, the surface exchange primarily depends on the surface available, which is the soil surface plus the leaf

area. Moreover, we found that the canopy structure is essential in controlling the turbulent transfer both horizontally and vertically. The stomatal aperture can be viewed as the second major biological factor controlling the exchange of NH_3 and O_3 between the surface and the atmosphere. For NH_3 , the nitrogen metabolism of the plant is also essential in controlling the stomatal compensation point through the NH_4^+ concentration in the apoplast and the pH. For the CO_2 , the biological control of the plant is critical *via* the photosynthesis, the autotrophic respiration, but more generally *via* the plant nitrogen metabolism, including symbiotic fixation.

The litter decomposition was found to be essential in NH_3 emissions from grasslands but also in oilseed rape, over short time scales. Moreover, organic matter decomposition at the soil surface or in the soil is an essential process controlling long term carbon and nitrogen balances. In the soil, the nitrogen and carbon metabolisms are essential in controlling the GHG emissions and the heterotrophic respiration but also the NH_3 long term exchange via the NO_3^- and NH_4^+ concentration in the soil. Soil biological activity also controls the NO emissions which very slightly affects the O_3 fluxes locally but to a larger extent at the regional and global scale.

However, in a managed ecosystem, all these biological processes are at least perturbed and at most controlled by management. The canopy specie and genotype as well as the dates of sowing and harvesting are chosen by the farmer. The specie composition during the growth and the biological aggressions are controlled by pesticides applications. The nitrogen status of the ecosystem is controlled by nitrogen applications as fertiliser, and the field receives various organic residual matters depending on the stocks accumulated in other part of the farm. The quantity of residues left in the field is also controlled and the soil itself is perturbed by cultivation harvesting and pesticide application, leading to significant GHG, reduced nitrogen and particle emissions to the atmosphere. Moreover, the wet and dry deposition of nitrogen can be primarily attributed to anthropogenic activities. Finally, ozone is also a typical anthropogenic pollutant, which affects the plant growth.

It may therefore be argued that the major control of the pollutant, GHG and particle exchanges between managed ecosystems and the atmosphere is by the human activity. This shows the great responsibility but also the opportunity we have to optimise the management of these ecosystems not only in terms of economical and social benefits but also in terms of environmental benefits.

7. FUTURE RESEARCHES

7.1. Challenges faced by agriculture as a key activity controlling GHG emissions, reactive nitrogen cycling and atmospheric pollutants exchange

As discussed in the introduction, agriculture is accounting for around 10% of the total anthropogenic greenhouse gas (GHG) emissions, but there are great uncertainties on both the N₂O and CO₂ contribution of agriculture (Ceschia et al., 2010; Smith et al., 2007). There is an even larger uncertainty in the effect of managements on the future contribution of agriculture to GHG emissions, with current issues regarding fertilisation, tillage (Angers et al., 1997; Baker et al., 2007), but also the links between the N and C balances of agro-ecosystems (Ammann et al., 2007), and a rising concern regarding the prospects of diminishing phosphorus availability. But arable land, and more generally managed land, is also playing a central role in atmospheric pollution as the major contributor of specific pollutant, like pesticides (Bedos et al., 2002) and ammonia (Sommer et al., 2003), but also particles (Faburé et al., 2011).

Agriculture is also a major pathway of the nitrogen cycle and represents the main entry of anthropogenic reactive nitrogen in this cycle as synthetic fertiliser and NO emissions (6% global emissions, IPCC, 2007) (the second most important pathways being NO_x emissions from combustion). But agricultural lands represent a large fraction of the terrestrial surface and they contribute a great deal to pollutant recapture, like for O₃ (Memmesheimer et al., 1997) or nitrogen compounds (NH₃, NO₂, HNO₃) (Flechard et al., 2011).

If our lifestyle does not change drastically on the global scale, this reactive nitrogen production is expected to increase with the increasing demand for food consumption and biofuel (Erisman and Sutton, 2008; Galloway et al., 2008). Regarding pesticides, future consumption is uncertain: In the one hand increasing cultivation of pesticides resistant GMO suggests an increasing consumption of pesticides in the future. In the other hand, the increasing awareness of potential harmful effects of the pesticides may lead to a decrease of the number of pesticides used (Ecophyto 2018). The average ozone concentration is also expected to increase by 40-60% by 2100 (Meehl et al., 2007). These impacts on the environment, health and welfare are starting to be estimated in terms of costs to the society. (Sutton et al., 2011) have estimated that excess nitrogen in the environment costs the European Union between 70 and 320 billion € per year. Similarly, the impact of increasing ozone concentration is estimated to cost about 12-35 billions \$ annually (Avnery et al., 2011a; Avnery et al., 2011b).

Optimizing the management of agriculture in the prospect of its long term sustainability in carbon and greenhouse gases emission, but also in pesticides and nitrogen losses is therefore a key challenge for the society (Spiertz, 2010). Such a challenge asks the research community to be able to produce predictive models that combines complex biogeochemical cycling of nitrogen, carbon and pollutants, with plant and soil functioning and agronomical practices in a socio-economical context. This is, in turn, a key challenge for the research community, which is asked to keep producing new knowledge on complex biochemical processes while simultaneously contributing to integrate this knowledge in agronomical and economical models.

7.2. Proposed approach

To answer the key challenges previously emphasised, a central scientific objective that I wish to work on is to *“improve the quantification of the fluxes of C, N, greenhouse gases and reactive gases between managed land and the atmosphere and understand their interactions over the long term”*. It is indeed essential to better quantify these fluxes and to understand the underlying processes for improving the prediction capacity of the global warming models, but also for optimising the cropping systems and the management options in terms of environmental threat. Moreover, there is a rising awareness that all environmental threats are linked and should be considered together. As an example, ozone is a pollutant for human health, it is a known greenhouse gas, but it also has a positive feedback impact on CO₂ absorption by terrestrial ecosystems. Therefore, over the long term the interactions between C, N but also O₃ and aerosols should be taken into account, as there may be positive or negative feedbacks between them. A second example is ammonia, which is a known atmospheric pollutant leading to aerosols formation, which themselves have a negative feedback on the warming potential. But NH₃ is a threat to semi natural ecosystems too and also lead to indirect N₂O emissions. Therefore when studying NH₃ effects to the environment and potential mitigation option, we need to think more globally in terms of nitrogen cycle and at a scale that includes indirect effects.

I wish to contribute to this central question by working on two research axes which are linked together and well within the scope of my laboratory research interests.

- *Improving the predictive capacity of GHG and pollutant exchange models by coupling the ecosystem functioning with the sources and sinks of pollutants and GHG including chemistry within the canopy.*
- *Quantifying the GHG and pollutant fluxes, in current and innovative agronomical systems and their effects on the linked C and N balances over the long term.*

These two axes of researches are briefly described in the following.

7.3. Improving the predictive capacity of GHG and pollutant exchange models

Greenhouse gases, nitrogen and pollutant fluxes should be considered together as they all interact with each other. In this first research axe, I wish to contribute by (1) improving our understanding of the mostly uncertain pollutant exchange processes (in the short term O₃, NH₃, NO_x and in the longer term VOCs, and aerosols), and (2) coupling ecosystem models, surface exchange models, biogenic source models and within canopy chemistry models.

I wish to contribute to process understanding (1) by field measurements of O₃, NO_x, NH₃ and VOCs fluxes over arable land with up-to-date methodologies like QCL, eddy-covariance, REA, focussing on key uncertainties: litter emissions of NH₃ and VOCs, NO₂. Flux chamber studies will be used to better understand some of the key processes involving environment and biological control, like O₃ deposition onto bare soil and cuticles and its response to humidity, the interaction between NO_x and O₃ exchange in the canopies, or NH₃ litter emissions.

Regarding the model coupling (2), I wish to contribute by coupling CERES-EGC model (agro-ecosystem and soil carbon and nitrogen model), (Gabrielle et al., 2006) with the Surf atm model (soil-vegetation-atmosphere transfer model) (Personne et al., 2009) and the Volt'air model (soil transfer of NH_3 and pesticides) (Génermont and Cellier, 1997). I contribute to this work, which is currently in progress, by both steering up a working group and participating in the coupling between ecosystem models and physical transfer model. We aim at including root absorption of nutrients, and stomatal compensation point in such a model. This issue will also benefit from the work of a PhD student starting in the end of 2011 which will couple NO emission from soils, with VOCs emissions from leaves, soil and residual organic matter, and O_3 deposition, together with the MuSICA model (Ogee et al., 2003) and the previous coupled model with the addition of an in-canopy chemical reaction model. The idea is to adapt existing atmospheric chemistry modules for in-canopy reactions accounting for the specific turbulence within the canopy. Finally the benefits of extending the Lagrangian Stochastic approach to account for chemical reaction within the canopy will be evaluated.

Regarding the strategy, this work will benefit from our involvement in the ECLAIRE (Effects of climate change on air pollution impacts and response strategies for European ecosystems) project, led by CEH Edinburgh starting in 2012, for which I am the PI for INRA. It will also be supported by the measurements undertaken in the ICOS (Integrated Carbon Observation System) arable site of Grignon of which I have the responsibility. This topic will further benefit from the methodological developments made in our laboratory: The ROSAA analyser for NH_3 flux measurements, the ongoing O_3 and NO eddy covariance measurements, the NH_3 and O_3 flux chamber currently used in our lab, and the experience of the staff in GC-MS of organic pollutants. This work will be conducted in collaboration with colleagues from my laboratory, and INRA Ephyse regarding the MusiCA model (Ogee et al., 2003) and the O_3 deposition model (Lamaud et al., 2009), but also with LSCE (Juliette Lathière) which is currently working on similar questions for forest. Further collaborations are envisaged with Denis Maro (IRSN) to study coupled fluxes of reactive nitrogen compounds and aerosols.

One of the main difficulties I identify in these researches will be to avoid double counts in the models development at the national scale especially and the European scale too. For that, we should pay special attention in actively participating in the construction of an efficient network on modelling, while at the same time affirming our specificities in surface exchange modelling of pollutants (especially reactive nitrogen and ozone) and GHG. The working group set up in our laboratory for coupling CERES-EGC with Surf atm and Volt'air, and the collaboration with Ephyse should help strengthening the position of INRA at the national scale, and concretising our collaboration with the LSCE and the LISA on integrating our models in regional scale transport models is a target over the next three years. Moreover, attention will also be paid to coordinate these developments with the existing INRA modelling platforms. Finally, the production of high quality data on pollutant and GHG fluxes from field and chamber flux measurements is regarded as an essential part of the work which will allow validating the models and identifying key issues in future researches.

7.4. Quantifying the GHG and pollutant fluxes, and the C and N balances in agro ecosystems over the long term

GHG and pollutant fluxes above agro-ecosystems are still very uncertain, and despite great efforts in the methodologies and new instrument development there are still great uncertainties in long term measurements of cumulated fluxes of CO₂, N₂O or CH₄, in one hand, and on the nitrogen and carbon balance and their links, on the other hand. One of the key issue regarding flux measurements is the yet not fully understood causes of the non closure of the energy balance above agro ecosystems (Mauder et al., 2010). Especially the question arises as to how this unbalance should be considered to correct scalar fluxes. Another issue is the effect of gap filling methodologies on the CO₂ net ecosystem exchange. The uncertainties are even greater on nitrogen fluxes, and the existing references are sparse over longer terms. The main efforts should be put on refining reactive nitrogen flux measurements: NH₃ and NO₂ fluxes but also HNO₃ and their daily variability as well as N containing aerosols and volatile organic compounds. The difficulty in this later case is that these fluxes are usually non conservative in the surface boundary layer due to chemical interactions or local horizontal advection. Regarding the carbon and nitrogen balances over the long term, the main issue is: how to reconcile the flux method with the soil carbon and nitrogen balance method? The current uncertainties concern the spatial and time variability of the fluxes and stocks at the field scale (Davis et al., 2010), the N₂ fluxes which can not be measured directly, as well as other uncertainties regarding dissolved organic carbon leaching and deposition of organic nitrogen. Precise measurements of C and N imports and exports should also not be forgotten.

Beyond the need to refine the quantification and our understanding of the GHG, C, N and pollutant fluxes between agro-ecosystems and the atmosphere, there is a need to optimise the management of these ecosystems in terms of their environmental services and impacts and to propose innovative cropping systems. In terms of environmental impacts, current issues that should be studied concern the optimisation of fertiliser use by reducing NO₃⁻ and NH₃ losses, and accounting for wet and dry deposition of nitrogen, or using leguminous cover crops in the rotation. The reduction of pesticides use, by reducing losses by volatilisation following application should also be a target. The reduction of GHG emissions and the carbon storage in the soil should also be a target, which could be achieved by optimising nitrogen supply and residues return to the field, as well as organic matter applications. In terms of environmental services, the application of residual organic matter in agricultural field, as well as the implication of using residues from methanisation on the fluxes and balances of nitrogen and carbon is an important issue that should be studied. The precise role of crops in urbanised regions in O₃ and NO₂ deposition at the regional scale is another key issue that should be studied.

Quantifying the GHG and pollutant fluxes, and the C and N balances in agro ecosystems over the long term requires focussing on the field scale to be able to understand the underlying complex biological physical and chemical processes. However, since agro-ecosystems are highly managed, and since the impacts of agriculture can be indirect (indirect N₂O emissions), a larger scale should be considered which comprises the whole farm to account for the anthropogenic fluxes of nitrogen and carbon, but which also includes the catchment area. This is the work undertaken in the NitroScape model (Duretz,

2011) developed under the supervision of Jean-Louis Drouet and Pierre Cellier in the NitroEurope project (Drouet et al. 2011). Although this scale will not be the main focus of my work I wish to contribute to this topic by both sharing the field-scale biosphere-atmosphere exchange models and my knowledge and models on short-range dispersion and deposition of gaseous and particulate pollutants.

To achieve this work, my main investment will be in coordinating the long-term measurements field site in Grignon, under the ICOS (Integrated Carbon Observation System) project for which I am the PI for Grignon. This involves measurement of CO₂ fluxes, soil and plant C and N pools, imports and exports from the field, plant biomass, with all complementary measurements needed for interpreting and modelling. Additionally, N₂O and O₃ flux measurements will be performed by static chamber and Eddy-Covariance, respectively. The site will also be part of the INGOS (Integrated non-CO₂ Greenhouse gas Observation System) infrastructure network which should allow us to improve the measurement methods for N₂O.

In terms of measurement methods I wish to be involved in setting up and testing measurements of N₂O and NH₃ fluxes by Eddy-covariance using a Quantum Cascade Laser (QCL) tunable diode laser analyser which we will receive this year, as well as NO and NO₂ eddy-covariance measurements with chemiluminescent analysers (Loubet et al., 2011c). The strategy regarding these measurement methods will be to focus on key periods with intensive measurements. I will also contribute to this work in developing simple methods to estimate NH₃ volatilisation following fertiliser application, based on the inverse modelling approaches I developed (Loubet et al., 2010) coupled with passive diffusion sampler measurements (Loubet et al., 2011a). This simple method is planned to be used in multiple sites in France to improve our quantification of NH₃ losses following fertiliser application. Finally, specific experiments will be conducted to evaluate the potential N₂ emissions from the field.

Moreover, we are currently thinking of testing new rotations on ICOS site, which may include leguminous cover crops, or oilseed rapes. Moreover a methaniser will be installed in the AgroParisTech farm (which is the farm running the ICOS field site). This will give use the opportunity to study the effects of applying the digested residues onto the field, especially in terms of nitrogen fluxes and carbon balance. This part of the work will be conducted in collaboration with agronomists and soil scientist in Grignon.

In terms of strategy, this work will be supported by INRA through ICOS, but also the INGOS and the ECLAIRE projects. This work will benefit from networking with French and European colleagues involved in ICOS, and especially those working on arable lands (INRA Mons, INRA Lusignan, CESBIO). I will moreover pay a special attention in linking this work with the model developments exposed previously. This should be achieved by building PhD subjects based on a good balance of field measurement and model development and testing and in collaboration with other researches from the laboratory and the national network. The priorities should be on modelling fluxes of reactive nitrogen (NH₃, NO₂) in agro-ecosystems, quantifying COVs fluxes from agro-ecosystems and quantifying the impact of innovative rotations on GHG and C and N fluxes.

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ANNEXE A. CINQ PUBLICATIONS SIGNIFICATIVES

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