Report No. **193**

epa Research
Climate - Water - Sustainability
Identifying pressures • Informing policy • Developing solutions

Ambient Atmospheric Ammonia in Ireland, 2013-2014

Authors: Brian Doyle, Thomas Cummins, Cara Augustenborg and Julian Aherne

Comhshaol, Pobal agus Rialtas Áitiúil
Environment, Community and Local Government

www.epa.ie

ENVIRONMENTAL PROTECTION AGENCY

The Environmental Protection Agency (EPA) is responsible for protecting and improving the environment as a valuable asset for the people of Ireland. We are committed to protecting people and the environment from the harmful effects of radiation and pollution.

The work of the EPA can be divided into three main areas:

Regulation: *We implement effective regulation and environmental compliance systems to deliver good environmental outcomes and target those who don't comply.*

Knowledge: *We provide high quality, targeted and timely environmental data, information and assessment to inform decision making at all levels.*

Advocacy: *We work with others to advocate for a clean, productive and well protected environment and for sustainable environmental behaviour.*

Our Responsibilities

Licensing

We regulate the following activities so that they do not endanger human health or harm the environment:

- waste facilities *(e.g. landfills, incinerators, waste transfer stations)*;
- large scale industrial activities (*e.g. pharmaceutical, cement manufacturing, power plants)*;
- intensive agriculture *(e.g. pigs, poultry)*;
- the contained use and controlled release of Genetically Modified Organisms *(GMOs)*;
- sources of ionising radiation *(e.g. x-ray and radiotherapy equipment, industrial sources)*;
- large petrol storage facilities;
- waste water discharges;
- dumping at sea activities.

National Environmental Enforcement

- Conducting an annual programme of audits and inspections of EPA licensed facilities.
- Overseeing local authorities' environmental protection responsibilities.
- Supervising the supply of drinking water by public water suppliers.
- Working with local authorities and other agencies to tackle environmental crime by co-ordinating a national enforcement network, targeting offenders and overseeing remediation.
- Enforcing Regulations such as Waste Electrical and Electronic Equipment (WEEE), Restriction of Hazardous Substances (RoHS) and substances that deplete the ozone layer.
- Prosecuting those who flout environmental law and damage the environment.

Water Management

- Monitoring and reporting on the quality of rivers, lakes, transitional and coastal waters of Ireland and groundwaters; measuring water levels and river flows.
- National coordination and oversight of the Water Framework Directive.
- Monitoring and reporting on Bathing Water Quality.

Monitoring, Analysing and Reporting on the Environment

- Monitoring air quality and implementing the EU Clean Air for Europe (CAFÉ) Directive.
- Independent reporting to inform decision making by national and local government *(e.g. periodic reporting on the State of Ireland's Environment and Indicator Reports)*.

Regulating Ireland's Greenhouse Gas Emissions

- Preparing Ireland's greenhouse gas inventories and projections.
- Implementing the Emissions Trading Directive, for over 100 of the largest producers of carbon dioxide in Ireland.

Environmental Research and Development

- Funding environmental research to identify pressures, inform policy and provide solutions in the areas of climate, water and sustainability.

Strategic Environmental Assessment

- Assessing the impact of proposed plans and programmes on the Irish environment *(e.g. major development plans)*.

Radiological Protection

- Monitoring radiation levels, assessing exposure of people in Ireland to ionising radiation.
- Assisting in developing national plans for emergencies arising from nuclear accidents.
- Monitoring developments abroad relating to nuclear installations and radiological safety.
- Providing, or overseeing the provision of, specialist radiation protection services.

Guidance, Accessible Information and Education

- Providing advice and guidance to industry and the public on environmental and radiological protection topics.
- Providing timely and easily accessible environmental information to encourage public participation in environmental decision-making *(e.g. My Local Environment, Radon Maps)*.
- Advising Government on matters relating to radiological safety and emergency response.
- Developing a National Hazardous Waste Management Plan to prevent and manage hazardous waste.

Awareness Raising and Behavioural Change

- Generating greater environmental awareness and influencing positive behavioural change by supporting businesses, communities and householders to become more resource efficient.
- Promoting radon testing in homes and workplaces and encouraging remediation where necessary.

Management and structure of the EPA

The EPA is managed by a full time Board, consisting of a Director General and five Directors. The work is carried out across five Offices:

- Office of Environmental Sustainability
- Office of Environmental Enforcement
- Office of Evidence and Assessment
- Office of Radiological Protection
- Office of Communications and Corporate Services

The EPA is assisted by an Advisory Committee of twelve members who meet regularly to discuss issues of concern and provide advice to the Board.

EPA RESEARCH PROGRAMME 2014–2020

Ambient Atmospheric Ammonia in Ireland, 2013–2014

(2012-CCRP-MS.8)

EPA Research Report

Prepared for the Environmental Protection Agency

by

UCD Soil Science, UCD School of Agriculture and Food Science, University College Dublin;
Environmental Resource Studies, Trent University; and
Impact Research Management

Authors:

Brian Doyle, Thomas Cummins, Cara Augustenborg and Julian Aherne

ENVIRONMENTAL PROTECTION AGENCY
An Ghníomhaireacht um Chaomhnú Comhshaoil
PO Box 3000, Johnstown Castle, Co. Wexford, Ireland

Telephone: +353 53 916 0600 Fax: +353 53 916 0699
Email: info@epa.ie Website: www.epa.ie

ACKNOWLEDGEMENTS

This report is published as part of the EPA Research Programme 2014–2020. The programme is financed by the Irish Government and administered by the Environmental Protection Agency, which has the statutory function of co-ordinating and promoting environmental research.

The project team would like to thank Professor Ted Farrell for serving on the Steering Group, Anne Killion and Gillian McGrath of UCD Soil Science, and Met Éireann for facilitating communication with the climatological network. We recall here the earlier contribution of our colleagues Yvonne de Kluizenaar and Roel van den Beuken. We particularly want to thank the volunteer network operators, listed on page iii, to whom we are deeply indebted.

DISCLAIMER

The EPA Research Programme addresses the need for research in Ireland to inform policy and other stakeholders on a range of questions in relation to environmental protection. These reports are intended as contributions to the necessary debate on the protection of the environment.

EPA RESEARCH PROGRAMME 2014–2020
Published by the Environmental Protection Agency, Ireland

ISBN: 978-1-84095-673-3 July 2017

Price: Free Online version

Project Partners

Thomas Cummins
UCD Soil Science
UCD School of Agriculture and Food Science
University College Dublin
Dublin
Ireland
Tel.: +353 1 716 7744
Email: thomas.cummins@ucd.ie

Julian Aherne
Environmental Resource Studies
Trent University
Peterborough
Ontario
Canada
Tel.: +1 705 748 1011
Email: jaherne@trentu.ca

Volunteer Network Operators

Participant	**Station**	**Organisation**
Mr Patrick Fitzmaurice	Athleague	Met Éireann
Mr Desmond McHugh	Ballinamore	Met Éireann
Ms Margaret Meehan, Mr David Meehan	Ballincurrig	Met Éireann
Ms Marie McCahey	Carrickmacross	Met Éireann
Mr Patsy Bennett	Clonroche	Met Éireann
Mr David Dodd	Clonskeagh	EPA
Mr Gerard Kenny, Ms Tracy Leogue	Derrygreenagh	Bord na Móna
Mr David Farrell	Dooary	University College Dublin (UCD)
Dr Siobhan Jordan	Dundalk Institute of Technology (IT)	Dundalk IT
Ms Nora Power	Dungarvan	Met Éireann
Mr John Gallagher	Glenties Hatchery	North Western Regional Fisheries Board (NWRFB)
Mr Gerard Murphy	Killarney	NPWS
Dr Siobhan Jordan	Leiter Cavan	Dundalk IT
Mr Christy Healy	Littleton	Bord na Móna
Dr Darius Ceburnis	Mace Head	National University of Ireland, Galway (NUIG)/Met Éireann
Mrs Paula Hart, Mr Christy Hart	Naas	–
Ms Ailish McCabe	Navan	Met Éireann/Boliden
Ms Isabella Donnelly	Oak Park	EPA
Ms Michelle McNally, Mr Paddy Douglas	Phoenix Park, Winetavern Street	Dublin City Council
Mr Padraig Kavanagh	Shannon Airport	Met Éireann
Mr Patrick Dooley	Sliabh Bloom	Met Éireann
Mr Brendan Murphy	Sligo Airport	Met Éireann
Mr Jonathan Sykes	Springfield Castle	Met Éireann
Mr Martin Sweeney	Straide	Met Éireann

Contents

List of Figures

List of Tables

Executive Summary

Ammonia (NH_3) is a gas and a reduced form of nitrogen. It is released to the atmosphere mostly from farm-animal wastes and nitrogen fertilisers, depending on husbandry and nutrient-management practices. A potential pollutant, ammonia is the most abundant form of gas-phase reduced nitrogen in the atmosphere and contributes to both the formation of particulate matter and the deposition of reactive nitrogen on land surfaces. Sources of atmospheric ammonia increased throughout the 20th century as a result of fertiliser production and intensive farming practices, increasing nitrogen deposition in sensitive ecosystems. There are limited monitoring data on ambient atmospheric ammonia in Ireland since the last survey in 1999–2000. The present network monitored ambient atmospheric ammonia concentrations in air away from point sources, across Ireland, during 2013–2014. The objectives of the project were:

1. to establish a national network to measure ambient atmospheric ammonia concentrations and produce a national concentration map;
2. to evaluate both the present and prior networks to achieve a better understanding of the spatial and temporal variability of atmospheric ammonia in Ireland;
3. to estimate the magnitude of total reduced nitrogen deposition in Ireland by combining dry deposition of ammonia and wet deposition of ammonium estimates.

Ambient atmospheric ammonia concentrations were measured at 25 monitoring stations across Ireland between June 2013 and July 2014, using passive diffusive samplers, exposed in triplicate on a 2-week cycle. Atmospheric ammonia concentrations show spatial variation similar to that of the 1999–2000 study, with higher concentrations of ammonia observed towards the north-east midlands and the south-east. The station with the lowest mean concentration (0.48 μg/m^3) was Mace Head, Connemara, County Galway, while the highest mean (2.96 μg/m^3) was at Leiter Cavan. The annual average, 1.72 μg/m^3, from all 25 sites, was higher than the 1.45 μg/m^3 average of the 1999–2000 study. This observed mean is above the 1 μg/m^3 critical level (where lichens and bryophytes are key to ecosystem integrity), and below the 3 μg/m^3 critical level (for all other vegetation). Critical levels are levels of pollutants in the atmosphere above which direct adverse effects on receptors may occur, according to present knowledge. The critical levels of atmospheric ammonia concentrations quoted above are recommended by the Convention on Long-range Transboundary Air Pollution. This study also found higher concentrations of ammonia in the air in Dublin city centre than in nearby suburban sites, probably from urban sources such as vehicle exhaust and sewage emissions. Seasonal variations in ammonia concentrations were observed but were not significant.

Wet deposition of ammonium was determined by taking interpolated ammonium concentrations from precipitation data from 16 stations and combining them with mapped long-term annual rainfall accumulation data from Met Éireann. Dry deposition of ammonia was mapped by multiplying interpolated atmospheric ammonia concentrations (from the present study) by literature-derived, surface-specific deposition velocities applied to CORINE (Coordination of Information on the Environment) landcover classes. National estimates of dry deposition of ammonia, wet deposition of ammonium, and total reduced nitrogen deposition (the sum of wet and dry) for the whole area of Ireland were found to be 32.9, 19.2 and 52.1 kt of nitrogen present as reduced nitrogen per year respectively. Reduced nitrogen deposition is dominated by dry deposition of ammonia. Of the ammonia emission estimate of 107.8 kt for 2013 (EPA, 2015), therefore, roughly half is deposited within Ireland. The deposition maps from both monitoring campaigns suggest that sensitive ecosystems within defined areas may be threatened by reduced nitrogen deposition.

Changing agricultural activity, such as increasing cattle, pig and poultry populations, will cause increases in atmospheric emissions of ammonia, leading to increased deposition of reduced nitrogen, with potential adverse impacts on sensitive ecosystems. Future research should focus on improving the spatial and temporal air concentration data. A permanent, nationwide monitoring network is required to provide quantitative atmospheric ammonia data, especially in the context of the national Food Harvest 2020 and Food Wise 2025 government strategies, which aim to increase production in the beef and dairy sectors (DAFM, 2015). This project improves our knowledge of ambient atmospheric ammonia concentration levels, their spatial and temporal variation across the country, and the spatial distribution of wet ammonium, dry ammonia and reduced nitrogen deposition in Ireland.

Policy Implications

The project demonstrates action by Ireland to encourage research and monitoring, as required under the Gothenburg Protocol to the United Nations Economic Commission for Europe Convention on Long-range Transboundary Air Pollution. Developing a permanent monitoring network (Chapter 6) would further support the aims of the Protocol.

Clear relationships have been shown between nitrogen-intensive agricultural activities and ammonia concentrations, and such activities are expected to increase under the Food Harvest 2020 and Food Wise 2025 plans. Therefore, ammonia emissions and concentrations can be expected to increase. This finding is important to underpin strategies for preventing air pollution from ammonia as agricultural activity increases.

The methods used here to assess reduced nitrogen deposition, when combined with improved deposition velocities and with assessment of oxidised forms of nitrogen, will contribute an independent assessment of total nitrogen deposition. This will be relevant to discussions around expected revised ceilings under the National Emission Ceilings Directive. Furthermore, the possible withdrawal of the UK from the constraints of the directive may create the potential for increased ammonia emissions in Northern Ireland.

The ammonia concentrations, deposition and high-resolution interaction of deposition with land surfaces are important in understanding environmental impacts on nitrogen-sensitive ecosystems, specifically peatlands, semi-natural grasslands, lakes and forests. The concentration and deposition mapping used here can contribute to models for assessing transport and deposition to specific ecosystems, and for evaluating the likely impacts of projected increases in emissions as agricultural activity increases.

It is recommended that a permanent network be established to continuously monitor ambient atmospheric ammonia concentrations away from point sources. Ideally, such a network would benefit from the continued operation of European Monitoring and Evaluation Programme sites operated by EPA and Met Éireann at Oak Park, Johnstown Castle/Carnsore, Malin Head and Valentia, and of sites in Northern Ireland. The network should operate using passive samplers, with a smaller number of co-located denuder samplers.

1 Introduction

This project, "Ambient Atmospheric Ammonia in Ireland, 2013–2014", is referred to in this report as Ammonia2. It was funded by the Environmental Protection Agency (EPA) under its Science, Technology, Research and Innovation for the Environment (STRIVE) programme. The ammonia-monitoring campaign has been set up and run within University College Dublin (UCD) School of Agriculture and Food Science, in collaboration with Trent University, Ontario, Canada, which provided analytical support. The study was project managed by Dr Cara Augustenborg, Impact Research Management. This study builds on an earlier, similar investigation, in 1999–2000, published by de Kluizenaar and Farrell (2000), referred to here as Ammonia1.

Ammonia (chemical formula NH_3) is a naturally occurring reactive trace gas in the atmosphere. At high concentrations it has adverse environmental impacts, including the eutrophication of semi-natural terrestrial ecosystems and the formation of secondary particulate matter (PM), which can have implications for human health. In Ireland, agriculture is the principal NH_3 emission source; cattle populations in particular are significantly linked to total NH_3 emissions (EPA, 2012). The Irish Government's current strategies for growth in agriculture, Food Harvest 2020 and Food Wise 2025 (DAFM, 2015), aim to increase milk output by 50% and beef output by 20% in value above 2007–2009 levels, which will require an increase in herd numbers. In its recent environmental assessment for Ireland, the EPA (2012) states that atmospheric NH_3 levels will rise and become a problem if cattle numbers increase to their pre-2000 levels. The proposed increase in cattle numbers may lead to increased atmospheric NH_3 emissions, and higher ambient NH_3 concentrations. Up-to-date knowledge of national atmospheric NH_3 concentrations is needed, given the 15-year gap since the previous study, and also in the light of current government policy to encourage growth in the agriculture sector.

In Ireland, there is currently no continuous monitoring of ambient atmospheric NH_3 gas concentrations. Up to 2011, atmospheric sampling of NH_3 was carried out at three environmental monitoring sites operated by UCD and Coillte. These were the International Cooperative Programme (ICP) Forests Level II sites at Ballinastoe, County Wicklow, Brackloon, County Mayo, and Cloosh, County Galway. The observations recorded at these sites were consistent with the national emissions inventory in showing no long-term change in NH_3 concentration for remote sites (Aherne, 2011). The EPA currently monitors atmospheric particulate ammonium (NH_4^+) at three sites in Ireland (Malin, County Donegal, Carnsore, County Wexford, and Oakpark, County Carlow) as part of the European Monitoring and Evaluation Programme (EMEP) (Leinert *et al.,* 2008). The EMEP is a scientifically based and policy-driven programme under the Convention on Long-range Transboundary Air Pollution (CLRTAP) for international co-operation to solve transboundary air pollution problems. Ambient atmospheric NH_3 is monitored continuously at three sites in Northern Ireland (Lough Navar, County Fermanagh, Hillsborough, County Down, and Coleraine, County Derry), under the UK National Ammonia Monitoring Network (NAMN, 2016). Ammonia is not covered by the CAFE Directive on ambient air quality (Directive 2008/50/EC) and is not part of the national ambient air quality network managed by the EPA.

The Ammonia1 study is the only previous national-scale atmospheric NH_3 monitoring campaign in Ireland, operated from 1999 to 2000 by UCD (de Kluizenaar and Farrell, 2000). This 40-station network indicated two distinct regions with high concentrations of NH_3 in the air: the north midlands and south midlands. The areas of high NH_3 concentrations were spatially related to agricultural intensity, specifically populations of cattle and of pigs and poultry. Maps of dry deposition of NH_3, wet deposition of NH_4^+ and total deposition of reduced nitrogen (NH_x) indicated areas of higher NH_x deposition and displayed a similar spatial pattern to the air concentrations (de Kluizenaar and Farrell, 2000). These maps are compared with the outputs of this study in Chapters 4 and 5.

The methods of data collection and analysis employed by the Ammonia1 project guided those used by Ammonia2, particularly the use of Willems badge passive samplers to collect atmospheric NH_3. The Ammonia1 network was more spatially dense, however, with 40 stations as opposed to Ammonia2's 25. Also, the samplers were exposed weekly for Ammonia1 compared with fortnightly for Ammonia2. One major difference between the two projects was the provision of urban monitoring stations in the Ammonia2 network. Prior to the Ammonia2 study there had been no urban monitoring of ambient NH_3 in Ireland. As part of the Ammonia2 monitoring project, an exploratory set of three sites in Dublin was established.

The Ammonia2 project used similar techniques to the Ammonia1 project in the estimation of wet deposition of NH_4^+, dry deposition of NH_3 and total deposition of NH_x. A detailed description of the techniques involved is included in Chapter 3 of this report. The most up-to-date datasets available were used for the Ammonia2 deposition mapping, for example the 2012 Coordination of Information on the Environment (CORINE) land-cover data, in tandem with the NH_3 concentrations observed during the operation of the Ammonia2 network.

1.1 Policy Relevance

The United Nations Economic Commission for Europe (UNECE) established the CLRTAP. Parties to the convention must limit, reduce and prevent air pollution by developing policies and strategies, information exchange, consultation, research and monitoring. While Ireland is a signatory to the convention, it has not yet ratified the protocol, signed by Ireland at Gothenburg in 1999 and amended in 2012, which is concerned with NH_3 emissions. The Gothenburg Protocol requires that:

> Each Party shall … [act with the] aim of reducing emissions of … ammonia … [and] … shall encourage research, development, monitoring and cooperation …

This project intends to contribute to the research and monitoring of the long-range transboundary transport of NH_3 and to influence Irish policy and strategy development. The outputs from the project will provide information to exchange with other members of CLRTAP. The EU Directive on National Emission Ceilings (NEC) (Directive 2001/81/EC) established emission ceilings for such acidifying and eutrophying substances as NH_3. Data produced from this study will contribute to the knowledge base for Ireland to comply with that directive and other EU strategies on air pollution.

This project aims to help improve Ireland's capacity to assess and analyse environment impacts of NH_3 in the context of ecosystem sensitivity and critical loads. The research is intended to inform and improve reporting to the UNECE CLRTAP and the EU NEC Directive. Furthermore, it is possible that atmospheric NH_3 levels may increase and become a problem if cattle numbers rise as foreseen by the Food Harvest 2020 and Food Wise 2025 strategies. Therefore, this project will provide data and deposition mapping to give information on the possibility of rising NH_3 levels, and as a reference for 2020–2025.

1.2 Objectives

The objectives of the project were:

1. to establish a national network to measure ambient atmospheric ammonia concentrations and produce a national concentration map;
2. to evaluate both the present and prior networks to achieve a better understanding of the spatial and temporal variability of atmospheric ammonia in Ireland;
3. to estimate the magnitude of total reduced nitrogen deposition in Ireland by combining dry deposition of ammonia and wet deposition of ammonium estimates.

1.3 Report structure

The report is divided as follows. Chapter 2 reviews the sources, sinks and fate of NH_3 in the atmosphere. It also includes a review of the environmental impacts of atmospheric NH_3 and methods for measuring atmospheric NH_3. Chapter 3 describes the methods used to collect and analyse the data used in the study, including the workings of the Willems badge passive sampler, the network design and site selection, mapping NH_3 concentrations and measuring nitrogen deposition. Chapters 4 and 5 combine results and discussion, presenting the national atmospheric NH_3 concentration map and the wet, dry and NH_x deposition maps, and comparing findings with the earlier Ammonia1 project. Chapter 6 presents conclusions and recommendations. Supplementary material is provided in the appendices.

2 Atmospheric Ammonia and Reduced Nitrogen Deposition

Atmospheric NH_3 gas is emitted to the atmosphere both naturally and as a result of human industrial activities such as agriculture and transport. The principal sources of NH_3 emission to the atmosphere are agricultural; livestock wastes and fertilisers are particularly significant (Buijsman *et al.*, 1987; Sutton *et al.*, 1995; Whitehead, 1995; Anderson *et al.*, 2003; Paulot *et al.*, 2014). It has been estimated that, in most western European countries, up to 90% of NH_3 in the atmosphere originates directly from agricultural sources (Sutton *et al.*, 1995). Concentrations of NH_3 in the air in western Europe are therefore also highly spatially correlated with livestock populations; they increase in proportion to cattle, sheep, pig and poultry numbers (Buijsman *et al.*, 1987; Sutton *et al.*, 2001a; Erisman *et al.*, 2007; Skjøth *et al.*, 2011). In Ireland, cattle populations show a strong correlation with atmospheric NH_3 concentrations (EPA, 2012) and contribute at least 75% of total emissions (Hyde *et al.*, 2003). Cattle, for example, eat plant protein and excrete waste nitrogen mostly in the form of urea, $CO(NH_2)_2$. Between 60 and 90% of the nitrogen in cattle urine is in the form of urea, and NH_3 is volatilised from urea (Whitehead, 1995). Synthetic urea is also used as a grassland fertiliser and, when it is applied to the sward surface, NH_3 is readily volatilised from it (Whitehead, 1995). When dissolved in soil water, the urea in both urine and fertiliser is hydrolysed by urease, a common soil microbial enzyme, producing ammonium carbonate, $(NH_4)_2CO_3$. This is then converted to NH_4^+ and hydroxyl (OH^-) ions; under alkaline conditions, they react together to form volatile NH_3 gas, which escapes to the atmosphere (Collins *et al.*, 1986). An abbreviated nitrogen-cycle diagram, emphasising the role of NH_3, is in Figure 2.1. In nitrogen-limited ecosystems, nitrogen is cycled tightly among plants, animals, and soil organic matter. Agricultural systems tend to concentrate nitrogen, both in fertilisers and in animal slurries, which allows opportunities for NH_3 to leak to the atmosphere.

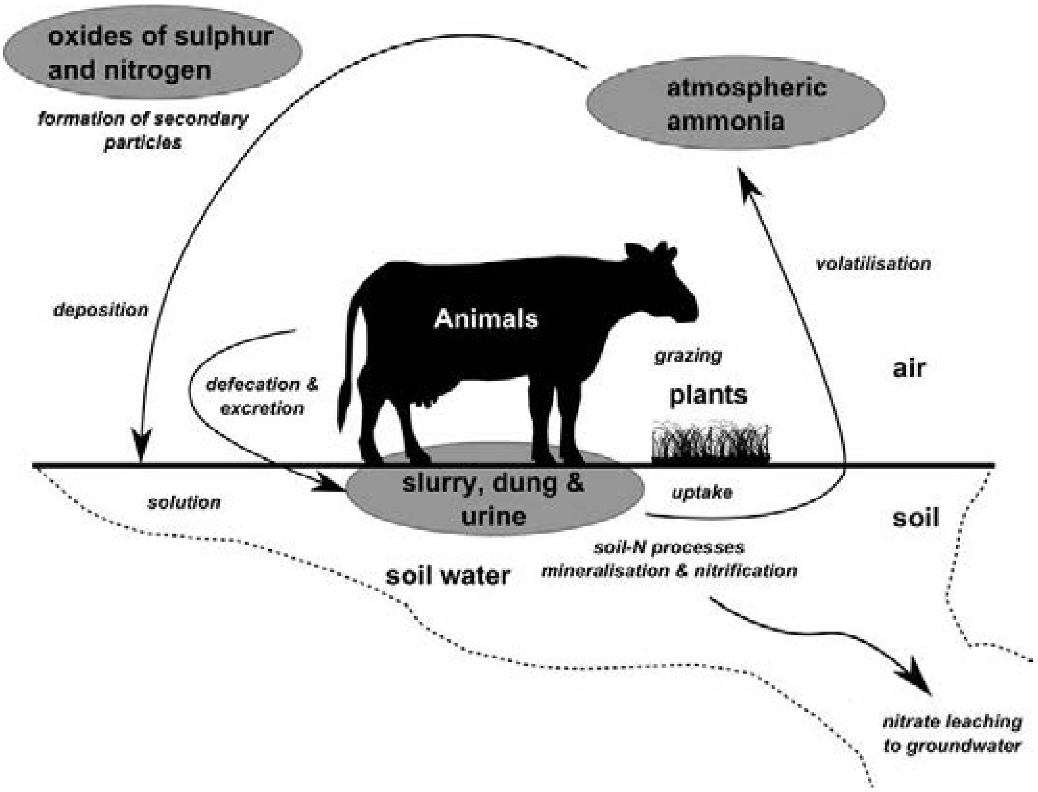


Figure 2.1. Abbreviated nitrogen cycle, emphasising the role of NH_3.

This loss can be managed, by matching nitrogen supply to plant and animal requirements, and avoiding conditions of localised surplus nitrogen at the soil surface.

The amount of NH_3 volatilised from urea applied to soil depends on soil properties (urease activity, organic matter content) (McGarry *et al.*, 1987), cation exchange capacity (Whitehead, 1995), soil pH and acid-buffering capacity (O'Toole *et al.*, 1985) and weather (Black *et al.*, 1985; Hatch *et al.*, 1990; Lockyer and Whitehead, 1990; Sutton *et al.*, 2013), including temperature (McGarry *et al.*, 1987; Whitehead, 1995) and rainfall (Black *et al.*, 1984, 1985; McGarry *et al.*, 1987).

Non-agricultural sources of NH_3 are nitrogen-fertiliser production, coal and biomass burning, waste incineration, wastewater treatment, landfill, horses, pet dogs and cats, wild animals and seabirds (Sutton *et al.*, 2000). Transport emissions are caused by road vehicles fitted with three-way catalytic converters, which are designed to remove nitrogen oxides (NO_x) from the exhaust gases and expel NH_3 as a by-product (Cape *et al.*, 2004). According to the EPA in Ireland, road transport produces a small proportion of emissions of NH_3 (< 1%) (EPA, 2015). Sutton *et al.* (2000) estimated that transport-related NH_3 emissions were 3.1% of total emissions for the UK in 1996. Recent advances in catalytic converters, however, appear to have reduced this urban source of NH_3 substantially (Kean *et al.*, 2009). Ammonia in the atmosphere is also emitted directly from humans through sweat and breath; rates of emission are highly variable, but are estimated to be in the region of 17 g of nitrogen present as ammonia (NH_3-N) per person per year (Sutton *et al.*, 2000).

2.1 Ammonia in the Atmosphere

The annual (1999) Irish average NH_3 concentration measured by de Kluizenaar and Farrell (2000) across 40 sites in Ireland was 1.45 µg/m^3. Annual means from each site ranged between 0.14 and 7.24 µg/m^3. Measured concentrations from the UK show the largest NH_3 concentrations at sites in regions with high NH_3 emissions, such as Hinderclay Fen in East Anglia (pig and poultry emissions), where the 2008 annual mean was 8.68 µg/m^3 and ranged between 4.2 and 19.9 µg/m^3. The smallest NH_3 concentrations were observed at remote sites in the north and west of the UK, which are in less populated areas with few NH_3 emission sources. Such sites, e.g. Inverpolly and Strathvaich Dam in northern Scotland, have annual means of < 0.1 µg/m^3 of NH_3 (DEFRA, 2009). Annual mean NH_3 concentrations measured in rural Delaware, a poultry-producing region in the eastern USA, ranged from 0.5 to 6 µg/m^3, with a mean value of 1.6 µg/m^3 (Skudlark *et al.*, 2005). The presence of intensively managed livestock has been shown to substantially increase air concentrations of NH_3 close to the source. A study of intensive agricultural areas in the Netherlands typically showed atmospheric NH_3 concentrations ranging between 10 and 40 µg/m^3 (Duyzer *et al.*, 2001). Urban sources of NH_3 are also significant. Ambient air concentrations of ~ 2 µg/m^3 of NH_3 at an urban site suggest that, away from intensive agricultural areas, urban regions have the highest ambient NH_3 concentrations (Zbieranowski and Aherne, 2012a). Data from a site in Rome with heavy traffic show that the average NH_3 concentration ranged from 13.5 to 21.6 µg/m^3. That was quite high in comparison with the daily concentration at a rural station, which ranged between 1.2 and 3.9 µg/m^3 (Perrino *et al.*, 2002).

2.2 Residence Time and Deposition Mechanisms from the Atmosphere

On agricultural land, gaseous NH_3 is generally emitted at ground level from diffuse sources, such as urine patches in pasture, and land treated with slurry and fertilisers. As it enters the atmosphere it tends to move laterally over surrounding vegetation, and a substantial proportion of the emitted NH_3 may be deposited and absorbed by vegetation in the immediate vicinity (Whitehead, 1995; Vogt *et al.*, 2013). The deposition processes by which this occurs are known as dry deposition (when NH_3 gas directly impacts and is absorbed on solid surfaces such as soil or vegetation) and wet deposition (when NH_3 gas becomes part of precipitation by solution or transformation and incorporation, and is deposited on earth). Wet and dry deposition rates and quantities depend on factors including meteorological conditions, surface conditions, and the physical and chemical properties of the gases, particles and surfaces in question. Once gaseous NH_3 is emitted to the atmosphere, it also transforms quite rapidly into NH_4^+. As NH_3 is the main alkaline compound in the atmosphere, it reacts with acidic compounds such as sulphur dioxide (SO_2) and NO_x to form NH_4^+ aerosols (mainly ammonium sulphate and ammonium nitrate). Ammonium aerosols are a significant component of fine PM, measured as $PM_{2.5}$ (particles smaller than 2.5 µm). A global estimate of air-pollution effects found agricultural emissions to be the main source of surplus deaths attributable to air pollution in Europe. The estimate has large uncertainties, but the premature mortality attributable to air pollution in Europe is in the hundreds of thousands annually (Lelieveld *et al.*, 2015), making NH_3 an important emission for human health. Total estimates for Ireland are several orders of magnitude lower, with uncertainties so large that no conclusions can be drawn for this small geographical area. NH_4^+ aerosols are, like NH_3 gas, also removed from the atmosphere to soil and vegetation surfaces by wet and dry deposition. As an aerosol, however, NH_4^+ has been shown to persist in the atmosphere for several weeks and to be transported over much greater distances than NH_3 gas (Warneck, 1988). Asman and van Jaarsveld (1990) developed a statistical transport model, cited by van den Beuken (1997), according to which, of the cumulative calculated deposition in western Europe, downwind from a 1-m-high source, 44% of the emitted NH_3 is dry deposited as NH_3, 6% is wet deposited as NH_3, 14% is dry deposited as NH_4^+ and 36% is wet deposited as NH_4^+ (Figure 2.2).

Sutton *et al*. (1992) measured the deposition of ammoniacal nitrogen at two moorland sites and found that the dry deposition of NH_3 was similar in magnitude to the wet deposition of NH_4^+. The residence time of NH_3 in the atmosphere depends on factors such as the conversion rate of NH_3 to NH_4^+ and the rates of dry and wet deposition of each species, but it is generally accepted that NH_3 is resident in the atmosphere for between 0.8 and 4 days, and NH_4^+ between 5 and 19 days (Sutton *et al.*, 1993; Fangmeier *et al.*, 1994). NH_3 is not transported over large distances, as it is rapidly converted to NH_4^+ aerosol at a rate of about 30% per hour (Asman and van Jaarsveld, 1990, cited by van den Beuken, 1997). There is generally less NH_3 than NH_4^+ in the atmosphere, except in localised areas where large amounts of NH_3 are volatilising (Warneck, 1988). It is also important to note that NH_3 may flow in both directions between the air, on the one hand, and vegetation and soils, on the other. Surfaces such as leaves and soils may emit as well as absorb atmospheric NH_3 (Whitehead, 1995).

2.3 Environmental Impacts of Atmospheric Ammonia

High levels of gaseous NH_3 are toxic to most plant species and cause detrimental physiological effects, including visible damage to foliage (Fangmeier *et al.*, 1994; Nordin *et al.*, 2011). Only close to point sources do atmospheric NH_3 concentrations reach levels that can damage leaves. For example, NH_3 from poultry housing facilities has been reported to damage foliage on nearby trees (Roelofs *et al.*, 1985). The EU considers 8 µg/m^3 the critical level above which NH_3 concentrations directly harm plants, although this may be set too high (Cape *et al.*, 2009).

The volatilisation of NH_3 removes valuable nutrient nitrogen from the soil to the atmosphere, representing a

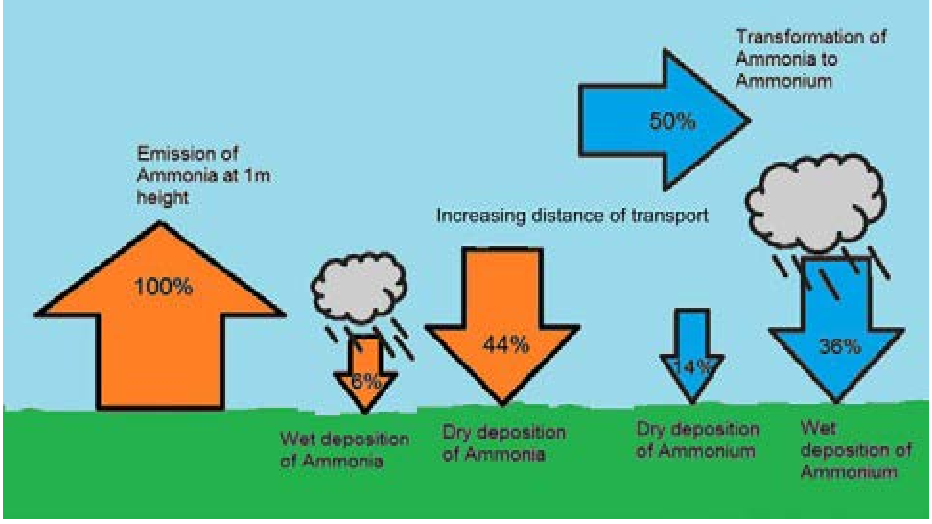


Figure 2.2. The fate of gaseous NH_3 (orange arrows) in the atmosphere. The largest arrow on the left represents emission by a 1-m-high source of NH_3; the arrows to the right represent the mechanism of deposition. Half of emitted NH_3 is converted to NH_4^+ (blue arrows) and may be transported further from the source. Source: Asman and van Jaarsveld (1990), cited by van den Beuken (1994).

significant loss to the farmer. An inevitable consequence of NH_3 volatilisation and subsequent deposition is that ammoniacal nitrogen is distributed over a much greater area than would otherwise take place. At local scales, therefore, a net transfer of nitrogen occurs, from areas with high NH_3 emissions, such as intensively farmed land, to the surrounding countryside. The absorption of this plant-available nitrogen by soils and vegetation may have a beneficial effect locally and increase the supply of nutrient nitrogen to nearby crops and pastures, although that is unlikely, since these vegetations are unlikely to be nitrogen-limited. Within areas of natural or semi-natural vegetation, such absorption may cause unwelcome changes to the mix of species, and in such circumstances atmospheric NH_3 becomes polluting.

2.4 Critical Loads

The concept of critical loads has been developed to protect ecosystems from the adverse effects of atmospheric pollution. A critical load is defined as "a quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge" (Nilsson and Grennfelt, 1988). Empirical critical loads set threshold levels below which no harmful effect is observed to occur across a range of habitats. Stevens *et al.* (2004) have shown that, across Europe, species richness has declined significantly in Natura 2000 sites that receive more than 10 kg of nitrogen per hectare per year. In a recent study, the total nitrogen deposition to Irish grasslands has been calculated to range between 2 and 22 kg/ha per year (Henry and Aherne, 2014), shown in Figure 2.3.

Exceedance was predicted for 35% of mapped acid grasslands in Ireland, based on an empirical critical load of 15 kg of nitrogen per hectare per year. Such exceedances are likely to cause a decline in species diversity within acid grassland ecosystems in Ireland. In Europe, widespread exceedances of critical loads of nutrient nitrogen are predicted for 2020, primarily owing to the deposition of NH_x (Posch *et al.,* 2011a). Bobbink and Hettelingh (2011) revised specific critical loads of nitrogen for ecosystems, as follows:

- forest: 10–15 kg/ha per year;
- heathland: 10–25 kg/ha per year;
- raised and blanket bogs: 5–10 kg/ha per year.

Problems occur for many plant species in natural and semi-natural ecosystems such as heathland and raised bogs, as they can compete only where nitrogen is in low supply (Roelofs, 1986). Many of the plant species in these ecosystems are adapted to low-nutrient environments. For example, the grass *Molinia caerulea* may become dominant and replace *Calluna vulgaris*. Such a

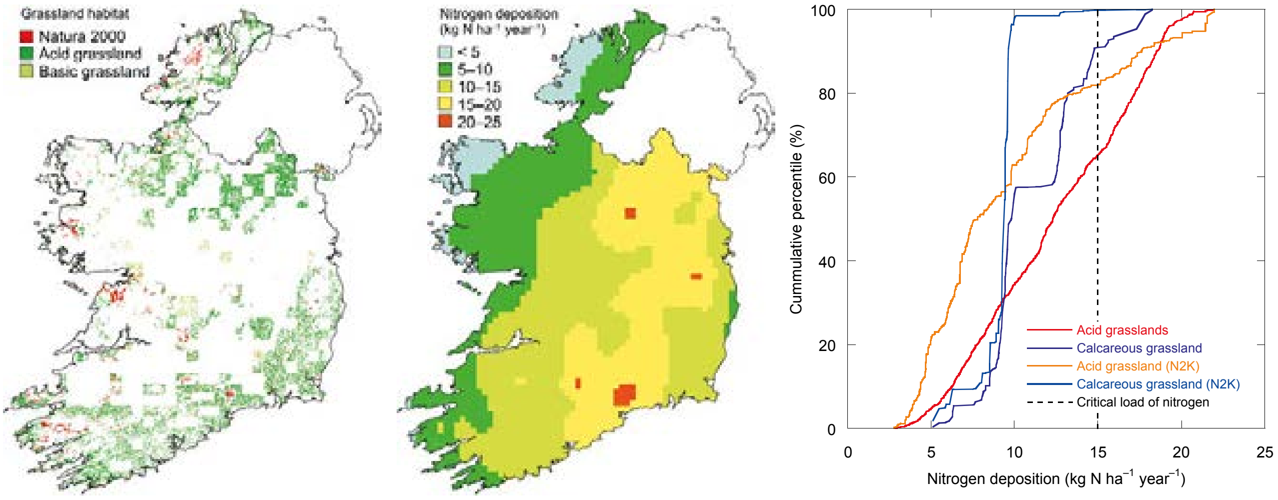


Figure 2.3. Critical load of nutrient nitrogen exceedance in semi-natural grasslands. Left: semi-natural grassland, with areas of same protected as Natura 2000 sites. Centre: total nitrogen deposition (wet + dry), kg/ha per year on a 5 km × 5 km grid. Right: cumulative frequency distributions of nitrogen deposition to semi-natural grasslands and protected semi-natural grasslands (N2K) on acid and calcareous mineral soils. Critical load of nutrient nitrogen is set at 15 kg/ha per year, with critical load exceedances to the right of the dashed line. Source: adapted from Henry and Aherne (2014).

replacement, identified by Bobbink (1991), is illustrated in Figure 2.4.

It also appears that the species of nitrogen that is deposited is important to the effect on the ecosystem. For example, Verhoeven *et al.* (2011) suggest that, if nitrogen is deposited as oxidised species, there is no detrimental impact on the mix of organisms in a raised bog ecosystem. If nitrogen is deposited in reduced, ammoniacal forms (NH_3 and NH_4^+), however, it can have a negative affect on bryophyte vegetation, possibly shifting it from sedge and herb species to grasses and shrubs.

Relevant information from studies on the impacts of nitrogen on natural and semi-natural ecosystems was incorporated into the existing European database on empirical critical levels (Bobbink and Hettelingh, 2011). Critical levels are defined as concentrations of pollutants in the atmosphere above which direct adverse effects on receptors, such as human beings, plants, ecosystems or materials, may occur according to present knowledge (UNECE, 2004). Critical loads, which refer to a mass transfer to a receptor, and critical levels, which are based on concentrations, are needed to assess impacts of air pollution on ecosystems and on organisms respectively. Critical loads of acidifying substances and nutrient nitrogen, and critical levels of ozone, are assessed for Ireland (Aherne, forthcoming). The current critical annual mean NH_3 levels are 1 µg/m where lichens and bryophytes form a key part of the ecosystem integrity, and 3 µg/m for all other vegetation (Bobbink and Hettelingh, 2011).

Along with changes to plant biodiversity, increased NH_3 deposition may also contribute to soil acidification and the leaching of nitrates and soil nutrients. Most of the nitrogen deposited in ammoniacal form is either nitrified or taken up by plants. In both cases, the soil pH tends to be reduced (Sutton *et al.*, 1993). In strongly acidic soils (pH < 4.5) a build-up of exchangeable NH_4^+ is possible as nitrification is inhibited at low pH ranges. This accumulation may result in the displacement of the nutrient cations K^+, Ca^{2+} and Mg^{2+} from cation exchange sites and their subsequent leaching from the soil (Sutton *et al.*, 1993).

Atmospheric NH_3 may also, under certain circumstances, directly affect human health through the formation and inhalation of secondary particles. NH_3 reacts with SO_2 and NO_x to form NH_4^+ aerosols (mainly ammonium sulphate and ammonium nitrate). Although European emissions of sulphur oxides (SO_x) and NO_x declined by 54% and 26% respectively in 2001–2010, NH_3 emissions fell by less than 10% during the same period. A successful PM abatement strategy across Europe appears effective only if NH_3 emissions are also reduced in combination with continuing SO_x and NO_x reductions (Bessagnet *et al.*, 2014). While better knowledge of the relative toxicities of different fine particulate substances is needed to direct air pollution strategy, it is clear that fine particles formed from agricultural

Figure 2.4. Response of a low-nitrogen ecosystem to increased nitrogen inputs. Chalk grassland vegetation in the Netherlands: (left) without nitrogen addition; (right) after three years of nitrogen addition (100 kg/ha per year as NH_4NO_3). Source: photos R. Bobbink, from Bobbink and Hetteling (2011).

Table 2.1. Exposure limits for NH_3 set by the Occupational Safety and Health Administration (OSHA) in the USA (ATSDR, 2004)

Exposure period	Parts per million	µg/m^3
8 hours	25	17,000
15 minutes	35	27,000

emissions, including NH_3, are a significant contribution to ill-health worldwide (Lelieveld *et al.*, 2015). High concentrations may arise from certain domestic cleaning products, from animal housing and slurry handling in agriculture, and from waste management and other industries. Workplace exposure limits for NH_3 are shown in Table 2.1.

2.5 Legislative Framework Limiting Ammonia Emissions in the European Union

In recent years, there has been an EU-wide effort to reduce nitrogen emissions through legislation. For example, emission-reduction targets for NH_3 are set by the Gothenburg Protocol to the CLRTAP and the NEC Directive, with the primary aims of lessening acidification and eutrophication. Parties to the convention must limit, reduce and prevent air pollution through development of policies and strategies, information exchange, consultation, research and monitoring. The NEC Directive established emission ceilings for acidifying and eutrophying substances including NH_3. In addition, abatement of NH_3 emissions is also required by Directive 2010/75/EU on industrial emissions and the Nitrates and Water Framework Directives (Directive 91/676/EEC and Directive 2000/60/EC), and emission limits for heavy-duty vehicles have become mandatory for all new registrations since 2014 (EC, 2015).

In Ireland, nationwide emissions of NH_3 are below the level set by the NEC Directive. A peak occurred in 1998 with an estimated emission of 122.7 kt, breaching the national emissions ceiling limit of 116 kt at that time. However, since 1998, estimated emissions have gradually reduced and the 2013 estimate of 107.8 kt for 2013 is below the NEC limit (EPA, 2015) (Figure 2.5). Ammonia trends differ from those of the other NEC substances, with emissions of SO_2, volatile organic compounds and NO_x all decreasing, while country's emissions of NH_3 remained relatively static over 1990–2012 (CSO, 2014: table 1.7). Moreover, observed wet deposition of NH_4^+ to terrestrial ecosystems is steady, showing no long-term trends during 1990–2012 (CSO, 2014).

2.6 Ammonia-Monitoring Networks

Atmospheric NH_3 concentrations were first determined in the mid- to late 19th century, with the majority of the observations made in urban locations (by Fresenius in Wiesbaden, Germany, in 1849 and by Smith in London

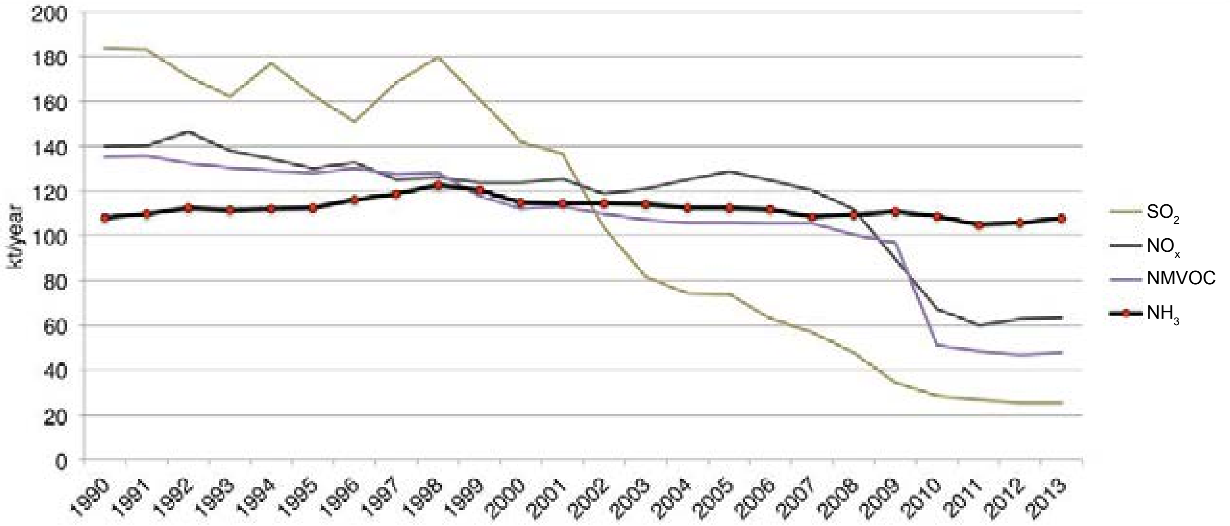


Figure 2.5. Adjusted emissions of major air pollutants for Ireland, 1990–2013. Annual emission limits under the NEC Directive are 42 kt of SO_2, 65 kt of NO_x, 55 kt of non-methane volatile organic compounds and 116 kt of NH_3. NMVOC, non-methane volatile organic compounds. Source: Duffy *et al.*, 2015; EPA, 2015.

in 1872; Sutton *et al.*, 2008). The scientific methods for investigating atmospheric NH_3 concentrations from the mid- to late 19th century are generally considered to be robust and reliable, although little is known about the volumes of air sampled in those early observations, which contributes to a degree of uncertainty (Sutton *et al.*, 2008).

The first true trans-national atmospheric and precipitation monitoring network was established in the 1950s as the European Air Chemistry Network of 49 stations across Finland, Sweden, Norway, Denmark and the UK. Both wet NH_4^+ and particulate NH_x were measured at each station. Monitoring equipment for each station was installed within a custom-designed insulated cabinet, which collected both air and precipitation (Egnér and Eriksson, 1955).

By the 1980s, environmental researchers across Europe began to take an interest in NH_3 as a pollutant in its own right. It originated with Dutch concerns about high agricultural NH_3 emissions (Sutton *et al.*, 2008). Studies by Erisman *et al.* (1988) and Vermetten *et al.* (1990) reflect this concern. One major study from this period by Allen *et al.* (1988) is of interest because it attempted to map spatial variation of NH_3 and NH_4^+ at a regional (35 km radius) scale. The study was conducted over 17 months, measuring concentrations at 19 sites in a variety of urban and rural locations. The results displayed high seasonal and local variations in NH_3 concentrations due to local (mostly livestock farming) sources.

The UK NAMN is a good example of a nationwide NH_3-monitoring network. It was first established in 1996 with 70 sampling locations; following a review in 1998 the number rose to over 80. Presently the UK NAMN measures gaseous NH_3 every month at 85 sites across the UK (NAMN, 2016). The network layout is in Figure 2.6. The network uses two sampling methods: a low-cost denuder filter-pack system was developed for long-term sampling periods, and a passive sampling method is also used. The latter method is cheaper and suitable for more sites, but requires calibration by co-location with denuders.

Because of the high spatial variability of atmospheric NH_3 concentrations, it was recognised that it was not feasible to monitor at a high density on a national scale. The monitoring network was designed, however, to provide sufficient data to fine-tune an atmospheric NH_3 emission and transport model known as the Fine Resolution Ammonia Exchange (FRAME) (Singles *et al.*, 1998). Direct measurements from the network and outputs from the FRAME model were combined to estimate NH_3 dry deposition across the UK.

The EMEP was set up in 1977 to determine the impact and extent of the alarming increase of acid precipitation across Europe at that time (EMEP, 2004). In 1979 the EMEP became an integrated part of the CLRTAP, and it now plays a major role in developing emission-reduction targets for negotiating emission-control agreements in the form of protocols to the convention (EMEP, 2004). The 1999 Gothenburg Protocol to the CLRTAP set national NH_3 emission ceiling limits for participating European countries, recognising that the deposition of nitrogen compounds may lead to unwanted fertilisation and eutrophication of sensitive ecosystems (UNECE, 2013). The EMEP network has a network of sites in 37 countries, which take hourly and/or daily measurements (EMEP, 2011) to capture the relationship between pollution and weather patterns. Data from the network have been reported since 1977. Initially the priority measurements were SO_2 and sulphate in air, and pH and sulphate in precipitation. Since 1977 the range of measurements has gradually increased to include all main components of precipitation, plus ozone and nitrogen compounds in air. Direct measurements of NH_3 air concentrations, however, are not recorded at every EMEP monitoring station. Equipment at the EMEP sites in Ireland is shown in Figure 2.7, and the site network in Ireland is shown in Figure 2.8.

Ammonia monitoring is also carried out in the AmmoniaN2K project as part of research into emissions from livestock housing, led by UCD (Tom Curran and Daithi Kelleghan, 2015, UCD School of Biosystems Engineering, University College Dublin, personal communication). The AmmoniaN2K project has been established to examine the transfer of NH_3 from emission sources to nearby Natura 2000 sites, relating emission concentrations to inferred local effects on biota. However, this monitoring was not used for the purposes of the Ammonia2 research study reported here, as it was based on point emission sources.

2.7 Measuring Ambient Atmospheric Ammonia

Sampling techniques can be divided into active or denuder sampling, in which air is drawn at a known rate through a trap for the target substance, and passive or

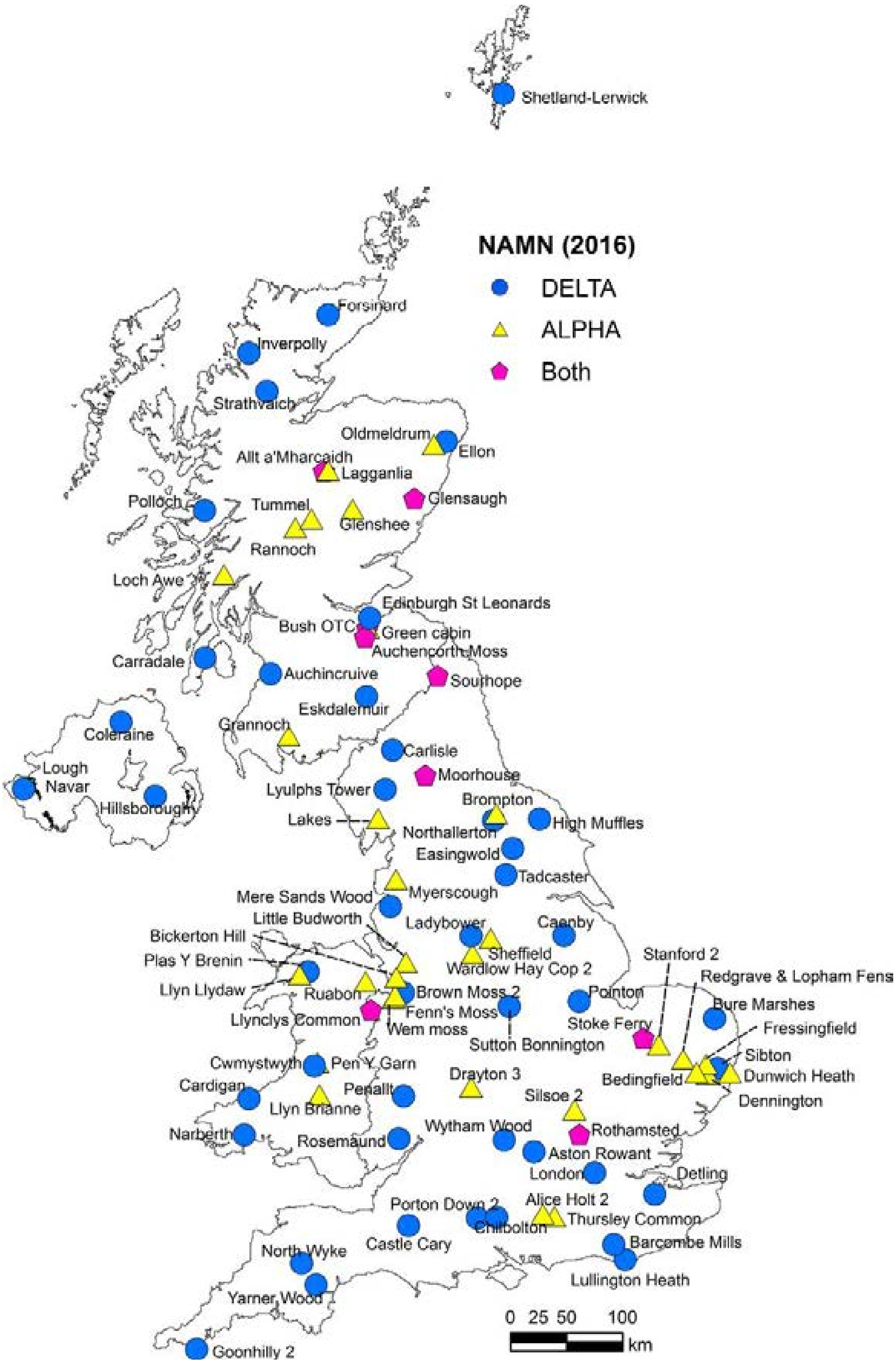


Figure 2.6. Sites in the UK NAMN. DELTA are active denuder samplers; ALPHA are passive samplers. Co-location of denuder and passive samplers allows comparison. Source: Sim Tang, Department for Environment, Food and Rural Affairs (DEFRA), UK Eutrophying and Acidifying Atmospheric Pollutants Network (UKEAP), August 2016, personal communication.

Figure 2.7. Equipment at Oak Park, County Carlow, one of six Irish sites in the EMEP network. Left: Eigenbrodt daily wet-only precipitation sampler, which accumulates one bottle per day, opening during precipitation events and staying closed otherwise. Right: Digitel high-volume daily air sampler, which collects PM_{10} on filter papers from 730 m^3 of air per day (Leinert *et al.*, 2008). In both cases, samples are stored in the enclosure until taken for laboratory analysis of ions.

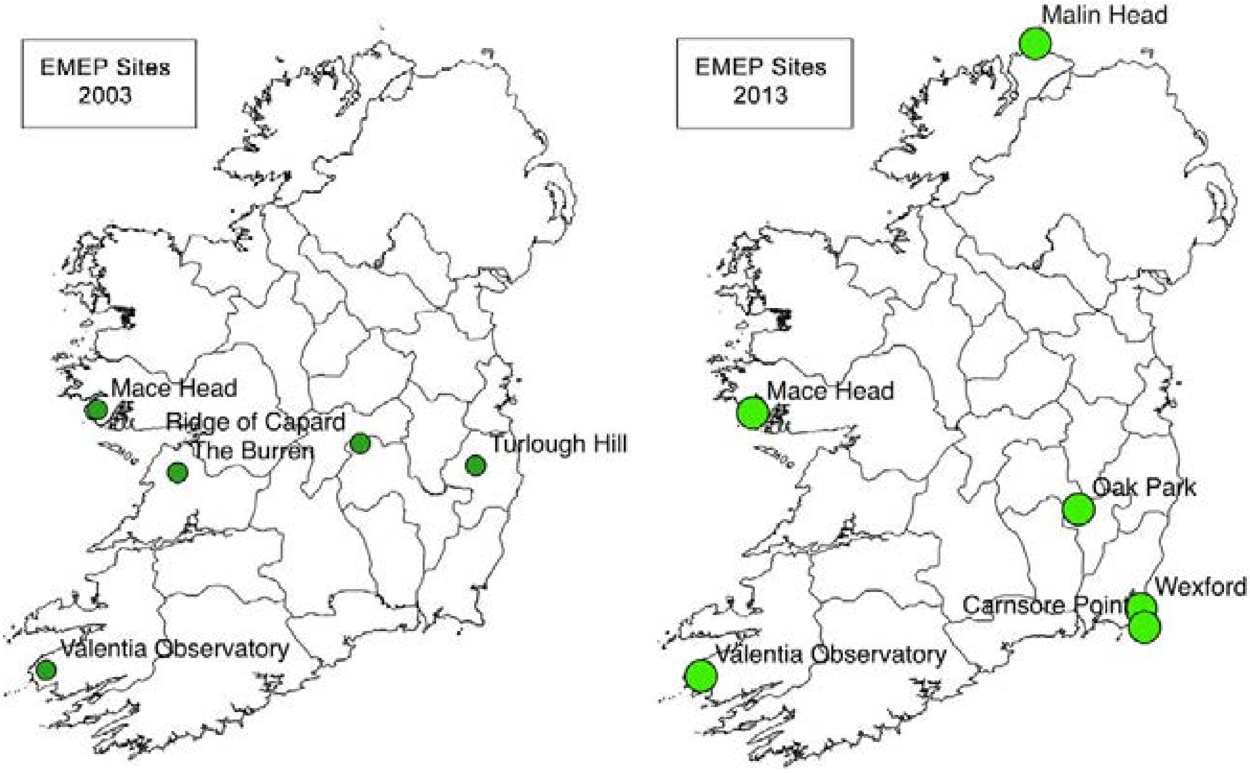


Figure 2.8. EMEP sites in Ireland, 2003 (left) and 2013 (right).

diffusive types, which rely on sampler body dimensions and shape to define a diffusion space to control transfer of the target gas to a trap surface. In each case, the trap surface is coated with an acid, which captures the NH_3 by protonation to NH_4^+, which is adsorbed or reacts, and is retained; as NH_3 is removed from the adjacent gas, a concentration gradient is established, maintaining a continued flow of gas to the trap surface.

2.7.1 Diffusive samplers

Berlin *et al.* (EC, 1987) defined the diffusive sampler as follows: "A diffusive sampler is a device which is capable of taking samples of gas or vapour pollutants from the atmosphere at a rate controlled by a physical process, such as diffusion through a static air layer or permeation through a membrane, but which does not involve the active movement of the air through the sampler."

It should be noted that the adjective "passive" is also used when describing these samplers. The term "passive" emphasises the process by which this type of sampler operates, namely diffusing gas from the atmosphere, along a path of defined dimensions, onto an absorbing medium, without the aid of a mechanically pumped source of air. According to Brown (1993), qualitative passive sampling techniques were used to test workplace environments as early as the 1930s; however, it took another 40 years for robust quantitative diffusive sampling to be applied, as in 1973 a tube-form sampler for SO_2 was described (Palmes and Gunnison, 1973). Tube-type diffusive samplers are hollow cylindrical tubes, closed at one end. The closed (top) end of the tube contains either a filter paper or a stainless steel grid, which is coated with an absorbent that collects the gas of interest. Since its introduction, numerous samplers, based on the original Palmes tube design, have been developed for ambient air monitoring. In each case, the length and/or diameter of the tube is modified to achieve the desired sampling rate (Tang *et al.*, 2001). Tube-type designs, with their long diffusion path lengths, are designed to be low-sensitivity samplers, suitable for long-term monitoring or in regions with high background ambient concentrations. Further experimentation with the geometry of the Palmes tube sampler led to the development of the badge-type diffusive sampler. Badge-type samplers, so called because of their broader and flatter shape, have higher analyte uptake rates than tube-type samplers because of their relatively large opening and short diffusion length. It was found that, by decreasing the diffusive path length in relation to the cross-sectional area of the sorbent surface, uptake rates for the target analyte could be increased substantially, thus increasing the sensitivity of the sampler.

Diffusive sampling relies on the principles of Fick's first law, which states that the mass flux of a substance goes from regions of high concentration to regions of low concentration, with a rate that is proportional to the concentration gradient of that substance in that one (spatial) dimension, and can be expressed as:

$$J = \frac{D}{L \times \left(C_1 - C_2\right)} \qquad \text{(Equation 2.1)}$$

where J = mass flux (amount of substance per unit area per unit time, µg/m per second), D = diffusion coefficient of substance (m^2/s), L = length of static air layer in the sampler (diffusion length) (m), C_1 = concentration of substance at the beginning of the diffusion layer (i.e. where $L = 0$) ($\mu g/m^3$) and C_2 = concentration of substance at the end of the diffusion layer ($\mu g/m^3$) (e.g. Brown, 2000). The mass of the substance that can diffuse to a suitable sorbent within a certain time is determined by Equation 2.2, which is derived from Equation 2.1:

$$m_s = \frac{D \times A \times \left(C_1 - C_2\right) \times t}{L} \qquad \text{(Equation 2.2)}$$

where m_s = mass of the substance which is sorbed by diffusion (µg), D = diffusion coefficient (m^2/s), A = cross-sectional area of the diffusion path (m^2), C_1 = concentration of the substance at the beginning of the diffusion layer ($\mu g/m^3$), C_2 = concentration of substance at the end of the diffusion layer ($\mu g/m^3$), t = exposure time (s) and L = length of the static air layer in sampler (m) (Brown, 2000). Figure 2.9 illustrates the diffusion process and indicates a simple cylindrical passive sampler.

The open end of the sampler at position 1 is the beginning of the diffusion path, where the target gas has a concentration of C_1. A sorbent at position 2 coating the interior base of the sampler, indicated by the dashed line S, will reduce the gas-phase concentration, C_2, to zero (ideally) due to sorption or chemical reaction. The sorption of the target gas at position 2 allows for its net flow along the diffusion length L. The shaded arrows indicate the direction of the flux within the sampler. Ideally, C_1 is equal to the concentration of the given target gas in the air outside the diffusive sampler C, and

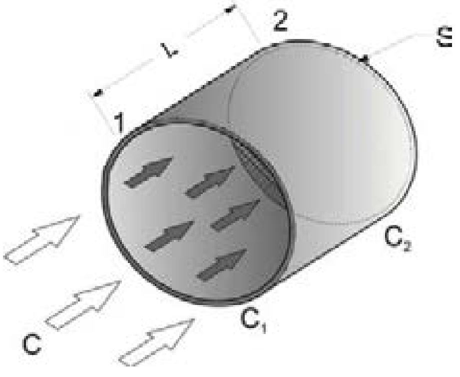


Figure 2.9. Diagram of the diffusion process within a simple passive sampler (adapted from Brown, 2000). See text for explanation of symbols.

C_2 equals zero ('zero-sink' condition). In this ideal case, the magnitude of the diffusive uptake rate U (µg/m^3 per second) can be found by using Equation 2.3:

$$U = \frac{D \times A}{L} \qquad \text{(Equation 2.3)}$$

The diffusive uptake rate U is therefore dependent only on the diffusion coefficient of the given analyte, D, and on the geometry of the diffusive sampler used (Brown, 2000). Substituting U for DA/L and rearranging Equation 2.2:

$$U = \frac{m_s}{C \times t} \qquad \text{(Equation 2.4)}$$

where U = magnitude of the diffusive uptake rate (µg/m^3 per second), m_s = mass of the substance sorbed by diffusion (µg), C = concentration of substance in the air outside the diffusive sampler (µg/m^3) and t = exposure time (s) (Brown, 2000). Also, if the exposure time is included in Equation 2.3, the magnitude of the volume of air sampled can be calculated by using Equation 2.5 (Tang *et al.*, 2001).

$$V = \frac{D \times A \times t}{L} \qquad \text{(Equation 2.5)}$$

Equations 2.1–2.5 apply under ideal conditions. In practice there are a number of factors that must be accounted for when designing and deploying passive samplers in order to get accurate results.

2.7.2 The Willems badge diffusive sampler

The diffusive sampler developed by Willems (1988, 1989, 1993) has a short diffusion length, increasing the sensitivity of the sampler, and uses a polytetrafluoroethylene (PTFE) diffusion filter to create a stable stagnant air layer within the sampler (Figure 2.10).

The sampler body consists of a rigid polystyrene cylinder, closed at one end. The cylinder has an internal diameter of 28 mm and an internal depth of 8 mm. The internal base of the cylinder contains a glass-fibre filter coated with tartaric acid, an absorbent for gaseous NH_3. A 2-mm retainer ring separates the absorbent acid layer and a PTFE diffusion filter, creating a 2-mm-thick stagnant air layer above the absorbent surface. The PTFE filter is kept in place by the insertion of a 3-mm polystyrene retainer ring. The assembly is sealed by a polyethylene cap. The absorbent filter at the base of the sampler is made from glass fibre mesh (Whatman GF/A). These materials do not react with the reagents or with the target gas. The PTFE diffusion filter membrane (Schleicher and Schuell TE-38) has pores of 5 µm diameter and is reinforced with polyester fibres, giving the membrane thickness and rigidity.

2.7.3 The working principles of the Willems badge

The Willems badge works on the principle of diffusion of NH_3 through the PTFE filter and the 2-mm static air layer followed by chemisorption to the absorbent

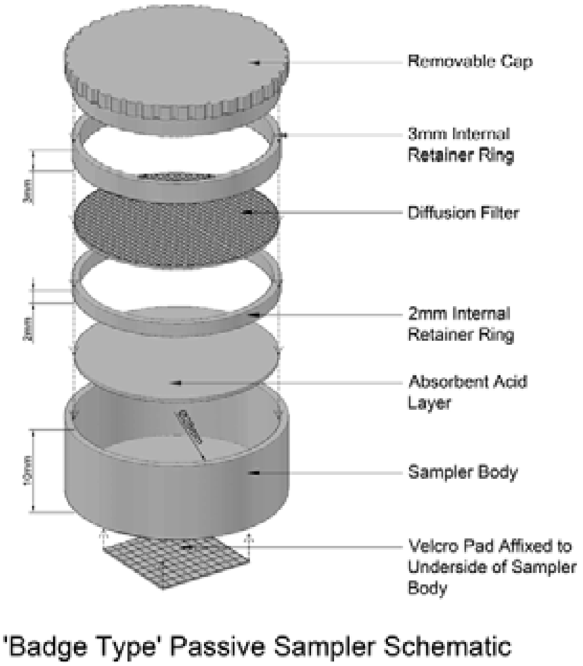


Figure 2.10. Exploded diagram showing the construction of the Willems badge passive-diffusive sampler.

acid coated filter at the base of the sampler. When the gas is removed from the air onto the acid layer, a concentration gradient of gas is created, and there is a consequent flow towards the sorbent. Chemical and physical resistances have an influence on the diffusion process within the sampler. Analogous to Ohm's law of electrical resistance (voltage = current × resistance) and using Equation 2.1, the following equation can be constructed:

$$(C_1 - C_2) = J \times R_p \qquad \text{(Equation 2.6)}$$

where J = flux per unit area per unit time (µg/m^2 per second) and R_p = sum of physical resistances of the badge for NH_3. This physical resistance may be sub-divided into three composite resistances: R_b, the boundary layer resistance; R_m, the membrane resistance; and R_d, the diffusion resistance (Figure 2.11).

$$R_p = R_d + R_m + R_b \qquad \text{(Equation 2.7)}$$

The diffusion resistance, R_d, is built into Equation 2.1, as it is a function of the diffusion coefficient and the diffusion length (L/D). The magnitude of the membrane resistance R_m depends on the properties of the PTFE membrane, namely its thickness, porosity and tortuosity. The boundary layer resistance, R_b, is caused by the formation of a static air boundary layer within the shelter of the rim of the badge, above the diffusion membrane. This space is necessary within the badge to fit the 3-mm internal retainer ring that keeps the Teflon diffusion filter in place and also allows the badge lid to be closed and sealed. The magnitude of the boundary layer resistance is linked to the velocity of the external wind by an effect known as "wind shortening". It has been determined that, when the external air velocity is 1.2 m/s or higher, R_b is small and constant (Willems, 1993). In addition to the three physical resistances discussed above, there is also a chemical resistance. The chemical resistance may be derived, under steady-state conditions, from the following equation (Adema, 1993, cited by van den Beuken, 1994):

$$C_0 = J \times k^{-1} \times k_a^{-1} \qquad \text{(Equation 2.8)}$$

where C_0 = gas concentration at the surface of the filter (µg/m^2), J = flux per unit area per unit time (µg/m^2 per second), k = reaction velocity (m^3/mol per second) and k_a = filter activity (mol/m^2). The chemical resistance, R_c, is defined as:

$$R_c = k^{-1} \times k_a^{-1} \qquad \text{(Equation 2.9)}$$

and is generally found to be small. The chemical resistance can now be added to Equation 2.6:

$$(C_1 - C_2) = J \times (R_p + R_c) = J \times R_t \qquad \text{(Equation 2.10)}$$

The total resistance of the Willems badge, R_t, has been determined empirically by simultaneous measurements with badges and a reference method. At wind velocities higher than 1 m /s^{-1}, which result in a negligible boundary resistance, R_t, the total resistance was determined by Willems (1988) using a denuder as a reference method. The total resistance can now be calculated using the following equation:

$$R_t = \frac{C_{ref} \times A \times t}{Q} \qquad \text{(Equation 2.11)}$$

where R_t = total resistance (s/m), C_{ref} = concentration of the analyte measured with a reference method (µg/m^3), A = reaction filter surface area[1] (5.309×10^{-4}m^2), t = sampling time (s) and Q = amount of analyte on the reaction filter (µg).[2] The total resistance, R_t, was found to be 164 s/m. With the measured total resistance, the concentration of target gas in the air can be calculated

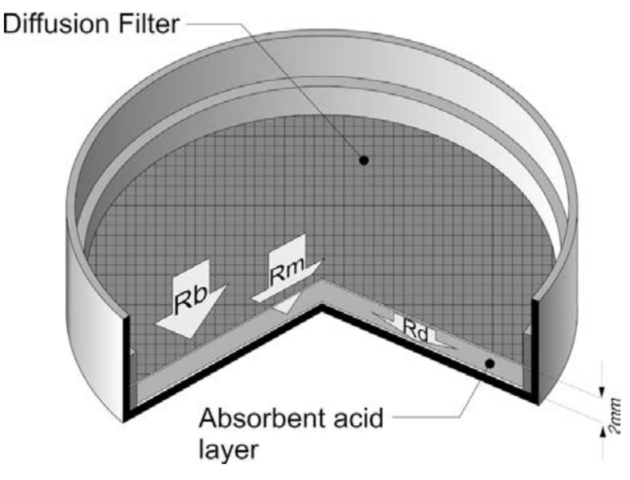


Figure 2.11. Diagram of assembled Willems badge indicating the three physical resistances R_b, R_m and R_d.

---

[1] Badge body diameter is 28 mm (Figure 2.10). The 1-mm-thick retaining-ring wall reduces the absorbent surface diameter by 2 mm. Therefore, the absorbing surface is [(0.026 ÷ 2) m]2 × π = 0.0005309 m2.

[2] The measured substance is ammonium, NH4+, which is recalculated and expressed throughout this report as Q, in µg of NH3. 1 µg NH4+ = 0.9497 µg NH3.

from the sampled amount of analyte on the reaction filter (Q) and the sampling time (*t*) according to the following equation:

$$C = \frac{Q \times R_t}{A \times t} \qquad \text{(Equation 2.12)}$$

where C = average concentration during exposure (µg/m^3). Total resistance, R_t, of the Willems badge has been empirically validated for Irish conditions using a High Efficiency Annular Denuder (van den Beuken, 1994) as a reference method.

2.7.4 *Factors affecting sampler performance*

The movement of ambient air and the orientation of the sampler relative to the external air flow affect the performance of the diffusive sampler because of their influence on the effective diffusion path length (Pozzoli and Cottica, 1987; Zurlo and Andreoletti, 1987; Brown, 2000).

The sorbent must have high sorption capacity for the target gas, and low vapour pressure of the sorbed material or of the reaction product. Tartaric acid was found to be an appropriate coating medium for the Willems badge sampler, although citric and oxalic acids perform similarly (Rabaud *et al.*, 2001).

High wind speeds during sampling may lead to an underestimation of the diffusive uptake rate and, more importantly, may also damage the samplers directly. Samplers should be placed in open sites at a sufficient distance from obstacles such as buildings or walls that are likely to create turbulent air flows. Some protection from precipitation is also important for all types of sampler, as rain or melted snow can interfere with the sampling surfaces.

Diffusive samplers are small and can travel by post. Although each sampler is sealed, sampler batches should also travel within a sealed container during transport, at a constant low temperature, and away from possible contamination sources such as petroleum or aviation fuel (Brown, 2000). They can also have a sorbent pack included to scrub any NH_3 within the container. Additional sample blanks, i.e. travel blanks, should accompany the samplers during transit.

2.8 Calculating Dry Deposition Velocities

To map reduced nitrogen deposition, dry deposition of NH_3 must be mapped separately from wet deposition of NH_4^+, and the results combined. Estimate dry deposition of NH_3 requires an inferential modelling technique. Measured NH_3 concentration (µg/m^3) is combined with a deposition velocity (m/s), and the flux (µg/m^2 per second) from the atmosphere to the ground is obtained.

Directly measuring the dry deposition of an atmospheric component is difficult, and the behaviour of NH_3 at local scales makes its quantification even more of a challenge. The deposition of NH_3 involves many complex processes, especially because of its high reactivity and strong water solubility. They include the formation of particulate ammonium nitrate (NH_4NO_3) in the presence of nitric acid (HNO_3), bi-directional transport paths, non-stomatal uptake by foliage, co-deposition of NH_3 and SO_2 forming ammonium sulphate [$(NH_4)_2SO_4$], and other factors (Sutton *et al.*, 2007).

Dry deposition velocities are calculated for different surface or vegetation types by using a resistance model that describes both the transport of a component to, and its absorption at, a given surface. The dry deposition velocity (V_d) is the rate at which a gaseous component is deposited onto a surface. It is measured in centimetres per second.

Resistances are modelled using observations of meteorological and surface exchange processes for different receptor surfaces with varying atmospheric concentrations of the measured component, as described by Erisman *et al.* (1994). The resistance model represents the resistance of the gas to three stages of transport from the atmosphere, through the boundary layer and finally to the receptor surface. The first stage is transport through the atmosphere to the receptor surface (R_a); the second stage is transport through the quasi-laminar layer at the receptor surface (R_b); and the third stage is the capture of the gas or particle at the receptor surface (R_c) (Erisman *et al.*, 1994). In this model the dry deposition velocity is represented as the reciprocal of the sum of the three resistances:

$$V_d = \frac{1}{\left(R_a + R_b + R_c\right)} \qquad \text{(Equation 2.13)}$$

When a deposition velocity is known for a receptor, the rate of deposition per unit area, or flux, may be calculated. The flux is determined from the measured air concentration and deposition velocity at a certain height (*z*) by the following equation:

$$F = V_d(z) \times C(z) \qquad \text{(Equation 2.14)}$$

where F = flux (g/m^2 per second), $C(z)$ = concentration of the atmospheric component at height z (µg/m^3), $V_d(z)$ = deposition velocity at height z (cm/s) and z = reference height above a surface (m) (Erisman *et al.*, 1994). Figure 2.12 illustrates the nominal location of each of the resistances.

There are complications, however, when modelling dry deposition velocities for chemical species such as NH_3 that have surface sources in addition to the atmospheric source. In the resistance model described above, it is assumed that the surface concentration is zero. However, there may be a non-zero concentration of NH_3 that at the surface (the surface may emit NH_3). Therefore, for gases such as NH_3 that have a compensation point (c_p), the flux is estimated as:

$$F = V_d(z) \times [C(z) - c_p] \qquad \text{(Equation 2.15)}$$

NH_3 dry deposition velocity for a specific receptor may therefore be found from the flux/concentration ratio (Erisman *et al.*, 1994):

$$V_d(z) = F \div [C(z) - c_p] \qquad \text{(Equation 2.16)}$$

By measuring NH_3 concentrations in air, and the dry deposition flux over a given area, using micrometeorological techniques, a deposition velocity may be calculated. According to Sutton (1994), micrometeorological measurements provide the best approach for measuring NH_3 fluxes and resistances in the field. Micrometeorological techniques use high-frequency measurements of the atmospheric concentration of the analyte in tandem with meteorological measurements

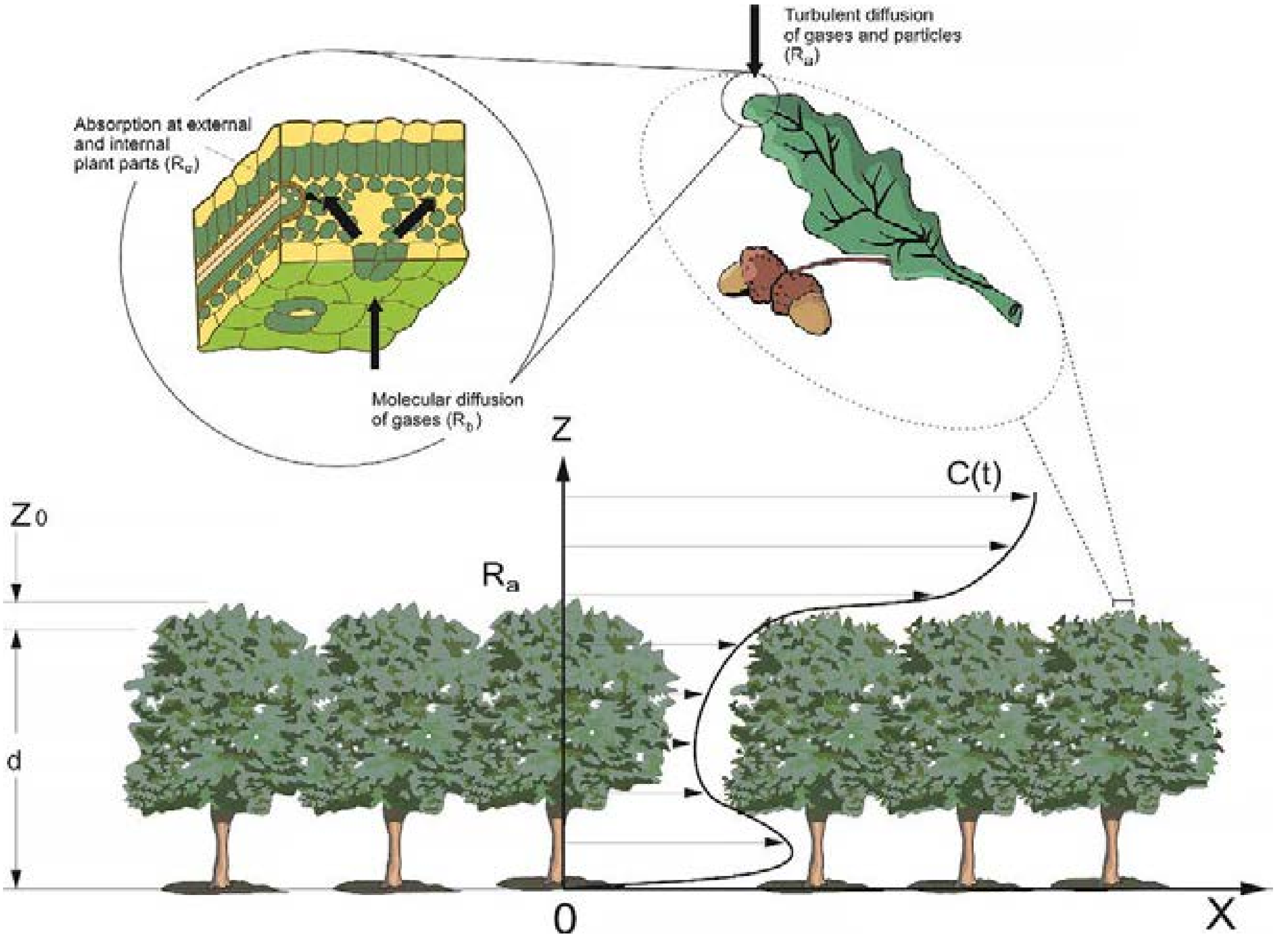


Figure 2.12. Nominal location of the three ecosystem resistances used to calculate the dry deposition velocity. Source: after van den Beuken (1994).

such as wind speed, wet and dry bulb air temperatures, net radiation and heat fluxes. Micrometeorological techniques are, however, extremely labour- and equipment-intensive and allow the measurement of component fluxes only over limited areas and for limited periods.

Dry deposition values for different surface types were selected from those given by de Kluizenaar and Farrell (EPA, 2000), who reviewed both modelled and measured surface-specific NH_3-deposition velocities (V_d).

3 Network Operation Methods

Following analysis of the Ammonia1 concentration data it was possible to classify the sites based on statistically similar groups. The analysis, based on the annual median NH_3 concentration observed during that survey at each site, showed that the sites could be divided into three broad groupings: western seaboard, mid-range and midlands (Figure 3.1). Given the very low annual concentrations recorded at sites along the western seaboard, the monitoring station density within the western seaboard region was reduced from the Ammonia1 network, while monitoring-site density in the north and south midlands was maintained for the Ammonia2 study.

Sites within the Ammonia2 monitoring network were then selected based on the following criteria: they were to be distributed across Ireland, each at least 5 km distant from major point sources of NH_3, such as large pig farms and poultry farms, and at lesser minimum distances from lesser sources, at locations where volunteer site personnel were available, and situated at climatological stations or locations with similar conditions. Where possible, original sites from the Ammonia1 network were given priority. The 25 selected sites are shown in Figure 3.1. The Ammonia1 network operated with 40 stations for Ireland's approximately 84,400 km^2, giving a network density of 1750 km^2 per station. The 25 stations of the Ammonia2 network result in a coverage of closer to 2800 km^2 per station, which is in line with the monitoring network in the UK (3000 km^2 per station).

The western seaboard is monitored by four sites: Glenties, Sligo Airport, Mace Head and Killarney. A small urban transect of three sites was also established in Dublin, representing the urban core (Winetavern Street), the suburbs (Clonskeagh) and a mid-way site (Phoenix Park). Most selected stations are part of the network of climatological stations operated by Met Éireann. They broadly follow World Meteorological Organization (WMO) standards for site and exposure requirements:

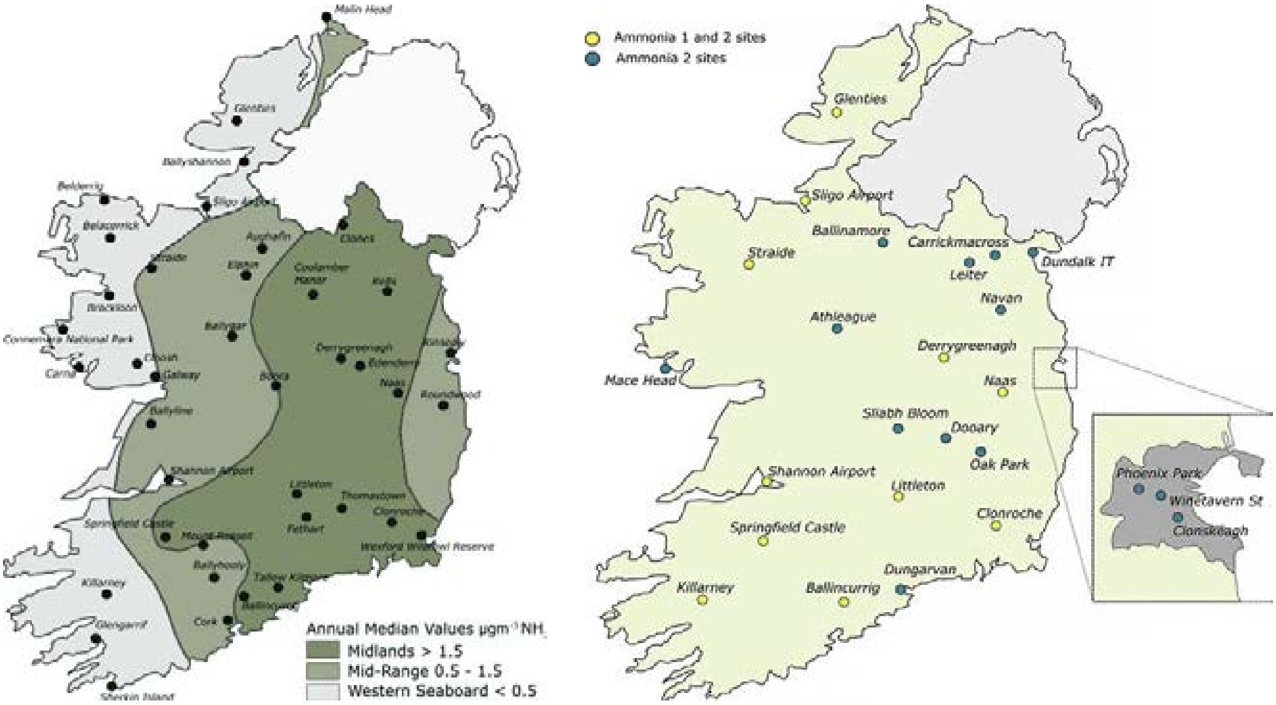


Figure 3.1. Left: the 1999–2000 NH_3 monitoring network sites (Ammonia1); shading indicates similar annual median NH_3 concentrations. Right: the Ammonia2 network sites. Inset: the three sites in urban Dublin.

> The site enclosure should be a level piece of ground, covered with short grass, and surrounded by open fencing or palings to exclude unauthorised persons.
>
> There should be no steeply sloping ground in the vicinity and the site should not be in a hollow. If these conditions are not complied with, the observations may show peculiarities of entirely local significance.
>
> The site should be well away from trees, buildings, walls or other obstructions.
>
> (WMO, 2008)

The suitability of each of the selected sites was evaluated after a site visit and it was included in the network only if it passed the site suitability criteria. One site in the network is illustrated in Figure 3.2. The site assessment form is given in Appendix 1.

Site inspections and sampler deployment took place between 28 May and 14 June 2013. A site assessment form (Appendix 1) was completed at each site. The network volunteer on site was instructed on how to handle the Willems badge samplers during exposure, storing and shipping. A sampling field-sheet was used for each sampler exposure period; this is given in Appendix 2. Site details are given in Table 3.1.

3.1 Network Operation

The first sets of samplers for the monitoring network were deployed between 28 May and 14 June 2013 at 21 stations. The first co-ordinated swap-over of badges occurred on 17 June 2013. By exposure period 4, beginning on 15 July 2014, all 25 of the monitoring stations were up and running on the network. Monitoring ended on 28 July 2014 and consisted of 28 fortnightly exposures and 1 4-week exposure. In total the monitoring campaign ran for 60 weeks.

Eighty samplers were required for each 2-week exposure (25 sites × 3 samplers per site + 5 travel blanks = 80). Batches of 160 prepared samplers, for 2 exposures, were shipped every 4 weeks from Trent University, Ontario, Canada, to UCD, and stored at 4°C

Figure 3.2. Willems badge NH_3 samplers of the Ammonia2 network, attached under the edge of the Stevenson screen enclosure at Carrickmacross climatological station, County Monaghan. Red tape identifies the preparation batch in the Trent University lab. The samplers are sheltered from falling rain, but open on their lower sides to allow free air movement. Site assessment includes considering adjacent shelter, and the size and proximity of any NH_3 point sources.

Table 3.1. Monitoring site details

Site name	Easting (m)	Northing (m)	Altitude (m)	Sampling start	Sampling end	Site description
Athleague	181786.92	257494.47	61	30/06/2013	28/07/2014	Garden, house, farmland
Ballinamore	210565.65	310828.73	103	24/05/2013	28/07/2014	Farmland
Ballincurrig	186255.11	084299.99	175	06/06/2013	28/07/2014	Garden, house, farmland
Carrickmacross	281742.51	303601.05	64	12/06/2013	28/07/2014	Garden, house, farmland
Clonroche	282385.94	133108.92	118	17/07/2013	28/07/2014	Garden, house, farmland
Clonskeagh	317695.44	230483.12	22	03/07/2013	29/07/2014	Car park, offices, suburban
Derrygreenagh	249402.05	238162.90	100	07/06/2013	25/07/2014	Work facility, cutover bog
Dooary	250567.69	188247.89	240	14/06/2013	28/07/2014	Garden, house, farmland, forest
Dundalk Institute of Technology	305346.31	305155.03	24	12/06/2013	28/07/2014	Car park, campus, edge of town
Dungarvan	221780.69	092855.28	19	06/06/2013	28/07/2014	Garden, farmland
Glenties	181530.66	393744.22	63	31/05/2013	28/07/2014	Salmon hatchery, farmland
Killarney	096952.36	086347.25	41	05/06/2013	29/07/2014	Parkland
Leiter, Cavan	248693.00	302011.00	141	17/06/2013	28/07/2014	Garden, house, farmland
Littleton	220376.32	151177.72	136	07/06/2013	07/08/2014	Cutover bog
Mace Head	073402.30	232270.56	15	29/05/2013	28/07/2014	Exposed coast
Naas	286354.26	217151.94	c. 84	28/05/2013	14/07/2014	Garden, house, farmland
Navan	284814.29	268440.11	52	28/05/2013	05/08/2014	Farmland
Oak Park	272650.00	179657.00	145	03/07/2013	28/07/2014	Farmland
Phoenix Park	309930.00	236101.00	52	29/05/2013	28/07/2014	Offices, urban parkland
Shannon Airport	137212.74	160814.89	12	13/06/2013	28/07/2014	Busy international airport
Sliabh Bloom	219855.20	193659.81	210	04/06/2013	28/07/2014	Garden, house, farmland
Sligo Airport	161037.00	336897.63	8	31/05/2013	28/07/2014	Quiet regional airport, coast
Springfield Castle	135214.44	122368.00	106	05/06/2013	28/07/2014	Garden, house, farmland
Straide	126049.83	297866.90	21	30/05/2013	28/07/2014	Garden, house, farmland
Winetavern Street	315104.00	234058.00	c. 10	29/05/2013	28/07/2014	Car park entrance, busy urban setting

Phoenix Park and Winetavern St sampler height, 3.5 m; all other sites sampler height, 1.2 m.

until dispatched by post. Shipments from Trent included cooler-packs and small containers of tartaric acid to scrub NH_3 inside the package.

Each site posting for each 2-week exposure period consisted of a sealed zip-lock bag containing three samplers, a field-sheet for recording the sampler exposure times, a set of gloves for handling the samplers, and a pre-paid and addressed return envelope. After each exposure period the site operators posted the samplers and field-sheets back to UCD. Samplers were stored at 4°C and then shipped back to Trent University for analysis.

Five travel blank samplers accompanied each batch of samplers. The travel blanks were stored with the main batch of samplers until deployment. When the samplers were posted to the field, a monitoring site was chosen and the travel blanks were posted along with that site's samplers. The operators were instructed to keep the travel blanks, unopened, in a refrigerator and to post them back with their accompanying samplers after the exposure period was over. Different sites within the network were chosen for the travel blanks during each exposure period. The travel blanks were returned to Trent University along with their batch of exposed badges. The travel blanks accompanied the samplers, unopened, through all stages of their journey, and are therefore representative of a standard set of samplers, deployed in the network yet unopened. Background levels of NH_3 that the badges pick up during transport and storage can thereby be assessed.

Samplers were swapped every fortnight on Mondays, except at the Oak Park site, which swapped on Wednesday for operational reasons. Operators were reminded of the impending date by text or email.

The samplers were exposed for a standard 2-week period throughout the campaign except for one exposure period of 4-weeks' duration, which occurred at Christmas 2013. This extended exposure period was planned and co-ordinated across all the sites, to reduce the risk of irregular sample periods during the holiday season.

3.2 Returns of Diffusive Samplers

There were 29 separate exposure periods in the monitoring campaign, and 2099 Willems badges were deployed to and returned from the field. Badges were considered lost if they were unfit for analysis. Throughout the whole campaign, 6 sites lost all 3 badges for 1 exposure period, 4 sites lost 2 badges for 1 exposure period and 26 sites lost 1 badge for 1 exposure period. A total of 52 badges were lost or contaminated during the campaign, representing a 2.4% loss. The reasons that badges were lost include if the badges were missing or damaged after the exposure period; if the filters were found to be uneven or gaps in the filter were observed; if badges were found on the ground by the operator; and if the caps sealing the badges were not fully closed on return to UCD. Details of badge returns are shown in Appendix 4.

The Willems badges were exposed for, in total, 232,848 hours during the campaign. From all the sites, 8896 hours were recorded deviating from (either exceeding or below) the target exposure hours, which represents a 3.7% variation from a perfect exposure time record.

In terms of operation efficiency, the NH_3 monitoring network was a success. A low percentage (2.4%) of samplers were lost, damaged or contaminated in the field or in transit and the samplers were also exposed for the correct times, resulting in a very low variation (3.7%) from a perfect exposure record. The samplers were also exposed in some very stormy conditions during the year. For example, at Mace Head on 12 February 2014, hurricane-force winds of 65 knots (120 km/h) were reported, equalling the fifth-highest wind speed recorded in Ireland. The samplers were returned intact from Mace Head during this exposure period. The smooth running of the network, the low levels of sampler losses and the excellent time keeping were the result of the reliability, consistency and attention to detail by the volunteer operators throughout the course of the study.

3.3 Laboratory Analysis

The Willems badge diffusive samplers were assembled and, after exposure, disassembled and analysed in laboratories at Trent University. The samplers were assembled and disassembled within the controlled environment of a glove-box fitted with an NH_3 filtration system. The NH_3-free air within the glove-box ensures that contamination is minimised when preparing the samplers for exposure and also when analysing the exposed samplers. On arrival at Trent University the samplers were stored in cool, dark conditions in a refrigerator. The NH_3 collected on the samplers was analysed by spectrophotometric determination. For each batch of samplers analysed, a standard curve was generated from a set of six calibration standards of known NH_3 concentration. An ultraviolet–visible spectrometer (Perkin Elmer Lambda 2) was used at a wavelength of 655 nm for the analysis of the samples. Data from the network were generated as spectrophotometric absorbance values, and the amount of time each set of badges was exposed at each site was taken from the field-sheet. The absorbance value measured from each badge and its exposure time were then converted to an air concentration value for each of the samplers. Travel and laboratory blanks for each batch of samplers were also analysed. Preparation and analysis of the samplers follow the original Willems analytical procedure as described by de Kluizenaar and Farrell (2000), and reproduced in Appendix 3.

3.4 Laboratory and Travel Blanks

A total of 138 laboratory blanks were assembled for the study, or about five laboratory blank badges for each 2-week exposure cycle. An average of 1.403 µg of NH_3 (*Q*) was measured on the filters of the laboratory blanks following exposure, equating to a fortnightly average air concentration of 0.358 µg/m^3 of NH_3. The standard deviation of 0.023 µg laboratory blank absorbance of NH_3 equates to an air concentration value of 0.189 µg/m^3. The average coefficient of variation between the laboratory blank badge values across all 29 exposures was 23%.

The detection limit of the Willems badge was estimated as twice the standard deviation of the average laboratory blank for the 2-week exposure. A value of 0.379 µg/m^3 of NH_3 was calculated as the detection limit. Analytically, observations below this limit were detectable but these values are uncertain, as there are no significant differences between the laboratory blank values and the observed values. Of the 701 sets of triplicate exposures during the campaign, 11 recorded values (1.5%) were below the detection limit but above their laboratory blank value (five of these, 45% of the total, are from the Mace Head site). These values are shown in italics when reported. A total of 45 exposures (6.4%) have measured values below their respective laboratory blank values; 10 of these (22%) were from the Mace Head site. These exposure values were indistinguishable from the laboratory blanks and designated as ‘none detected’ (ND).

Figure 3.3 shows a boxplot of the range of NH_3 in µg absorbed (*Q*, expressed as NH_3) on the filters of laboratory blanks, travel blanks and each monitoring station.

The laboratory blanks recorded significantly lower amounts of NH_3 sampled (*Q*) than the exposed sites, based on a Mann–Whitney U test. The same test confirms, however, that the laboratory blanks also show significantly lower amounts than the travel blanks and that the travel blanks have statistically similar *Q* values to three low-range sites (Figure 3.3). This test result implies that the travel blanks were picking up NH_3 during transit from the laboratory to the study sites and back again. Previous similar studies (de Kluizenaar and Farrell, 2000; Zbieranowski and Aherne, 2012a) have shown laboratory blanks with statistically similar *Q* values to travel blanks, indicating that the sealed badge-cap and zip-lock bags protected the samplers from contamination between assembly, exposure and analysis during those studies. One probable reason for the higher *Q* values on the travel blanks recorded during this study is that the samplers travelled further and for longer than in the other cited studies. Although the travel blank *Q* values are statistically similar to those of the Killarney, Mace Head and Glenties sites, these sites have the lowest recorded NH_3 concentration averages and their *Q* values are also significantly different from the other sites across the network. A total of 8% of the measured values recorded for the study are below the 0.379 µg/m³ detection limit; almost 60% of this total are measurements from the three low-range sites.

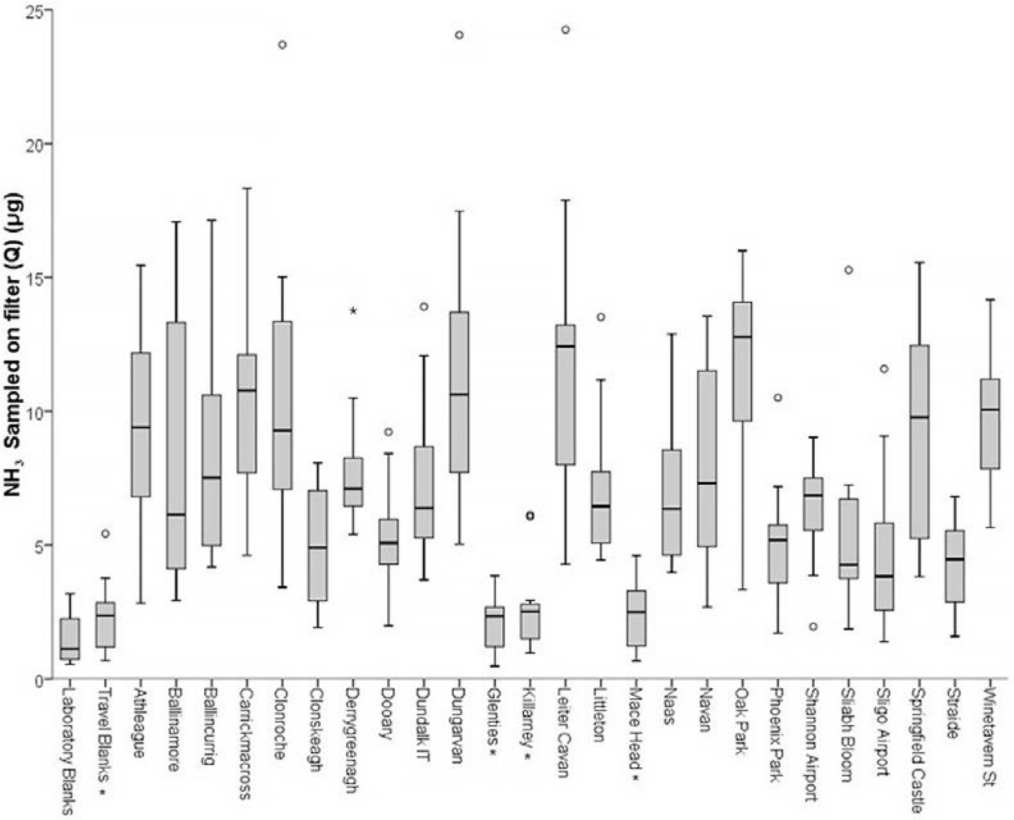


Figure 3.3. Boxplot of range of NH_3 amounts, *Q*, µg NH_3 absorbed on laboratory blanks, travel blanks and monitoring station samplers. The box represents the interquartile range; the median for each source is shown by the line within each box. Sites that are statistically indistinguishable from travel blanks are denoted with an asterisk on the *x*-axis label. Values below the detection limit are included in the boxplot.

3.5 Evaluating Diffusive Samplers

The performance of the Willems badge samplers was evaluated by exposure period assessment, and by co-location assessment with a denuder method.

For the exposure period assessments, five sites within the existing network were chosen to deploy extra sets of samplers. Multiple sets of badges were exposed at the same location over varying periods and the uptake rate for each set of badges were compared. The exposure period assessment allows comparison of NH_3 uptake between sets of badges over different times. Extra triplicate sets of samplers were exposed at each site for a 4-week period. In addition, further triplicate sets were exposed for four 1-week periods. Ideally, four separate badges exposed consecutively over 4 weeks should record the same amount of NH_3 as one badge exposed for 4 weeks in the same location. The standard fortnightly samplers were also exposed at these sites.

The amounts (Q) of NH_4^+ on the reaction filters of the samplers exposed for 2 and 4 weeks were compared with the sum of amounts from samplers exposed for successive weekly periods, to assess their performance over different exposure periods. This exposure period monitoring took place at the same five sites over two separate periods: the first was for 4 weeks in November and December 2013, chosen to assess winter (low atmospheric NH_3) conditions; the second period ran for 4 weeks in April and May 2014, assessing the badges' uptake rates during more elevated NH_3 conditions in the late spring. The five sites, namely Sligo Airport (County Sligo), Athleague (County Roscommon), Ballincurrig (County Cork), Derrygreenagh (County Westmeath), and Navan (County Meath), were chosen as a geographical spread across the country, along an expected gradient of NH_3 concentrations.

Linear regressions were conducted from both assessment periods. In all regression tests, the NH_3 air concentrations from the 2-week exposure periods were assigned as the independent variable, as this is the standard exposure period used for the main study. At the five study sites, the aggregated air concentrations from two 2-week exposures were compared with the aggregated concentrations from four 1-week exposures, and also with one 4-week exposure. The two regressions were carried out over two test periods. For each individual test, an R^2 value, a mean prediction error (MPE) and a root mean squared error (RMSE) were calculated. The results are shown in Table 3.2.

An MPE value of 1 indicates no loss of data. The negative MPE values from both trials show that there is a loss of data between the weekly monitoring periods and the fortnightly monitoring periods. Similarly, positive MPE values show that there is also a loss of data between the fortnightly monitoring periods and the 4-week monitoring periods. There are higher correlations (R^2 values) between the weekly and fortnightly periods for both trials than between the fortnightly and 4-week periods.

The correlation graph in Figure 3.4 represents the errors from both trials. The reference lines in the graph shows the 1:1 line for the 2-week NH_3 concentrations, from five monitoring stations. The black squares comparing NH_3 concentrations between 1- and 2-week periods are mostly above the reference line. This indicates NH_3 loss between the 1- and 2-week sample periods. The black circles compare the 2-week and 4-week sampling. Most are below the reference line, indicating a loss of NH_3 between 2- and 4-week periods. The results of the exposure period monitoring tests show that data loss (decreasing NH_3 concentration) is occurring with increasing exposure duration.

Table 3.2. Linear regressions comparing 2-week with 1-week exposures and 2-week with 4-week exposures from two trial periods

Exposures	R^2	MPE	RMSE
Trial period 1			
2 weeks vs 1 week	0.789	–0.312	0.436
2 weeks vs 4 weeks	0.653	0.523	0.463
Trial period 2			
2 weeks vs 1 week	0.847	–0.185	0.163
2 weeks vs 4 weeks	0.083	0.133	0.379

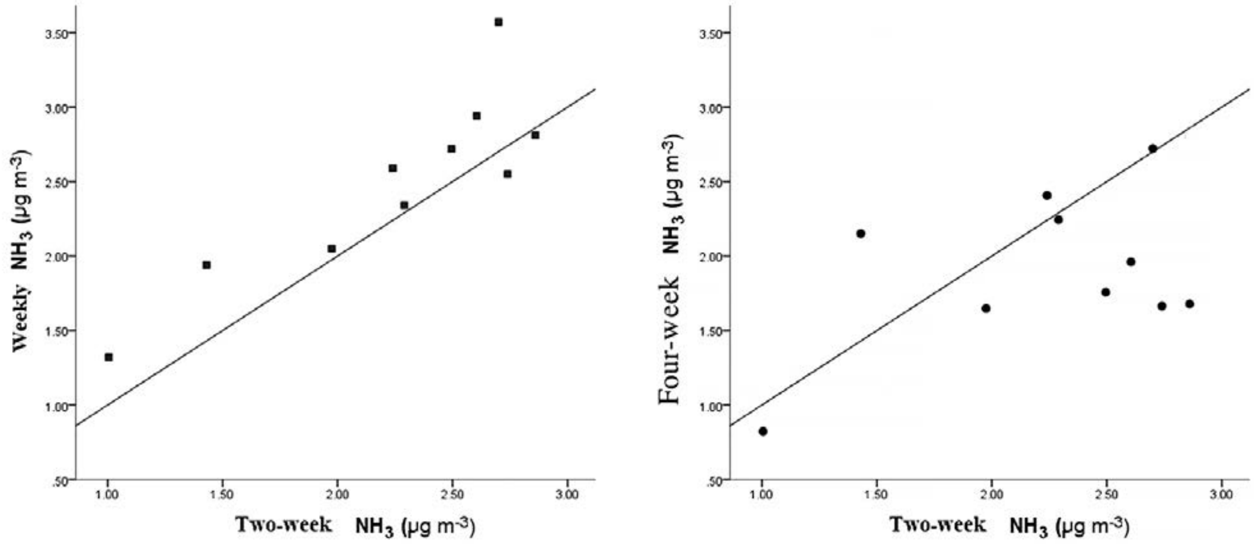


Figure 3.4. Ambient NH_3 concentrations comparing 1-, 2- and 4-week exposures, from two 4-week trial periods at five monitoring sites. The *x*-axes are aggregated 2-week exposures; the left graph plots these against aggregated 1-week exposures, and the right graph against the 4-week exposures. The 1:1 line is shown; points tending towards the shorter-period axis indicate NH_3 loss over longer sampling periods, although the effect is not significant and adjustments can be made to correct it.

Ideally the NH_3 recorded on the badges should remain constant between time periods. Two weekly exposures at one site should equal one fortnightly exposure, for example. The trials suggest that perhaps the total resistance constant R_t requires slight adjustment. The adjustment required would be very small, however, as the magnitude of the decreasing concentrations (the error) was below the detection limit.

The Willems badge samplers were appraised further by directly comparing the uptake rate of NH_3 on a triplicate set of badges with a reference method (an active denuder). For this co-location assessment, triplicate sets of Willems samplers were exposed for two separate trial periods, adjacent to an active denuder system at Hillsborough, County Down, a station within the UK National Ammonia Monitoring Network. The trial periods matched the denuder's routine operation for the calendar months of June and July 2014. The precision of NH_3 concentrations measured by passive samplers compared with a reference method should be <±20% (Sutton *et al.,* 2001b). The coefficients of variation of the measured concentrations between the two methods, badge and denuder, were below 10% for both test periods.

3.6 Mapping of Air Concentrations

An NH_3 concentration map was constructed using the GIS (geographic information system) software ArcMap 10.2 produced by Esri. Empirical Bayesian kriging was used to create the predicted coverage. Geostatistical interpolation techniques, such as kriging, explore and examine the statistical properties of the measured data points, quantify the spatial autocorrelation among these points and account for the spatial configuration of the sample points around the prediction location (de Smith *et al.*, 2009).

This geoprocessing routine was chosen as being suitable for small datasets, and requiring minimal interactive modelling (Pilz and Spöck, 2008). Although the data transformation carried out by the routine is reportedly particularly sensitive to outliers, a Dixon's *Q* test confirmed that no outliers exist within the mean concentration values for the monitoring sites.

The geostatistical interpolation method used, empirical Bayesian kriging, assumes that the data-point values represent a sample from some underlying surface function and that this sample must first be analysed to create a suitable model that will provide the best possible estimate of the underlying function. This model, which is called a variogram, may then be used to predict values at unsampled locations.

4 Ambient Ammonia Concentrations in Ireland, June 2013–July 2014

Summary measured values of NH_3 concentrations are given in Table 4.1.

The average atmospheric NH_3 concentration from the 25 sites during the course of the study was 1.72 µg/m³. This is higher than the 1.45 µg/m³ average from the 40 sites in the Ammonia1 study (de Kluizenaar and Farrell, 2000), although this comparison is affected by the reduced number of western seaboard sites in Ammonia2. The Ammonia2 average value is lower than the average value of 2.50 µg/m³ recorded during the 2013–2014 monitoring period at three stations in Northern Ireland [Dr Yuk Sim Tang, Department for Environment, Food and Rural Affairs (DEFRA), UK Eutrophying and Acidifying Atmospheric Pollutants Network (UKEAP), personal communication, 2015], although this comparison is limited by comparing denuders in Northern Ireland with passive samplers.

Table 4.1. Mean ambient NH_3 concentrations (µg/m³) and summary statistics for each site from June 2013 to July 2014. All measured values are included in the calculations.

Site name	*n*	Mean	Min.	Max.	Median	Range	Accep%	CV%
Athleague	28	2.07	0.72	4.24	1.90	3.52	100	41
Ballinamore	29	1.92	ND	4.35	1.76	3.87	93	60
Ballincurrig	28	2.04	0.79	4.38	1.84	3.59	100	48
Carrickmacross	27	2.50	1.01	10.51	2.65	9.51	100	71
Clonroche	25	2.83	0.67	9.63	2.26	8.96	100	84
Clonskeagh	27	1.19	ND	2.13	1.10	1.64	93	42
Derrygreenagh	28	1.99	0.60	3.51	2.06	2.91	100	30
Dooary	29	1.26	ND	2.36	1.23	2.04	93	37
Dundalk Institute of Technology	29	1.88	0.85	3.60	1.70	2.75	100	40
Dungarvan	28	2.41	1.15	6.14	2.15	4.99	100	44
Glenties	29	0.70	ND	2.11	0.59	1.91	72	76
Killarney	29	0.65	ND	1.62	0.59	1.28	79	58
Leiter, County Cavan	28	2.96	1.05	7.81	3.07	6.76	100	52
Littleton	28	1.53	0.51	2.84	1.46	2.33	100	39
Mace Head	28	0.48	ND	1.18	0.42	0.93	64	59
Naas	26	1.67	0.53	3.21	1.63	2.68	100	34
Navan	26	1.77	ND	3.47	1.54	3.01	96	50
Oak Park	27	2.67	0.84	4.02	2.72	3.18	100	35
Phoenix Park	28	1.11	ND	2.68	1.24	2.04	86	51
Shannon Airport	29	1.53	ND	2.53	1.59	2.00	93	39
Sliabh Bloom	29	1.14	ND	3.89	1.06	3.43	93	58
Sligo Airport	28	1.01	ND	2.33	0.75	1.94	86	62
Springfield Castle	29	2.29	0.75	4.24	2.55	3.48	100	43
Straide	29	1.10	ND	1.85	1.12	1.50	97	41
Winetavern Street	29	2.27	0.80	4.08	2.39	3.28	100	33
Mean	28	1.72	0.61	3.95	1.66	3.34	94	49

Accep%, percentage of measured values where the CV% is acceptable; CV%, ratio of the standard deviation to the mean expressed as a percentage; max., maximum; min., minimum; ND, none detected.

4.1 Spatial Variation of Ammonia Concentrations

The mean values over the monitoring period for individual sites ranged from 0.48 µg/m^3 at Mace Head to 2.96 µg/m^3 at Leiter, with a mean concentration of 1.72 µg/m^3 for all 25 sites over the study period (Table 4.1).

The maximum concentration was 10.51 µg/m^3, recorded at Carrickmacross, County Monaghan, in June 2013. Many measurements, at many sites, were below the detection limit (ND in Table 4.1), while the minimum detectable concentration (above ND, and distinguishable from laboratory blank measurements) was 0.20 µg/m^3, recorded at Glenties, County Donegal, in December 2013. Concentrations from each exposure period were highly variable between locations; the greatest single 2-week exposure range was 9.98 µg/m^3, in June 2013 between Carrickmacross and Naas monitoring stations. Three sites on the western seaboard, namely Killarney, Mace Head and Glenties, recorded the lowest site mean concentrations from the campaign, 0.65 µg/m^3, 0.48 µg/m^3 and 0.70 µg/m^3 respectively, while four sites in the east of the country, Leiter, Clonroche, Oak Park and Carrickmacross, displayed relatively high average concentrations, 2.96 µg/m^3, 2.83 µg/m^3, 2.67 µg/m^3 and 2.50 µg/m^3 respectively (Table 4.1).

The spatial variation in ambient atmospheric NH_3 concentration is mapped in Figure 4.1. The map represents background concentrations, as monitoring sites were away from point sources; closer to emitters, concentrations will be higher. The urban stations displayed spatial variability: the outer suburban stations, Clonskeagh and Phoenix Park, showed annual averages of 1.19 µg/m^3 and 1.11 µg/m^3 respectively, considerably lower than the city centre station, Winetavern St, which had an annual average of 2.27 µg/m^3. The concentration variation

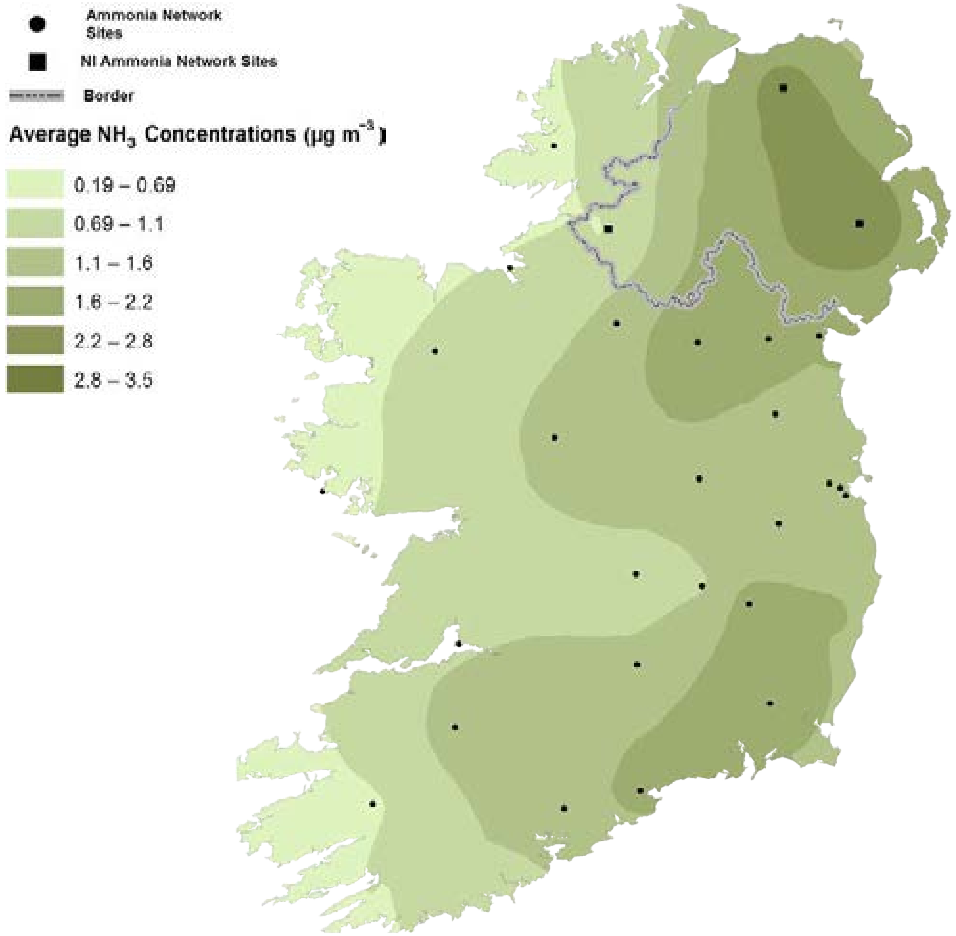


Figure 4.1. Mean atmospheric NH_3 concentrations, interpolated from measurements at 25 sites in Ireland and 3 sites in Northern Ireland between June 2013 and July 2014. Northern Ireland data courtesy of Dr Yuk Sim Tang, Department for Environment, Food and Rural Affairs (DEFRA), UK Eutrophying and Acidifying Atmospheric Pollutants Network (UKEAP), 2015, personal communication.

among the three Dublin sites is on a spatial scale that cannot be displayed on the national map (Figure 4.1).

A distinct, and consistent, spatial trend of increasing values from west to east appears to be a major feature of atmospheric NH_3 concentrations in Ireland and was also found in the 1999–2000 network. Concentrations are found to be higher in the midlands than at the coast and are notably lower along the western seaboard thanks to the arrival of Atlantic air containing lower levels of atmospheric NH_3. The spatial trend of increasing NH_3 concentrations from west to east is shown in Figure 4.2.

The low NH_3 air concentrations observed on the western seaboard may be interpreted as caused by the landfall of oceanic air, which carries a much lower concentration of atmospheric NH_3 than do continental air masses, as well as by a lower level of agricultural activity in these areas. For example, Pio *et al.* (1996) found average air concentrations from continental sources containing $0.37 \pm 0.24\,\mu g/m^3$ NH_3-N compared with maritime air containing $0.13 \pm 0.09\,\mu g/m^3$ NH_3-N on the west coast of Portugal, suggesting that Atlantic air masses contained roughly one-third the NH_3 concentration of continental air masses. The three sites with the lowest average concentrations from the study are on the western seaboard: Killarney, Mace Head and Glenties. Mace Head recorded the lowest mean concentration ($0.48\,\mu g/m^3$) for the network. Given its location in the extreme west of Connemara, concentrations recorded at the Mace Head site may represent close to the average concentration of NH_3 in oceanic air masses. It should be noted that the Mace Head site, run by National University of Ireland, Galway (NUIG), is an internationally renowned atmospheric research station and participates in many monitoring networks including EMEP, WMO, GAW (Global Atmosphere Watch) and ACTRIS (Aerosols, Clouds, and Trace gases Research InfraStructure Network) (http://www.macehead.org).

The observed zones of elevated NH_3 air concentrations towards the north-east midlands and the south-east correspond to observed spatial patterns of agricultural activity. For example, the north-eastern counties of Monaghan, Meath, Westmeath, Cavan and Louth have higher cattle populations and also a cluster of EPA-licensed pig and poultry facilities. Locally high cattle populations in the south-east, namely south County Waterford and County Wexford, are also represented on the NH_3 concentration map.

There are two regions on the map where the spatial correlation between agricultural activity and observed NH_3 concentrations is not entirely apparent, however; they are in south Cork and the southern midlands. South County Cork contains a higher population of cattle than the surrounding region. The lower atmospheric NH_3 concentrations mapped in this region may be explained simply by lack of data (i.e. absence of a monitoring

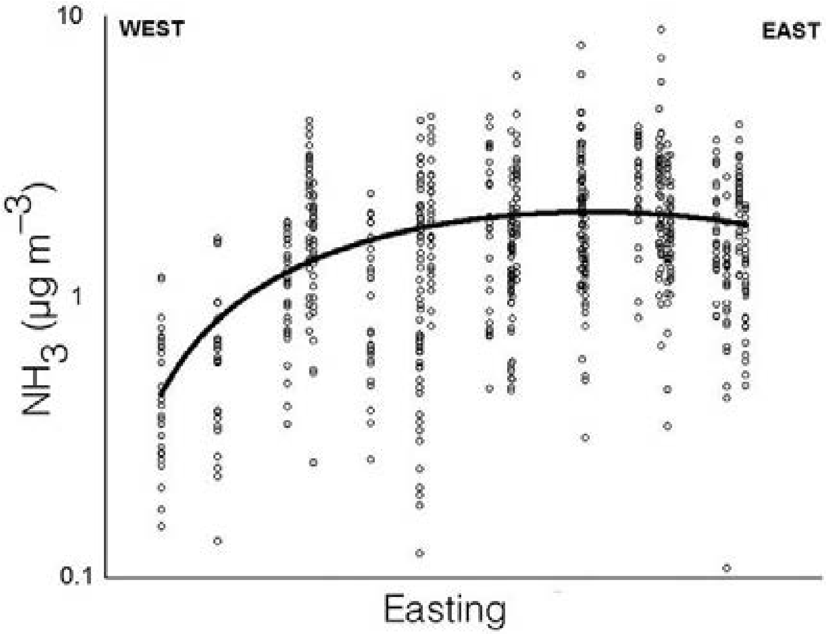


Figure 4.2. NH_3 concentrations (µg/m³) on a log scale (*y*-axis) vs eastings. Values are grouped by site, plotted from west to east. The trend line is constructed based on the annual mean value per site.

station) and by proximity to the Atlantic coast. The second region, centred around north Tipperary, County Offaly and County Laois, also has higher cattle populations than surrounding areas but shows up as a distinct area of low NH_3 concentration on the map. One possible reason for this anomaly is choice of site location. The Sliabh Bloom site on the Offaly–Tipperary border and the Dooary site in County Laois recorded lower mean NH_3 concentrations than adjacent sites. Both sites are, however, in elevated positions in the landscape: Dooary, at 240 m above sea level, is at the highest altitude in the network and Sliabh Bloom is slightly lower at 210 m above sea level. The Dooary site is located close to a large conifer plantation, a known sink of atmospheric NH_3 (van den Beuken, 1994), and the Sliabh Bloom site is in south-sloping mountain farmland above the agricultural plains of north Tipperary. Although both sites are in agricultural areas, their elevation and landscape positions may mean that they do not fully represent the ambient NH_3 concentrations that a nearby site at lower elevations might record. These two sites have a profound influence on the pattern of NH_3 concentrations on the map, suggesting that the apparent zone of lower concentrations towards the east midlands may be misleading.

The suburban Dublin sites of Phoenix Park and Clonskeagh have similar mean NH_3 concentration values of 1.11 and 1.19 µg/m^3 respectively, significantly lower than the 2.27 µg/m^3 concentration recorded at Winetavern St, the busy urban core site. The suburban sites also show levels slightly lower than those recorded in Dublin's agricultural hinterland in Navan and Naas. The higher concentration displayed in Winetavern St is therefore spatially isolated and a probable urban effect, explained perhaps by transport and possibly sewer emissions. Comparable results were reported in 2012 by Zbieranowski and Aherne in southern Ontario, Canada, where an urban site recorded concentrations of ~2 µg/m^3 and intensive agricultural sites ($n = 4$) recorded an annual average of 2.8 µg/m^3, which suggested that, apart from intensive agricultural areas, urban centres have the highest ambient NH_3 concentrations.

Lough Navar displayed the lowest mean concentration in the Northern Irish network (0.51 µg/m^3). The two easterly sites in the Northern Irish network, Coleraine, County Derry, and Hillsborough, County Down, have the two highest recorded NH_3 concentrations in the island of Ireland for the monitoring period: 3.49 and 3.50 µg/m^3 respectively. It must be stressed, however, that the three sites in the Northern Irish network recorded NH_3 concentrations with a different technique (active denuder) and over a different time cycle (one calendar month) from the Ammonia2 network. A direct comparison of atmospheric NH_3 concentrations between monitoring stations across the two different networks must be approached with caution. However, at an island-wide scale, the inclusion of both networks in the NH_3 concentration map shown in Figure 4.1 is acceptable.

An atmospheric NH_3 monitoring study in 2004 in Northern Ireland reported mean annual averages of between 4 and 6 µg/m^3 at three sites, and annual averages in excess of 6 µg/m^3 at two sites (Tang *et al.*, 2004). There were a total of 15 sites in the 2004 Northern Ireland network and the majority of the high-concentration sites were located to the east.

In the UK, a background coastal site, Goonhilly in Cornwall, had a yearly average of 0.51 µg/m^3 in 2013, similar to concentrations in Irish Atlantic sites such as Mace Head, where the yearly average was 0.48 µg/m^3. A rural background site, Drayton, in the English midlands, close to Stratford-upon-Avon, recorded a yearly average NH_3 concentration of 1.71 µg/m^3 in 2013. However, a site in the more intensively farmed east of England, at Dennington in Suffolk, recorded an average NH_3 concentration of 3.76 µg/m^3 during the same year (NAMN, 2016). Atmospheric NH_3 concentrations in the Netherlands are higher; for example, a passive sampler network operating for 1 year found concentrations ranging from 1 to 18 µg/m^3, with an average of 6.6 µg/m^3 from all sites (van Pul *et al.*, 2004). In Switzerland the mean annual NH_3 concentration in ambient air from a network of 41 sites was found to be 2.5 µg/m^3, ranging from 0.4 to 7.5 µg/m^3 (Thöni *et al.*, 2004), reflecting variation from high-NH_3 locations, in intensive agricultural land, to low-NH_3 regions, in remote alpine areas.

4.2 Temporal Variability of Ammonia Concentrations

Atmospheric NH_3 concentrations measured at the study sites varied temporally, as can be seen in time-series shown in Figure 4.3. The greatest absolute range of NH_3 concentrations over the course of monitoring for a single site was 9.51 µg/m^{-3}, from Carrickmacross, County Monaghan. However, the greatest relative variation of NH_3 concentrations was recorded in Clonroche, County Wexford (CV = 84%). A one-way ANOVA (analysis of variation) test was carried out on the mean

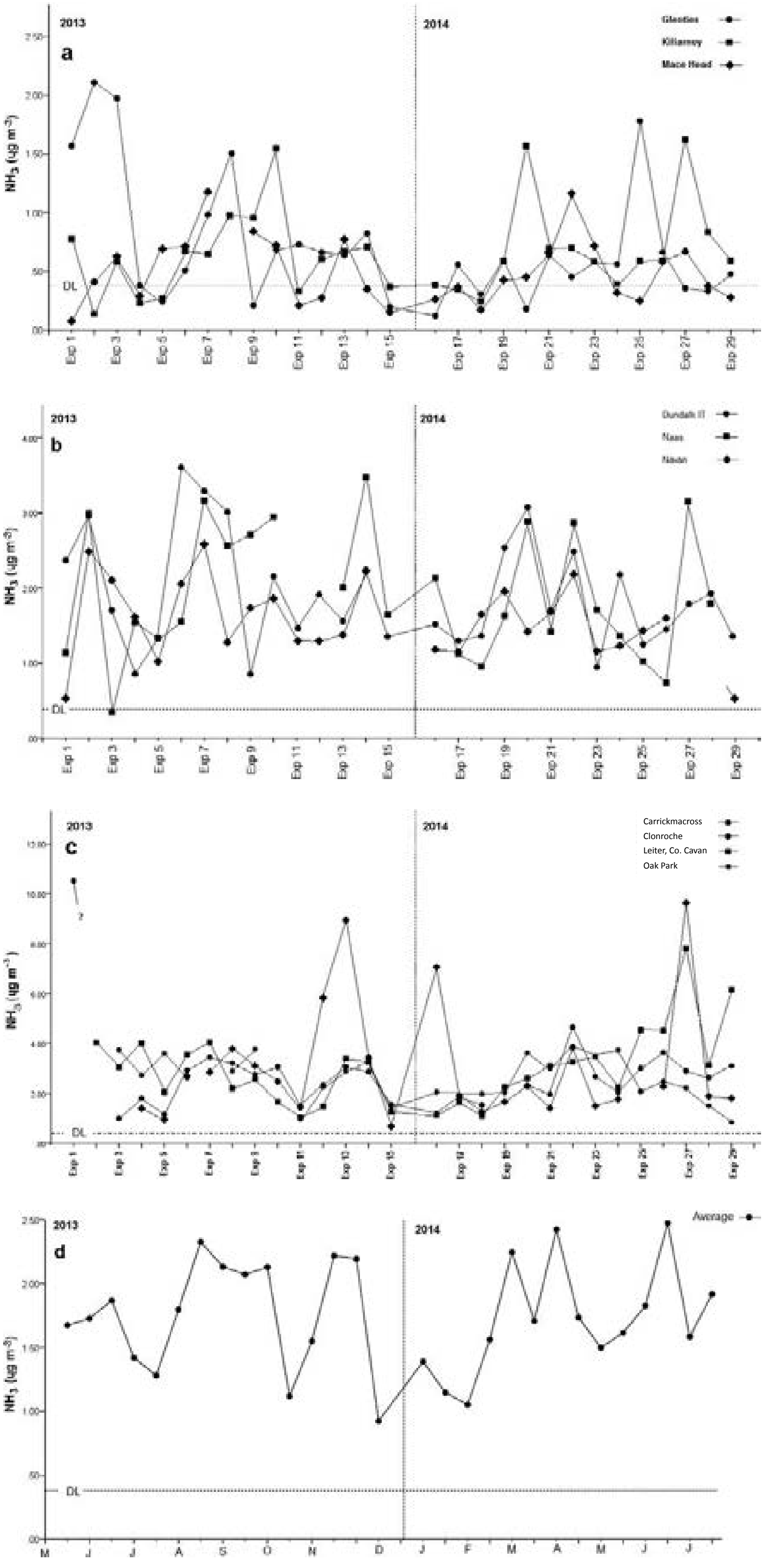


Figure 4.3. Time-series of ambient atmospheric NH_3 concentrations at selected study sites (June 2013 to July 2014). (a) Low-concentration sites; (b) medium-concentration sites; (c) high-concentration sites; (d) average measurements from all sites (*n* = 25). The detection limit (DL) is shown in each graph.

concentration values for the sites between seasons. The test showed that there was no significant effect of seasons on NH_3 concentrations at the $p<0.05$ level [$F(3,96)=1.495$, $p=0.22$].

There was temporal variation in the concentrations measured, although the observed trends (Figure 4.3) are not strong. Seasonal differences between mean NH_3 concentrations are not significant. The variations may be better explained by the timing of agricultural activity and by weather patterns during the year. The temporal graphs show peaks of concentrations in spring, consistent with slurry spreading. The slightly lower concentrations observed during the late spring and summer months are indicative of favourable growing conditions for grass and crops and possibly less manure application. The dip in atmospheric NH_3 concentration during this period is possibly due to a ‘crossing over’ of the compensation point (Farquhar *et al.*, 1980), where net NH_3 deposition has replaced net emission in the landscape. The concentrations increase again in autumn, possibly reflecting increasing agricultural activity and also a prolonged spell of warm and dry weather at this time. The observed decrease in concentrations during the winter months correspond to reduced agricultural activity and lower temperatures.

A similar seasonal variation of atmospheric NH_3 concentrations was reported in Northern Ireland in 2004, with peaks observed in spring and autumn and reduced concentrations during the summer and winter (Tang *et al.*, 2004). Similar seasonal patterns were also found in Scotland and Hungary and were also linked to agricultural activity (Horváth and Sutton, 1998; Burkhardt *et al.*, 1998). Buijsman *et al.* (1998) reported large temporal variations in atmospheric NH_3 in the Netherlands, with the highest concentrations occurring in spring, summer and autumn. The effect of climate on atmospheric NH_3 concentrations is highlighted in a Canadian study, where a seasonal trend is immediately obvious because of the extremely cold winters in that region (Zbieranowski and Aherne, 2012b). In Ireland, weather fluctuations also appear to have an influence on temporal variations of NH_3 concentration, as they sometimes dictate the timing of manure and fertiliser application. The peaks of concentration at sites generally coincide with spells of dry weather. A single exposure period with increased NH_3 concentrations has a large influence on the annual mean concentration at an individual site. The results from the network therefore stress the importance of long-term continuous monitoring in fully ascertaining the effect of weather events on temporal variation.

A paired *t*-test was carried out on annual average values between sites that were common to both the Ammonia1 and Ammonia2 studies. The results from the test showed that there was no statistical difference between the NH_3 concentrations recorded in the two studies (*t*-statistic$=0.361$; $p=0.725$). Summary statistics for sites shared by the Ammonia1 and Ammonia2 networks are shown in Table 4.2.

Ammonia concentrations from the Ammona1 and Ammonia2 surveys are shown by the maps in Figure 4.4.

Table 4.2. Mean ambient NH_3 concentrations (µg m^{-3}) and summary statistics for each site comparing Ammonia1 (1999) with Ammonia2 (2013–2014)

Site name	Mean1	Mean2	Med1	Med2	Min1	Min2	Max1	Max2
Ballincurrig	2.43	2.04	2.34	1.84	0.44	0.79	6.73	4.38
Clonroche	1.62	2.83	1.27	2.26	0.47	0.67	14.20	9.63
Derrygreenagh	1.48	1.99	1.39	2.06	0.53	0.60	2.70	3.51
Glenties	0.25	0.70	0.18	0.59	0.04	ND	1.06	2.11
Killarney	0.27	0.65	0.24	0.59	0.05	ND	0.85	1.62
Littleton	1.58	1.53	1.48	1.46	0.51	0.51	4.65	2.84
Naas	3.37	1.67	2.56	1.63	0.04	0.53	11.60	3.21
Shannon Airport	1.63	1.53	1.18	1.59	0.42	ND	6.48	2.53
Sligo Airport	0.56	1.01	0.53	0.75	0.06	ND	1.34	2.33
Springfield Castle	2.06	2.29	1.70	2.55	0.54	0.75	4.78	4.24
Straide	1.21	1.10	1.16	1.12	0.41	ND	3.41	1.85
Mean	1.50	1.58	1.28	1.49	0.32	0.64	5.25	3.48

Max, maximum; med, median; min, minimum; ND, none detected. Suffixes 1 and 2 refer to the two network periods.

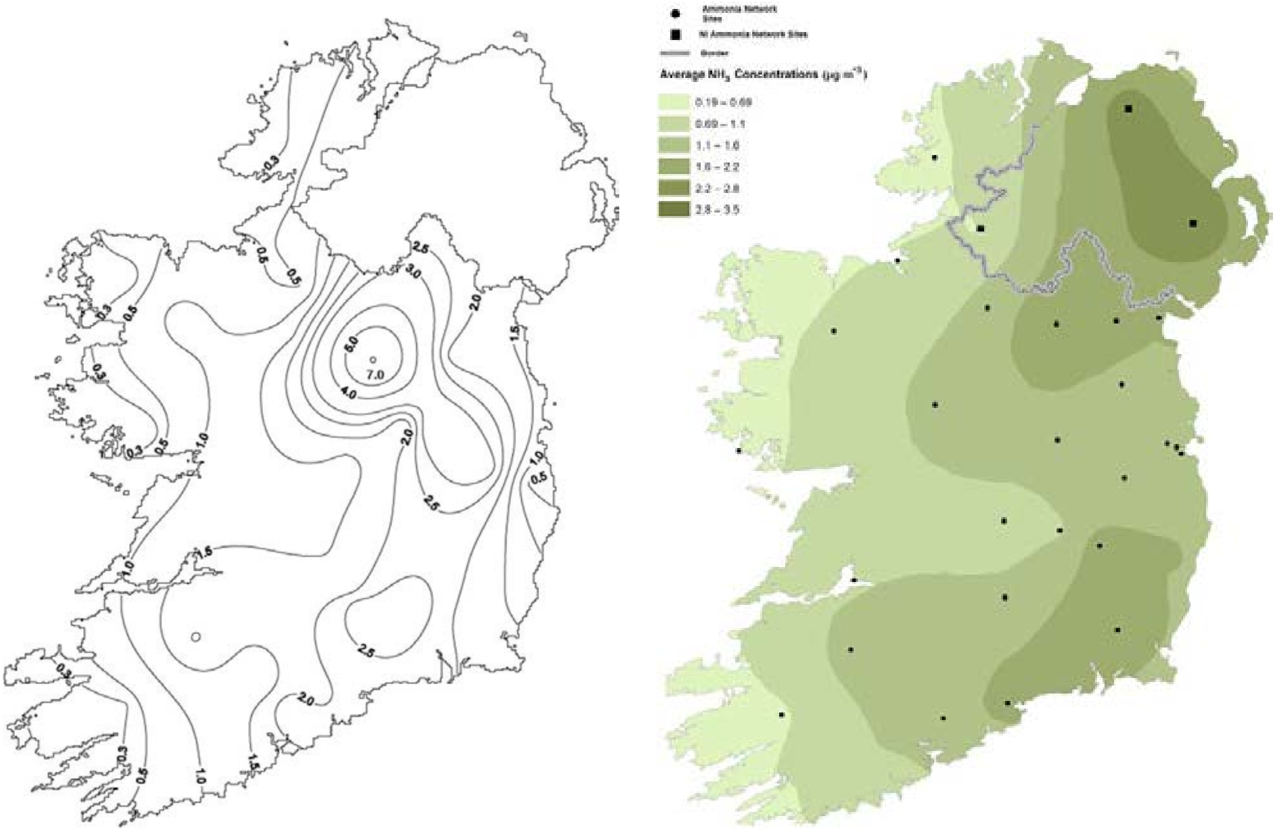


Figure 4.4. Concentrations of atmospheric gaseous NH_3 from the Ammonia1, 1990 (left), and Ammonia2, 2013–2014 (right), networks (μg/m^3). Paired *t*-testing of sites common to the two surveys does not indicate any significant difference between NH_3 concentrations in the two monitoring periods.

4.3 Correlation of Atmospheric Ammonia Concentrations with Agricultural Statistics

The relationships between atmospheric NH_3 concentrations and agricultural statistics were examined. Spatial data about livestock populations (total cattle, total sheep) and also total area (ha) under pasture, silage and arable land from statistics available from the Central Statistics Office (CSO) for 2010 were used. Data for each category are stored by district electoral division (DED). Data for pig and poultry populations are available only by county.

In a GIS study, a buffer of 10 km in radius was constructed around each monitoring station, and data from each category were totalled within each buffer. Where the buffer truncated a DED, a percentage area-based calculation was applied to estimate the total to be included within each buffer. Pig and poultry population data were calculated into estimated NH_3 emissions per county. A series of regressions was then conducted between each category and the observed annual average NH_3 concentration for each monitoring site.

From the regression analysis between atmospheric NH_3 concentrations and agricultural statistics, correlations were observed. The strongest relationships were observed between NH_3 concentrations and area of arable land ($R^2 = 0.569$) (Figure 4.5), area under silage ($R^2 = 0.513$) and area under pasture ($R^2 = 0.419$). A positive relationship was found between NH_3 concentrations and cattle population ($R^2 = 0.454$, $p < 0.05$) (Figure 4.5). A relationship between sheep population and NH_3 was not observed.

A relationship was also observed between calculated pig and poultry NH_3 emissions per county and NH_3 concentrations per site ($R^2 = 0.437$), shown in Figure 4.6. The emissions were calculated from 2010 CSO data about pig and poultry populations by county.

Atmospheric NH_3 increases with increases in cattle populations and areas under arable, pasture and silage within a 10-km radius from each site and, for county-based statistics, with pig and poultry inventory emissions. For cattle populations, the *p*-value of 0.015 indicates that there is a 98.5% certainty that a linear relationship exists with measured NH_3 concentrations

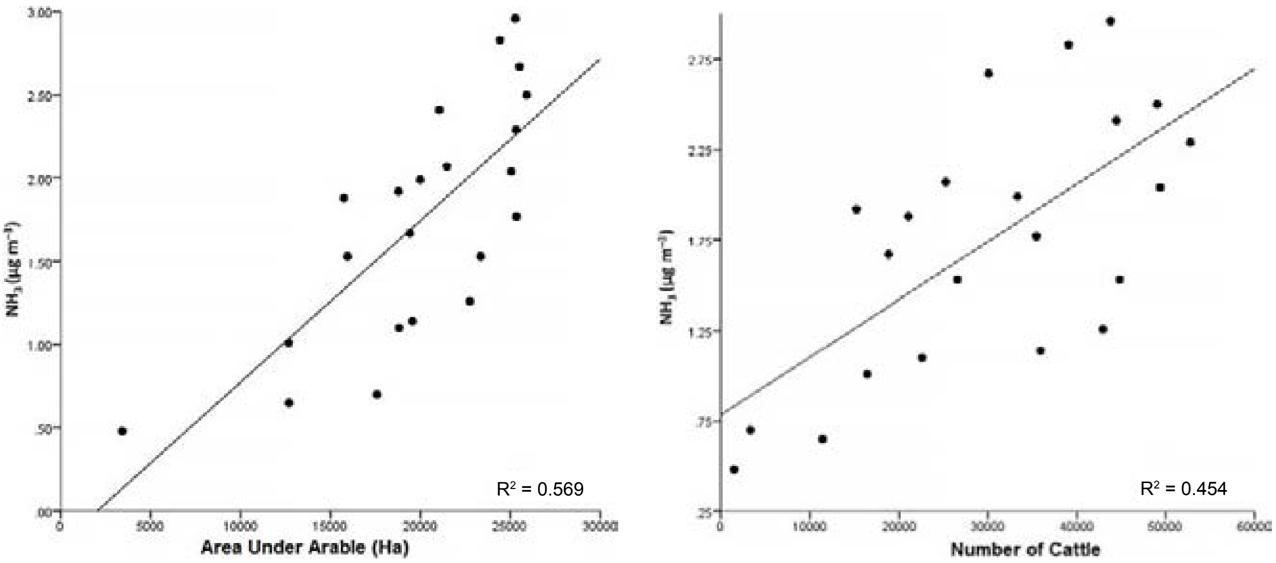


Figure 4.5. Spatial correlations between atmospheric NH_3 concentrations (*y*-axis) and total arable area (left) and total cattle population (right) from a 10-km-radius buffer constructed around each rural monitoring site. Three urban sites, Winetavern St, Clonskeagh and Phoenix Park, were not included in the analysis.

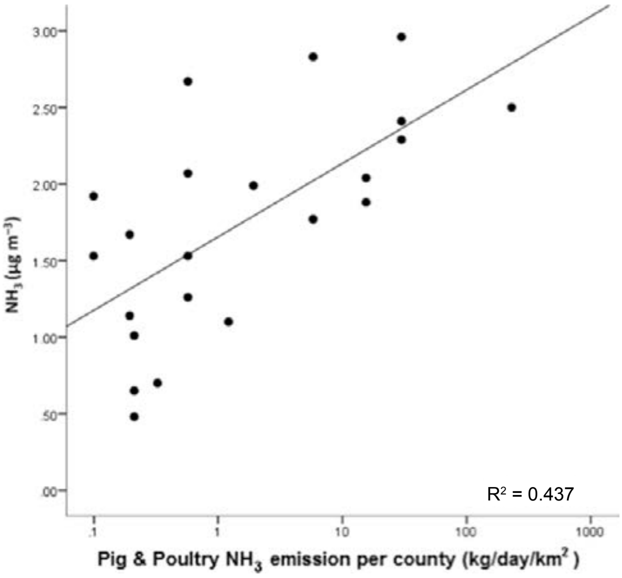


Figure 4.6. Spatial correlation between atmospheric NH_3 concentrations (*y*-axis) and calculated pig and poultry emissions by county (*x*-axis, log scale). Three urban sites, Winetavern St, Clonskeagh and Phoenix Park, were not included in the analysis.

among sites. An increase in cattle numbers may therefore be expected to lead to an increase in atmospheric NH_3. The strongest R^2 relationship observed was between NH_3 concentrations and area under arable land. This relationship reflects the link between organic and mineral fertiliser application to land and observed atmospheric NH_3 concentration. Similar relationships observed between area under silage and area under pasture (not shown) are also indicative of this link.

4.4 Critical Levels of Ammonia

The annual average ambient NH_3 concentration, 1.72 µg/m³, is above the critical level of 1 µg/m³ where lichens and bryophytes form a key part of the ecosystem. Annual averages from the three sites on the western seaboard are below this critical level. The remaining 22 sites have annual means above this critical level. Irish ecosystems where lichens and bryophytes are key species may be under threat from loss of biodiversity, in regions distant from the Atlantic seaboard.

The critical level of 3 µg/m³ ambient NH_3 for ecosystems where lichens and bryophytes are not key to ecosystem integrity (Cape *et al*., 2009) was not exceeded by the mean NH_3 concentration from any of the 25 sites. Exceedances occur over shorter periods; this value was exceeded by the maximum fortnightly values at 15 sites, and never exceeded at the remaining 10 sites.

The 8 µg/m³ critical level for human health impacts was not exceeded at any site based on mean or median values across the full monitoring period. However, individual measurements, which each represent a 2-week period, do exceed this critical value. Exceedance occurred at Clonroche and Carrickmacross, as indicated by their site maximum values in Table 4.1. It should be noted in this context that these monitoring sites were explicitly sited away from NH_3 point sources. Levels of ambient atmospheric NH_3 significant for human health may occur in locations nearer to large or small point sources.

5 Reduced Nitrogen Deposition in Ireland, June 2013–July 2014

5.1 Wet Deposition of Nitrogen Present as Ammonium

Wet deposition of NH_4^+ is assessed by sampling and analysis of bulk precipitation, combined with measuring the amount of precipitation. Bulk precipitation is measured in continuously open funnel collectors, into which rain and snow can fall, being collected as liquid in a receiving bottle. Some dry deposition also occurs, as the funnel is open all the time. An overview of methods applicable to datasets used here is given by Hansen *et al*. (2013).

The amounts of NH_4^+ deposited by atmospheric wet deposition can be calculated by multiplying the chemical concentration in precipitation by the accumulated precipitation amount (measured as a depth, mm/year). The wet NH_4^+ deposition map may therefore be a combination of quite spatially dense rainfall volume measurements with spatially relatively sparse precipitation chemistry measurements. This approach to mapping wet deposition is also recommended by the federal environment agency of Germany (the Umweltbundesamt, UBA), which states: “in most regions the long-term spatial variation in the wet deposition of NH_4^+ is determined predominantly by variations in precipitation amount and less by variations in ion concentrations” (UBA, 2004). It is important therefore to interpolate the precipitation fields from the best available data – the dense network of collectors provided by the Met Éireann network – rather than simply interpolate the measured wet deposition rates gathered by the less dense EMEP precipitation chemistry network. Also, as spatial variations in NH_4^+ concentrations in precipitation are generally small across most regions, it is recommended to interpolate measured solute concentrations separately and estimate wet deposition as the product of the mapped (interpolated) solute concentration and the mapped precipitation depth.

Data for long-term average annual precipitation depths (mm/year) were provided by Met Éireann, for the 30-year period 1981–2010 (Figure 5.1), as described by Walsh (2012). Wet deposition of NH_4^+ was determined by combining precipitation depths with an interpolated map of measured NH_4^+ concentrations in bulk precipitation, following methodologies described by Aherne and Farrell (2002).

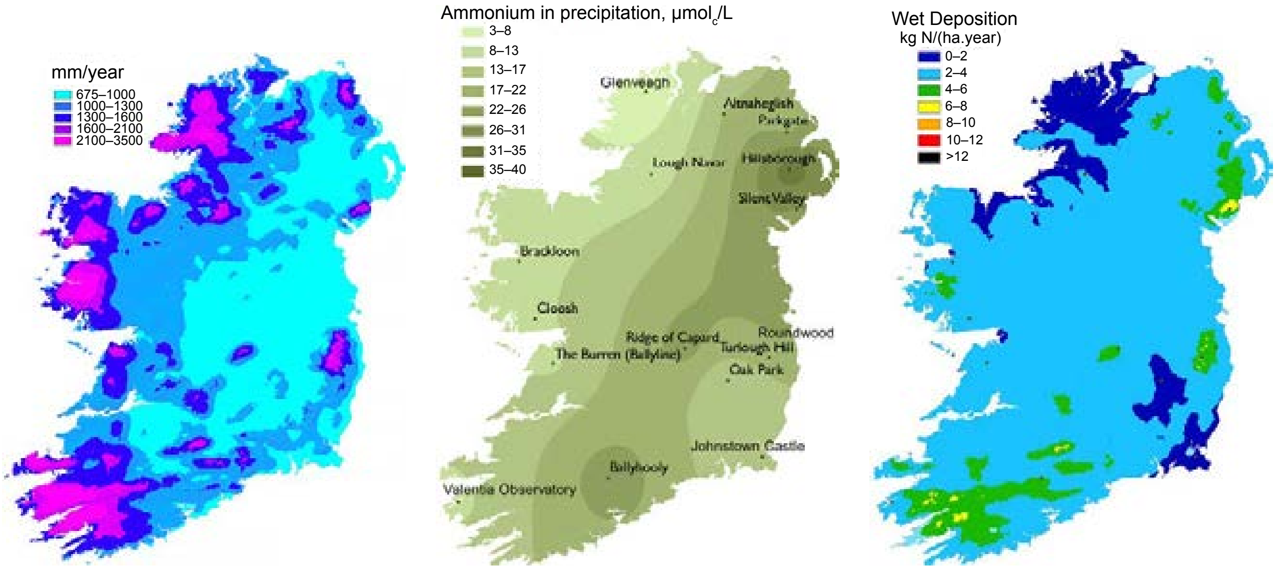


Figure 5.1. Wet deposition of NH_4^+-N. Left: annual precipitation depth, 1980–2010 (mm/year) from Met Éireann. Centre: precipitation chemistry monitoring stations, and long-term annual mean volume-weighted and precipitation-corrected NH_4^+-N concentrations in precipitation, obtained by empirical Bayesian kriging (μmol/L). Right: wet deposition of NH_4^+-N (kg/ha per year).

Observed long-term annual average concentrations of NH_4^+ in bulk precipitation from 16 stations across the island of Ireland, shown in Table 5.1, were used to construct an interpolated map, Figure 5.1. Data were not used from any station with an operating period of less than 3 years. Four stations – Brackloon, Cloosh, Lough Navar and Valentia Observatory – had observation periods of 20 years. The average number of monitoring years across all sites used is ~10 years. Seven of the sites, namely Glenveagh, Johnstown Castle, Lough Navar, Oak Park, Ridge of Capard, The Burren and Valentia Observatory, contributed to the EMEP. Three of the sites, Brackloon, Cloosh and Roundwood, are forest plots with bulk precipitation samplers under the UNECE ICP Forests monitoring network (Johnson *et al.*, 2013, 2015). Precipitation was collected using bulk samplers and also wet-only samplers.

The long-term mean NH_4^+ concentration from each site was normalised to the mapped long-term rainfall data from Met Éireann. The deposition flux was then converted back to a concentration, which is a precipitation-normalised NH_4^+ concentration. The concentration map was converted to a 1 km × 1 km raster map and combined with the rainfall data map from Met Éireann to produce the final wet deposition map.

To report the total wet deposition of NH_4^+-N, the deposition value from each 1 km × 1 km grid square in the country was summed, and converted to kilograms of NH_4^+-N per hectare per year.

The total wet deposition of NH_4^+ for Ireland is estimated as 19.2 kt of NH_4^+-N per hectare per year.

The distribution of wet-deposited NH_4^+-N (Figure 5.1) does not display the strong west–east trend of increasing deposition that is apparent in the concentration map (Figure 4.1). The spatial variation in the wet deposition of NH_4^+ displayed in the map is largely determined by the spatial variation of precipitation volumes. This effect is most noticeable in the south-west, where increased precipitation over upland regions shows up as areas of increased NH_4^+ deposition. Increased wet deposition of NH_4^+ is also visible on the west coast, in the Maumturk Mountains; in the midlands, in the Sliabh Bloom range; and on the east coast, in the Wicklow Mountains. Areas

Table 5.1. Precipitation chemistry monitoring stations, location (Irish Grid), start and end years, sampling frequency, observed and predicted bulk precipitation and observed and precipitation-corrected long-term annual average volume-weighted concentrations

Site	Easting (m)	Northing (m)	Start year	End year	Sampling period	Observed bulk precipitation (mm/year)	NH_4^+-N ($\mu mol_{\pm}$/L)	Predicted bulk precipitation (mm/year)	Normalised NH_4^+-N ($\mu mol_{\pm}$/L)
Altnaheglish	269800	404100	1991	1994	2 weeks	1409	19.81	1536	18.17
Ballyhooly	172300	98000	1991	1994	1 week	1158	27.18	1187	26.52
Brackloon	097300	279900	1991	2011	1 week	1298	14.00	1669	10.89
Cloosh	111044	232358	1991	2011	1 week	1514	11.82	1581	11.32
Glenveagh[a]	204225	422517	2006	2011	1 day	1016	6.15	1612	3.88
Hillsborough	324323	357645	1991	2000	1 week	728	46.07	904	37.10
Johnstown Castle[a]	302292	115830	2006	2011	1 day	786	15.21	1056	11.32
Lough Navar[a,b]	208633	353976	1991	2011	1 day	1228	11.42	1511	9.28
Oak Park[a]	272910	180072	2005	2011	1 day	642	15.12	827	11.74
Parkgate	322700	389700	1991	1994	2 weeks	1066	21.12	1073	20.98
Ridge of Capard[a]	236822	207483	1997	2001	1 day	1176	30.32	1399	25.49
Roundwood/ Ballinastoe	319204	208408	2005	2011	1 week	1368	24.05	1514	21.73
Silent Valley	330600	324300	1991	1994	2 weeks	1594	28.04	1709	26.15
The Burren (Ballyline)[a]	126158	194926	1997	2002	1 day	891	18.86	1486	11.31
Turlough Hill	307322	199297	1991	2002	1 day	1229	25.61	1616	19.48
Valentia Observatory	046341	078097	1991	2011	1 day	1612	10.65	1575	10.90

[a]Stations contributing to the EMEP.

[b]Daily observations until 1999, fortnightly since 2001.

Source: Henry and Aherne (2014).

of lower wet deposition are apparent in the north-west and south-east. The lower concentrations in the north-west may be explained by low atmospheric NH_3 levels, resulting in low NH_4^+ deposition in this region. There are relatively low wet deposited NH_4^+ levels in the south-east, which are associated with relatively low precipitation volumes in the south-east.

There is some uncertainty in the wet deposition of NH_4^+ map, largely as a result of the limited spatial resolution of the precipitation chemistry data. Atmospheric NH_4^+ data from only seven sites in the Ireland were available up to 2011 (Table 5.1). Therefore, earlier time-series were included to improve coverage. Since no significant temporal trend was discovered in this dataset for NH_4^+ in precipitation (Henry and Aherne, 2014), it was assumed that the inclusion of the extended data would not unduly influence or bias the wet deposition map.

The majority of stations within the precipitation chemistry networks use open-funnel bulk collectors. This also creates uncertainty because dry deposited NH_3 may also collect on the funnel surface and get washed into the collector, and thus increase the precipitation concentrations. To ensure accuracy in this regard, wet-only samplers (samplers that open only during precipitation events) should be used.

Figure 5.2 compares the spatial distribution of wet deposited NH_4^+ for the Ammonia1 and Ammonia2 networks. Both show a smaller east–west trend than the concentration map (Figure 4.1).

5.2 Dry Deposition of Nitrogen Present as Ammonium

Atmospheric NH_3 has a short atmospheric residence time and is emitted at varying source strengths, primarily from low-altitude agricultural sources (Whitehead, 1995). As a result, atmospheric concentrations may show steep horizontal and vertical gradients, displaying spatial variations of concentration by a factor of three to four at sub-kilometre scales (Asman *et al.*, 1988). The actual network density of approximately 2700 km^2 per station is at a resolution that will not detect sub-kilometre (farm-scale) variation, but will detect regional trends.

The calculation of dry deposition velocities is achieved by the careful measurement of a complex set of atmosphere-to-surface interactions (Erisman *et al.*, 1994). Each velocity is ecosystem and climate specific, and should not be generalised. The literature furnishes deposition velocity values that were discovered for ecosystems in other countries. Applying them to the

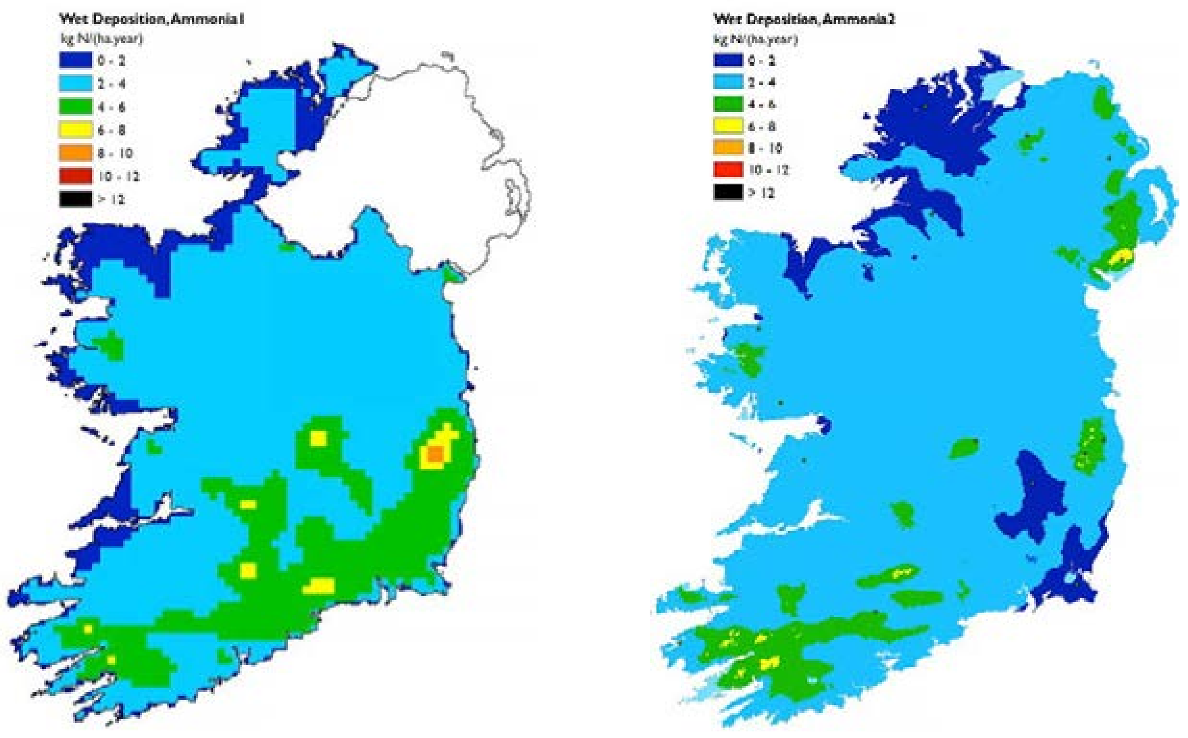


Figure 5.2. Wet deposition of NH_4-N (kg N per hectare per year). Left: Ammonia1 survey, 1999. Right: Ammonia2 survey, 2013–2014.

present study introduces uncertainty to the deposition estimates. The recent review of deposition velocities by Schrader and Brümmer (2014) highlights the uncertainties in calculating deposition velocities, and in assigning them to specific landcover types. The review suggests that, historically, certain velocities may have been set too high. Even a small change of magnitude to a deposition velocity assigned to a specific landcover will have a major effect on the final deposition calculation at a national scale. However, the deposition velocities for the present study were not revised in the light of the recent review and were chosen to align with the Ammonia1 study (Table 5.2). The principal reason was to ensure that direct comparisons could be made of the magnitude of dry deposited NH_3 and NH_x deposition between Ammonia1 and the present study.

Dry deposition is estimated by an inferential modelling technique. Measured NH_3 concentration (µg/m^3) is combined with a deposition velocity (m/s), and the flux (µg/m^2 per second) from the atmosphere to the ground is obtained. Using derived deposition velocities for defined land use categories is based on highly simplified assumptions about the relationship between near-ground NH_3 concentrations and the respective dry deposition fluxes. These simplifications are necessary and unavoidable when extending deposition velocities from the single-plot scale to regional and national coverages (Schrader and Brümmer, 2014). Because of the technical difficulties and labour-intensive methodologies encountered when measuring dry deposition velocities, relatively few campaigns have been undertaken.

De Kluizenaar and Farrell (2000) reviewed surface-specific NH_3 deposition velocities (V_d), both modelled and measured. Their review gathered results from 15 studies, reporting a total of 22 deposition velocities for seven land classes. The deposition velocities that were selected from their review were also used for the present study, to allow direct comparison, and are reproduced in Table 5.2.

The interpolated and mapped atmospheric NH_3 concentrations, discovered from the network (Figure 4.1), were converted to a 1 km × 1 km raster map. This process calculated an ambient atmospheric NH_3 concentration value for each 1-km^2 grid square in the country. The grid is based on the Irish National Grid co-ordinate system. Using the same base grid, the 2012 CORINE landcover database for Ireland was converted to a surface-specific deposition velocity map. Deposition velocities used were those of de Kluizenaar and Farrell (2000; Table 5.2). GIS tools were used to firstly amalgamate and then assign CORINE landcover classes into respective deposition classes.

The 1 km × 1 km cells of air concentrations (µg/m^3) on the rasterised NH_3 concentration map were multiplied by the surface-specific deposition raster cells (m/s) to produce a dry deposition map (µg/m^2 per second). The inferential technique used to produce the map assumes that the dry deposition is linearly correlated with atmospheric NH_3 air concentrations and, moreover, that the annual average dry deposition velocity (V_d) is dependent on the surface type only. No lateral transport processes were considered in constructing this map.

To report the total dry deposition of NH_3-N, the deposition value from each 1 km × 1 km grid square in the country was summed and converted to kilograms of NH_3-N per hectare per year.

The dry deposition map of NH_3 is shown in Figure 5.3. It reflects the strong west–east gradient of increasing NH_3 concentrations found on the ambient NH_3 concentration map in Figure 4.2. The western seaboard has a background dry deposition rate of NH_3 of between 2 and 4 kg of nitrogen per hectare per year; however, the transition to landcover types such as moorland and forest plantations on uplands in the region results in increased NH_3 deposition in these areas. The effect is noticeable in Sligo and Mayo over the Ox Mountains, in the Sliabh Aughty (extensively forested upland in County Galway) and also over the highlands in County Cork and Kerry. Deposition rates increase towards the north-east and south-east of the country, reflecting the increase in NH_3 air concentrations. Here the effect of landcover changes in uplands is also noticeable. In the north-east, elevated regions of deposition are apparent on the Cooley peninsula and on the Monaghan–Enniskillen border. In the south-east, examples of increased deposition are apparent in the Wicklow and Blackstairs Mountains, and in the Comeragh and Galtee Mountains too. Decreased dry deposition in urban areas in the east and south is also apparent. Low deposition velocities assigned to urban landcovers in Dublin, Cork and Limerick show up clearly on the map. The total dry deposition of NH_3 is estimated as 32.9 kt of NH_3-N per hectare per year.

Figure 5.4 allows comparison of dry deposition for the Ammonia1 and Ammonia2 studies. The increased spatial resolution of the Ammonia2 map relates to improved landcover information.

Table 5.2. Deposition classes and their associated NH_3 deposition velocities, V_d

Landcover type	V_d (cm/s)
Coniferous forest	
Coniferous forest	3.0
Mixed forest	
Mixed forest	2.5
Broad-leaved forest	
Broad-leaved forest	2.0
Traditional woodland – scrub	
Moors and heathland	
Moors and heathland	1.5
Peat bogs	
Urban areas	
Continuous urban fabric	0.5
Discontinuous urban fabric	
Industrial or commercial units	
Road and rail networks and associated lands	
Port areas	
Airports	
Agricultural lands, grasslands, waters, bare land and others	
Non-irrigated arable land	1.0
Pastures	
Annual crops associated with permanent crops	
Complex cultivation patterns	
Land principally occupied by agriculture, with significant areas of natural vegetation	
Natural grassland	
Inland marshes	
Intertidal flats	
Water courses	
Water bodies	
Costal lagoons	
Sea and ocean	
Beaches, dunes, sands	
Bare rocks	
Sparsely vegetated areas	
Burnt areas	
Mineral extraction sites	
Dump sites	
Construction sites	
Green urban areas	
Sport and leisure areas	

Deposition classes (in italics) are amalgamated from CORINE landcover classes (sub-categories).
Source: selected from literature by de Kluizenaar and Farrell (2000).

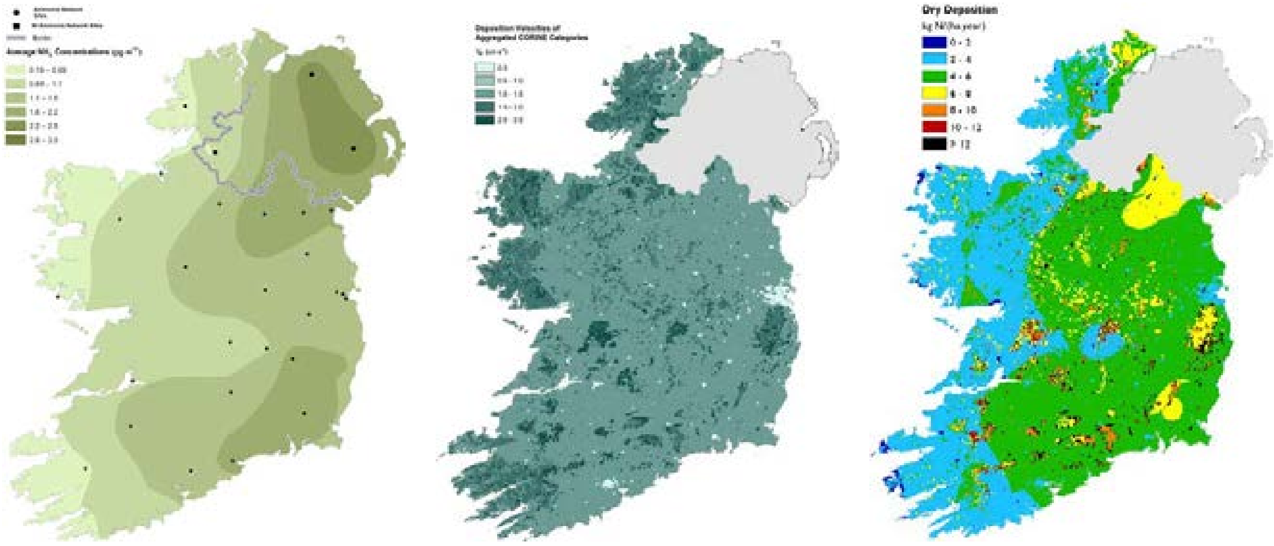


Figure 5.3. Dry deposition of NH_4-N. Left: NH_3 concentrations from this study, June 2013 to July 2014 (reduced from Figure 4.1). Centre: deposition velocities following de Kluizenaar and Farrell (2000) applied to aggregated CORINE 2012 landcover classes. Right: dry deposition of NH_3-N (kg/ha per year).

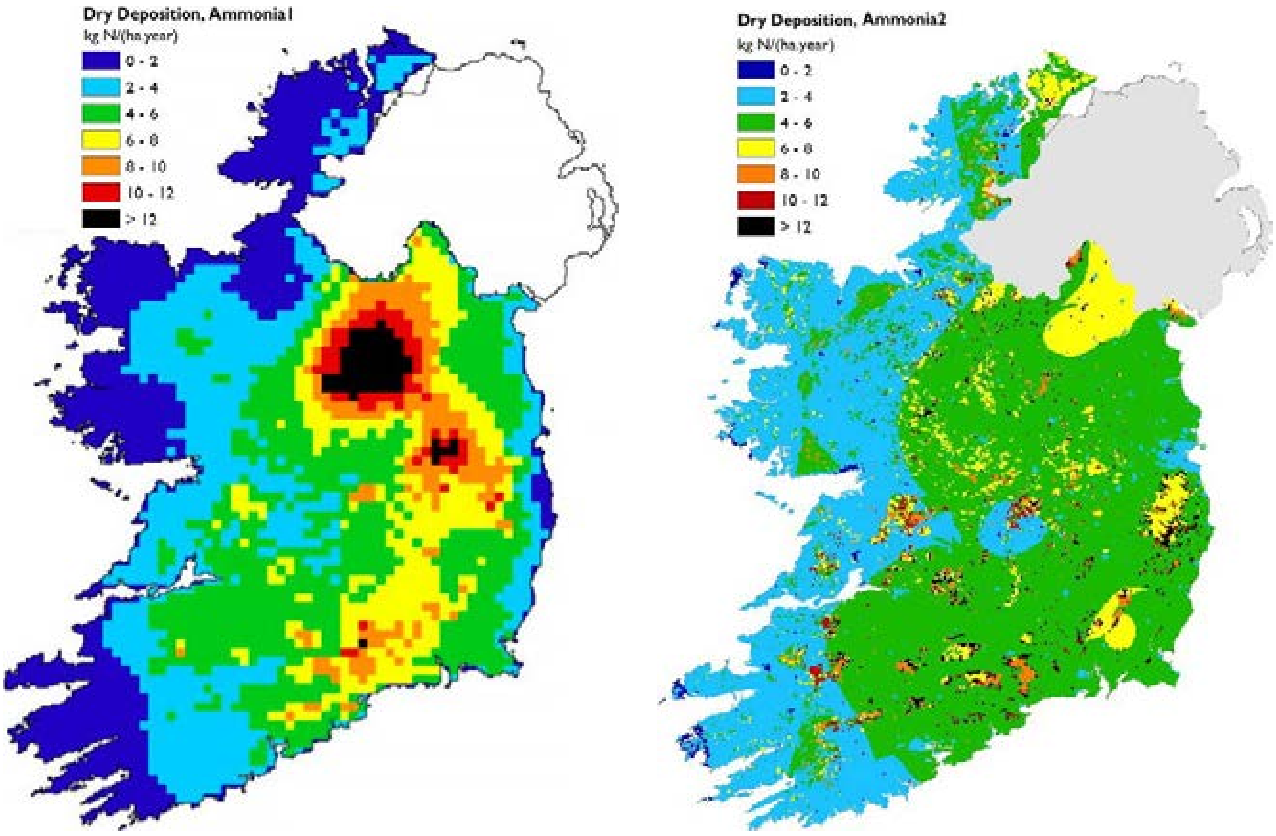


Figure 5.4. Dry deposition from Ammonia1 (left) and Ammonia2 (right). All values are kilograms of NH_4^+-N per hectare per year.

5.3 Total Reduced Nitrogen Deposition

The map of NH_x deposition, Figure 5.5, displays a general trend of increasing nitrogen deposition towards the east and south, due to higher levels of agricultural activity in these areas. Background deposition rates on the western seaboard are mostly between 4 and 6 kg of NH_x per hectare per year, which increases on mountains or where landcovers are assigned higher deposition velocities, especially forest. Towards the east the background deposition rate increases to between 6 and 8 kg/ha per year, with two areas in the midlands, the Sliabh Aughty Mountains and the Sliabh Bloom Mountains, showing increased deposition rates. A large area of the map, in the north-east, centred on County Monaghan, has a background deposition rate of 8 to 10 kg/ha per year. Within that area are two areas of significantly elevated deposition, on the Cooley peninsula and on the Monaghan–Enniskillen border. Another area with significant background deposition stretches from the Kerry and Cork mountains along the south coast to the Wicklow Mountains in the east. Within this more linear feature there are considerable areas with greater deposition, mostly on high ground. However, the Wicklow Mountains contain the area of highest NH_x deposition in the country, more than 12 kg/ha per year.

Critical load ranges of 5–10 kg of nitrogen per hectare per year for bogs, 10–15 kg/ha per year for forest and 10–20 kg/ha per year for heathland (Posch *et al.*, 2011b) may be exceeded in some areas. The north-east and the east and south coasts (Figure 5.5) may contain sensitive ecosystems where the nitrogen critical load is exceeded by the deposition of NH_x alone. Critical loads here refer to nutrient nitrogen, which includes oxidised

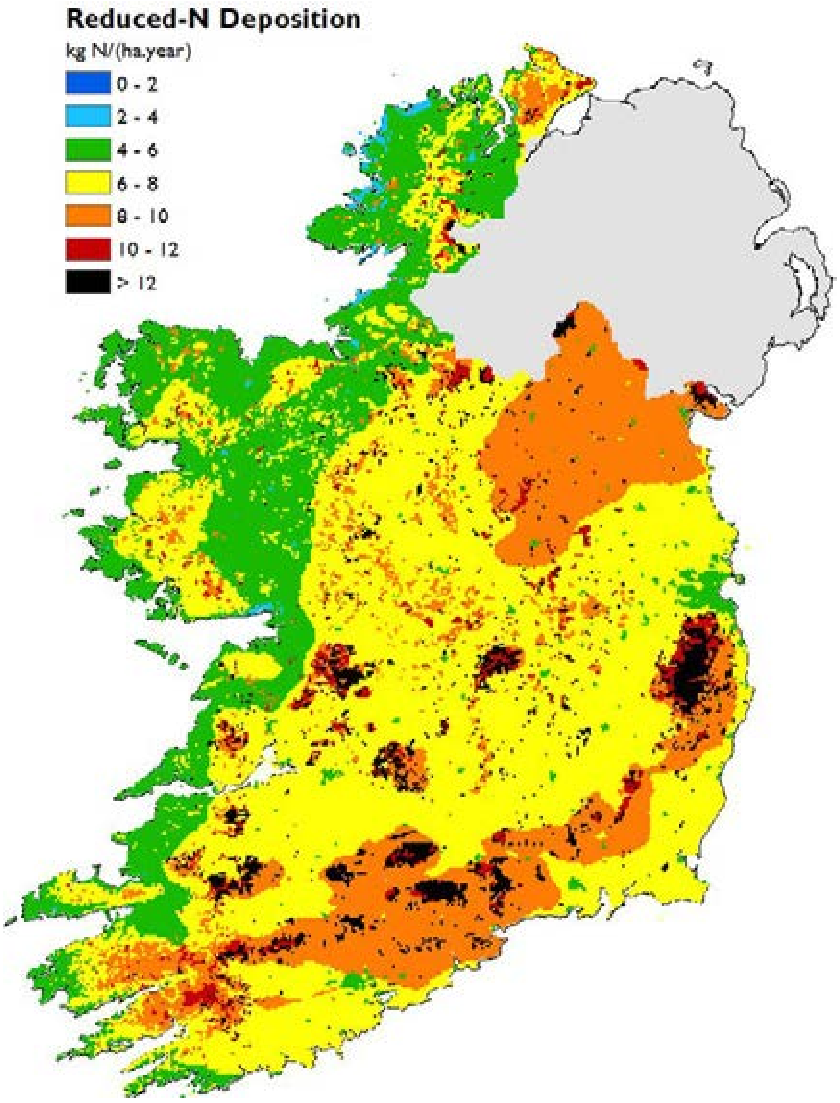


Figure 5.5. Annual NH_x-N deposition (kg/ha per year), as the sum of wet deposition and dry deposition.

Table 5.3. Reduced nitrogen emissions and deposition (kt/ha per year)

Study	Process	Conditions	Wet	Dry	Total
Ammonia1	Deposition	Veg. classes; dv = 1–3 cm/s	23.3	31.3	54.7
Ammonia2	Deposition	Veg. classes; dv = 1–3 cm/s	19.2	32.9	52.1
Henry and Aherne (2014)	Deposition	Uniform grassland; dv = 1.5 cm/s			67.6
EPA (2015)	Emission	Year 2013			107.8

dv, deposition velocity.

forms not estimated here. The magnitude of estimated NH_x deposition within these regions suggests that sensitive ecosystems may be adversely impacted.

The estimated NH_x deposition is 52.1 kt of NH_x-N per year (Table 5.3). The dry, wet and total deposition estimates from the present study are generally similar to those estimated by de Kluizenaar and Farrell (2000). The dry deposition estimated by the present study is 32.9 kt of NH_3-N per hectare per year, slightly higher than the estimate from the Ammonia1 study, which was 31.3 kt/ha per year. The present study estimates the wet deposition of NH_4^+ to be 19.2 kt of NH_4^+-N per hectare per year, lower than the 23.3 kt/ha per year estimated by Ammonia1. The total deposition from the present study is also lower, at 52.1 kt of NH_x-N per hectare per year compared with 54.7 kt/ha per year. Henry and Aherne (2014) report an NH_x deposition estimate of 67.6 kt of NH_x-N per hectare per year, assuming uniform grassland cover and an NH_3 deposition velocity of 1.5 cm/s. NH_3-N emissions of 107.8 kt were reported for Ireland in 2013 (EPA, 2015). Estimated NH_x deposition therefore amounts to approximately half of the NH_3 emitted in Ireland. The other half may have several fates: it could be exported and deposited on other landmasses and the sea, or converted by oxidation to other forms and deposited within Ireland.

The spatial distributions of total deposition of NH_x from the Ammonia1 and Ammonia2 studies (Figure 5.6) are broadly similar, especially in the south of the country, with the same areas (mostly upland areas) receiving increased deposition. In the northern half of the country, the location of the large area of elevated

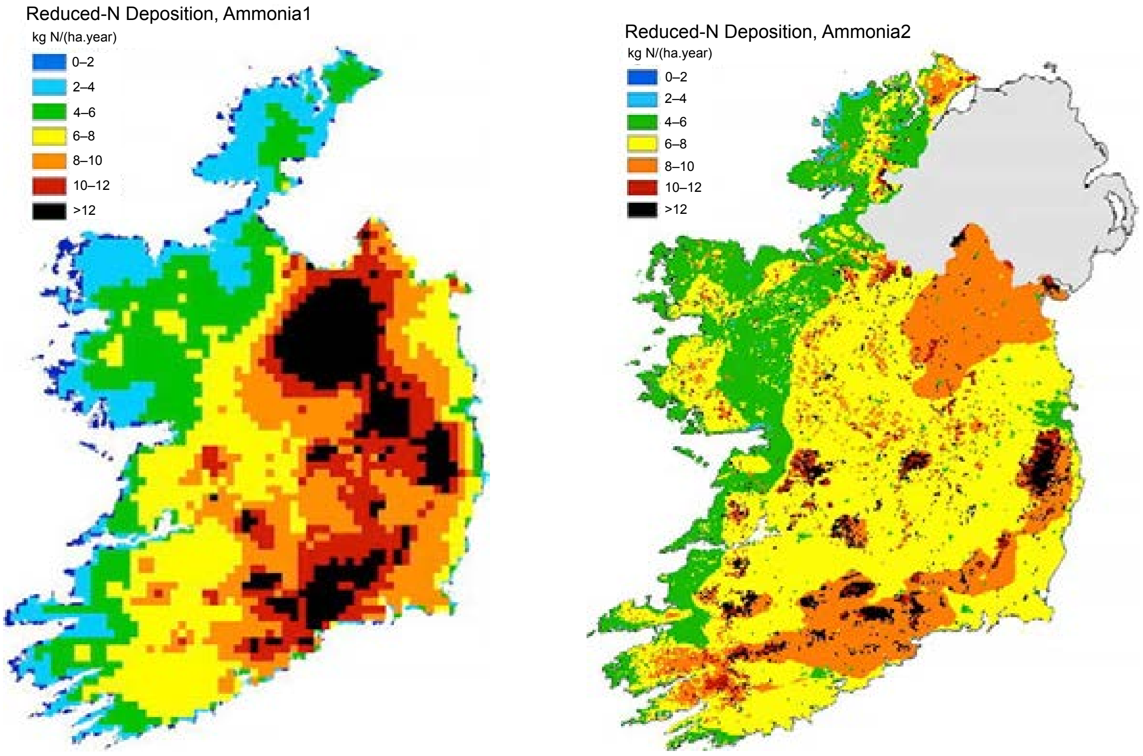


Figure 5.6. Reduced nitrogen deposition from Ammonia1 (left) and Ammonia2 (right). Sources: Ammonia1 map from de Kluizenaar and Farrell (2000); Ammonia2 map reduced from Figure 5.5.

deposition that occurs in the north-east, in both studies, shifts location from a more westerly position (centred in County Longford) in the Ammonia1 study to a more northerly position (centred in County Monaghan) in the Ammonia2 study.

The noted low wet deposition in the south-east does not obviously affect the total deposition distribution. The relatively high annual average atmospheric NH_3 concentrations recorded in this region during 2013–2014 (Oak Park 2.67 $\mu g/m^3$ and Clonroche 2.84 $\mu g/m^3$) indicate that dry deposition is the dominant influence in this area.

The dominant form of NH_x deposition in Ireland is the dry deposition of NH_3. The present study suggests that dry deposition accounts for approximately 60% of NH_x deposition. This dominance of dry deposition over wet deposition in Ireland is supported by the literature (Warneck, 1988; van den Beuken, 1997; de Kluizenaar and Farrell, 2000). The spatial distribution of dry NH_3 deposition in Ireland is highly correlated with the spatial distribution of NH_3 emissions, which in turn is linked almost exclusively to agricultural activity (EPA, 2015). The present study also shows that measured atmospheric NH_3 concentrations are correlated with agricultural activity (Figures 4.5 and 4.6). A study conducted in Northern Ireland in 2004 reported that dry NH_3 deposition was the largest contributor to the total nitrogen deposition at each monitoring site, confirming that dry deposition of NH_3 dominates nitrogen deposition in Northern Ireland too. It was concluded in the study that the dominance of dry deposition of NH_3 over all other sources is due to significant intensive agricultural activity in Northern Ireland (Tang *et al.*, 2004). The low spatial variation of wet deposited NH_4^+ (Figure 5.1) is consistent with it being a secondary reaction product, ultimately derived from atmospheric NH_3, with a longer residence time in the atmosphere allowing greater mixing and dispersal (Fangmeier *et al.*, 1994). Variation in the wet deposition of NH_4^+ in Ireland is determined predominantly by variations in precipitation amount, with the increases on higher ground, where there is more precipitation (UBA, 2004). Also, as nitrate and NH_4^+ aerosols are extremely efficient cloud condensation nuclei, increased wet deposition of NH_4^+ occurs as these clouds are washed out over higher ground by falling rain or snow. Networks do not generally take measurements at high elevation in complex terrain, so these effects are generally omitted from network measurements (Dore *et al.*, 1992). Figure 5.6 compares the deposition maps with those from the Ammonia1 study.

6 Conclusions and Recommendations

6.1 Conclusions

1. Ambient atmospheric NH_3 concentrations have been measured for Ireland, away from point sources, for just over a calendar year, June 2013 to July 2014. The mean NH_3 concentration was 1.72 µg/m^3. Mean concentrations have been mapped (Figure 4.1).
2. There is a strong west–east gradient of increasing concentration across the country (Figure 4.2) with two separate areas of elevated atmospheric NH_3 concentration, in the north-east and south-east (Figure 4.1). These results concur with findings by de Kluizenaar and Farrell (2000).
3. There has been no significant change in the spatial variation in NH_3 concentrations between the Ammonia1 and Ammonia2 studies (Figure 4.4).
4. Positive linear relationships exist between atmospheric NH_3 concentrations and high-resolution statistics for cattle populations, areas under arable agriculture (Figure 4.5), pasture and silage, and with county-level documented emissions for pig and poultry facilities (Figure 4.6).
5. Irish ecosystems where lichens and bryophytes are key species may be under threat from loss of biodiversity, as critical levels are exceeded in regions distant from the Atlantic seaboard (section 4.4).
6. The spatial distribution of NH_x-N deposition generally follows the spatial distribution of ambient atmospheric NH_3 air concentrations (Figures 4.1 and 5.5), and the spatial patterns of deposition are also similar to those of the Ammonia1 study (Figure 5.6).
7. The magnitudes of wet, dry and total NH_x deposition in Ireland are similar to those of the Ammonia1 study (Figures 5.2, 5.4 and 5.6). Dry deposition of NH_3 is the dominant form of NH_x deposition in Ireland (63%) (Table 5.3). According to the estimated levels of NH_x-N deposition shown on the NH_x deposition map (Figure 5.5), higher levels of NH_x deposition are seen in the uplands away from the west coast.

Deposition monitoring at the ICP Forests Level II monitoring sites Brackloon and Roundwood provides direct measurement of the mass transfer of NH_4^+ below the rough forest vegetation cover, and thereby an independent means to assess deposition empirically. This monitoring is important to evaluating the total mass-transfer to vegetated surfaces, which represents significantly more nutrient nitrogen than is deposited by bulk precipitation.

At time of writing (June 2016), the NEC Directive is being reviewed. Annexes to the revised draft directive identify NH_3 as an important air pollutant (David Dodd, Department of the Environment, Community and Local Government, personal communication, 2016):

> Ammonia (NH_3) is widely regarded as a neglected pollutant. Whereas EU levels of sulphur dioxide (SO_2) are expected to have been reduced by 72% by 2020, compared to 2000, and nitrous oxides (N_2O) by 53%, ammonia has only declined by 7% ... This is of concern because the ecological impacts of ammonia, for instance through toxic effects on plants … are considered to be more problematic than other types of reactive nitrogen, such as nitrogen oxides (NO_x).

Also at the time of writing, the UK (including Northern Ireland) is likely to withdraw imminently from the constraints of the NEC Directive. That would have important implications for NH_3 emissions, among other issues. This increases the need for NH_3 monitoring in Ireland, notably in those border regions where trans-boundary exchange is likely.

The Ammonia1 project recommendations (de Kluizenaar and Farrell, 2000) are consistent with findings of this study: NH_3 concentrations are regionally high, and sufficient to exceed thresholds for impacts on ecosystems. Critical load exceedance for nutrient nitrogen is affected by NH_3. Ammonia is the most important component in nitrogen deposition in Ireland. There is a need for a national monitoring network for ambient atmospheric NH_3.

Adding to these earlier recommendations is the awareness of NH_3 as a contributor to the formation of $PM_{2.5}$, to which it is a major contributor. Air pollution is now the main environmental cause of premature death in Europe, with the role of ammonia in formation of particles as a leading mechanism (EEA, 2015; Lelieveld *et al*., 2015). The emphasis in NH_3 research and monitoring should continue to recognise the effects on ecosystems, while effects on human health through formation of $PM_{2.5}$ should now take priority.

6.2 Recommendations for a Permanent National Ammonia Network

Continuous, island-wide monitoring of NH_3 is needed, given the dynamic nature of emissions, as well as longer-term variation in response to climate change and changes in agricultural activity that are expected to be driven by current policies under Food Harvest 2020 and Food Wise 2025 (DAFM, 2015), current negotiations on the NEC Directive, and the position of Ireland's NH_3 emissions close to the target ceiling. Recommendations as a set of guiding principles, and a specific set of site and infrastructure prescriptions including existing capacity, are presented below.

A permanent ammonia-monitoring network for Ireland is recommended. The proposed sites, existing and new measurement infrastructure are shown in Table 6.1. The principles guiding these selections are:

1. The proposed network depends on the continued operation of EMEP sites by Met Éireann and EPA at Oak Park, Johnstown Castle/Carnsore, Malin Head and Valentia.
2. Passive samplers should be added at these core sites.
3. Denuders should be installed at sites across Ireland, and co-location of passive samplers for calibration should be possible at any site.
4. Passive samplers should be installed, for continuous, long-term operation, with site density weighted by regional nitrogen-emission intensity. Sites chosen should be suitable for meteorological measurements, away from point NH_3 sources, and ideally supported by other long-term monitoring. A total of 15 sites for Ireland, 18 for the island of Ireland, is recommended. Ireland benefits from continuation of existing UK NAMN denuder sites at Hillsborough, Lough Navar and Coleraine (NAMN, 2016).

Further site selection would be needed in some areas as detailed in the report, such as south Cork and the south midlands regions, because the topography may have affected NH_3 levels.

Cost estimation for such a network is based on support from existing institutions and from volunteer network operators, without whose input the burden would be greatly higher. Using outline costs for the Willems badge passive sampler as operated in this study, denuder operating costs suggested by collaborators, a half-time operator and institutional overheads, we suggest a guideline one-off setup cost of €40,000, and annual operating costs of €30,000/year.

At the time of writing, we believe the EPA intends to undertake NH_3 monitoring at the current EMEP sites of Oakpark, Johnstown Castle or Carnsore Point, Malin Head and Mace Head. Valentia is already monitoring NH_3. This is very much to be welcomed. Emphasis on background coastal sites is noted, and it is further recommended that at least one more inland site, at Clones, be added to this small network. However, there is an immediate need to include other locations in an expanded NH_3 monitoring network, as per Table 6.1, at or near to known sources of agricultural NH_3 emissions.

6.3 Recommendations for Further Research

Research is required to ascertain deposition velocities, using micrometeorological measurement methods, for Irish grassland, moorland and forest ecosystems. Deposition velocities used here to allow comparison with the findings of de Kluizenaar and Farrell (2000) are probably too high, but significant uncertainty surrounds the choice of suitable deposition velocities.

Further research is required to investigate urban NH_3 concentrations. Somewhat higher values are reported here for the single city-centre location, which is exposed to high traffic volumes. Experience in Toronto and other cities indicates urban areas as specific NH_3 sources (Zbieranowski and Aherne, 2012).

Accurate models of the spatial distribution of NH_3 emissions are an essential input to models of atmospheric transport and deposition. This is especially important

Table 6.1. Proposed permanent NH_3 monitoring network sites and infrastructure. Ticked boxes indicate existing infrastructure. Unticked boxes are where proposed installations should be made. Sites in Northern Ireland are included for completeness.

Site	Networks	Operation	Aerosol NH_4^+	Precipitation NH_4^+	Denuder NH_4^+ and NH_3	Passive NH_3
Oak Park	EMEP Ammonia2	EPA Met Éireann	☑	☑		☐
Johnstown Castle/Carnsore	EMEP	EPA Met Éireann	☑	☑		☐
Malin Head	EMEP Synoptic stations	EPA Met Éireann	☑	☑		☐
Valentia	EMEP Synoptic stations	Met Éireann	☑ (plus NH_3)	☑		
Belmullet	Synoptic stations	Met Éireann		☑		☐
Clones	Synoptic stations	Met Éireann		☑		☐
Roundwood	Ammonia1&2 ICP Forests	UCD		☑		☐
Brackloon	ICP Forests ICP Integrated Monitoring	UCD		☑	☐	☐
[East midlands site]	[new site]	[to be found]				☐
Winetavern St	Ammonia2	Dublin City Council				☐
Athleague	Ammonia2	Volunteer				☐
Carrickmacross	Ammonia2	Volunteer				☐
Dundalk Institute of Technology	Ammonia2	Volunteer			☐	☐
Littleton	Ammonia1&2	Volunteer				☐
[Glaslough area]	[new site]	[to be found]			☐	☐
Derrygreenagh	Ammonia1&2	Volunteer				☐
Ballincurrig	Ammonia1&2	Volunteer			☐	☐
Killarney	Ammonia1&2	Volunteer				☐
Coleraine	UK NAMN				☑	
Hillsborough	UK NAMN			☑	☑	
Lough Navar	UK NAMN		☑ (plus NH_3)	☑	☑	

when resulting deposition maps are used to calculate the spatial distribution of critical loads exceedance or to determine suitable abatement strategies. The methodologies used to create the deposition maps for the present study are valid and suitable for use at a national scale, although they may usefully be refined. Improvements to model the distribution of agricultural NH_3 emissions have been carried out in the UK, and similar work could be undertaken in Ireland. Modelling at a parish scale, Dragosits *et al.* (1998) employed a specific spatial-weighted redistribution of NH_3 emission sources onto suitable landcover types at a 1-km-grid level. The refined model allowed more realistic spatial NH_3 emission estimates, especially for semi-natural and natural areas by relocating emission sources from upland areas to the more intensively farmed lowland areas. This method is also applicable to Ireland. The modelled distribution of NH_3 emissions should be improved for Ireland.

The atmospheric NH_3 concentration map should be improved by using detailed modelled emission data, with an atmospheric transport model that supports Irish meteorological factors – such as the FRAME model (e.g. Fournier *et al.*, 2002) – in conjunction with NH_3 concentration values. Concentration and deposition estimates obtained by modelling should be validated by measured monitoring data, provided by a long-term monitoring network.

At an international level the impacts of air pollution deposition, in particular from nitrogen, are increasingly being understood and this can be seen through the increased interaction between the Habitats Directive and air pollution policy, in particular through the CLRTAP. Semi-natural ecosystems within areas of high NH_3 concentration may suffer loss of biodiversity, based on the critical concentration values of 1 µg/m^3 where lichens and bryophytes form a key part of the ecosystem and 3 µg/m^3 for other semi-natural ecosystems. Semi-natural ecosystems within areas of continuous high atmospheric concentration may be under threat, indicated by exceedance of a critical level of 3 µg/m^3 on annually averaged concentrations (Bobbink and Hettelingh, 2011). Research is required to identify if specific semi-natural ecosystems are under threat from NH_3 and to assess the potential impacts to those ecosystems, using the approach of assessing critical load of nutrient nitrogen. As part of this effort, a related EPA-funded project, AmmoniaN2K, has been established to examine the transfer of NH_3 from emission sources to nearby Natura 2000 sites, relating emission concentrations to inferred local effects on biota (Daithi Kelleghan and Tom Curran, UCD School of Biosystems Engineering, University College Dublin, 2015, personal communication).

EPA also funds research by University College Cork on the source apportionment of $PM_{2.5}$ levels at a number of towns across the country. This research is ongoing but preliminary results indicate that NH_3 emissions contribute to the total $PM_{2.5}$ at the monitoring sites through the formation of secondary particulates from gaseous precursors. These findings are important, as they show that particulate levels, which are a key parameter of air quality in terms of health impact, can be reduced by reducing precursor compounds such as NH_3 (Lelieveld *et al.*, 2015). This research (http://www.ucc.ie/en/crac/research/sapphire/) should be published in 2017 (John McEntagart, EPA, 6 April 2016, personal communication).

References

Adema, E.H., 1993. *Some Notes about the Mechanism of Dry Deposition*. Department of Air Quality, Agricultural University Wageningen, Wageningen, the Netherlands.

Aherne, J., 2011. Ammonia monitoring at forest plots. Presentation at FORFLUX Biogeochemistry of Irish Forests [RSF 07510] Advisory Group Meeting, 5–6 December 2011, Dublin. Available online: http://people.trentu.ca/jaherne/forflux/20111205 T2 forflux.pdf (accessed August 2016).

Aherne, J., Henry, J. and Wolniewicz, M., 2016. *Development of Critical Loads for Ireland: Simulating Impacts on Systems (SIOS) (2008-CCRP-4.1a).* CCRP Report. EPA, Johnstown Castle, Ireland.

Aherne, J. and Farrell, E.P., 2002. Deposition of sulphur, nitrogen and acidity in precipitation over Ireland: chemistry, spatial distribution and long-term trends. *Atmospheric Environment* 36: 1379–1389. Available online: http://www.sciencedirect.com/science/article/pii/S1352231001005076 (accessed August 2016).

Allen, A.G., Harrison, R.M. and Wake, M.T., 1988. A meso-scale study of the behaviour of atmospheric ammonia and ammonium. *Atmospheric Environment* 22: 1347–1353.

Anderson, N., Strader, R. and Davidson, C., 2003. Airborne reduced nitrogen: ammonia emissions from agriculture and other sources. *Environment International* 29: 277–286. Available online: http://www.sciencedirect.com/science/article/pii/S0160412002001861 (accessed August 2016).

Asman, W.A.H. and van Jaarsveld, H.A., 1990. *A Variable-Resolution Statistical Transport Model Applied for Ammonia and Ammonium.* National Institute of Public Health and Enviromental Protection, Bilthoven, the Netherlands.

Asman, W.A.H., Drukker, B. and Janssen, A.J., 1988. Modelled historical concentrations and depositions of ammonia and ammonium in Europe. *Atmospheric Environment* 22: 725–735.

ATSDR (Agency for Toxic Substances & Disease Registry), 2004. *Toxicological Profile for Ammonia*. ATSDR, Atlanta, GA. Available online: http://www.atsdr.cdc.gov/phs/phs.asp?id=9&tid=2 (accessed August 2016).

Bessagnet, B., Beauchamp, M., Guerreiro, C. *et al.,* 2014. Can further mitigation of ammonia emissions reduce exceedances of particulate matter air quality standards? *Environmental Science and Policy* 44: 149–163. Available online: http://www.sciencedirect.com/science/article/pii/S1462901114001348 (accessed August 2016).

Black, A.S., Sherlock, R.R., Smith, N.P. *et al*., 1984. Effect of previous urine application on ammonia volatilisation from 3 nitrogen fertilisers. *New Zealand Journal of Agricultural Research* 27: 413–416.

Black, A.S., Sherlock, R.R., Smith, N.P. *et al*., 1985. Effects of form of nitrogen, season, and urea application rate on ammonia volatilisation from pastures. *New Zealand Journal of Agricultural Research* 28: 469–474.

Bobbink, R., 1991. Effects of nutrient enrichment in Dutch chalk grassland. *Journal of Applied Ecology* 28: 28–41.

Bobbink, R. and Hettelingh, J.-P., 2011. *Review and revision of empirical critical loads and dose–response relationships: Proceedings of an Expert Workshop, Noordwijkerhout, 23–25 June 2010*. Available online: http://www.iap.ch/publikationen/bobbink_hettelingh_2010_empirical_critical_loads.pdf (accessed August 2016).

Brown, R.H., 1993. The use of diffusive samplers for monitoring of ambient air. *Pure and Applied Chemistry* 65: 1859–1874. Available online: http://old.iupac.org/publications/pac/1993/pdf/6508x1859.pdf (accessed August 2016).

Brown, R.H., 2000. Monitoring the ambient environment with diffusive samplers: theory and practical considerations. *Journal of Environmental Monitoring* 2: 1–9.

Buijsman, E., Maas, H.F.M. and Asman, W.A.H., 1987. Anthropogenic NH_3 emissions in Europe. *Atmospheric Environment* 21: 1009–1022.

Buijsman, E., Aben, J.M.M., Van Elzakker, B.G. *et al*., 1998. An automatic atmospheric ammonia network in the Netherlands set-up and results. *Atmospheric Environment* 32: 317–324.

Burkhardt, J., Sutton, M.A., Milford, C. *et al*., 1998. Ammonia concentrations at a site in Southern Scotland from 2 yr of continuous measurements. *Atmospheric Environment* 32: 325–331.

Cape, J.N., Tang, Y.S., van Dijk, N. *et al*., 2004. Concentrations of ammonia and nitrogen dioxide at roadside verges, and their contribution to nitrogen deposition. *Environmental Pollution* 132: 469–478. Available online: http://www.sciencedirect.com/science/article/pii/S0269749104001952 (accessed August 2016).

Cape, J.N., van der Eerden, L.J., Leith, I.D. *et al*., 2009. Evidence for changing the critical level of ammonia. *Environmental Pollution* 157: 1033–1037.

Collins, J.F., Larney, F.J. and Morgan, M.A., 1986. Climate and soil management. In Keane, T. (ed), *Climate, Weather and Irish Agriculture*. Joint Working Group on Applied Agricultural Meteorology (AGMET), Dublin.

CSO (Central Statistics Office), 2014. *Environmental Indicators Ireland 2014*. CSO, Dublin. Available online: http://cso.ie/en/media/csoie/releasespublications/documents/environment/2014/eii2014.pdf (accessed August 2016).

DAFM (Department of Agriculture, Food and the Marine), 2015. *Food Harvest 2020*. DAFM, Dublin. Available online: http://www.agriculture.gov.ie/publications/2011/annualreviewandoutlookforagriculturefisheriesandfood20102011/nationaldevelopments/foodharvest2020/ (accessed 26 October 2016).

DEFRA (Department for Environment, Food and Rural Affairs), 2009. *UK Eutrophying and Acidifying Atmospheric Pollutants (UKEAP)*. DEFRA, London. Available online: http://uk-air.defra.gov.uk/assets/documents/reports/cat10/1011291545_AQ0616_UKEAP_2009_Annual_Report.pdf (accessed August 2016).

de Kluizenaar, Y. and Farrell, E.P., 2000. *8. Ammonia Monitoring in Ireland: A Full Year of Ammonia Monitoring, Set-Up & Results*. Research and Development Series No. 8. EPA, Johnstown Castle, Ireland.

de Smith, M.J., Goodchild, M.F. and Longley, P.A., 2009. *Geospatial Analysis: A Comprehensive Guide to Principles, Techniques and Software Tools*. Matador, Leicester.

Dore, A.J., Choularton, T.W. and Fowler, D., 1992. An improved wet deposition map of the United Kingdom incorporating the seeder-feeder effect over mountainous terrain. *Atmospheric Environment. Part A. General Topics* 26: 1375–1381. Available online: http://www.sciencedirect.com/science/article/pii/0960168692901222 (accessed August 2016).

Dragosits, U., Sutton, M.A., Place, C.J. *et al*., 1998. Modelling the spatial distribution of agricultural ammonia emissions in the UK. *Environmental Pollution* 102(Suppl. 1): 195–203. Available online: http://www.sciencedirect.com/science/article/pii/S026974919880033X (accessed August 2016).

Duffy, P., Hanley, E., Barry, S. *et al*., 2015. *Ireland Informative Inventory Report 2015: Air Pollutant Emissions in Ireland 1990–2013 Reported to the Secretariat of the UN/ECE Convention on Long-Range Transboundary Air Pollution.* EPA. Johnstown Castle, Ireland. Available online: http://erc.epa.ie/safer/downloadCheck.jsp?isoID=21&rID=10174&atID=2282811 (accessed August 2016).

Duyzer, J.H., Nijenhuis, B. and Weststrate, H., 2001. Monitoring and modelling of ammonia concentrations and deposition in agricultural areas of the Netherlands. *Water, Air, and Soil Pollution* 1: 131–144.

EC (European Commission), 1987. The Proceedings of an International Symposium organised by The Commission of the European Communities and the United Kingdom Health and Safety Executive “Diffusive Sampling: An Alternative Approach to Workplace Air Monitoring”. No 10555, Brussels and Luxembourg.

EC (European Commission), 2015. Transport & Environment. Available online: http://ec.europa.eu/environment/air/transport/road.htm (accessed August 2016).

EEA (European Environment Agency), 2015. *Air Quality in Europe 2015*. EEA Report No. 5/2015. Available online: http://www.eea.europa.eu/publications/air-quality-in-europe-2015 (accessed August 2016).

Egnér, H. and Eriksson, E., 1955. Current data on the chemical sampling of air and precipitation. *Tellus* 7: 134–137.

EMEP (European Monitoring and Evaluation Programme), 2004. Assessment Report EMEP Assessment Part I: European Perspective. Available online: http://emep.int/publ/reports/2004/assessment_2004.html (accessed August 2016).

EMEP (European Monitoring and Evaluation Programme), 2011. EMEP Measurement Data Online/EMEP Acidifying/Euthrophying Compounds/Station Maps 1980–2010. Available online: http://www.nilu.no/projects/ccc/emepdata.html (accessed August 2016).

EPA (Environmental Protection Agency), 2012. *Ireland’s Environment 2012: An Assessment*. Lehane, M. and O’Leary, B. (eds). EPA, Johnstown Castle, Ireland. Available online: http://www.epa.ie/pubs/reports/indicators/irelandsenvironment2012.html (accessed August 2016).

EPA (Environmental Protection Agency), 2015. *Ireland’s Transboundary Gas Emission in 2013*. EPA, Johnstown Castle, Ireland. Available online: http://www.epa.ie/pubs/reports/air/airemissions/NECD%20Summary%20Report%202015.pdf Summary Report 2015.pdf (accessed August 2016).

Erisman, J.W., Vermetten, A.W.M., Asman, W.A.H. *et al*., 1988. Vertical distribution of gasses and aerosols: the behaviour of ammonia and related components in the lower atmosphere. *Atmospheric Environment* 22: 1153–1160.

Erisman, J.W., Van Pul, A. and Wyers, P., 1994. Parametrization of surface resistance for the quantification of atmospheric deposition of acidifying pollutants and ozone. *Atmospheric Environment* 28: 2595–2607. Available online: http://www.sciencedirect.com/science/article/pii/1352231094904332 (accessed August 2016).

Erisman, J.W., Bleeker, A., Galloway, J. *et al*., 2007. Reduced nitrogen in ecology and the environment. *Environmental Pollution* 150: 140–149.

Fangmeier, G.D., Hadwiger-Fangmeier, A., Van der Eerden, L. *et al*., 1994. Effects of atmospheric ammonia on vegetation: a review. *Environmental Pollution* 86: 43–82.

Farquhar, G.D., Firth, P.M., Wetselaar, R. *et al*., 1980. On the gaseous exchange of ammonia between leaves and the environment: determination of the ammonia compensation point. *Plant Physiology* 66**:** 710–714.

Fournier, N., Pais, V.A., Sutton, M.A. *et al*., 2002. Parallelisation and application of a multi-layer atmospheric transport model to quantify dispersion and deposition of ammonia over the British Isles. *Environmental Pollution* 116: 95–107. Available online: http://www.sciencedirect.com/science/article/pii/S0269749101001464 (accessed August 2016).

Hansen, K., Thimonier A., Clarke N. *et al*., 2013. Atmospheric deposition to forest ecosystems. In Ferretti, M. and Fischer, R. (eds), *Forest Monitoring: Methods for Terrestrial Investigations in Europe with an Overview of North America and Asia*. Elsevier, Amsterdam.

Hatch, D.J., Jarvis, S.C. and Dollard, G.J., 1990. Measurements of ammonia emission from grazed grassland. *Environmental Pollution* 65: 333–346.

Henry, J. and Aherne, J., 2014. Nitrogen deposition and exceedance of critical loads for nutrient nitrogen in Irish grasslands. *Science of the Total Environment* 470–471: 216–223. Available online: http://www.sciencedirect.com/science/article/pii/S0048969713010851 (accessed August 2016).

Horváth, L. and Sutton, M.A., 1998. Long-term record of ammonia and ammonium concentrations at K-puszta, Hungary. *Atmospheric Environment* 3: 339–344.

Hyde, B.P., Carton, O.T., O'Toole, P., 2003. A new inventory of ammonia emissions from Irish agriculture. *Atmospheric Environment* 37: 55–62. Available online: http://www.sciencedirect.com/science/article/pii/S1352231002006921 (accessed August 2016).

Johnson, J.A., Aherne, J. and Cummins, T., 2013. Contrasting responses of two Sitka spruce forest plots in Ireland to reductions in sulphur emissions: results of 20 years of monitoring. *Biogeochemistry* 116: 15–37.

Johnson, J., Aherne, J. and Cummins, T., 2015. Base cation budgets under residue removal in temperate maritime plantation forests. *Forest Ecology and Management* 343: 144–156. Available online: http://www.sciencedirect.com/science/article/pii/S0378112715000419 (accessed August 2016).

Kean, A.J., Littlejohn, D., Ban-Weiss, G.A. *et al*., 2009. Trends in on-road vehicle emissions of ammonia. *Atmospheric Environment* 43: 1565–1570. Available online: http://www.sciencedirect.com/science/article/pii/S1352231008008881 (accessed August 2016).

Leinert, S., McGovern, F. and Jennings, S.G., 2008. *New Transboundary Air Pollution Monitoring Capacity for Ireland*. EPA ERC (Environmental Research Centre) Report 10, Johnstown Castle, Ireland.

Lelieveld, J., Evans, J.S., Fnais, M. *et al*., 2015. The contribution of outdoor air pollution sources to premature mortality on a global scale. *Nature* 525 (7569): 367–371.

Lockyer, D.R. and Whitehead, D.C., 1990. Volatilisation of ammonia from cattle urine applied to grassland. *Soil Biology and Biochemistry* 22: 1137–1142.

McGarry, S.J., O'Toole, P. and Morgan, M.A., 1987. Effects of soil temperature and moisture content on ammonia volatilisation from urea-treated pasture and tillage soils. *Irish Journal of Agricultural Research* 26: 173–182.

NAMN, 2016. National Ammonia Monitoring Network (NAMN). Available online: http://www.ecn.ac.uk/links/link-items/uk-national-ammonia-monitoring-network-namn (accessed August 2016).

Nilsson, J. and Grennfelt, P., 1988. *Critical Loads for Sulphur and Nitrogen*. Nordic Council of Ministers, Copenhagen, Denmark.

Nordin, A., Sheppard, L.J., Strengbom, J. *et al*., 2011. Background document. *Nitrogen Deposition and Natura 2000: Science and Practice in Determining Environmental Impacts*. COST (European Cooperation in Science and Technology). pp. 115–129.

O'Toole, P., Morgan, M.A. and McGarry, S.J.,1985. A comparative study of urease activities in pasture and tillage soils. *Communications in Soil and Plant Analysis* 16: 759–773.

Palmes, E.D. and Gunnison, A.F., 1973. Personal monitoring device for gaseous contaminants. *American Industrial Hygiene Association Journal* 34: 78–81.

Paulot, F., Dacob, D.J., Pinder, R.W. *et al.*, 2014. Ammonia emissions in the United States, European Union, and China derived by high-resolution inversion of ammonium wet deposition data: interpretation with a new agricultural emissions inventory (MASAGE_NH3). *Journal of Geophysical Research: Atmospheres* 119: 4343–4364.

Perrino, C., Catrambone, M., Di Menno Di Bucchianico, A. *et al.*, 2002. Gaseous ammonia in the urban area of Rome, Italy and its relationship with traffic emissions. *Atmospheric Environment* 36: 5385–5394. Available online: http://www.sciencedirect.com/science/article/pii/S1352231002004697 (accessed August 2016).

Pilz, J. and Spöck, G., 2008. Why do we need and how should we implement Bayesian kriging methods. *Stochastic Environmental Research and Risk Assessment* 22: 621–632.

Pio, C.A., Cerqueira, M.A., Castro, L.M. *et al.*, 1996. Sulphur and nitrogen compounds in variable marine/continental air masses at the southwest European coast. *Atmospheric Environment* 30: 3115–3127.

Posch, M., Aherne, J. and Hettelingh, J.-P., 2011a. Nitrogen critical loads using biodiversity-related critical limits. *Environmental Pollution* 159: 2223–2227. Available online: http://www.sciencedirect.com/science/article/pii/S0269749110005099 (accessed August 2016).

Posch, M., Slootweg, J. and Hettelingh, J.-P. (eds), 2011b. *Modelling Critical Thresholds and Temporal Changes of Geochemistry and Vegetation Diversity: CCE Status Report 2011*. Coordination Centre for Effects, Bilthoven, the Netherlands. Available online: http://hdl.handle.net/10029/258481 (accessed August 2016).

Pozzoli, L. and Cottica, D., 1987. An overview of the effects of temperature, pressure, humidity, storage and face velocity. In Berlin, A.B., Brown, R.H. and Saunders, K.J. (eds), *Diffusive Sampling: An Alternative Approach to Workplace Air Monitoring*. Royal Society of Chemistry, London.

Rabaud, N.E., James, T.A., Ashbaugh, L.L. *et al.*, 2001. A passive sampler for the determination of airborne ammonia concentrations near large-scale animal facilities. *Environmental Science & Technology* 35: 1190–1196.

Roelofs, J.G.M., 1986. The effect of airborne sulphur and nitrogen deposition on aquatic and terrestial heathland vegetation. *Experientia* 42: 372–377.

Roelofs, J.G.M., Kempers, A.J., Houdijke, A.L.F.M. *et al.*, 1985. The effects of air-borne ammonium sulphate on *Pinus nigra* var. *maritima* in the Netherlands. *Plants and Soils* 84: 45–56.

Schrader, F. and Brümmer, C., 2014. Land use specific ammonia deposition velocities: a review of recent studies (2004–2013). *Water, Air, and Soil Pollution* 225: 2114. Available online: http://www.ncbi.nlm.nih.gov/pmc/articles/PMC4176955/ (accessed August 2016).

Singles, R., Sutton, M.A. and Weston, K.J., 1998. A multi-layer model to describe the atmospheric transport and deposition of ammonia in Great Britain. *Atmospheric Environment* 32: 393–399.

Skjøth, C.A., Geels, C., Berge, H. *et al.*, 2011. Spatial and temporal variations in ammonia emissions: a freely accessible model code for Europe. *Atmospheric Chemistry and Physics* 11: 5221–5236.

Skudlark, J.R., Jennings, J.A., Roadman, M.J. *et al.*, 2005. Atmospheric nitrogen inputs to the Delaware Inland Bay: the role of ammonia. *Environmental Pollution* 135: 433–443.

Stevens, C.J., Dise, N.B., Mountford, O. *et al.*, 2004. Impact of nitrogen deposition on the species richness of grasslands. *Science* 303: 1876–1879.

Sutton, M.A., Moncrieff, J.B. and Fowler, D., 1992. Deposition of atmospheric ammonia to moorlands. *Environmental Pollution* 75: 15–24.

Sutton, M.A., Pitcairn, C.E.R. and Fowler, D., 1993. The exchange of ammonia between the atmosphere and plant communities. *Advances in Ecological Research* 24: 301–393.

Sutton, M.A., Asman, W.A.H. and Schjørring, J.K., 1994. Dry deposition of reduced nitrogen. *Tellus* 46B: 255–273.

Sutton, M.A., Place, C.J., Eager, M. *et al.*, 1995. Assessment of the magnitude of ammonia emissions in the United Kingdom. *Atmospheric Environment* 12: 1393–1411.

Sutton, M.A., Dragosits, U., Tang, Y.S. *et al.*, 2000. Ammonia emissions from non-agricultural sources in the UK. *Atmospheric Environment* 34: 855–869.

Sutton, M.A., Tang, Y.S., Dragosits, U. *et al.*, 2001a. A spatial analysis of atmospheric ammonia and ammonium in the U.K. *Scientific World* 1: 275–286.

Sutton, M.A., Miners, B., Tang, Y.S. *et al.*, 2001b. Comparison of low cost measurement techniques for long-term monitoring of atmospheric ammonia. *Journal of Environmental Monitoring* 3: 446–453.

Sutton, M.A., Nemitz, E., Erisman, J.W. *et al.*, 2007. Challenges in quantifying biosphere–atmosphere exchange of nitrogen species. *Environmental Pollution* 150: 125–139.

Sutton, M.A., Erisman, J.W., Dentener, F. *et al.*, 2008. Ammonia in the environment: from ancient times to the present. *Environmental Pollution* 156: 583–604.

Sutton, M.A., Reis, S., Riddick, S.N. *et al*., 2013. Towards a climate-dependent paradigm of ammonia emission and deposition. *Philosophical Transactions of the Royal Society of London B: Biological Sciences* 368(1621): 20130166.

Tang, Y.S., Cape, J.N. and Sutton, M.A., 2001. Development and types of passive samplers for monitoring atmospheric NO_2 and NH_3 concentrations. *Scientific World* 1: 513–529.

Tang, Y.S., van Dijk, N., Love, L. *et al*., 2004. *Ammonia Monitoring in Northern Ireland, Final Report*. Scotland and Northern Ireland Forum for Environmental Research, Edinburgh.

Thöni, L., Brang, P., Braun, S. *et al*., 2004. Ammonia monitoring in Switzerland with passive samplers: patterns, determinants and comparison with modelled concentrations. *Environmental Monitoring and Assessment* 98: 93–107.

UBA (Umweltbundesamt), 2004. *Manual on Methodologies and Criteria for Modelling and Mapping Critical Loads & Levels and Air Pollution Effects, Risks and Trends*. UNECE Convention on Long-range Transboundary Air Pollution. Federal Environmental Agency (UBA), Berlin. Available online: http://www.icpmapping.org/Mapping_Manual (accessed August 2016).

UNECE (United Nations Economic Commission for Europe), 2004. ICP Modelling and Mapping Critical Loads and Levels Approach. UNECE Convention on Long-range Transboundary Air Pollution Working Group on Effects. Available online: http://www.unece.org/env/lrtap/workinggroups/wge/definitions.html (accessed August 2016).

UNECE (United Nations Economic Commission for Europe), 2013. Guidance Document for Preventing and Abating Ammonia Emissions from Agricultural Sources. Available online: http://www.unece.org/fileadmin/DAM/env/documents/2012/EB/ECE_EB.AIR_120_ENG.pdf (accessed August 2016).

van den Beuken, R., 1994. *Passive Sampling of Atmospheric Ammonia at Forest Sites in Ireland and Ammonia Deposition Estimates*. Department of Air Quality, Agricultural University Wageningen, the Netherlands, and Department of Environmental Resource Management, University College Dublin, Dublin.

van den Beuken, R., 1997. *Mapping Emission and Dry Deposition of Ammonia in Ireland*. Forest Ecosystem Research Group, University College Dublin, Dublin.

van Pul, A., van Jaarsveld, H., van der Meulen, T. *et al*., 2004. Ammonia concentrations in the Netherlands: spatially detailed measurements and model calculations. *Atmospheric Environment* 38: 4045–4055.

Verhoeven, J.T.A., Beltman, B., Dorland, E. *et al*., 2011. Differential effects of ammonium and nitrate deposition on fen phanerogams and bryophytes. *Applied Vegetation Science* 14: 149–157.

Vermetten, A.W.M., Hofschreuder, P. and Versulis, A.H., 1990. *Air Pollution in Forest Canopies*. Agricultural University Wageningen, Wageningen, the Netherlands.

Vogt, E., Dragosits, U., Braban, C.F. *et al*., 2013. Heterogeneity of atmospheric ammonia at the landscape scale and consequences for environmental impact assessment. *Environmental Pollution* 179: 120–131.

Walsh, S., 2012. *A Summary of Climate Averages for Ireland*. Climatological Note 14. Met Éireann, Dublin. Available online: http://www.met.ie/climate-ireland/SummaryClimAvgs.pdf (accessed August 2016).

Warneck, P., 1988. *Chemistry of the Natural Atmosphere*. Academic Press, San Diego, CA.

Whitehead, D.C., 1995. *Grassland Nitrogen*. CAB International, Wallingford, UK.

Willems, J.J.H., 1988. *Spectrophotometric Analysis of Ammonia*. Agricultural University Wageningen, Wageningen, the Netherlands.

Willems, J.J.H., 1989. *Passive Sampling of Ammonia under Outdoor Conditions (Willems Badge)*. Agricultural University Wageningen, Wageningen, the Netherlands.

Willems, J.J.H., 1993. *Low-Cost Methods for Measuring Air Pollutants (A Training Program)*. Report R-635. Department of Air Quality, Agricultural University Wageningen, Wageningen, the Netherlands.

WMO (World Meteorological Organization), 2008. *Guide to Meteorological Instruments and Methods of Observation*. WMO, Geneva, Switzerland. Available online: http://library.wmo.int/pmb_ged/wmo_8_en-2012.pdf (accessed August 2016).

Zbieranowski, A.L. and Aherne, J., 2012a. Ambient concentrations of atmospheric ammonia, nitrogen dioxide and nitric acid across a rural–urban–agricultural transect in southern Ontario, Canada. *Atmospheric Environment* 62: 481–491. Available online: http://www.sciencedirect.com/science/article/pii/S1352231012008126 (accessed August 2016).

Zbieranowski, A.L. and Aherne, J., 2012b. Spatial and temporal concentration of ambient atmospheric ammonia in southern Ontario, Canada. *Atmospheric Environment* 62: 441–450.

Zurlo, N. and Andreoletti, F., 1987. Effect of air turbulence on diffusive sampling. In Berlin, A.B., Brown, R.H. and Saunders, K.J. (eds), *Diffusive Sampling: An Alternative Approach to Workplace Air Monitoring*. Royal Society of Chemistry, London.

Abbreviations

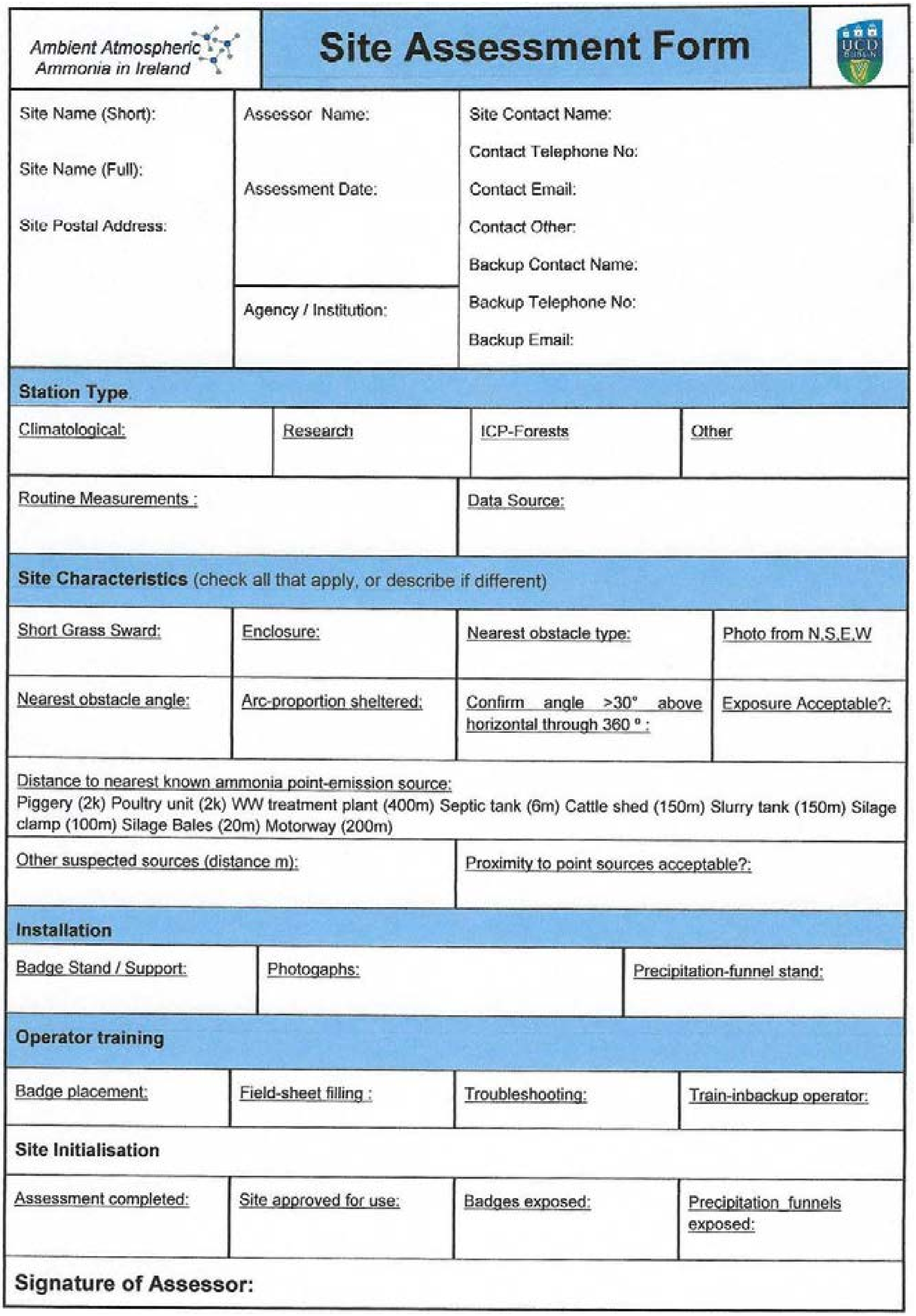
CLRTAP	Convention on Long-range Transboundary Air Pollution
CORINE	Coordination of Information on the Environment
EMEP	European Monitoring and Evaluation Programme
EPA	Environmental Protection Agency
FRAME	Fine Resolution Ammonia Exchange
GIS	Geographic information system
ICP	International Cooperative Programme
MPE	Mean prediction error
NAMN	National Ammonia Monitoring Network
ND	None detected
NEC Directive	Directive on National Emission Ceilings
NH_3	Ammonia
NH_3-N	Nitrogen present as ammonia
NH_4^+	Ammonium
NH_4-N	Nitrogen present as ammonium
NH_x	Reduced nitrogen
NH_x-N	Nitrogen present as reduced nitrogen
NO_x	Nitrogen oxides
PM	Particulate matter
$PM_{2.5}$	Particulate matter smaller than 2.5 µm
PTFE	Polytetrafluoroethylene
RMSE	Root mean squared error
SO_2	Sulphur dioxide
SO_x	Sulphur oxides
STRIVE	Science, Technology, Research and Innovation for the Environment
UCD	University College Dublin
UNECE	United Nations Economic Commission for Europe
WMO	World Meteorological Organization

Glossary

µg/m^3	Micrograms per cubic metre. The unit is used in this document for reporting atmospheric concentrations of the trace gas NH_3. This refers to micrograms of NH_3 in each cubic metre of air. Since temperature and pressure are not stated, the reader should assume it refers to sea-level pressure, and standard or ambient temperature. Extreme conditions would introduce other considerations
Ambient	Condition of the environment, without modification
Ammonia/ammonium	Ammonia (NH_3) transforms by protonation to ammonium (NH_4^+), reversibly. The proportion of each present is determined by the pH of the medium. Transfer of ammonia to surfaces, such as wet vegetation, is predominantly by transformation to ammonium, while release from surfaces is by deprotonation, with NH_3 liberated. In acid soil environments, all is present as ammonium. Other forms of reduced (as distinct from oxidised) nitrogen exist, but this narrower sense is used in this report
Annular denuder	See **denuder**
Atmospheric deposition	Transfer from atmosphere to earth surface, including vegetation surfaces, in precipitation and direct accumulation on surfaces such as dew and frost. See **deposition**
Badge	The colloquial term for the shallow, broad, cylindrical containers used here as sampling devices, with a fixing to attach the closed surface to a support, likened to pinning a badge (or “button” in American speech) to one’s clothes
Critical level	Concentration of a substance above which harm may occur to a sensitive receptor, according to present knowledge
Critical load	Mass transfer of a substance below which no harm will occur to a sensitive receptor, according to present knowledge
Denuder	Sampling device that removes (“denudes”) all of a target substance from a sampled medium. An annular denuder has its absorbing surfaces arranged as a pair of coaxial nested cylinders, enclosing a narrow cylindrical space. (These would be concentric rings, Latin “annuli”, in cross-section, like the rings of a tree; hence the name.) A tubular denuder has a single absorbing surface, on the inside of the tube. In either configuration, air is actively drawn through the denuder tube
Deposition	Transfer of substance from a medium to a surface. This may occur by many mechanisms, including falling hydrometeoric precipitation (rain, hail and snow), falling dust and phase transfers such as dew and frost
Deposition velocity	Either defined as the inverse sum of successive resistances or based on measurement of deposition. The unit of deposition velocity is cm/s
Diffusive sampler	A device to collect a substance, where the mechanism of capture involves a controlled transfer of target by molecular motion of the carrier (as distinct from motion by mass flow of carrier). Ammonia *diffuses* through air in the still-air zone of the sampler
Dry deposition	Transfer of substance to a surface by gas impact with adsorption or transformation at the surface, and by particulate transfer, probably with electrostatic adhesion for finer particles. This concept includes deposition to a wet surface, and is envisaged as total deposition minus that collected by open-funnel wet-only collectors (which have a lid that closes when precipitation is not falling). Dry deposition depends on factors including the roughness of vegetation, and so is dependent on land cover, with tall complex forest canopies experiencing high dry deposition

Empirical Bayesian kriging	A kriging method with automated calculations, towards building a valid kriging model
Kriging	A method of geostatistical interpolation, where a set of points in two dimensions (the *x*- and *y*-values), each with a value in a third dimension (the *z*-value), are used to generate a surface, based on regression of observed *z*-values, weighted according to spatial covariance
Reduced nitrogen	In this report, this term refers to ammonia (NH_3) and ammonium (NH_4^+), collectively NH_x. “Reduced” is the reverse of “oxidised” in this sense (not of “increased”)
Wet deposition	The transfer of liquid-phase substances from the atmosphere to vegetation or land surfaces. This excludes dry deposition, and is operationally defined by having funnel samplers open only during periods when precipitation is sensed. Wet deposition also means the substances deposited or the solute and solid component transferred

Appendix 1 Site Assessment Form



Ambient Atmospheric Ammonia in Ireland	**Site Assessment Form**

Site Name (Short): Site Name (Full): Site Postal Address:	Assessor Name: Assessment Date:	Site Contact Name: Contact Telephone No: Contact Email: Contact Other: Backup Contact Name: Backup Telephone No: Backup Email:
	Agency / Institution:	

Station Type

Climatological:	Research	ICP-Forests	Other

Routine Measurements :	Data Source:

Site Characteristics (check all that apply, or describe if different)

Short Grass Sward:	Enclosure:	Nearest obstacle type:	Photo from N,S,E,W
Nearest obstacle angle:	Arc-proportion sheltered:	Confirm angle >30° above horizontal through 360 ° :	Exposure Acceptable?:

Distance to nearest known ammonia point-emission source:
Piggery (2k) Poultry unit (2k) WW treatment plant (400m) Septic tank (6m) Cattle shed (150m) Slurry tank (150m) Silage clamp (100m) Silage Bales (20m) Motorway (200m)

Other suspected sources (distance m):	Proximity to point sources acceptable?:

Installation

Badge Stand / Support:	Photogaphs:	Precipitation-funnel stand:

Operator training

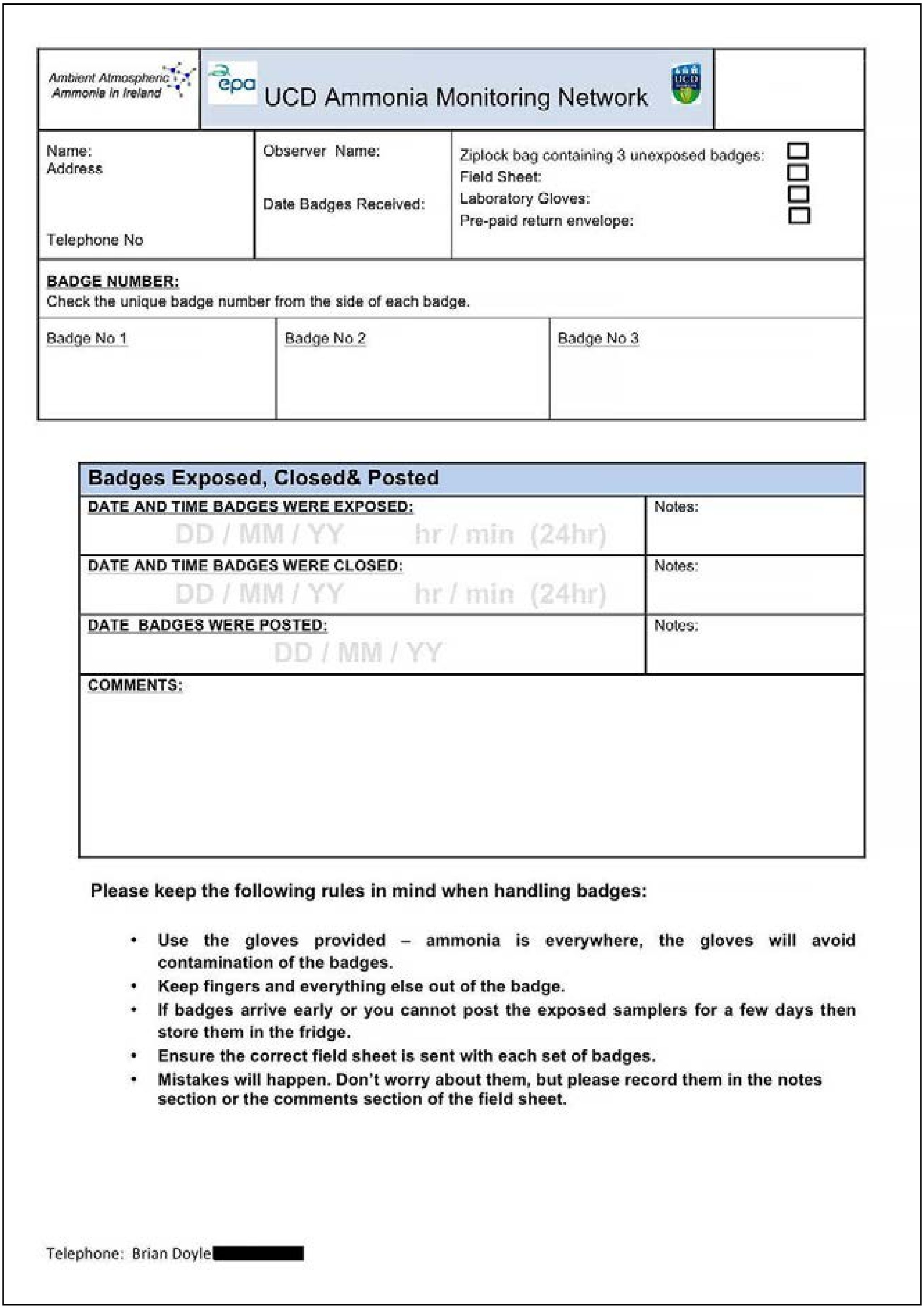
Badge placement:	Field-sheet filling :	Troubleshooting:	Train-inbackup operator:

Site Initialisation

Assessment completed:	Site approved for use:	Badges exposed:	Precipitation funnels exposed:

Signature of Assessor:

Appendix 2 Sampling Field-Sheet



Ambient Atmospheric Ammonia in Ireland

epa

UCD Ammonia Monitoring Network

Name:
Address

Telephone No

Observer Name:

Date Badges Received:

Ziplock bag containing 3 unexposed badges: ☐
Field Sheet: ☐
Laboratory Gloves: ☐
Pre-paid return envelope: ☐

BADGE NUMBER:
Check the unique badge number from the side of each badge.

Badge No 1	Badge No 2	Badge No 3

Badges Exposed, Closed& Posted

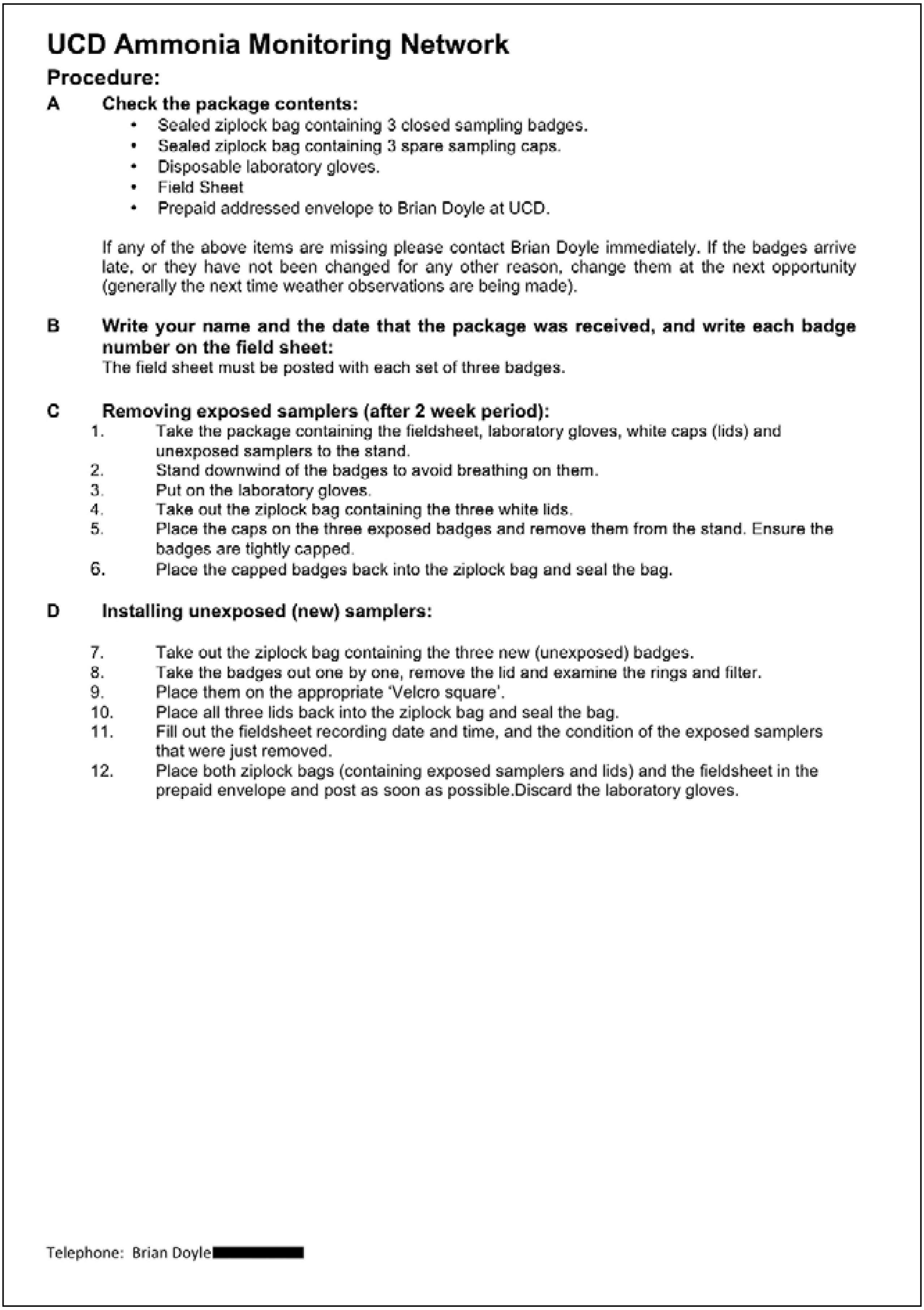
DATE AND TIME BADGES WERE EXPOSED: DD / MM / YY hr / min (24hr)	Notes:
DATE AND TIME BADGES WERE CLOSED: DD / MM / YY hr / min (24hr)	Notes:
DATE BADGES WERE POSTED: DD / MM / YY	Notes:

COMMENTS:

Please keep the following rules in mind when handling badges:

- Use the gloves provided – ammonia is everywhere, the gloves will avoid contamination of the badges.
- Keep fingers and everything else out of the badge.
- If badges arrive early or you cannot post the exposed samplers for a few days then store them in the fridge.
- Ensure the correct field sheet is sent with each set of badges.
- Mistakes will happen. Don't worry about them, but please record them in the notes section or the comments section of the field sheet.

Telephone: Brian Doyle [redacted]



UCD Ammonia Monitoring Network

Procedure:

A Check the package contents:

- Sealed ziplock bag containing 3 closed sampling badges.
- Sealed ziplock bag containing 3 spare sampling caps.
- Disposable laboratory gloves.
- Field Sheet
- Prepaid addressed envelope to Brian Doyle at UCD.

If any of the above items are missing please contact Brian Doyle immediately. If the badges arrive late, or they have not been changed for any other reason, change them at the next opportunity (generally the next time weather observations are being made).

B Write your name and the date that the package was received, and write each badge number on the field sheet:

The field sheet must be posted with each set of three badges.

C Removing exposed samplers (after 2 week period):

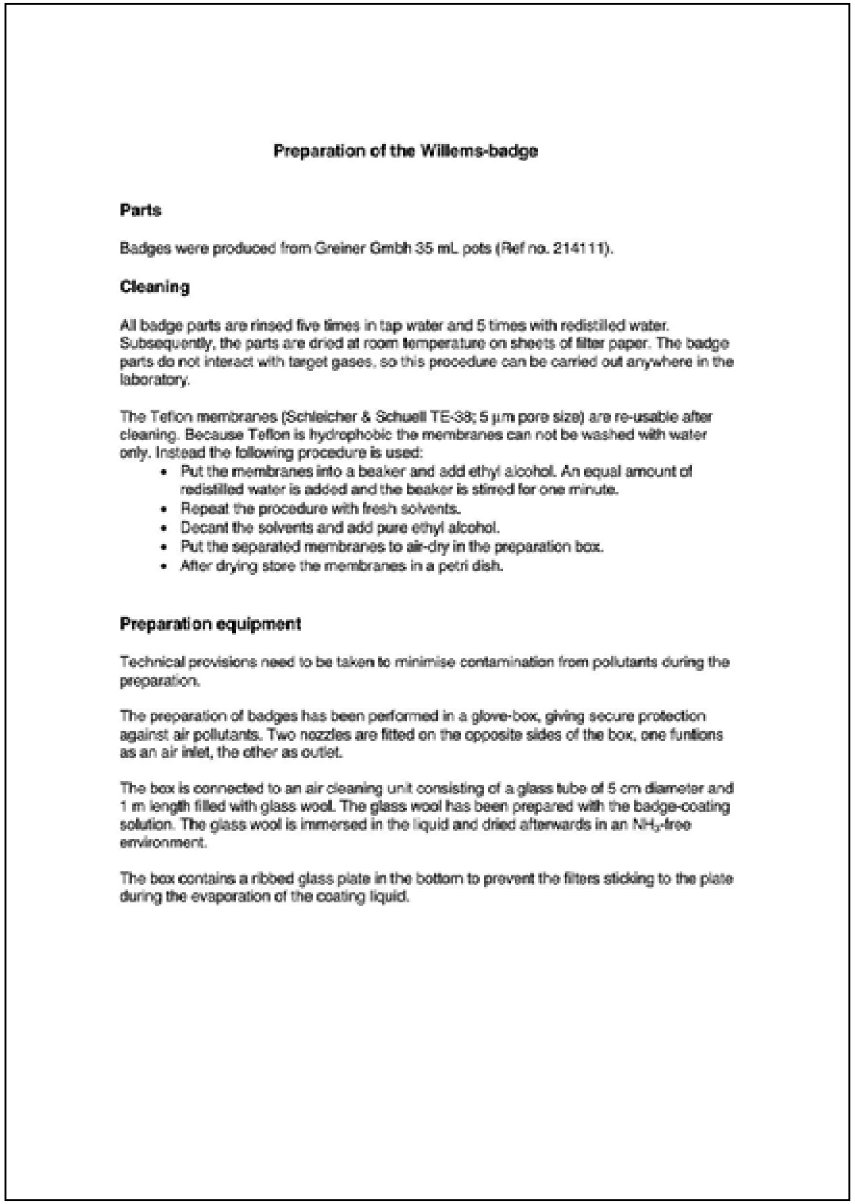
1. Take the package containing the fieldsheet, laboratory gloves, white caps (lids) and unexposed samplers to the stand.
2. Stand downwind of the badges to avoid breathing on them.
3. Put on the laboratory gloves.
4. Take out the ziplock bag containing the three white lids.
5. Place the caps on the three exposed badges and remove them from the stand. Ensure the badges are tightly capped.
6. Place the capped badges back into the ziplock bag and seal the bag.

D Installing unexposed (new) samplers:

7. Take out the ziplock bag containing the three new (unexposed) badges.
8. Take the badges out one by one, remove the lid and examine the rings and filter.
9. Place them on the appropriate ‘Velcro square’.
10. Place all three lids back into the ziplock bag and seal the bag.
11. Fill out the fieldsheet recording date and time, and the condition of the exposed samplers that were just removed.
12. Place both ziplock bags (containing exposed samplers and lids) and the fieldsheet in the prepaid envelope and post as soon as possible.Discard the laboratory gloves.

Telephone: Brian Doyle [redacted]

Appendix 3 Badge Preparation and Analysis (after de Kluizenaar and Farrell, 2000)



Preparation of the Willems-badge

Parts

Badges were produced from Greiner Gmbh 35 mL pots (Ref no. 214111).

Cleaning

All badge parts are rinsed five times in tap water and 5 times with redistilled water. Subsequently, the parts are dried at room temperature on sheets of filter paper. The badge parts do not interact with target gases, so this procedure can be carried out anywhere in the laboratory.

The Teflon membranes (Schleicher & Schuell TE-38; 5 µm pore size) are re-usable after cleaning. Because Teflon is hydrophobic the membranes can not be washed with water only. Instead the following procedure is used:

- Put the membranes into a beaker and add ethyl alcohol. An equal amount of redistilled water is added and the beaker is stirred for one minute.
- Repeat the procedure with fresh solvents.
- Decant the solvents and add pure ethyl alcohol.
- Put the separated membranes to air-dry in the preparation box.
- After drying store the membranes in a petri dish.

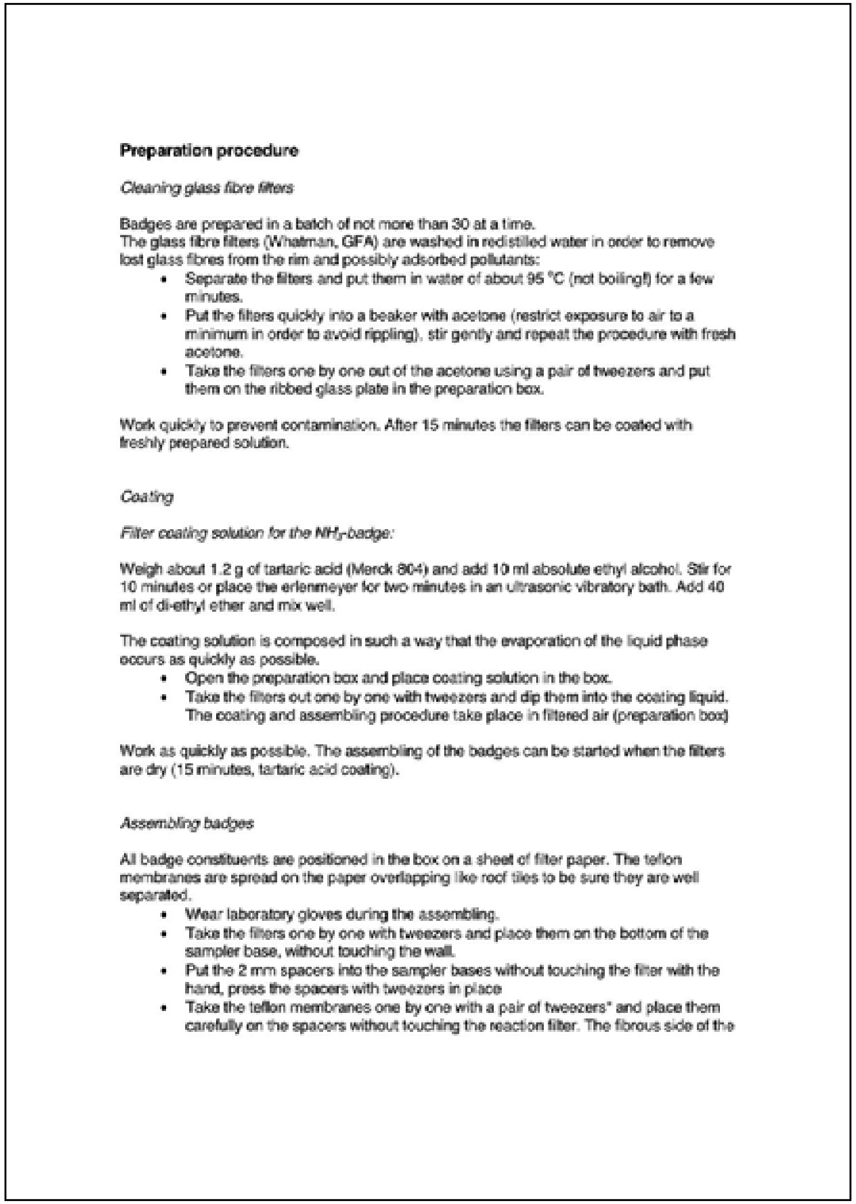
Preparation equipment

Technical provisions need to be taken to minimise contamination from pollutants during the preparation.

The preparation of badges has been performed in a glove-box, giving secure protection against air pollutants. Two nozzles are fitted on the opposite sides of the box, one funtions as an air inlet, the other as outlet.

The box is connected to an air cleaning unit consisting of a glass tube of 5 cm diameter and 1 m length filled with glass wool. The glass wool has been prepared with the badge-coating solution. The glass wool is immersed in the liquid and dried afterwards in an NH_3-free environment.

The box contains a ribbed glass plate in the bottom to prevent the filters sticking to the plate during the evaporation of the coating liquid.



Preparation procedure

Cleaning glass fibre filters

Badges are prepared in a batch of not more than 30 at a time.
The glass fibre filters (Whatman, GFA) are washed in redistilled water in order to remove lost glass fibres from the rim and possibly adsorbed pollutants:

- Separate the filters and put them in water of about 95 °C (not boiling!) for a few minutes.
- Put the filters quickly into a beaker with acetone (restrict exposure to air to a minimum in order to avoid rippling), stir gently and repeat the procedure with fresh acetone.
- Take the filters one by one out of the acetone using a pair of tweezers and put them on the ribbed glass plate in the preparation box.

Work quickly to prevent contamination. After 15 minutes the filters can be coated with freshly prepared solution.

Coating

Filter coating solution for the NH_3-badge:

Weigh about 1.2 g of tartaric acid (Merck 804) and add 10 ml absolute ethyl alcohol. Stir for 10 minutes or place the erlenmeyer for two minutes in an ultrasonic vibratory bath. Add 40 ml of di-ethyl ether and mix well.

The coating solution is composed in such a way that the evaporation of the liquid phase occurs as quickly as possible.

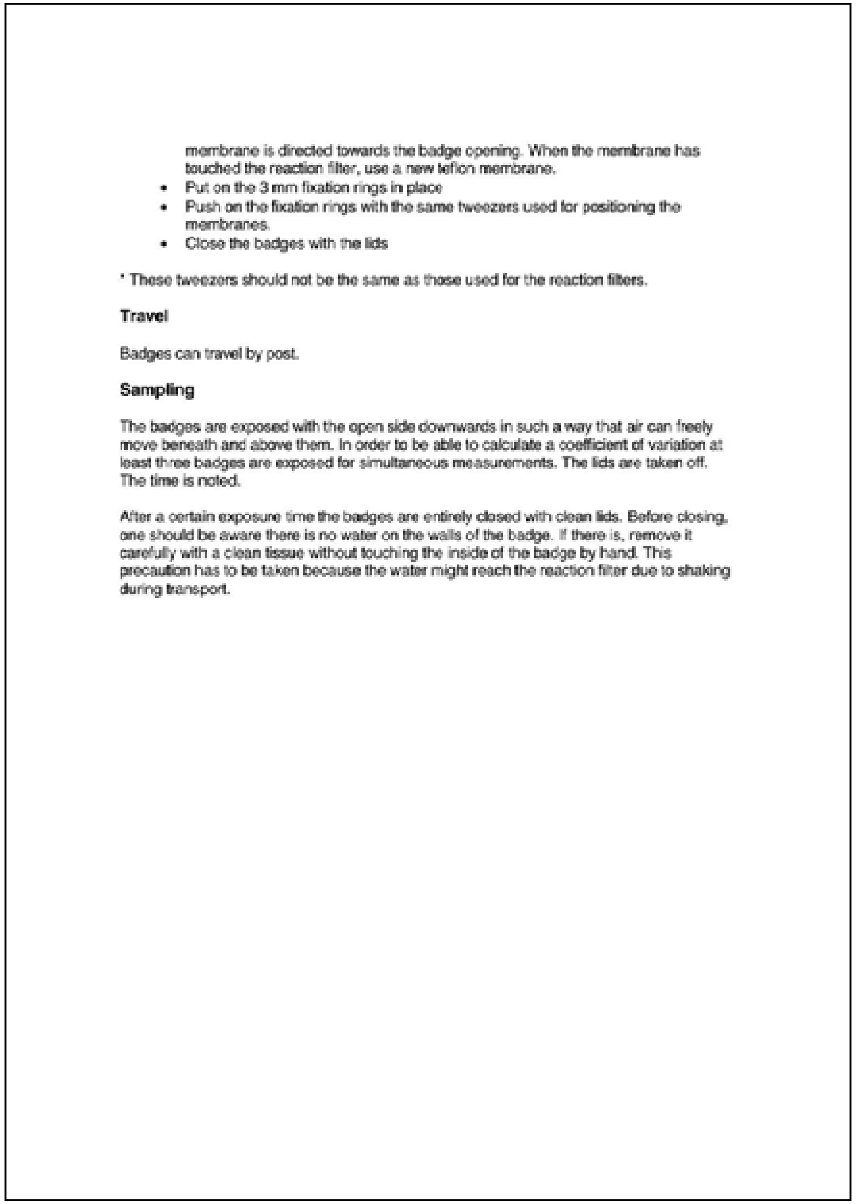
- Open the preparation box and place coating solution in the box.
- Take the filters out one by one with tweezers and dip them into the coating liquid. The coating and assembling procedure take place in filtered air (preparation box)

Work as quickly as possible. The assembling of the badges can be started when the filters are dry (15 minutes, tartaric acid coating).

Assembling badges

All badge constituents are positioned in the box on a sheet of filter paper. The teflon membranes are spread on the paper overlapping like roof tiles to be sure they are well separated.

- Wear laboratory gloves during the assembling.
- Take the filters one by one with tweezers and place them on the bottom of the sampler base, without touching the wall.
- Put the 2 mm spacers into the sampler bases without touching the filter with the hand, press the spacers with tweezers in place
- Take the teflon membranes one by one with a pair of tweezers* and place them carefully on the spacers without touching the reaction filter. The fibrous side of the



membrane is directed towards the badge opening. When the membrane has touched the reaction filter, use a new teflon membrane.
- Put on the 3 mm fixation rings in place
- Push on the fixation rings with the same tweezers used for positioning the membranes.
- Close the badges with the lids

* These tweezers should not be the same as those used for the reaction filters.

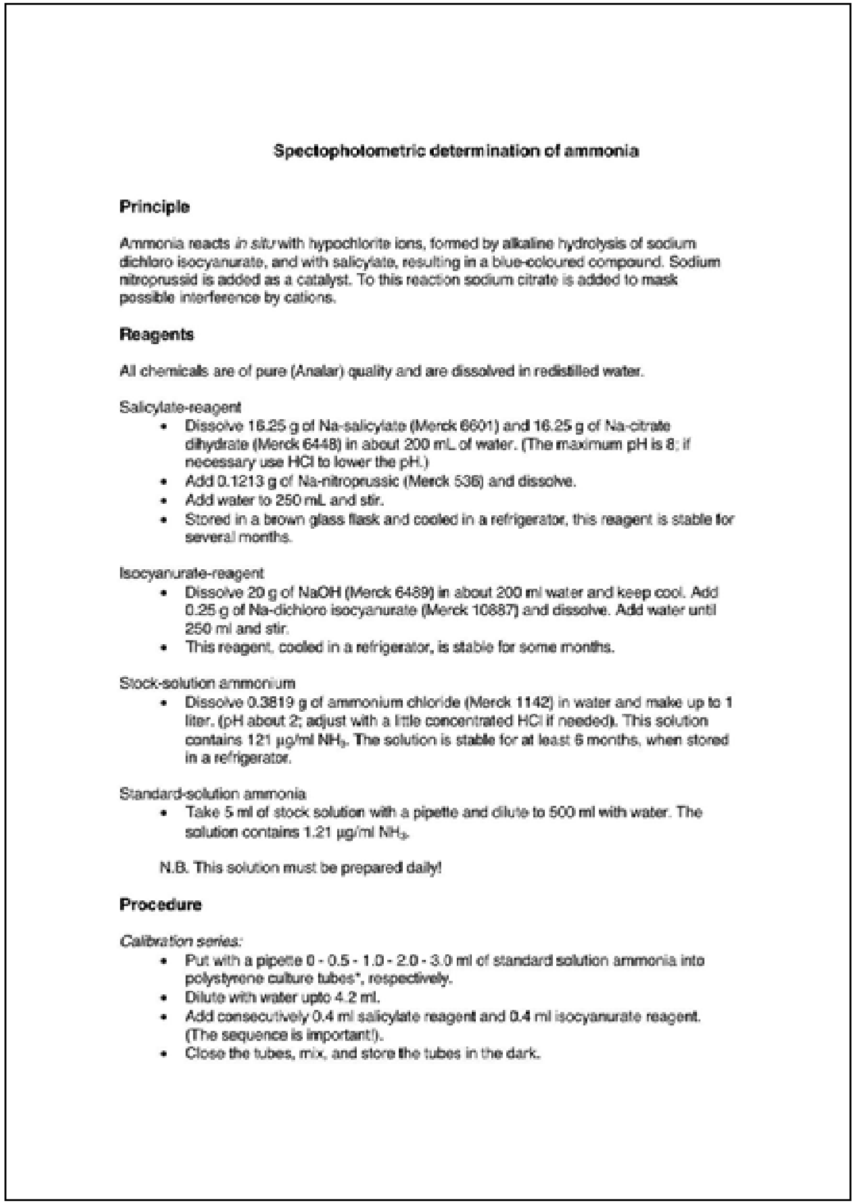
Travel

Badges can travel by post.

Sampling

The badges are exposed with the open side downwards in such a way that air can freely move beneath and above them. In order to be able to calculate a coefficient of variation at least three badges are exposed for simultaneous measurements. The lids are taken off. The time is noted.

After a certain exposure time the badges are entirely closed with clean lids. Before closing, one should be aware there is no water on the walls of the badge. If there is, remove it carefully with a clean tissue without touching the inside of the badge by hand. This precaution has to be taken because the water might reach the reaction filter due to shaking during transport.



Spectophotometric determination of ammonia

Principle

Ammonia reacts *in situ* with hypochlorite ions, formed by alkaline hydrolysis of sodium dichloro isocyanurate, and with salicylate, resulting in a blue-coloured compound. Sodium nitroprussid is added as a catalyst. To this reaction sodium citrate is added to mask possible interference by cations.

Reagents

All chemicals are of pure (Analar) quality and are dissolved in redistilled water.

Salicylate-reagent
- Dissolve 16.25 g of Na-salicylate (Merck 6601) and 16.25 g of Na-citrate dihydrate (Merck 6448) in about 200 mL of water. (The maximum pH is 8; if necessary use HCl to lower the pH.)
- Add 0.1213 g of Na-nitroprussic (Merck 536) and dissolve.
- Add water to 250 mL and stir.
- Stored in a brown glass flask and cooled in a refrigerator, this reagent is stable for several months.

Isocyanurate-reagent
- Dissolve 20 g of NaOH (Merck 6489) in about 200 ml water and keep cool. Add 0.25 g of Na-dichloro isocyanurate (Merck 10887) and dissolve. Add water until 250 ml and stir.
- This reagent, cooled in a refrigerator, is stable for some months.

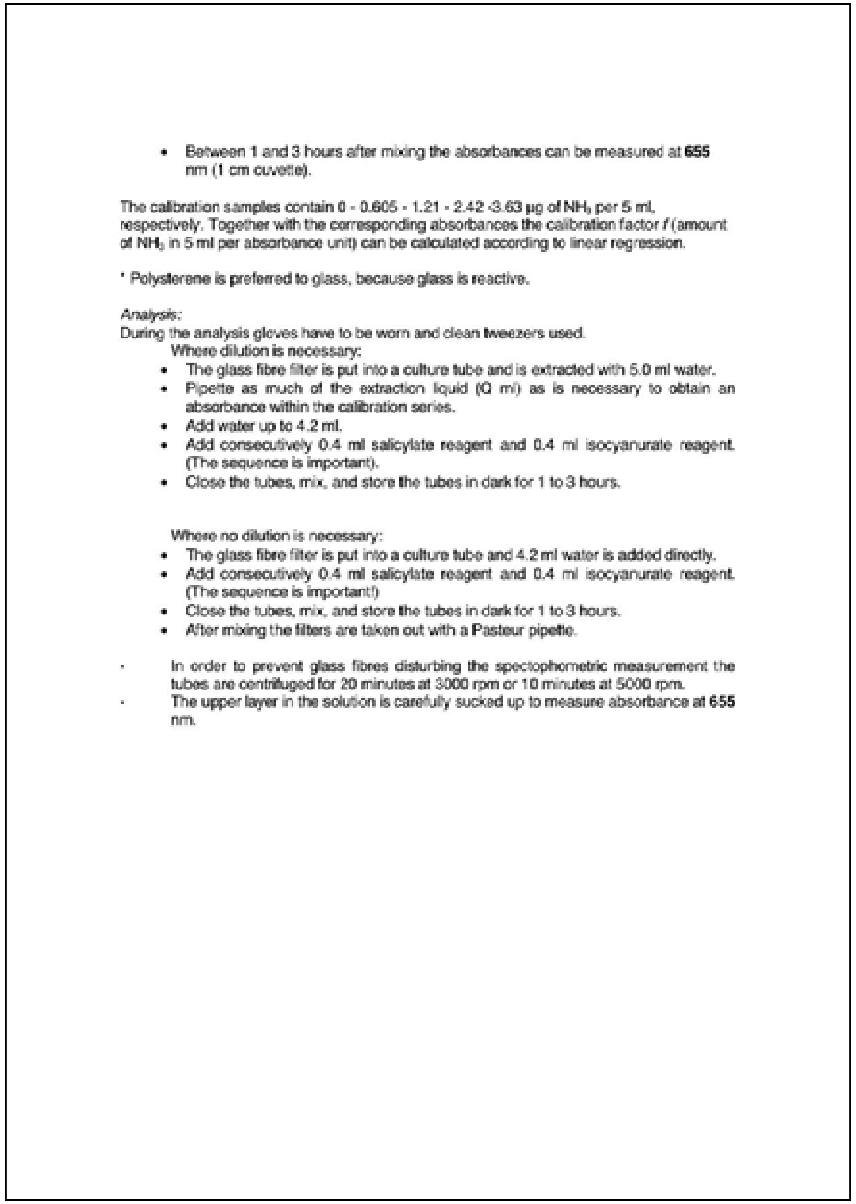
Stock-solution ammonium
- Dissolve 0.3819 g of ammonium chloride (Merck 1142) in water and make up to 1 liter. (pH about 2; adjust with a little concentrated HCl if needed). This solution contains 121 µg/ml NH_3. The solution is stable for at least 6 months, when stored in a refrigerator.

Standard-solution ammonia
- Take 5 ml of stock solution with a pipette and dilute to 500 ml with water. The solution contains 1.21 µg/ml NH_3.

N.B. This solution must be prepared daily!

Procedure

Calibration series:
- Put with a pipette 0 - 0.5 - 1.0 - 2.0 - 3.0 ml of standard solution ammonia into polystyrene culture tubes*, respectively.
- Dilute with water upto 4.2 ml.
- Add consecutively 0.4 ml salicylate reagent and 0.4 ml isocyanurate reagent. (The sequence is important!).
- Close the tubes, mix, and store the tubes in the dark.



- Between 1 and 3 hours after mixing the absorbances can be measured at **655** nm (1 cm cuvette).

The calibration samples contain 0 - 0.605 - 1.21 - 2.42 -3.63 µg of NH_3 per 5 ml, respectively. Together with the corresponding absorbances the calibration factor *f* (amount of NH_3 in 5 ml per absorbance unit) can be calculated according to linear regression.

* Polysterene is preferred to glass, because glass is reactive.

Analysis:
During the analysis gloves have to be worn and clean tweezers used.

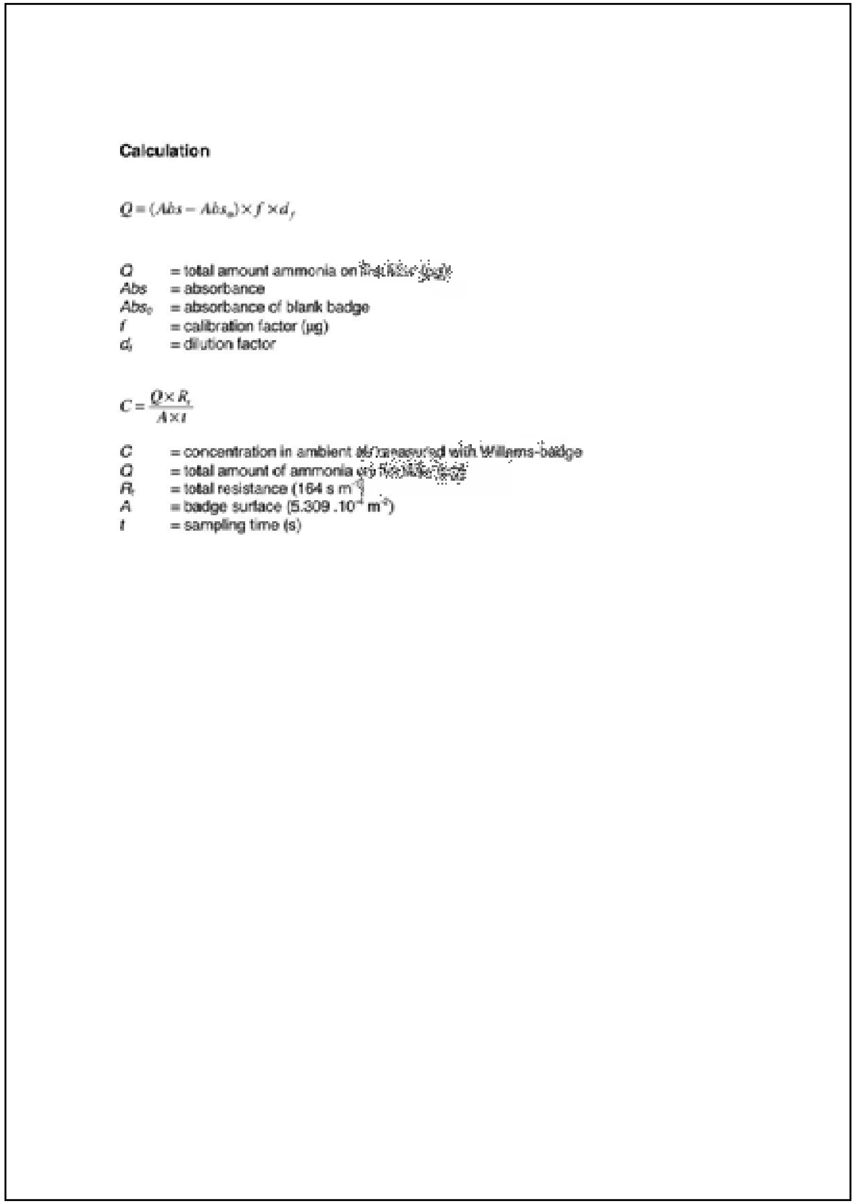
Where dilution is necessary:

- The glass fibre filter is put into a culture tube and is extracted with 5.0 ml water.
- Pipette as much of the extraction liquid (Q ml) as is necessary to obtain an absorbance within the calibration series.
- Add water up to 4.2 ml.
- Add consecutively 0.4 ml salicylate reagent and 0.4 ml isocyanurate reagent. (The sequence is important).
- Close the tubes, mix, and store the tubes in dark for 1 to 3 hours.

Where no dilution is necessary:

- The glass fibre filter is put into a culture tube and 4.2 ml water is added directly.
- Add consecutively 0.4 ml salicylate reagent and 0.4 ml isocyanurate reagent. (The sequence is important!)
- Close the tubes, mix, and store the tubes in dark for 1 to 3 hours.
- After mixing the filters are taken out with a Pasteur pipette.

- In order to prevent glass fibres disturbing the spectophometric measurement the tubes are centrifuged for 20 minutes at 3000 rpm or 10 minutes at 5000 rpm.
- The upper layer in the solution is carefully sucked up to measure absorbance at **655** nm.



Calculation

$$Q = (Abs - Abs_0) \times f \times d_f$$

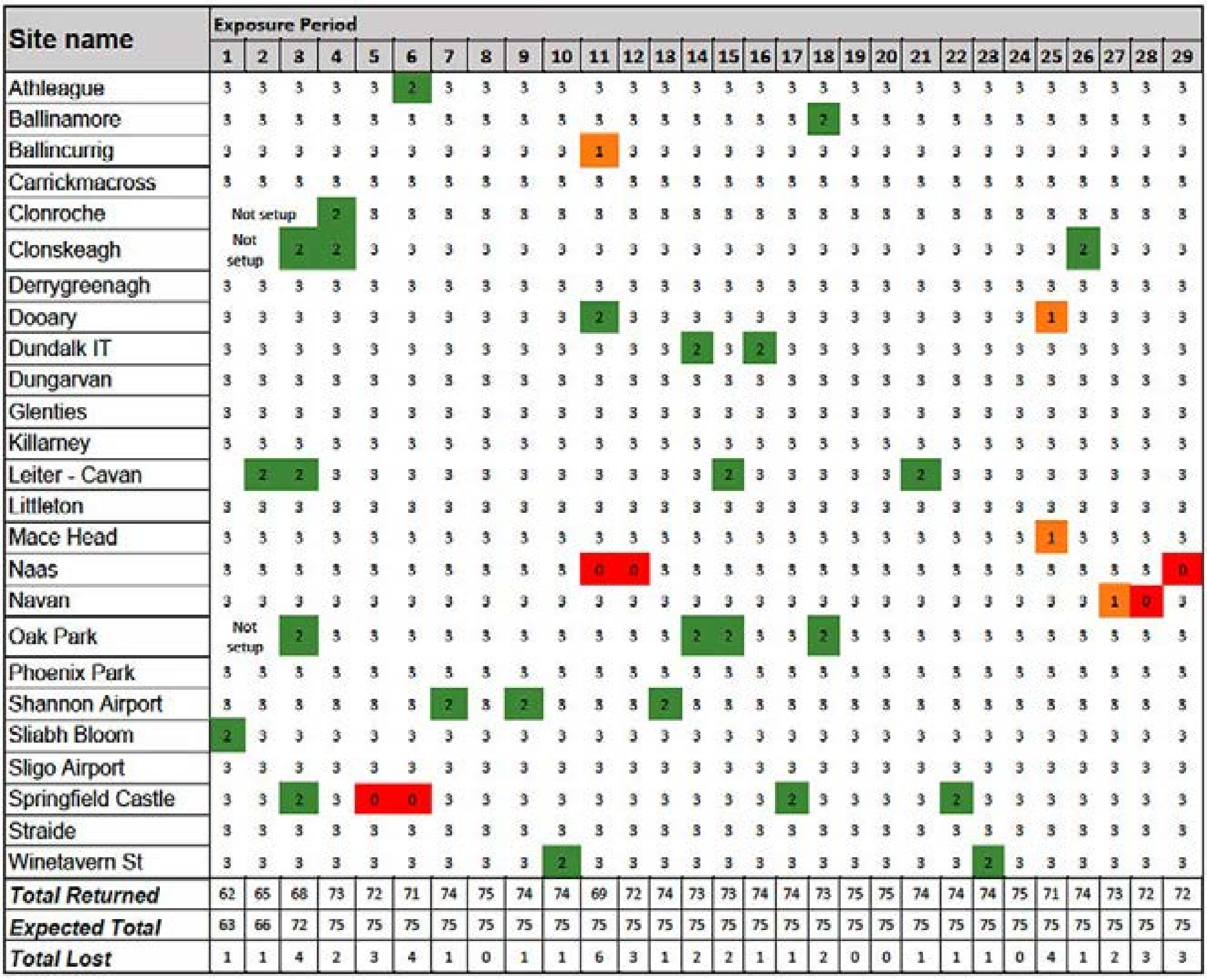
Q = total amount ammonia on the filter (µg)
Abs = absorbance
Abs_0 = absorbance of blank badge
f = calibration factor (µg)
d_f = dilution factor

$$C = \frac{Q \times R_t}{A \times t}$$

C = concentration in ambient air measured with Willems-badge
Q = total amount of ammonia on the filter (µg)
R_t = total resistance (164 s m^{-1})
A = badge surface (5.309 .10^{-4} m^2)
t = sampling time (s)

Appendix 4 Badge Returns

Badge return numbers from each site for each exposure period. Target returns are three badges from each site for each exposure period; highlighted cells show returns below target. Cells in green indicate an exposure period from one site where one badge was lost; orange, two badges lost; and red, three badges lost. Loss of three badges represents total data loss from the site for that exposure period.

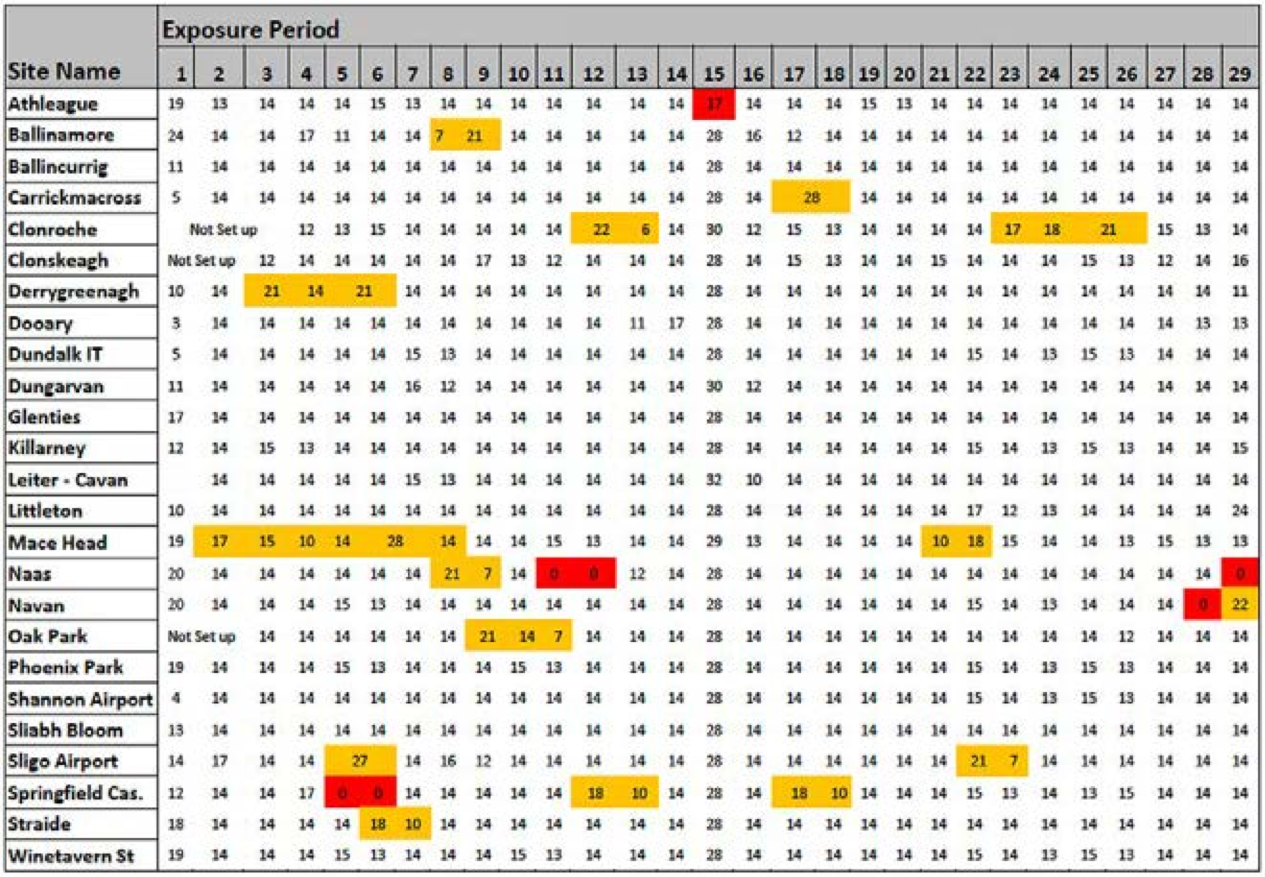


Site name	Exposure Period																												
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29
Athleague	3	3	3	3	3	2	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
Ballinamore	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	2	3	3	3	3	3	3	3	3	3	3	3
Ballincurrig	3	3	3	3	3	3	3	3	3	3	1	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
Carrickmacross	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
Clonroche	Not setup			2	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
Clonskeagh	Not setup		2	2	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	2	3	3	3
Derrygreenagh	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
Dooary	3	3	3	3	3	3	3	3	3	3	2	3	3	3	3	3	3	3	3	3	3	3	3	3	1	3	3	3	3
Dundalk IT	3	3	3	3	3	3	3	3	3	3	3	3	3	2	3	2	3	3	3	3	3	3	3	3	3	3	3	3	3
Dungarvan	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
Glenties	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
Killarney	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
Leiter - Cavan		2	2	3	3	3	3	3	3	3	3	3	3	3	2	3	3	3	3	3	2	3	3	3	3	3	3	3	3
Littleton	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
Mace Head	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	1	3	3	3	3
Naas	3	3	3	3	3	3	3	3	3	3	0	0	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	0
Navan	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	1	0	3
Oak Park	Not setup		2	3	3	3	3	3	3	3	3	3	3	2	2	3	3	2	3	3	3	3	3	3	3	3	3	3	3
Phoenix Park	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
Shannon Airport	3	3	3	3	3	3	2	3	2	3	3	3	2	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
Sliabh Bloom	2	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
Sligo Airport	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
Springfield Castle	3	3	2	3	0	0	3	3	3	3	3	3	3	3	3	3	2	3	3	3	2	3	3	3	3	3	3	3	3
Straide	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
Winetavern St	3	3	3	3	3	3	3	3	3	2	3	3	3	3	3	3	3	3	3	3	3	3	2	3	3	3	3	3	3
Total Returned	62	65	68	73	72	71	74	75	74	74	69	72	74	73	73	74	74	73	75	75	74	74	74	75	71	74	73	72	72
Expected Total	63	66	72	75	75	75	75	75	75	75	75	75	75	75	75	75	75	75	75	75	75	75	75	75	75	75	75	75	75
Total Lost	1	1	4	2	3	4	1	0	1	1	6	3	1	2	2	1	1	2	0	0	1	1	1	0	4	1	2	3	3

Clonroche, Clonskeagh and Oak Park sites began sampling at a later date.

Appendix 5 Exposure Periods

Numbers of days badges were exposed at each site for each exposure period. Orange: irregular periods, but no data lost. Red: some or all days missing, with data lost. Period 1 had variable length for all sites; period 15 was planned as 28 days.



Site Name	Exposure Period																												
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29
Athleague	19	13	14	14	14	15	13	14	14	14	14	14	14	14	17	14	14	14	15	13	14	14	14	14	14	14	14	14	14
Ballinamore	24	14	14	17	11	14	14	7	21	14	14	14	14	14	28	16	12	14	14	14	14	14	14	14	14	14	14	14	14
Ballincurrig	11	14	14	14	14	14	14	14	14	14	14	14	14	14	28	14	14	14	14	14	14	14	14	14	14	14	14	14	14
Carrickmacross	5	14	14	14	14	14	14	14	14	14	14	14	14	14	28	14	28		14	14	14	14	14	14	14	14	14	14	14
Clonroche	Not Set up			12	13	15	14	14	14	14	14	22	6	14	30	12	15	13	14	14	14	14	17	18	21		15	13	14
Clonskeagh	Not Set up		12	14	14	14	14	14	17	13	12	14	14	14	28	14	15	13	14	14	15	14	14	14	15	13	12	14	16
Derrygreenagh	10	14	21	14	21		14	14	14	14	14	14	14	14	28	14	14	14	14	14	14	14	14	14	14	14	14	14	11
Dooary	3	14	14	14	14	14	14	14	14	14	14	14	11	17	28	14	14	14	14	14	14	14	14	14	14	14	14	13	13
Dundalk IT	5	14	14	14	14	14	15	13	14	14	14	14	14	14	28	14	14	14	14	14	14	15	14	13	15	13	14	14	14
Dungarvan	11	14	14	14	14	14	16	12	14	14	14	14	14	14	30	12	14	14	14	14	14	14	14	14	14	14	14	14	14
Glenties	17	14	14	14	14	14	14	14	14	14	14	14	14	14	28	14	14	14	14	14	14	14	14	14	14	14	14	14	14
Killarney	12	14	15	13	14	14	14	14	14	14	14	14	14	14	28	14	14	14	14	14	14	15	14	13	15	13	14	14	15
Leiter - Cavan		14	14	14	14	14	15	13	14	14	14	14	14	14	32	10	14	14	14	14	14	14	14	14	14	14	14	14	14
Littleton	10	14	14	14	14	14	14	14	14	14	14	14	14	14	28	14	14	14	14	14	14	17	12	13	14	14	14	14	24
Mace Head	19	17	15	10	14	28		14	14	14	15	13	14	14	29	13	14	14	14	14	10	18	15	14	14	13	15	13	13
Naas	20	14	14	14	14	14	14	21	7	14	0	0	12	14	28	14	14	14	14	14	14	14	14	14	14	14	14	14	0
Navan	20	14	14	14	15	13	14	14	14	14	14	14	14	14	28	14	14	14	14	14	14	15	14	13	14	14	14	0	22
Oak Park	Not Set up		14	14	14	14	14	14	21	14	7	14	14	14	28	14	14	14	14	14	14	14	14	14	14	12	14	14	14
Phoenix Park	19	14	14	14	15	13	14	14	14	15	13	14	14	14	28	14	14	14	14	14	14	15	14	13	15	13	14	14	14
Shannon Airport	4	14	14	14	14	14	14	14	14	14	14	14	14	14	28	14	14	14	14	14	14	15	14	13	15	13	14	14	14
Sliabh Bloom	13	14	14	14	14	14	14	14	14	14	14	14	14	14	28	14	14	14	14	14	14	14	14	14	14	14	14	14	14
Sligo Airport	14	17	14	14	27		14	16	12	14	14	14	14	14	28	14	14	14	14	14	14	21	7	14	14	14	14	14	14
Springfield Cas.	12	14	14	17	0	0	14	14	14	14	14	18	10	14	28	14	18	10	14	14	14	15	13	14	13	15	14	14	14
Straide	18	14	14	14	14	18	10	14	14	14	14	14	14	14	28	14	14	14	14	14	14	14	14	14	14	14	14	14	14
Winetavern St	19	14	14	14	15	13	14	14	14	15	13	14	14	14	28	14	14	14	14	14	14	15	14	13	15	13	14	14	14

AN GHNÍOMHAIREACHT UM CHAOMHNÚ COMHSHAOIL
Tá an Ghníomhaireacht um Chaomhnú Comhshaoil (GCC) freagrach as an gcomhshaol a chaomhnú agus a fheabhsú mar shócmhainn luachmhar do mhuintir na hÉireann. Táimid tiomanta do dhaoine agus don chomhshaol a chosaint ó éifeachtaí díobhálacha na radaíochta agus an truaillithe.

Is féidir obair na Gníomhaireachta a roinnt ina trí phríomhréimse:

Rialú: *Déanaimid córais éifeachtacha rialaithe agus comhlíonta comhshaoil a chur i bhfeidhm chun torthaí maithe comhshaoil a sholáthar agus chun díriú orthu siúd nach gcloíonn leis na córais sin.*

Eolas: *Soláthraímid sonraí, faisnéis agus measúnú comhshaoil atá ar ardchaighdeán, spriocdhírithe agus tráthúil chun bonn eolais a chur faoin gcinnteoireacht ar gach leibhéal.*

Tacaíocht: *Bímid ag saothrú i gcomhar le grúpaí eile chun tacú le comhshaol atá glan, táirgiúil agus cosanta go maith, agus le hiompar a chuirfidh le comhshaol inbhuanaithe.*

Ár bhFreagrachtaí

Ceadúnú

Déanaimid na gníomhaíochtaí seo a leanas a rialú ionas nach ndéanann siad dochar do shláinte an phobail ná don chomhshaol:

- saoráidí dramhaíola *(m.sh. láithreáin líonta talún, loisceoirí, stáisiúin aistrithe dramhaíola)*;
- gníomhaíochtaí tionsclaíocha ar scála mór *(m.sh. déantúsaíocht cógaisíochta, déantúsaíocht stroighne, stáisiúin chumhachta)*;
- an diantalmhaíocht *(m.sh. muca, éanlaith)*;
- úsáid shrianta agus scaoileadh rialaithe Orgánach Géinmhodhnaithe *(OGM)*;
- foinsí radaíochta ianúcháin *(m.sh. trealamh x-gha agus radaiteiripe, foinsí tionsclaíocha)*;
- áiseanna móra stórála peitril;
- scardadh dramhuisce;
- gníomhaíochtaí dumpála ar farraige.

Forfheidhmiú Náisiúnta i leith Cúrsaí Comhshaoil

- Clár náisiúnta iniúchtaí agus cigireachtaí a dhéanamh gach bliain ar shaoráidí a bhfuil ceadúnas ón nGníomhaireacht acu.
- Maoirseacht a dhéanamh ar fhreagrachtaí cosanta comhshaoil na n-údarás áitiúil.
- Caighdeán an uisce óil, arna sholáthar ag soláthraithe uisce phoiblí, a mhaoirsiú.
- Obair le húdaráis áitiúla agus le gníomhaireachtaí eile chun dul i ngleic le coireanna comhshaoil trí chomhordú a dhéanamh ar líonra forfheidhmiúcháin náisiúnta, trí dhíriú ar chiontóirí, agus trí mhaoirsiú a dhéanamh ar leasúchán.
- Cur i bhfeidhm rialachán ar nós na Rialachán um Dhramhthrealamh Leictreach agus Leictreonach (DTLL), um Shrian ar Shubstaintí Guaiseacha agus na Rialachán um rialú ar shubstaintí a ídíonn an ciseal ózóin.
- An dlí a chur orthu siúd a bhriseann dlí an chomhshaoil agus a dhéanann dochar don chomhshaol.

Bainistíocht Uisce

- Monatóireacht agus tuairisciú a dhéanamh ar cháilíocht aibhneacha, lochanna, uiscí idirchriosacha agus cósta na hÉireann, agus screamhuiscí; leibhéil uisce agus sruthanna aibhneacha a thomhas.
- Comhordú náisiúnta agus maoirsiú a dhéanamh ar an gCreat-Treoir Uisce.
- Monatóireacht agus tuairisciú a dhéanamh ar Cháilíocht an Uisce Snámha.

Monatóireacht, Anailís agus Tuairisciú ar an gComhshaol

- Monatóireacht a dhéanamh ar cháilíocht an aeir agus Treoir an AE maidir le hAer Glan don Eoraip (CAFÉ) a chur chun feidhme.
- Tuairisciú neamhspleách le cabhrú le cinnteoireacht an rialtais náisiúnta agus na n-údarás áitiúil *(m.sh. tuairisciú tréimhsiúil ar staid Chomhshaol na hÉireann agus Tuarascálacha ar Tháscairí)*.

Rialú Astaíochtaí na nGás Ceaptha Teasa in Éirinn

- Fardail agus réamh-mheastacháin na hÉireann maidir le gáis cheaptha teasa a ullmhú.
- An Treoir maidir le Trádáil Astaíochtaí a chur chun feidhme i gcomhair breis agus 100 de na táirgeoirí dé-ocsaíde carbóin is mó in Éirinn.

Taighde agus Forbairt Comhshaoil

- Taighde comhshaoil a chistiú chun brúnna a shainaithint, bonn eolais a chur faoi bheartais, agus réitigh a sholáthar i réimsí na haeráide, an uisce agus na hinbhuanaitheachta.

Measúnacht Straitéiseach Timpeallachta

- Measúnacht a dhéanamh ar thionchar pleananna agus clár beartaithe ar an gcomhshaol in Éirinn *(m.sh. mórphleananna forbartha)*.

Cosaint Raideolaíoch

- Monatóireacht a dhéanamh ar leibhéil radaíochta, measúnacht a dhéanamh ar nochtadh mhuintir na hÉireann don radaíocht ianúcháin.
- Cabhrú le pleananna náisiúnta a fhorbairt le haghaidh éigeandálaí ag eascairt as taismí núicléacha.
- Monatóireacht a dhéanamh ar fhorbairtí thar lear a bhaineann le saoráidí núicléacha agus leis an tsábháilteacht raideolaíochta.
- Sainseirbhísí cosanta ar an radaíocht a sholáthar, nó maoirsiú a dhéanamh ar sholáthar na seirbhísí sin.

Treoir, Faisnéis Inrochtana agus Oideachas

- Comhairle agus treoir a chur ar fáil d'earnáil na tionsclaíochta agus don phobal maidir le hábhair a bhaineann le caomhnú an chomhshaoil agus leis an gcosaint raideolaíoch.
- Faisnéis thráthúil ar an gcomhshaol ar a bhfuil fáil éasca a chur ar fáil chun rannpháirtíocht an phobail a spreagadh sa chinnteoireacht i ndáil leis an gcomhshaol *(m.sh. Timpeall an Tí, léarscáileanna radóin)*.
- Comhairle a chur ar fáil don Rialtas maidir le hábhair a bhaineann leis an tsábháilteacht raideolaíoch agus le cúrsaí práinnfhreagartha.
- Plean Náisiúnta Bainistíochta Dramhaíola Guaisí a fhorbairt chun dramhaíl ghuaiseach a chosc agus a bhainistiú.

Múscailt Feasachta agus Athrú Iompraíochta

- Feasacht chomhshaoil níos fearr a ghiniúint agus dul i bhfeidhm ar athrú iompraíochta dearfach trí thacú le gnóthais, le pobail agus le teaghlaigh a bheith níos éifeachtúla ar acmhainní.
- Tástáil le haghaidh radóin a chur chun cinn i dtithe agus in ionaid oibre, agus gníomhartha leasúcháin a spreagadh nuair is gá.

Bainistíocht agus struchtúr na Gníomhaireachta um Chaomhnú Comhshaoil

Tá an ghníomhaíocht á bainistiú ag Bord lánaimseartha, ar a bhfuil Ard-Stiúrthóir agus cúigear Stiúrthóirí. Déantar an obair ar fud cúig cinn d'Oifigí:

- An Oifig um Inmharthanacht Comhshaoil
- An Oifig Forfheidhmithe i leith cúrsaí Comhshaoil
- An Oifig um Fianaise is Measúnú
- An Oifig um Cosaint Raideolaíoch
- An Oifig Cumarsáide agus Seirbhísí Corparáideacha

Tá Coiste Comhairleach ag an nGníomhaireacht le cabhrú léi. Tá dáréag comhaltaí air agus tagann siad le chéile go rialta le plé a dhéanamh ar ábhair imní agus le comhairle a chur ar an mBord.

EPA Research Report 193

Ambient Atmospheric Ammonia in Ireland, 2013-2014

Authors: Brian Doyle, Thomas Cummins,
Cara Augustenborg and Julian Aherne

Ammonia is a reactive atmospheric trace-gas, and part of the nitrogen cycle. Ammonia gas is released to the atmosphere mostly from farm-animal wastes and nitrogen fertilisers, depending on husbandry and nutrient-management practices. A potential pollutant, atmospheric ammonia has direct effects on human and vegetation health, and contributes to both the formation of particulate matter and the deposition of reactive nitrogen on land surfaces. Fine particulate matter impacts human health, while nitrogen deposition potentially affects forest health, reduces biodiversity in sensitive ecosystems, and contributes to soil acidification.

Identifying Pressures

Sources of atmospheric ammonia increased throughout the 20th century as a result of N-fertiliser production and intensive farming practices, increasing nitrogen deposition in sensitive ecosystems. There are limited monitoring data on ambient atmospheric ammonia in Ireland since a previous, comparable survey in 1999–2000. In this study, ambient atmospheric ammonia concentrations were measured at 25 monitoring sites across Ireland between June 2013 and July 2014, using passive diffusive samplers, exposed in triplicate on a 2-week cycle, away from point sources of ammonia. Monitoring shows higher concentrations of ammonia towards the north-east midlands and the south-east of Ireland, both areas of relatively intensive agricultural activity. Concentrations are associated with regional activity indicators for pig and poultry farming, cattle, and crop production.

Informing Policy

The ammonia concentrations observed are above the threshold for potential impacts on the most-sensitive ecosystems, but below those for the less-sensitive semi-natural vegetation types, as determined by the Convention on Long-Range Transboundary Air Pollution. A new observation here is that ammonia levels are also elevated in the Dublin urban area. Since clear relationships are shown between nitrogen-intensive agricultural activity and ammonia concentrations, this study is relevant to revision of emission limits under a revised National Emission Ceilings Directive.

Developing Solutions

This study proposes that a permanent monitoring network is required to provide quantitative atmospheric ammonia measurements, especially in the context of the national Food Harvest 2020 and Food Wise 2025 government strategies, which aim to increase production across multiple agricultural sectors. Such a network would give continuous monitoring of atmospheric ammonia, allowing detection of long-term trends, and forming a basis for modelling to assess the likely effect on ecosystems and human health. Since this method establishes background concentrations of ammonia away from point emission sources, it is essential as a basis for impact assessment around new and existing emission sources, and evaluating the effects of nearby sources on specific sensitive and protected ecosystems.

EPA Research: McCumiskey House,
Richiew, Clonskeagh, Dublin 14.

Phone: 01 268 0100
Twitter: @EPAResearchNews
Email: research@epa.ie

www.epa.ie

EPA Research Webpages
www.epa.ie/researchandeducation/research/