Quantification of atmospheric water soluble inorganic and organic nitrogen

Juan Manuel González Benítez

Centre for Ecology & Hydrology
NATURAL ENVIRONMENT RESEARCH COUNCIL

Ph. D. thesis
The University of Edinburgh
2010

Declaration

This thesis has been composed by myself and all the work herein is my own work, except where explicitly otherwise stated, and this work has not been submitted for any other degree or professional qualification.

Juan Manuel González Benítez

March 2010

Acknowledgements

I would like to thank my supervisors Professor Neil Cape and Dr Mathew Heal for all their guidance, good advice, encouragement, patience, help and support throughout my entire PhD. I would also like to thank the University of Edinburgh for providing the funding for my scholarship, and the NERC and the Centre for Ecology & Hydrology (CEH) for providing the infrastructure, instruments, equipment and materials needed to carry out this project.

Very special thanks must go to the NitroEurope Network, in particular to Dr. Marta Mitosinkova, from the Slovak Hydrometeorological Institute, Dr. Sonja Vidic, from the Meteorological and Hydrological Service of Croatia, Dr. László Horváth, from the Hungarian Meteorological Service, Dr. Markus Jocher, from the Agroscope Reckenholz-Tänikon Research Station (ART), Zürich, Switzerland, Dr. Ulla Makkonen, from the Finnish Meteorological Institute, and Dr. Ariën Stolk, from the National Institute for Public Health and the Environment (RIVM), in the Netherlands, for sub-sampling and providing data so generously to us. Without their help a very important part of this project would not have been possible.

A big thanks to Lara for her invaluable advice and guidance on the statistical analysis of the data, and for her support and encouragement in very crucial moments of my PhD. Also to Netty and Sim for being so patient and helping me so much with the analytical instrumentation, and Daniela and Stephanie for their help in the Easter Bush sampling campaign, and to my officemates Pawel, James, Sanna and Esther, for all the laughs, support, discussions, advice and such an amazingly fun and hard-working atmosphere, and to everybody at the CEH, I feel privileged to have had the opportunity of doing my PhD in such a great place.

Big thanks also to Isabella, Gaétan, Joss, Arancha and Natalia for their support and encouragement in the final and the hardest stages of my PhD, and of course to my parents and sister for their support all the way through.

Abstract

The key aims of this project were: (i) investigation of atmospheric nitrogen deposition, focused on discrimination between bulk, wet and dry deposition, and between particulate matter and gas phase, (ii) accurate quantification of the contributions of dissolved organic and inorganic nitrogen to each type of deposition, and (iii) exploration of the origin and potential sources of atmospheric water soluble organic nitrogen (WSON). This project was particularly focused on the WSON fraction because, despite it being a potentially important source of bioavailable reactive nitrogen, a number of questions regarding its deposition mechanism (wet vs. dry), composition and origin (natural, anthropogenic or mixed) remain unanswered.

There are two major difficulties in WSON determination: (i) the diversity of organic nitrogen compounds compared with the inorganic forms, and (ii) the lack of a direct determination method: the derivation of organic nitrogen concentrations in an aqueous sample involves the determination of the dissolved inorganic nitrogen (DIN) species concentration, comprising nitrate and ammonium, the determination of the total dissolved nitrogen (TDN) concentration, and the subtraction of the DIN concentrations from the TDN concentration. TDN determination requires a preparatory digestion step: high-temperature catalytic oxidation was the method used in this study. Ion chromatography (IC) was the method of choice for nitrate determination, whilst ammonium determination was by IC for rain samples, and by flow injection analysis for air samples collected into aqueous media.

This thesis is structured in 3 main parts: the first part examines weekly rain data over a period of 22 months from June 2005 to March 2007 collected in 2 types of rain collector (bulk deposition and “dry+wet” deposition) located in a semi-rural area 15 km southwest of Edinburgh, UK (N55°51′44″, W3°12′19″). Bulk deposition collectors were the standard rain gauges used in the UK national network for monitoring precipitation composition. “Dry+wet” deposition collectors were flushing rain gauges equipped with a rain detector, a spray nozzle, a 2-way valve and two independent bottles to collect funnel washings (dry deposition) and true wet deposition. A key objective in this part of the work was the accurate quantification of inorganic and organic water-soluble nitrogen species contribution to each type of

deposition. On average, for the 27 weekly samples with 3 valid replicates for the 2 types of collectors, DON represented 23% of the TDN in bulk deposition. Dry deposition of particles and gas on the funnel surface, rather than rain, contributed over half of all N-containing species (inorganic and organic). Some discrepancies were found between bulk and flushing rain gauges, for deposition of both TDN and DON, suggesting biological conversion and loss of inorganic N in the flushing samplers.

The second stage of this project was the investigation of in situ atmospheric concentrations of WSN species, both organic and inorganic. Simultaneous daily measurements of ammonium, nitrate and WSON were made between July and November 2008 at the same semi-rural site in south-east Scotland. Discrimination between material from the gas and particle phases was achieved by means of Cofer scrubbers and PTFE membrane filters, respectively. Average concentrations of NH_3 (determined as NH_4^+), NO_2/HNO_3 (determined as NO_3^-) and WSON in the gas phase were 82 ± 54 nmol N m^{-3}, 2.6 ± 2.5 nmol N m^{-3} and 18 ± 12 nmol N m^{-3} respectively, and in the particle phase were 20 ± 24 nmol N m^{-3}, 10 ± 9 nmol N m^{-3} and 8 ± 7 nmol N m^{-3} respectively (± represent standard deviation across all valid daily samples, not error of triplicate samples). Except for oxidised inorganic N, average concentrations in the gas phase were larger than in the particle phase. No evidence of solely agricultural or solely combustion sources of WSON was found, as no correlation in either phase between WSON and either NH_4^+ or NO_3^- could be established.

The final stage of this project was to gain a broader picture of nitrogen deposition across Europe. Rain samples were analysed for TDN and DIN from a network of 21 different sampling locations, from the south of Portugal to the north of Finland. The average DON contribution across the 21 sampling sites was ~ 19% and, according to the data gathered in this study, DON species appeared largely unrelated specifically to agricultural or to combustion nitrogen sources, although the results varied widely from site to site.

Overall, this work has shown that ON and its deposition comprises a significant component of total atmospheric reactive nitrogen.

Table of contents

1. Introduction

1.1. Background

1.1.1. Nitrogen: chemical forms and bioavailability

Nitrogen is an indispensable element to all forms of life, ranking fourth behind carbon, hydrogen and oxygen as the most common chemical element in living tissues (Vitousek et al., 1997). It is classified as an essential macronutrient, i.e. needed in large amounts relative to other important essential nutrients such as calcium, phosphorus, potassium, sulphur, and magnesium.

Diatomic nitrogen gas (N_2) constitutes 75.5% of Earth's atmospheric mass, and 99.96% of the global N, making it by far the largest pool of nitrogen (Atkinson, 2000, Scharenbroch and Lloyd, 2004). However, molecular nitrogen has a low solubility in water and, at the temperatures and pressures of the hydrosphere and atmosphere, it is relatively inert owing to the strength of its triple bond, non-polarity and high ionization potential (Pool et al., 2004). For this reason, processing, or fixation, is required to convert diatomic nitrogen into forms usable by living organisms.

Other chemical forms of nitrogen are nitrous oxide (N_2O), a mere 0.3 ppm in the atmosphere, but an important greenhouse gas (Houghton, 2004), and reactive nitrogen compounds (RNCs), defined as those compounds available to support plant and microbe growth (Dittman et al., 2007).

RNCs include inorganic species such as ammonium, ammonia gas, nitrate, nitric oxide, nitrogen dioxide and nitric acid, and organic forms such as nitrophenols, nitrobenzenes, acetonitrile, amines, organic nitrates, urea, chlorophyll, proteins, peptides, energy-transfer molecules (ATP and ADP), genetic material and amino acids. All these inorganic and organic forms of nitrogen readily bioavailable are also collectively called “fixed nitrogen” (the term “bioavailable” includes not only compounds supportive of plant and animal life, but also toxic compounds). The availability of RNCs is a major limiting factor for terrestrial ecosystem productivity (Jones and Willett, 2006). These compounds enter the terrestrial system through atmospheric deposition, biological or industrial fixation, and fertilization (Scharenbroch and Lloyd, 2004), and are continually transformed through a complex network of reactions called “the nitrogen cycle”.

1.1.2. The nitrogen cycle

The nitrogen cycle is the biogeochemical cycle that describes the network of reduction-oxidation transformations undergone by the nitrogen species as they move through interconnected reservoirs such as the atmosphere, the hydrosphere and the biosphere (Stevenson and Cole, 1999).

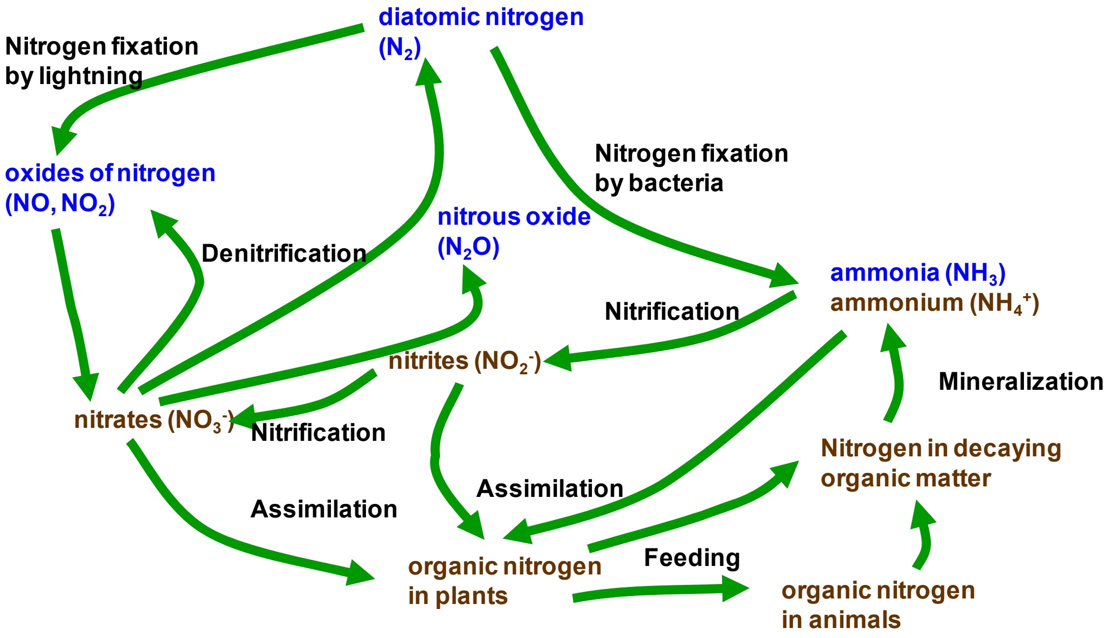


Figure 1.1: Schematic representation of the nitrogen cycle.

The main reduction-oxidation transformations in this cycle (Figure 1.1) include:

Nitrogen fixation: the process by which nitrogen is taken from its relatively inert diatomic form (N_2) in the atmosphere and converted into nitrogen compounds that can be used by plants. Nitrogen fixation is performed naturally by a number of different prokaryotes. Many higher plants, mainly legumes, and some animals such as termites, have formed associations with these microorganisms.

Assimilation: the process by which plants convert nitrate, nitrite and ammonium ions to organic nitrogen compounds. Plants absorb nitrate ions from the soil via their root hairs. The first step of assimilation is the reduction of the absorbed nitrate ions to nitrite ions, which is catalyzed by the enzyme nitrate reductase. The second step is the reduction of nitrite ions to ammonium ions, which is catalyzed by the enzyme nitrite reductase. The final step, called amination, consists of the incorporation of ammonium ions into amino acids (Raven and Smith, 1976). There is also some evidence of direct uptake of organic nitrogen by plants, principally in environments where nitrogen is a limited resource (Jones et al., 2005, Persson and Nasholm, 2001).

Mineralization: the process by which ammonium is released due to organic nitrogen degradation. This process is carried out by bacteria or, in some cases, fungi (Campbell and Reece, 2002). Just as the ammonia created through nitrogen fixation becomes available for other biological processes, so does the ammonium created in the process of decomposing animal waste and dead plants and animals.

Nitrification: the biological oxidation of ammonia with oxygen into nitrite ions followed by the oxidation of these nitrite ions into nitrate ions. The oxidation of ammonia into nitrite and the oxidation of nitrite into nitrate are performed by two different bacteria: the first step (oxidation of ammonia into nitrite) is carried out by bacteria of the genus Nitrosomonas and Nitrosococcus, which use ammonia as an electron donor in respiration. The second step (oxidation of nitrite into nitrate) is mainly carried out by bacteria of the genus Nitrobacter, which use nitrite ions as an electron donor in respiration (Juretschko et al., 1998). In most environments both organisms are found together, so consequently nitrate is usually the final product.

Denitrification: this is the process that completes the nitrogen cycle by reducing nitrate and nitrite ions in the soil into diatomic nitrogen, which is released back into the atmosphere. This process is performed by denitrifying bacteria, most of them belonging to the genera Psuedomonas, Micrococcus, Achromobacter and Bacillus. It consists of four sequential reactions, catalyzed by the enzymes nitrate reductase, nitrite reductase, nitric oxide reductase, and nitrous oxide reductase.

Nitrate → nitrite → nitric oxide → nitrous oxide → dinitrogen gas

During this process not only N_2, but also NO and N_2O are released to the atmosphere. In general, denitrification occurs when oxygen (which is a more favourable electron acceptor) is depleted, and bacteria turn to nitrate or nitrite as the electron acceptor. For this reason, it is in some soils, groundwater, wetlands, poorly ventilated areas of the ocean and in seafloor sediments where denitrification takes place. Some authors maintain that nitrogen is the main component of Earth's atmosphere due to the continued activity of denitrifying microorganisms throughout geological history (Stevenson and Cole, 1999).

All the transformations and fluxes included in the nitrogen cycle are controlled by mediating factors such as temperature, pH, light intensity, compound concentration, moisture content, etc, which adds further complexity to the cycle.

1.1.3. Pre-industrial nitrogen fixation

In pre-industrial times, the only routes to fix RNCs out of the atmosphere were the high-voltage electrical discharges of lightning (~8% of the non-anthropogenic RNCs) and biological fixation (Stevenson and Cole, 1999). The high temperature and energy released by lightning can oxidize atmospheric diatomic nitrogen, mainly to nitric oxide (NO), but also to nitrogen dioxide (NO_2). In subsequent reactions, more nitrogen dioxide is produced when nitric oxide reacts with atmospheric ozone.

Biological nitrogen fixation (Reaction 1) occurs when atmospheric nitrogen is converted to ammonia by diazotrophs, microorganisms such as cyanobacteria (blue-green algae) and rhizobia (bacteria contained within the nodules of the roots of nitrogen fixing plants).

$N_2 + 8H^+ + 8e^- + 16\ ATP \rightarrow 2NH_3 + H_2 + 16ADP + 16\ P$ (Reaction 1)

This reaction is catalyzed by the nitrogenase enzyme. In free-living diazotrophs, the nitrogenase-generated ammonium is assimilated into glutamate. In nitrogen-fixing plants, the nitrogen compounds produced by the rhizobia symbiotic bacteria are assimilated by the plant in the form of amino acids, helping the plant to grow and compete with other plants. When the plant dies, the nitrogen helps to fertilize the soil. The great majority of legumes have this association, but also some other plant families have similar associations.

As mentioned above, the amount of fixed nitrogen available is a major limiting factor in Earth's capability to sustain life. Due to this key constraint, the world's population growth, from 1.5 billion at the beginning of the 20th century to 6 billion today, would not have been possible without one of the most important scientific discoveries in history: the industrial synthesis and mass production of ammonia.

1.1.4. Human alteration of the nitrogen cycle

1.1.4.1. Historic introduction to anthropogenic RNCs

In 1898, Sir William Crookes (Figure 1.2), at that time president of the British Association for the Advancement of Science, wrote: "… all civilized nations stand in deadly peril of not having enough to eat." (Giffen, 1899). The peril was that, according to the nitrogen available, the farmers would be unable to satisfy the increasing demand for food. In order to solve this problem, Sir William suggested that chemists should develop methods for artificially fixing atmospheric nitrogen.

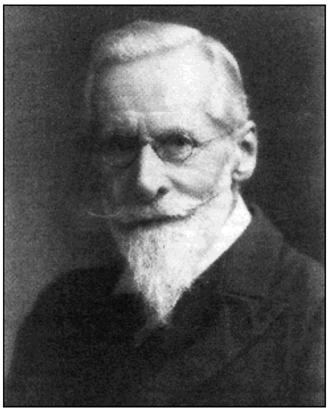


Figure 1.2: Sir William Crookes, 1832-1919.
Picture source: http://en.wikipedia.org/wiki/William_Crookes.

By 1905 Fritz Haber (Figure 1.3) had achieved this objective (Figure 1.4). Using osmium and uranium as catalysts, and in high pressure and temperature conditions, he reacted nitrogen gas (generated by the Linde process), and hydrogen gas to create ammonia (Stoltzenberg, 2005).

Figure 1.3: Fritz Haber, 1868-1934. Picture source: http://en.wikipedia.org/wiki/Fritz_Haber

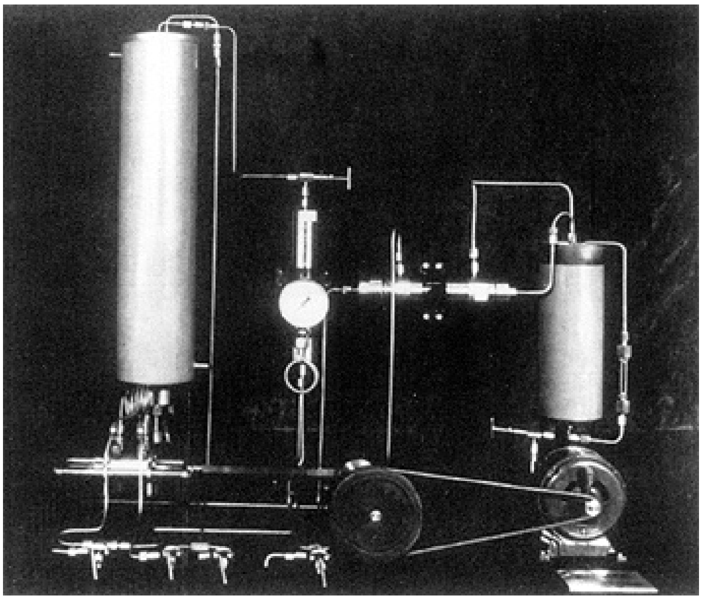


Figure 1.4: Fritz Haber's ammonia production apparatus, 1905.
Picture source: http://en.wikipedia.org/wiki/Haber_process

By 1913 Carl Bosch (Figure 1.5) had developed this method into an industrial process which became known as the Haber-Bosch method. In this process the catalyst used for ammonia production was iron, instead of osmium and uranium, and the nitric acid produced from the ammonia was then used to manufacture nitrogen fertilizers and explosives (Fryzuk, 2004).

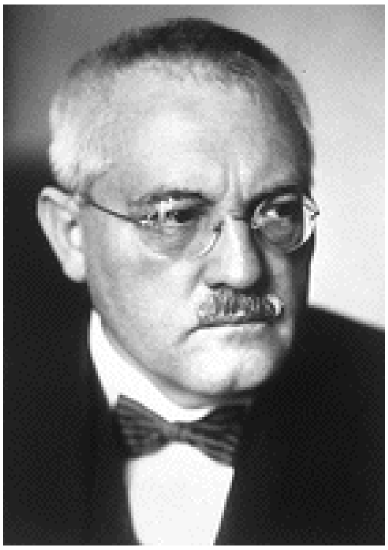


Figure 1.5: Carl Bosch, 1874-1940.
Picture source: http://en.wikipedia.org/wiki/Carl_Bosch

Until the late 1970s, most of the synthetic nitrogen fertilizer produced was applied in developed countries. However, use in these regions has now stabilized while fertilizer applications in developing countries have increased dramatically in order to meet the escalating demand for food of a growing population (Vitousek et al., 1997). Without nitrogen fertilizers, probably one-third of the world's current agricultural production would be lost. Nearly 40% of the world's dietary protein now comes from synthetic fertilizers, and 2 billion people might not be alive today without them (Galloway et al., 2008). However, the current amount of nitrogen fertilizers applied to the soil is very often far larger than the amount of nitrogen required by a crop to grow, and the present-day global production of nitrogen fertilizers is more than 80 Tg per year, compared to less than 1 Tg per year 90 years ago (Aneja et al., 2008), with many calls for reconsideration of the current level of fertilizer use, such as the Nanjing Declaration in 2004 (Erisman, 2004).

In addition to processes relating to synthetic fertilizer production and use, other sources of anthropogenic RNCs to the environment are:

High-temperature fossil fuel combustion reactions in motor vehicles and in industrial and utility boilers (approximately 20 million tons per year), which produce nitric oxide (NO) and nitrogen dioxide (NO_2) because the high temperatures and pressures reached cause atmospheric N_2 and O_2 to react via radical chain reactions (Heeb et al., 2008). In addition to this, the burning of fossil fuels releases back to the atmosphere fixed nitrogen stored for millions of years in those geological formations (Vitousek et al., 1997), although this fraction contributes only a small proportion.

Agricultural plantings of nitrogen-fixing crops (20 to 25 million tons per year). The replacement of large areas of diverse vegetation with nitrogen-fixing monocultures of rice and leguminous crops such as alfalfa, soybeans and peas has greatly increased the input of reactive nitrogen in those lands (Smil, 1999, Vitousek et al., 1997).

Anthropogenic wastes (including untreated sewage and manure), which contribute approximately 25 million tons per year to the budget (Kinzig and Socolow, 1994). It is worth mentioning that the ammonia released from animal wastes as a result of the inefficient conversion of dietary nitrogen to animal product compromises ~40% of natural and anthropogenic ammonia emissions combined, being the largest source of atmospheric ammonia (Aneja et al., 2008).

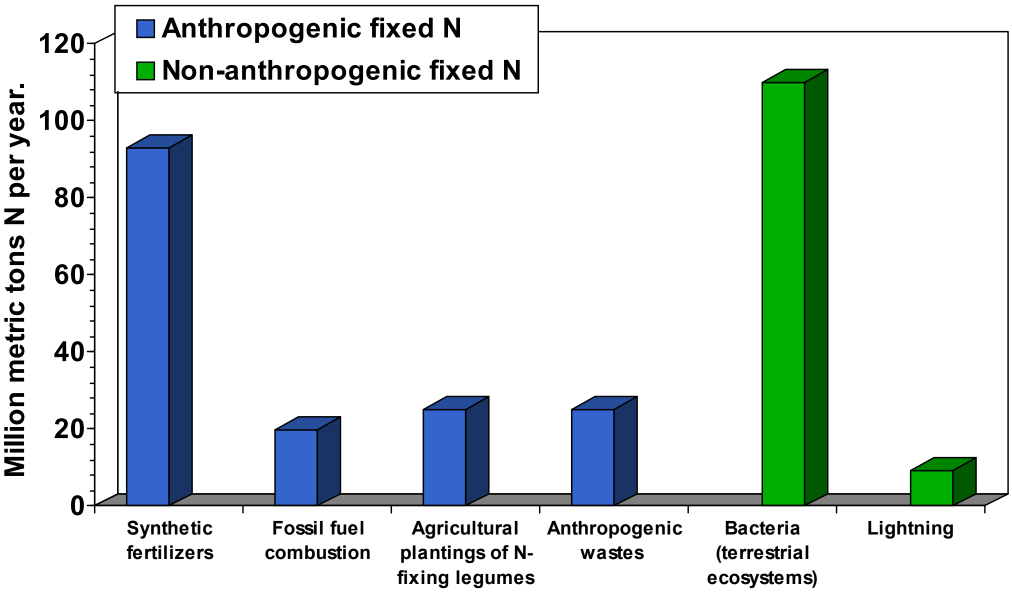


Figure 1.6: Summary of current sources of RNCs in terrestrial ecosystems.

As shown in Figure 1.6, anthropogenic nitrogen fixation now exceeds the amount of biologically fixed nitrogen on the continents (Burns, 2004). From this evidence, some authors distinguish between a "pre-industrial nitrogen cycle" and an "industrial nitrogen cascade" (Figure 1.7). In the pre-industrial nitrogen cycle atmospheric N_2 is fixed only by lighting and diazotroph microorganisms, and then returned back to the atmosphere by denitrifying bacteria and fungi. In the industrial nitrogen cascade the nitrogen cycle still occurs, but it is totally concealed by the overwhelming excess of anthropogenic fixed nitrogen flowing into the soil and atmosphere (Hooper, 2006). This huge pool of RNCs accumulated in the environment and cycling through different biogeochemical pathways leads to an important number of environmental issues, which are briefly described in the next section.

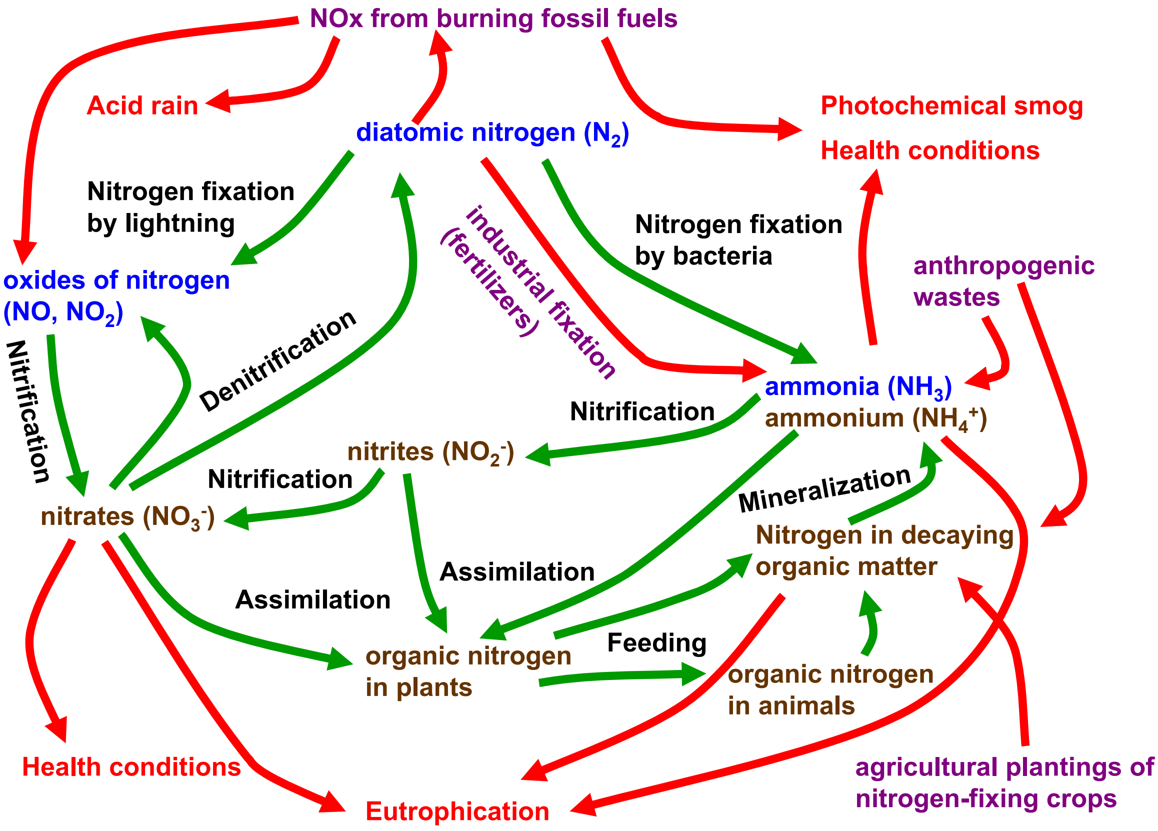


Figure 1.7: Schematic representation of the nitrogen cascade.

The anthropogenic flow of RNCs is unevenly spread across the Earth; some remote regions of the southern Hemisphere receive small input, whereas some areas such as northern Europe are being intensely transformed. However, no region remains unaffected, and, due to the dramatic changes which have occurred from the industrial revolution to the present day, the Stratigraphy Commission of the Geological Society of London has agreed with a proposal made by Nobel Prize-winning chemist Paul Crutzen suggesting that the Earth has left the Holocene and started a new epoch: the Anthropocene (NERC, 2008).

1.1.4.2. Environmental issues linked to anthropogenic nitrogen production

The potential environmental effects of the different RNCs released into the atmosphere will vary hugely depending on the compound and the pathway followed (Aneja et al., 2008). Once released into the atmosphere, RNCs can be transformed in chemical reactions, transported by winds, or returned to the surface by wet and dry deposition processes.

In the troposphere, RNCs such as nitric oxide (NO), nitrogen dioxide (NO_2), and nitrous and nitric acids (HNO_2, HNO_3) are involved in photochemical processes resulting in the formation of ozone (O_3) and the oxidation of hydrocarbons to form other lung irritants such as formaldehyde (CH_2O) and peroxyacetyl nitrate (PAN) (Heeb et al., 2008, Hooper, 2006, Wood et al., 2008). Nitric oxide (NO) is also an important precursor of acid rain (Vitousek et al., 1997) and an intermediate in stratospheric ozone depletion. Another consequence of RNCs' presence in the atmosphere is increased secondary aerosol production, which contributes to the particulate matter burden of ambient air and to decreased visibility, and is linked to negative effects on human health and to effects on local and global radiation budgets (Heeb et al., 2008, Petit and Bandosz, 2008, Whitehead et al., 2008).

In terrestrial ecosystems, elevated atmospheric RNC deposition rates might lead from a condition of nitrogen growth limitation to a condition of nitrogen saturation, which greatly contributes to environmental problems such as acidification and over-fertilization of soils and drainage waters, leading to forest decline (Aneja et al., 2008, Dittman et al., 2007, Ham and Tamiya, 2007, Ham et al., 2007, Wood et al., 2008), and eutrophication, probably the most damaging effect, as it leads to changes in species distribution and loss of biodiversity (Aneja et al., 2008). In water bodies, eutrophication leads to blooms of plankton and algae. When these organisms die and decompose, the bacteria that feed on them consume all the oxygen dissolved in the water, creating a "dead zone" which causes aquatic life to asphyxiate (Beman et al., 2005). In soils, eutrophication leads to losses of biodiversity among plants adapted to low-nitrogen soils, and subsequently, of the animals that depend on these plants. Heathlands are a very good example of susceptibility to this damaging effect. When N deposition increases in these ecosystems, the ability of heaths to compete with herbs decreases, favouring plant community substitution and the disappearance of the heathland (Cuesta et al., 2008). In addition to this, recent experiments have shown that ecosystems which, due to fertilization, have become species poor, have a far less stable plant productivity in the face of weather events such as droughts (Galloway et al., 1995).

Nitrogen saturation occurs when the availability of RNCs in a particular ecosystem exceeds the total combined plant and microbial nutritional demand in that ecosystem. Important biogeochemical responses to nitrogen saturation include: increased fluxes of nitrous oxide (N_2O) gas from soils, increased foliar nitrogen concentrations (Burns, 2004), and nitrate leaching into surface waters, which reduces the amount of nutrient cations in the soil. This condition affects sensitive tree species, decreases tree health and reduces acid neutralizing capacity in surface waters (Dittman et al., 2007).

There are also issues linked to human health: in water treatment, some organic nitrogen compounds dissolved in the water are an emerging concern as precursors for carcinogenic disinfection byproducts such as haloacetonitriles and N-nitrosodimethylamine (Ambonguilat et al., 2006, Lee and Westerhoff, 2005, Westerhoff and Mash, 2002).

In addition to the issues related to RNCs, there are also a few related to increased nitrous oxide (N_2O) emissions; its largest sources are associated with natural and agricultural ecosystems. However, N_2O concentration in the atmosphere has increased by 16% since pre-industrial times. Anthropogenic emissions of N_2O are linked to increasing fertilizer use, biomass burning and the chemical industry (e.g. nylon production). In the troposphere N_2O is a relatively inert infrared-absorbing greenhouse gas (lifetime of 100-150 years) and, despite its relatively low concentration in comparison with CO_2 (0.3 ppm vs. 370 ppm), its contribution to the anthropogenic enhancement of the greenhouse effect is proportionally larger (~4% vs. ~62%) (Graedel and Crutzen, 1993, Houghton, 2004). When transported to the stratosphere, N_2O becomes an intermediate in the destruction of stratospheric ozone (Aneja et al., 2008).

1.1.5. RNCs deposition control

Sampling and analysis methods for ammonium, nitrite and nitrate measurement have long been tested and validated. For this reason, European protocols for controlling nitrogen deposition have focused since the 1960s only on these components and, in fact, they have been very effective regarding the mentioned inorganic components (Cornell et al., 2003). In Europe, at the political level, the reactive nitrogen compounds restricted under the Gothenburg Protocol (UN-ECE, 1999) and the EU Directive 2001/81/EC (EU, 2001), both aiming to limit emissions of acidifying and eutrophying pollutants and ozone precursors, only include nitrogen oxides (NO_x) and ammonia (NH_3). The Gothenburg Protocol to "Abate Acidification, Eutrophication and Ground-level Ozone" entered into force on the 17th May 2005. Once the Protocol is fully implemented, Europe's sulphur emissions should be cut by at least 63%, its NO_x emissions by 41%, its volatile organic compounds (VOC) emissions by 40% and its ammonia emissions by 17% compared to 1990. It was estimated that by that time (2010), the area in Europe with excessive levels of acidification would shrink from 93 million hectares in 1990 to 15 million hectares, and that with excessive levels of eutrophication would fall from 165 million hectares in 1990 to 108 million hectares (if all the Member States meet their allocated targets by 2010).

To date, the main problem for producing a protocol for measuring deposition of water-soluble organic nitrogen (WSON) is the diversity of organic nitrogen compounds (Atkinson, 2000) compared with the inorganic forms. Due to these difficulties associated with organic nitrogen species analysis, most of the studies regarding N budgets have not included any organic species (Ham and Tamiya, 2007, Ham et al., 2007). However, atmospheric dissolved organic nitrogen (DON) deposition has been estimated to represent, on average, 32-36% of the total dissolved nitrogen (TDN), with important temporal fluctuations (Ham and Tamiya, 2007, Ham et al., 2007). According to a study carried out over a period of 2 years at seven sites across Britain, DON represents between 24 and 40% of the total nitrogen dissolved in rain over the UK (Cape et al., 2004). The location of the sampling site is a key factor in the DON fraction of the sample. In a recent study (Zhang et al., 2008) the DON contribution to the TDN deposition fluctuated from 4% to 79% across 15 different monitoring sites under study, and, on average, the DON contribution to TDN was ~30%, which is consistent with previous studies. In remote, unpolluted tropical sites, DON can represent up to 90% of the TDN in the rain (Pacheco et al., 2004).

It is not possible yet to describe the chemical composition of WSON, and hence, it is not possible to fully assess the bioavailability of the nitrogen associated with it, or to conclude whether the main sources of WSON to the atmosphere are anthropogenic or not (Cornell et al., 1995, Russell et al., 1998). Nevertheless, some progress has been made on this front, and readily bioavailable compounds such as urea and amino acids have been determined to contribute a significant part of the WSON, and it is increasingly clear that some more compounds included in the WSON may become bioavailable after chemical processing in a receiving ecosystem (Neff et al., 2002).

It is also believed that this organic nitrogen fraction includes synthetic compounds like pesticides such as atrazine (Ambonguilat et al., 2006), or reaction products from man-made emissions, such as nitrophenols (Luttke et al., 1997). Many authors believe that the WSON deposition rate is an important factor controlling N fluxes in terrestrial ecosystems (Ham and Tamiya, 2007), as WSON species might represent an important pool of unaccounted reactive nitrogen readily available to these ecosystems (Sharp et al., 2002). However, the information available is still limited and insufficient (Ham et al., 2007). In the near future, as nitrogen limits continue to become more stringent, the presence of water soluble organic nitrogen (WSON) might become the limiting factor in reaching total nitrogen limits (Dwyer et al., 2008, Ham and Tamiya, 2007). Ideally it should be routinely quantified alongside nitrate and ammonium (Jones and Willett, 2006), amino acids in particular (Forsum et al., 2006), and certainly be considered in any analysis of N budgets (Dittman et al., 2007, Ham et al., 2007, Krab et al., 2008).

1.1.6. Water-soluble organic nitrogen (WSON) and dissolved organic nitrogen (DON)

1.1.6.1. WSON and DON definitions

Both terms, water-soluble organic nitrogen (WSON) and dissolved organic nitrogen (DON), refer to a complex mixture of nitrogen-containing water-soluble organic species found in the environment. These include: simple compounds such as amino acids, amino sugars, purines and urea that are promptly metabolized by plants and microbes, high molecular weight compounds such as proteins, chlorophyll and DNA that are not easily metabolized (Christou et al., 2006, Dittman et al., 2007), and synthetic compounds like pesticides such as atrazine (Ambonguilat et al., 2006), or reaction products from man-made emissions, such as nitrophenols (Luttke et al., 1997).

The term water-soluble organic nitrogen (WSON) refers to nitrogen-containing water-soluble organic species that are in the atmosphere and have the potential to dissolve and be measured in aquatic media such as rainwater, cloudwater, streamwater, soilwater, oceans, etc.

The term dissolved organic nitrogen (DON) refers to those nitrogen-containing water-soluble organic species that are actually dissolved in water or soil, and are present in a given sample of aquatic media.

1.1.6.2. DON bioavailability

In aquatic ecosystems DON is often the major form of N, particularly in coastal/estuarine ecosystems, and therefore represents a potential source of N to phytoplankton and bacteria (Maie et al., 2006, Seitzinger and Sanders, 1999). In marine ecosystems, atmospheric inputs of organic nitrogen are estimated to be comparable to the input of inorganic nitrogen species (Matsumoto and Uematsu, 2005).

In soils DON represents the substrate from which ammonium and ultimately nitrate is naturally produced (Christou et al., 2006), and very often this organic nitrogen fraction is greater than the inorganic one (Goller et al., 2006, Jones and Willett, 2006), and some studies, contrary to a widespread opinion, have found that DON can be directly, not only indirectly (due to mineralization processes in the ecosystem), acquired by plants (Scharenbroch and Lloyd, 2004).

DON can be taken up directly by certain plants in the form of simple compounds such as urea and amino acids, however, further evidence demonstrating that this is a major plant N acquisition pathway is still needed (Jones et al., 2005). In the case of widespread subarctic moss species, their ability to take up nitrogen directly from free amino acids in the soil might represent an important competitive advantage in those cold biomes where inorganic nitrogen sources are scarce (Krab et al., 2008). Furthermore, plants possessing a greater capacity to take up dissolved organic N could pre-empt the uptake of N by plants that are more reliant on inorganic forms of N produced by mineralization (Jones et al., 2005). For instance, a number of measurements in ecosystems with very high stocks of organic N in the soil, such as taiga ecosystems, indicate that the inorganic N fluxes represent less than 50% of the annual requirement of the vegetation (Jones and Kielland, 2002, Kranabetter et al., 2007). Organic N uptake has, therefore, the potential to contribute to plant nutrition across the entire gradient of soil productivity.

In all agroecosystems DON represents a significant N pool, and its concentration is less sensitive to land use than DIN concentration, with low input agricultural systems dominated by ammonium and intensive agricultural systems dominated by nitrate. Intensive agricultural systems are defined in this context as land receiving regular fertilizers and producing high yields (Christou et al., 2005).

1.1.6.3. Sources and origin of WSON

In spite of the importance of atmospheric WSON in the global N budget, sources of WSON have not yet been understood sufficiently. Some theories suggest oceans, agricultural activities and biomass burning as the main sources of atmospheric WSON (Calderón et al., 2007).

Oceans would contribute to the global atmospheric WSON fraction in the form of aerosolized sea spray, where significant amounts of amino acids such as glycine, serine, aspartic acid and alanine have been detected (Matsumoto and Uematsu, 2005), and gas-phase amines released in metabolic processes of marine animals and bacteria (Calderón et al., 2007).

Agricultural activities would contribute to the atmospheric WSON budget in the form of urea applied as fertilizer and aliphatic amines from animal husbandry operations (Calderón et al., 2007). Domestic wastewater discharges are another important source of amines. Dimethylamine is the most common amine in human urine. Other prevalent aliphatic amines are methylamine and trimethylamine, which are also naturally produced by different organisms (Calderón et al., 2007). These amines are likely to represent an important fraction of WSON in the gas phase, and they are present in appreciable quantities on fine particles. However, they are quite volatile substances and their concentrations were found to be below the limit of detection in rainwater samples (Calderón et al., 2007). Livestock farming could also release into the atmosphere an important amount of free amino acids and proteinaceous compounds, the largest reservoir of organic nitrogen in most organisms (Wu et al., 2007). Proteinaceous compounds in the atmospheric condensed phase can be decomposed to dissolved free amino acids by photocatalytic hydrolysis (Matsumoto and Uematsu, 2005).

Biomass burning would contribute, releasing into the atmosphere amino acids (mainly L-glycine, L-serine, L-alanine, L-threonine, L-arginine and L-asparagine), acetonitrile (CH_3CN), which is a marker for biomass burning, and humic acid-like compounds such as fulvic acids that can release additional free amino acids when photolysed by sunlight (Calderón et al., 2007).

An important and yet unanswered question is the atmospheric WSON origin: natural, anthropogenic or mixed? Due to the important contribution of the WSON fraction to the total N budget, this is a key question when assessing the scale of the human perturbation of the N cycle. To date, investigations of individual compounds and isotopic analysis have been unable to provide conclusive results regarding the origin of atmospheric WSON (Kelly et al., 2005). In a recent study over the East China Sea and western North Pacific it was suggested that WSON compounds in marine aerosols were mainly from anthropogenic origin, as they were associated with continental materials of anthropogenic origin, particularly ammonium in fine particles (Nakamura et al., 2006). On the other hand, another study (Pacheco et al., 2004) claimed that DON represents up to 90% of the total dissolved nitrogen (TDN) found in tropical continental rain in remote unpolluted sites, suggesting a natural origin.

Another crucial question is whether the main contributor to the DON fraction in terrestrial ecosystems is dry or wet deposition. Wet deposition denotes removal by clouds and falling precipitation, and dry deposition denotes the direct collection of gases and particulates on a surface. In this context, a number of methods and different designs have been described for rain sampling over the last 30 years (Dämmgen et al., 2005). However, despite several studies showing that dry deposition can contribute significantly to nitrogen in bulk precipitation (Cape and Leith, 2002), in many cases, precipitation composition is derived from measurements of bulk precipitation, i.e. the basic design comprises a funnel connected to a collecting bottle, and therefore does not discriminate between dry deposition to the surface of the funnel and nitrogen species dissolved in the rain. There have been many studies aimed at evaluating the contribution of dry deposition to bulk precipitation collectors (Cape et al., 2009, Lee and Longhurst, 1992) but none so far has explicitly considered the effect on water-soluble organic nitrogen.

In summary, very little is known with regard to organic nitrogen in the atmosphere and in precipitation, and to its source and sink budgets. To date very important questions remain unanswered: deposition mechanisms: wet vs. dry deposition; origin: natural, anthropogenic or mixed; composition and biological availability.

1.2. Aims of the Project

Further investigation of atmospheric nitrogen deposition and exploration of some of the unanswered questions presented in the previous section are the driving forces behind this project. Particular attention has been paid to questions dealing with deposition mechanisms (of both inorganic and organic water-soluble nitrogen species) and with potential origins of water-soluble organic nitrogen species. The key aims of this project are:

(i) investigation of atmospheric nitrogen deposition focused on discrimination between bulk, wet and dry deposition, and between particulate matter and gas phase,

(ii) accurate quantification of the contributions of dissolved organic and inorganic nitrogen to each type of deposition, and

(iii) further exploration of the origin and potential sources of atmospheric water soluble organic nitrogen.

In order to fulfil these objectives, this project was structured in 3 main stages: the first stage (Chapter 3) was devoted to the detailed study of atmospheric nitrogen deposition in a semi-rural area in south-east Scotland. Rain samples were collected in standard rain gauges and flushing rain gauges, allowing discrimination between bulk, wet and dry deposition of nitrogen species. A key objective in this stage was the accurate quantification of inorganic and organic water-soluble nitrogen species contribution to each type of deposition.

In the first stage of this project it was discovered that dry deposition was by far a larger contributor to bulk deposition than wet deposition, both for organic and inorganic water-soluble nitrogen species. For this reason, the second stage of this project (Chapter 4) aimed at further exploration of atmospheric concentrations of water-soluble nitrogen species, both organic and inorganic. Discrimination between material from gas phase and particulate matter was achieved by means of Cofer scrubbers and PTFE membrane filters. Another key objective of this second stage was to investigate potential origins of the water-soluble organic nitrogen fraction, both in the gas phase and in particulate matter. Correlation studies of water-soluble organic nitrogen species with anthropogenic material from different sources were key tools for this investigation.

The thorough study of water-soluble organic and inorganic nitrogen fractions in bulk, wet and dry deposition, as well as in particulate matter and gas phase in the early stages of this project were focused on one single sampling site. For this reason, the final stage of this project (Chapter 5) was designed to gain a broader picture of nitrogen deposition across Europe: rain samples were analysed from a network of 21 different sampling locations, from the south of Portugal to the north of Finland. As in earlier stages, particular attention was paid to the organic fraction of N deposition and to the potential origin of this organic material: biogenic, anthropogenic or mixed.

1.3. Brief overview of the main techniques for N species determination in aqueous samples

Quantification of organic nitrogen dissolved in aqueous samples requires the measurement of the total nitrogen dissolved in the sample, from which the inorganic nitrogen is then subtracted (Cape et al., 2001, Cornell and Jickells, 1999, Cornell et al., 2003, Sharp et al., 2002). Total nitrogen includes all nitrogen-containing species (organic and inorganic) dissolved in the sample. Inorganic nitrogen includes all the nitrates (NO_3^-), nitrites (NO_2^-) and ammonium (NH_4^+) dissolved in the sample.

The most commonly used techniques for dissolved inorganic nitrogen (DIN) determination include a number of colorimetric methods, such as the indophenol blue method (Cornell and Jickells, 1999), and ion chromatography. Ion chromatography is the best method in this context, because it avoids any possible contribution of organic nitrogen, as sometimes happens in the indophenol blue method, which would result in organic nitrogen being underestimated (Cape et al., 2001, Rowland, 1983). Flow injection analysis instrumentation and methodology is also commonly used for ammonium determination in aqueous samples (Akse et al., 1998). Ion chromatography and flow injection analysis are the determination methods chosen for DIN determination in this project and they are described further in Chapter 2.

Other approaches to DIN determination include: a continuous flow analyzer (TRAACS 2000, Bran-Luebbe Inc.) for rainwater samples (Zhang et al., 2008), and capillary electrophoresis systems for nitrite (NO_2^-) and nitrate (NO_3^-) determination (Ham and Tamiya, 2007).

Determination of total dissolved nitrogen (TDN) requires a preparatory digestion step, either chemical or by combustion, to release the nitrogen from the organic molecules. According to the current literature, the main digestion methods available for TDN determination in aqueous samples are Kjeldahl digestion, UV digestion, alkaline persulfate oxidation and high-temperature catalytic oxidation (HTCO).

The Kjeldahl digestion is the oldest method (1883) and uses hot sulphuric acid to convert dissolved organic nitrogen (DON) to ammonium (Christou et al., 2006), followed by neutralisation, which liberates ammonia as a result of the pH increase, and finally, distillation and determination of ammonia by titration or colorimetric analysis (Nozawa et al., 2005). A limitation of this technique is that nitrogen compounds not present in the form of amines or amides are not efficiently converted to ammonium. Instead, they could be released as nitrogen oxides or diatomic nitrogen, and hence, not remain in solution (Doval et al., 1997, Yasuhara and Nokihara, 2001). This method fails to analyze samples with low nitrogen concentration such as rainwater (Vandenbruwane et al., 2007).

The UV digestion method consists of a photolytic breakdown of DON into ammonium, nitrite and nitrate by UV irradiation, followed by quantification by colorimetry or ion chromatography (Calderón et al., 2007, Cape et al., 2001, Scudlark et al., 1998). The problem associated with this method is that some compounds (such as sulphur-containing amino acids) resist UV photolysis, and hence the recoveries of these compounds are low (Hopkinson et al., 1993). In addition to this, if colorimetry is used for nitrate analysis, organic materials can interfere by producing a brown colour. This can be an issue if thymol is used as a biocide for preserving the samples.

The wet oxidation methods achieve chemical oxidation of DON to nitrate under alkaline conditions, by the addition of oxidants such as persulphate (Cape et al., 2001, Cornell et al., 2003, Scudlark et al., 1998).

The high-temperature catalytic oxidation (HTCO) methods aim for the complete combustion of all organic material to carbon dioxide (CO_2) and nitric oxide (NO), followed by quantitative detection of nitric oxide (NO) by chemiluminiscence (Cape et al., 2001, Cornell et al., 2003, Keene et al., 2002).

The two most common TDN digestion-determination methods in current use are HTCO and alkaline persulfate oxidation (Lee and Westerhoff, 2005). These methods have been directly compared by a number of authors, but there is no consensus regarding the superiority of one method over the other (Jones and Willett, 2006). In some studies (Vandenbruwane et al., 2007) the persulfate oxidation digestion method produced slightly higher TDN values than the HTCO method did, whereas in other studies (Cape et al., 2001) opposite results where found. The HTCO method is the determination method chosen for this project and it is explained further in Chapter 2.

2. Analytical methodology

2.1. Dissolved organic nitrogen (DON) determination in aqueous samples

There is no analytical method that yields direct quantification of dissolved organic nitrogen (DON) in water samples (Christou et al., 2006, Dittman et al., 2007, Ham and Tamiya, 2007, Jones and Willett, 2006, Kranabetter et al., 2007, Nakamura et al., 2006, Pacheco et al., 2004, Paul and Williams, 2005, Schwendenmann and Veldkamp, 2005, Vandenbruwane et al., 2007, Westerhoff and Mash, 2002, Zhang et al., 2008). For this reason, the derivation of DON concentrations involves several steps: (i) determination of the dissolved inorganic nitrogen (DIN) species concentration, (ii) determination of the total dissolved nitrogen (TDN) concentration, and (iii) subtraction of the DIN concentrations from the TDN concentration. In this context TDN includes all nitrogen-containing species (organic and inorganic) dissolved in the sample, and DIN includes nitrate, nitrite and ammonium dissolved in the sample. The nitrite concentration is usually negligible and not included in the analyses.

The main drawback of the indirect determination of DON is that it leads to increased analytical variance: since DON is calculated by the subtraction of several independently measured concentrations, the analytical variance for DON concentration is the summation of the variances of each one of the independently measured concentrations (Lee and Westerhoff, 2005, Vandenbruwane et al., 2007).

$$\text{var}([\text{DON}]) = \text{var}([\text{TDN}]) + \text{var}([\text{NO}_3^-]) + \text{var}([\text{NH}_4^+])$$

2.2. Nitrate determination in aqueous samples

Ion chromatography (IC) was the method of choice for nitrate determination. In IC, the separation mechanism consists of ion exchange on stationary phases with charged functional groups. The corresponding counter ions are located in the vicinity of the charged functional groups and can be exchanged with other ions of the same charge in the mobile phase. For each ion, the distribution between the mobile and the stationary phase is determined by the ion exchange equilibrium constant. The ion exchange equilibrium constant value depends on the ion’s affinity for the stationary phase of the ion exchanger (Schäfer et al., 2003).

The equipment used in this work included a Metrohm 766 IC Sample Processor connected to a Metrohm 761 Compact IC (Figure 2.1) equipped with a Metrosep A Supp 5 column, with an eluent of 3.2 mM carbonate and 1.0 mM bicarbonate. The limit of detection (LOD) for this equipment was 0.2 μM N for a 100 μL injection, calculated as 3 times the standard deviation (SD) of the entire set of standards at the lowest concentration point (sodium nitrate, 0.4 μM N) used during the study. Precision of this method, based on the coefficient of variation (CV) for sodium nitrate standards at 20 μM N concentration was 0.8 % on average within day, and also 0.8 % between days (i.e., for all measurements made). In this context CV is defined as [SD/average concentration] x 100 (Bronk et al., 2000). The anion analysis also quantified sulphate concentrations in the sample which, in addition to nitrate, is the main counter-ion of ammonium in the atmospheric aerosol.

2.3. Ammonium determination in aqueous samples

Two different methods were used for ammonium determination during this project: ion chromatography for rain samples (Chapter 3), and flow injection analysis for air samples collected into aqueous media (Chapter 4).

The equipment used for ammonium determination by ion chromatography included a Metrohm 733 IC Separation Center, equipped with a Metrosep C1 column for analysis and receiving eluent from a Metrohm 709 IC pump (Figure 2.1). The eluent comprised 24 mM boric acid / 5mM tartaric acid / 0.7 mM dipicolinic acid. The same autosampler (Metrohm 766 IC Sample Processor) was used for nitrate determination and ammonium determination, and then the sample was diverted to the two different IC columns. As with nitrate determination, the LOD for ammonium was 0.2 µM N for a 100 µL injection, calculated as 3 times the SD of the entire set of standards at the lowest concentration used during the study (ammonium sulphate, 0.5 µM N).

Figure 2.1: The ion chromatography (IC) equipment: a Metrohm 766 IC Sample Processor connected in parallel to a Metrohm 761 Compact IC equipped with a Metrosep A Supp 5 column (for anions analysis) and a Metrohm 733 IC Separation Center equipped with a Metrosep C1 column (for cations analysis).

The second method for ammonium determination used in this project was flow injection analysis using a FloRRia (Mechatronics Instruments BV) flow injection ammonium analyzer (Figure 2.2).

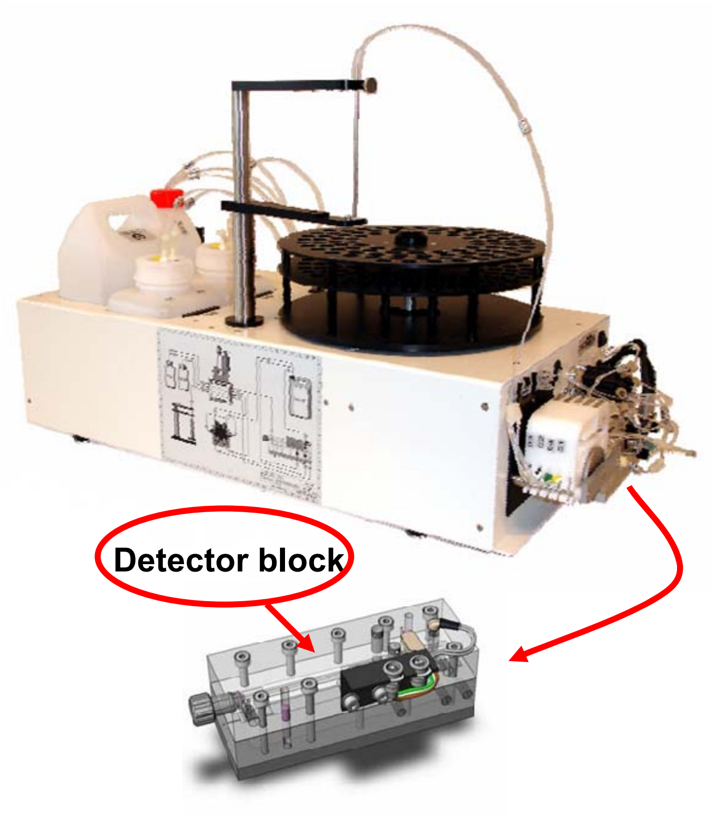


Figure 2.2: The flow injection ammonium analyzer (FloRRia, Mechatronics Instruments BV).

The only reagents required by this technique are deionised water (specific resistivity > 18 MΩ cm) and a 1 M sodium hydroxide, 100 ppb ammonium solution. The operational principle of this instrument is the conversion of ammonium in solution to ammonia gas at high pH (Akse et al., 1998). In the automated procedure, a small volume of sample (0.1 mL) is mixed with the alkaline carrier stream (1 M sodium hydroxide, pH >10.5). At these alkaline conditions the non-ionic and volatile ammonia form predominates in the carrier stream. The ammonia contained within samples injected into the carrier stream diffuses across a hydrophobic microporous PTFE membrane (0.22 µm pore size) into the flowing analytical stream consisting of deionised water (specific resistivity > 18 MΩ cm). The neutral pH of the analytical stream promotes ionization of the transported ammonia, resulting in an increase in conductivity in proportion to the initial sample ammonium concentration. The increase in conductivity in the analytical stream is compared relative to the conductivity of the deionised water (Figure 2.3).

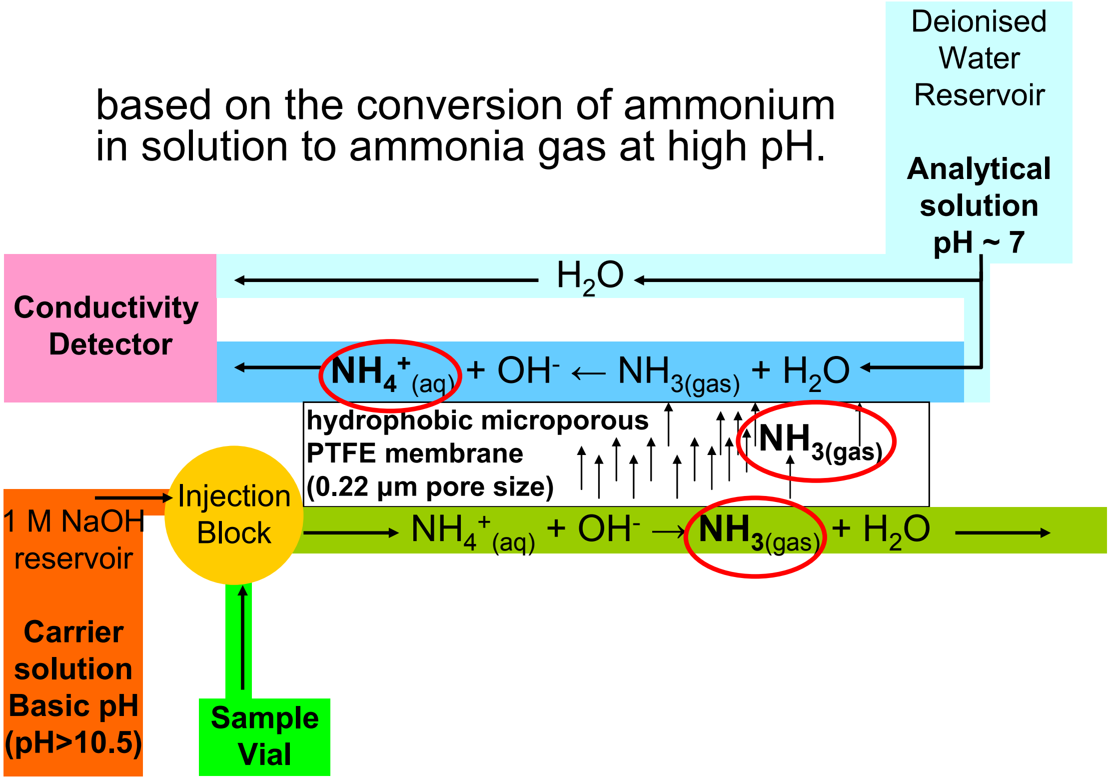


Figure 2.3: The principle of operation of a flow injection ammonium analyzer.

In this method ammonia is transported through the PTFE membrane by diffusion into the gas-filled pores. The source-sink situation created by the different predominance of species on opposite sides of the membrane maintains the maximal concentration gradient for ammonia across the membrane, ensuring unidirectional mass transfer of ammonia from the carrier stream into the analytical stream. To maximize efficiency of the gas phase transfer of ammonia through the membrane, the sample carrier stream and the analytical stream flow counter current to one another.

Using the FloRRia the LOD for ammonium was 0.7 µM N, calculated as 3 times the SD of the entire set of blanks produced during the study. The precision as determined from the CV for ammonium sulphate standards at 450 ppb concentration (24.9 uM N), was 1.8 % CV on average within day, and 2.3 % CV between day (i.e., for all measurements made).

2.4. Total dissolved nitrogen (TDN) determination in aqueous samples

TDN determination requires a preparatory digestion step. High-temperature catalytic oxidation (HTCO) was the method of choice in this study (Cape et al., 2001, Cornell et al., 2003, Keene et al., 2002). This method aims for the complete combustion of all organic material to CO_2 and nitric oxide (NO), followed by quantitative detection of NO by chemiluminescence. The instrument used for this technique was a nitrogen specific HPLC detector, ANTEK 8060-M (Figure 2.4), operated according to the manual. The analysis was conducted in flow-injection mode, with triplicate analyses of a 50 µL sample in a carrier of deionised water at a flow rate of 250 µL min^{-1}. The LOD for TDN was 1.3 µM N, calculated as 3 times the SD of the blank. In this context blanks were estimated by taking the y-intercepts of the standard regression lines based on each independent calibration with standard solutions of ammonium sulphate and sodium nitrate produced during the study. Precision of the ANTEK 8060-M, based on the CV for sodium nitrate standards at 25 µM N concentration was 2.4 % on average within day, and 4.0 % between days (i.e., for all measurements made).

Figure 2.4: The ANTEK 8060-M nitrogen specific HPLC detector.

2.4.1. Principle of operation of ANTEK 8060-M

The ANTEK 8060-M is a specific instrument for nitrogen analysis because all non-nitrogen containing compounds are transparent to the detector. The operation of the ANTEK is based on two reactions (Figure 2.5).

In the first reaction, the eluent (solvent matrix and sample) is routed to a pyrotube, placed inside a furnace, where it is reacted with oxygen at a temperature of 1050 °C (Cape et al., 2001). The products of this reaction are carbon dioxide, water, nitric oxide and other combustion products. In this step, all nitrogen-containing compounds are quantitatively converted to NO.

$\text{R-N} + \text{R-H} + O_2 \rightarrow CO_2 + H_2O + NO + \text{other combustion products}$

In this equation, R-N represents any compound containing nitrogen (organic or inorganic) and R-H represents any organic compound that does not contain nitrogen.

Following the oxidation step, the products are routed through a drying system to remove water, and then to the detector for quantification. The detector is equipped with an ozone generator and a reaction chamber. In the reaction chamber the nitric oxide is reacted with excess ozone to form nitrogen dioxide in an excited state (NO_2^*) and oxygen. The photons emitted as the excited-state molecules of nitrogen dioxide decay to the ground state are detected by a photomultiplier tube (kept at a constant temperature of 5 °C).

$NO + O_3 \rightarrow NO_2^* + O_2 \rightarrow NO_2 + h\nu$

The photon emission is proportional to the amount of nitrogen in the original sample. Using this technique, only chemically-bound nitrogen is detected, not diatomic nitrogen (N_2). Another advantage of this method is that any compound that contains nitrogen may be used to produce calibration curves.

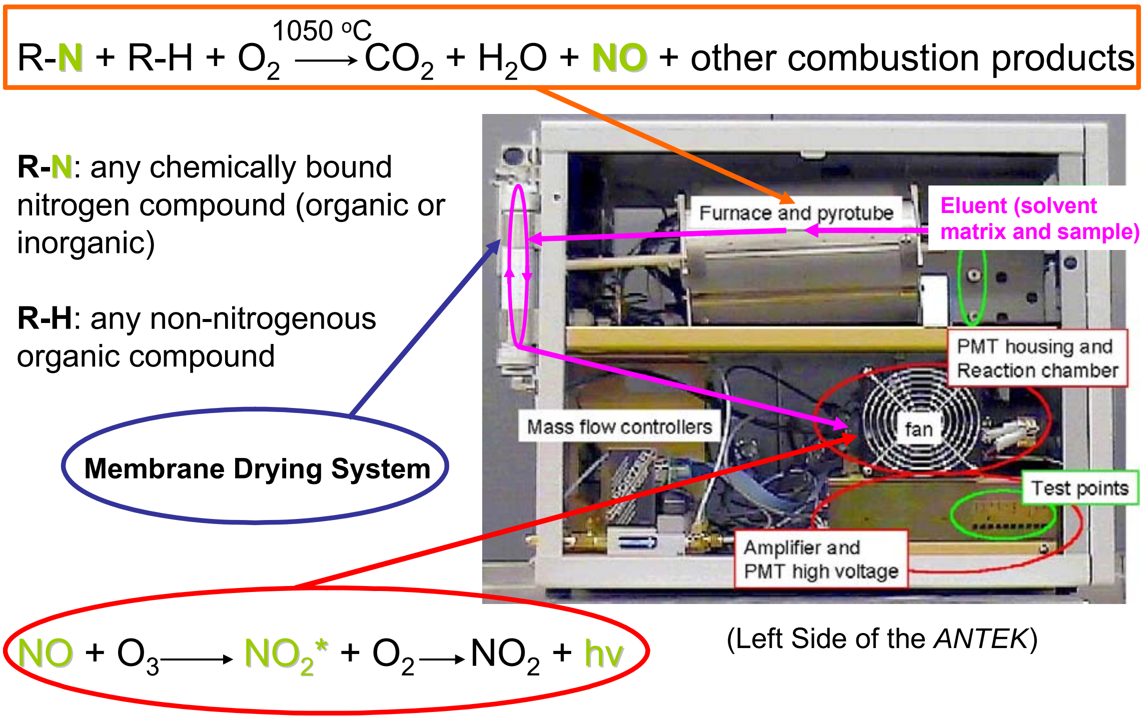


Figure 2.5: The principle of operation of the ANTEK 8060-M nitrogen specific HPLC detector.

2.4.2. Method development

Eluent flow rate into the pyrotube of the ANTEK 8060-M was optimized at 250 µL min^{-1} for 3 injections of 50 µL of sample per analysis. Slower eluent flow rate would produce wider and lower peaks in the chromatogram, causing peaks to overlap, whereas faster eluent flow rate would produce narrower and higher peaks in the chromatogram, which is usually desirable. However, the increase in height caused the peaks corresponding to the most concentrated standards to be off scale. More importantly, eluent flow rates larger than 250 µL min^{-1} caused technical problems in the instrument: it resulted in too much condensation at the end of the pyrotube. So much, that the vent block designed to deal with some excess of condensation could not cope, and as a consequence some moisture went all the way through the dryer to the 1.0 µm PTFE filter placed just before the reaction chamber, blocking the gas flow to the reaction chamber. The purpose of the 1.0 μm PTFE filter is to prevent particles and moisture to enter the reaction chamber.

As mentioned in the previous section, in theory, any compound that contains nitrogen can be used to produce calibration curves for the ANTEK 8060-M. However, the main problem encountered in the development of a reliable method for TDN determination in aqueous samples in this project was that very often the response to ammonium was lower than the response to nitrate (or to any other nitrogen-containing compound tested as potential calibration standards, such as caffeine and urea) (Figure 2.6).

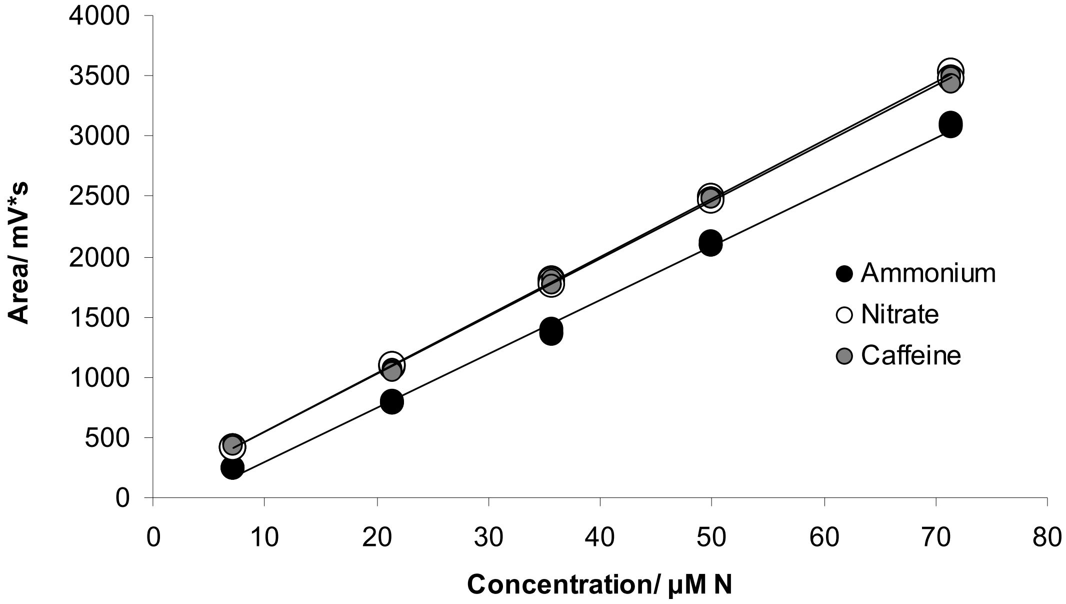


Figure 2.6: Comparison of responses to equimolar concentrations of ammonium sulphate, sodium nitrate and caffeine standards in the ANTEK 8060-M nitrogen specific HPLC detector. Across the entire concentration range, the area of the signal corresponding to nitrate and caffeine is always larger than that corresponding to ammonium.

Therefore, using the NH_4^+ calibration curve to determine TDN concentration in an aqueous sample would have overestimated TDN, whereas using the NO_3^- calibration curve would have underestimated TDN. To circumvent this problem, for TDN determinations in the first sampling campaign (Chapter 3), a correction factor (c.f.) was applied, where c.f. was the ratio of the slopes (m) corresponding to the calibration curves of NO_3^- and NH_4^+ standards in each batch of samples.

Mathematically:

$$\left[TDN\right] = m \times Area \rightarrow Area = \frac{\left[TDN\right]}{m} = \frac{\left[TDN\right]_{NH4+}}{m_{NH4+}} = \frac{\left[TDN\right]_{NO3-}}{m_{NO3-}} \therefore$$

$$\left[TDN\right]_{NO3-} = \frac{m_{NO3-}}{m_{NH4+}} \times \left[TDN\right]_{NH4+}$$

Therefore, the correction factor (c.f.) for this run is:

$$c.f = \frac{m_{NO3-}}{m_{NH4+}}$$

In these equations:

$\left[TDN\right]_{NH4+}$ is the TDN concentration determined with the NH_4^+ calibration curve.

$\left[TDN\right]_{NO3-}$ is the TDN concentration determined with the NO_3^- calibration curve.

$\left[NH_4^+\right]_{IC}$ is the NH_4^+ concentration in the sample, determined by ion chromatography.

Thus the formula used to obtain the corrected values of [TDN] was derived as follows:

$$\left[TDN\right]_{NH4+} - \left[NH_4^+\right]_{IC} = \left[NO_3^- + DON\right]_{NH4+}$$

$$[NO_3^- + ON]_{NO3-} = c.f. \times [NO_3^- + ON]_{NH_4^+}$$

$$\left[TDN\right]_{Corrected} = \left[NO_3^- + ON\right]_{NO3-} + \left[NH_4^+\right]_{IC} = c.f. \times \left[NO_3^- + ON\right]_{NH4+} + \left[NH_4^+\right]_{IC} \therefore$$

$$\left[TDN\right]_{Corrected} = c.f. \times \left(\left[TDN\right]_{NH4+} - \left[NH_4^+\right]_{IC}\right) + \left[NH_4^+\right]_{IC}$$

It was suspected that the low response to ammonium was linked to an ion exchange process between ammonium ions and some material retained on the surface of the inner walls of the PEEK tubing. The PEEK tubing (1/16” x 0.13 mm inner diameter) was present in two segments of approximately 30 cm each. The first segment linked the HPLC pump with the autosampler and the second segment linked the autosampler with the ANTEK 8060-M. As a first attempt to trying to improve the response to ammonium, the PEEK tubing was substituted with stainless steel tubing of the same inner diameter, and the eluent was slightly acidified (pH 4). However, since no clear improvement in ammonium response was observed, the initial PEEK tubing was replaced because peak resolution was slightly better with PEEK tubing than with stainless steel tubing.

A real improvement in ammonium response was observed using a mixture of 10% (V/V) methanol in water as eluent and running a vial containing pure methanol approximately every 10 samples. The purpose of using pure methanol in between samples was to flush from the inner walls of the tubing any “sticky” material that might have started to build up. This procedure seemed to work well, as the first peak of the methanol sample chromatogram was usually notably larger than the second one, and the second one slightly larger than the third, indicating that some material was indeed being flushed from the inner walls. More importantly, the response to ammonium standards increased to the same as the response to nitrate standards (Figure 2.7). Therefore, for samples from the second sampling campaign (air samples collected into aqueous media, Chapter 4) and the third sampling campaign (rain samples from NITROEUROPE sites, Chapter 5) it was not necessary to apply any correction factor to the TDN determination. Furthermore, since the mixture of 10% (V/V) methanol in water is more volatile than pure water, switching to this eluant helped to prevent potential condensation issues in the vent block located at the end of the pyrotube in the ANTEK-8060, which had previously caused problems with a noisy baseline.

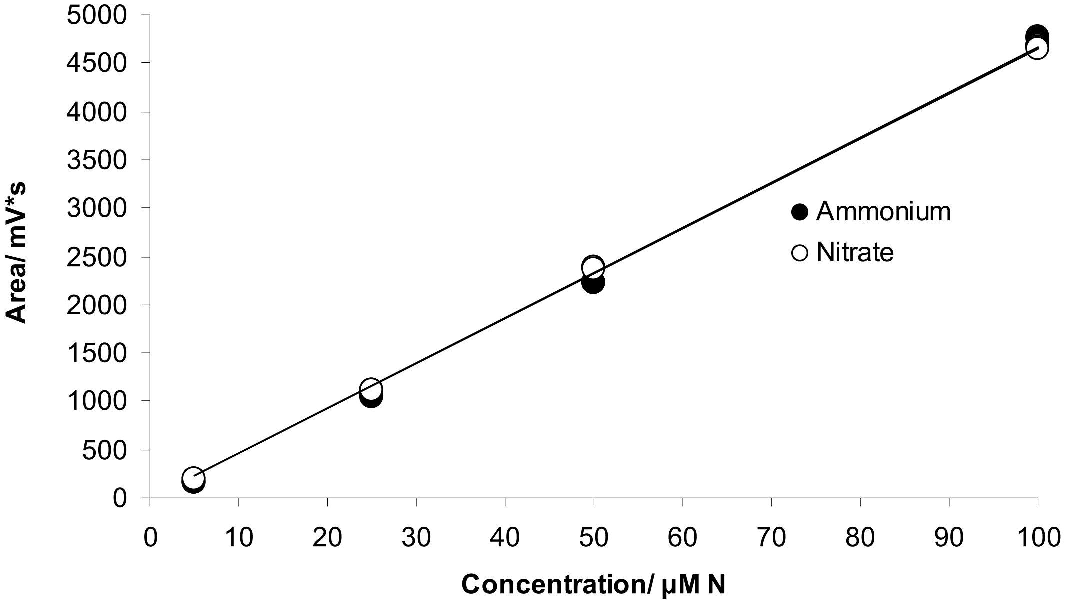


Figure 2.7: Comparison of responses to equimolar concentrations of ammonium sulphate and sodium nitrate standards in the ANTEK 8060-M nitrogen specific HPLC detector using a mixture of 10% (V/V) methanol in water as eluent and one vial of pure methanol every 10 samples. The area of the signal corresponding to nitrate and ammonium is very similar across the entire concentration range.

2.5. Summary of statistical tests applied to the data analysis

2-way analysis of variance (ANOVA): tool used for assessing the effect of different sources of variation in a dataset; e.g. sample date and sample type (wet or dry deposition).

T-test for equality of means: as in the case of 2-way ANOVA, this test assesses the different sources of variation in the dataset under analysis.

Pearson's test: in the context of this project, this test assesses correlation between two different species (e.g. ammonium and WSON concentrations) within the dataset under study.

Levene's test for equality of variances: this test assesses whether variability within two different datasets is statistically significant.

All these statistical tests are based on the evaluation of the null hypothesis. This is given by the p-value (measurement of the probability of occurrence of the null hypothesis). Usually, the limit for a significant interaction is set at $p < 0.05$ (less than 5 chances in 100), and the limit for a highly significant interaction is set at $p < 0.01$ (less than 1 chance in 100).

All the statistical tests listed assume that all the populations being compared follow a normal distribution. In those cases in which the data were not normally distributed, a transformation was applied (e. g. log, square root, Box-Cox).

In all the datasets under analysis, normal distribution was assessed by the means of Shapiro-Wilk test.

3. Atmospheric nitrogen in bulk, wet and dry deposition at the Centre for Ecology & Hydrology (CEH)

The aim of this work was to quantify the bulk, wet and dry deposition of water-soluble inorganic and organic nitrogen-containing species. This chapter reports on data from weekly collections of precipitation samples collected over a period of 22 months, from June 2005 to March 2007.

All samples were simultaneously collected in two types of rain collector (bulk deposition and “dry + wet” deposition). The bulk deposition collectors are denoted as “standard rain gauges” in this chapter, and were of the same design as used in the UK national network for monitoring precipitation composition. The “dry + wet” deposition collectors are denoted as flushing rain gauges in this chapter, and were of a novel type designed by Prof. J.N. Cape which will be described in detail in section 3.1.1. In this context, wet deposition denotes collection of actively falling precipitation, and dry deposition denotes the direct collection of gases and particles on a surface.

3.1. Experimental

3.1.1. Study site and collection methods

Precipitation was sampled weekly from June 2005 to April 2007 at the Centre for Ecology & Hydrology, in a ‘science park’ and within 1 km of mixed farming (arable and dairy) 15 km southwest of Edinburgh, UK (N55°51’44’’, W3°12’19’’). Two types of rain collector were used in this study: standard rain collectors and flushing rain collectors. Three rain collectors of each type were mounted 1.5 m above ground, in a 5 m-side square, in the middle of a grass field (Figure 3.1).

Figure 3.1: Standard rain collectors and flushing rain collectors at the CEH, Edinburgh.

The standard rain collectors consisted of a polypropylene funnel diameter 152 mm mounted directly in a polypropylene collecting bottle, and is the design used in the UK national network for monitoring precipitation composition (Cape et al., 2001). The flushing rain collectors (Cape et al., 2009) are equipped with a rain detector (conductivity array), a spray nozzle, an identical polypropylene funnel to the standard collector, a 2-way PTFE motorised valve, and two independent collecting bottles at ground level, connected to the funnels by 1.5m lengths of silicone tubing enclosed in an opaque flexible PVC tube (to exclude light and minimise biological activity) (Figure 3.2). When a rain event is detected, the funnel is rinsed with a fixed volume of 10% methanol in distilled water and the washings are collected in one of the sampling bottles as a measure of dry deposition on the funnel surface since the last precipitation event. One minute after the rinsing, the 2-way valve is switched to allow the subsequent rain, free from any contamination by prior dry deposition, to enter the second rain sample bottle. At the end of a rain event, signalled by the rain detector, the valve is switched again to the 'divert' position to seal the rain sample bottle from the atmosphere.

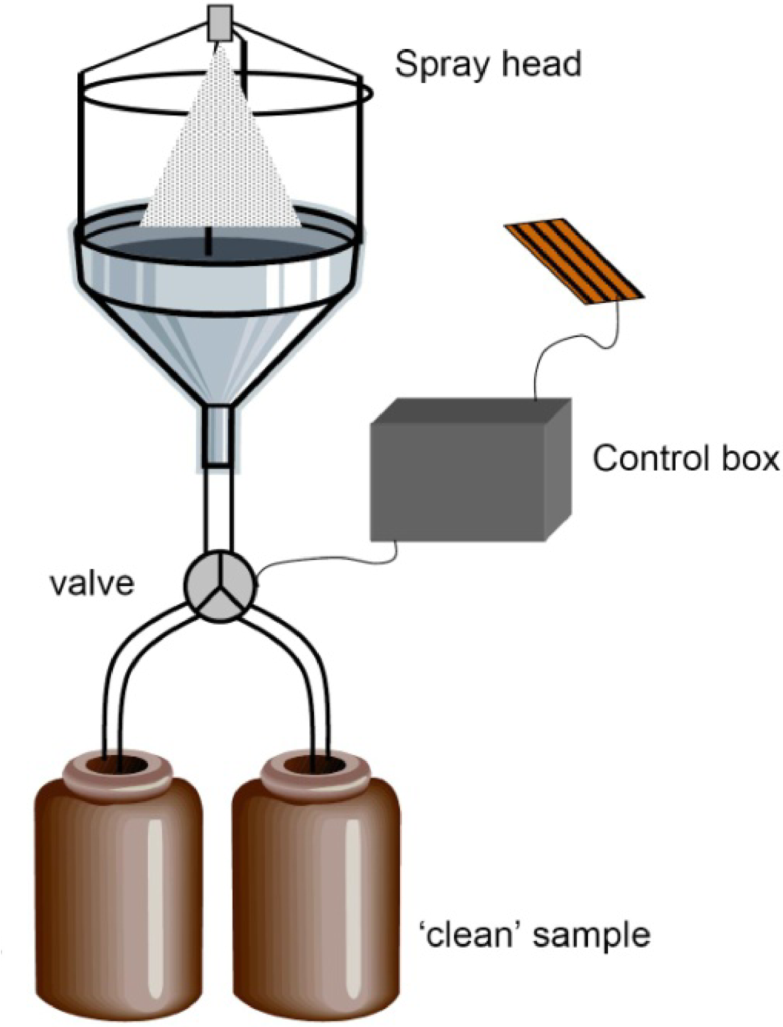


Figure 3.2: Schematic diagram of flushing collector. Source: Cape J.N., Dijk N.v., Tang Y.S., 2009. Measurement of dry deposition to bulk precipitation collectors using a novel flushing sampler. Journal of Environmental Monitoring, 11, 353-358.

3.1.2. Sample preservation

Nitrogen-containing compounds in precipitation are especially vulnerable to biological degradation (Cape et al., 2001, Hadi and Cape, 1995). For this reason there is a need for preservation of the sample during the processes of collection, transportation and storage. In this study, a small amount of a biocide solution was added to the collection bottles prior to sampling. Thymol (2-isopropyl-5-methyl phenol) was the biocide of choice in this study, as it is non-volatile, effective at low concentrations, and presents few toxicity problems for disposal. 100 mg L^{-1} was previously determined to be the optimum concentration (Cape et al., 2001, Hadi and Cape, 1995). This was the target concentration when sample bottles for rainfall and washings were charged with 25 mg thymol per litre of capacity before use (1 mL and 0.5 mL of 50 g L^{-1} methanol solution for rain and washings, respectively). The final thymol concentration in each sample was therefore variable, depending on the amount of rain during each particular week. However, the biocidal effect is not diminished greatly even if the sample bottle is filled (Cape et al., 2001). Collected rain samples were stored at 4 °C before analysis. Samples were filtered through a 0.2 μm pore-size inorganic membrane filter (Whatman, Anotop 10 IC) before chemical analysis.

3.1.3. Chemical analyses

Ion chromatography (IC) was the method of choice for DIN determination (nitrate and ammonium). In this work, the limit of detection (LOD) for both species was 0.2 μM N (further details in Chapter 2, sections 2.2 and 2.3).

TDN determination requires a preparatory digestion step. The method of choice was high-temperature catalytic oxidation (HTCO). In this work, the LOD for TDN was 1.3 μM N (further details in Chapter 2, section 2.4).

The quantification of dissolved organic nitrogen (DON) species concentrations involves the determination of the dissolved inorganic nitrogen (DIN) species and the total dissolved nitrogen (TDN) concentrations, and the subtraction of the DIN concentrations from the TDN concentration.

As explained in Chapter 2, the analytical equipment used in this study measures the concentrations of the different species in each weekly sample. However, in order to compare dry deposition with wet and bulk deposition, it is necessary to use "absolute" amounts of the deposited species (as the volume of sample collected in dry deposition is not the volume of rain collected, but the summation of the volume of solvent flushed by the rain gauge mechanism at the beginning of each rain event).

The unit used to quantify the "absolute" amount of N in this study is μmoles N m^{-2} wk^{-1}. The unit used for producing calibration curves and quantification of responses from all the analytical instruments is μM N wk^{-1}. The conversion equation is:

$$\mu\text{moles N m}^{-2}\text{ wk}^{-1} = \frac{\mu\text{M N x total volume of sample collected (L)}}{\text{area of funnel (m}^2\text{)}}\text{ m}^{-2}\text{ wk}^{-1}$$

3.1.4. Criteria used to establish sample quality

Two criteria were used to identify valid precipitation samples: (i) free from obvious contamination: K^+ concentration must be lower than 20 μM, as K^+ is a good marker for biological contamination (in this study, normally due to bird droppings). 6% of the samples collected were discarded for this reason. (ii) The sample must have sufficient amount of rainfall: the minimum volume was set at 50 mL. Samples with lower volumes were discarded, as they are more vulnerable to alterations in original composition, mainly due to evaporation or condensation processes. 7.5% of the samples collected were discarded for this reason.

The sampling period comprised 92 weeks, from 17th June 2005 to 28th March 2007. For statistical analyses only those weeks with three valid collector replicates for each type of collector were included, limiting the set of samples to 41 weeks. Weeks with three valid samples but with relative standard deviation (RSD) in the total dissolved nitrogen (TDN) greater than 50%, either in bulk deposition or in (dry + wet) deposition, were regarded as "suspicious" and removed from the statistical analysis, as the important discrepancies observed in those weeks within collectors of the same type (either standard rain gauges or flushing rain gauges) might suggest that an unnoticed problem had occurred in one or more of the collectors during that particular period. Seven of the 41 remaining weeks were discarded for this reason. Two additional weeks were removed from the statistical analysis, as mineral nitrogen fertilizer was being applied to a nearby field on these dates. In total there are 32 weeks with valid triplicates: 27 weeks with "washing mechanism on" + 5 weeks with "washing mechanism off".

3.2. Results

3.2.1. Dissolved organic nitrogen (DON)

Dissolved organic nitrogen (DON) represents a significant fraction of the N-containing species in all types of rain gauge (bulk, washings and wet deposition) over the whole period of study. Figures 3.3-3.5 show the time series of the average amount of DON and dissolved inorganic nitrogen (DIN) collected in the bulk, wet deposition and funnel washings (dry deposition) fractions, respectively, as μmoles N m^{-2} wk^{-1}.

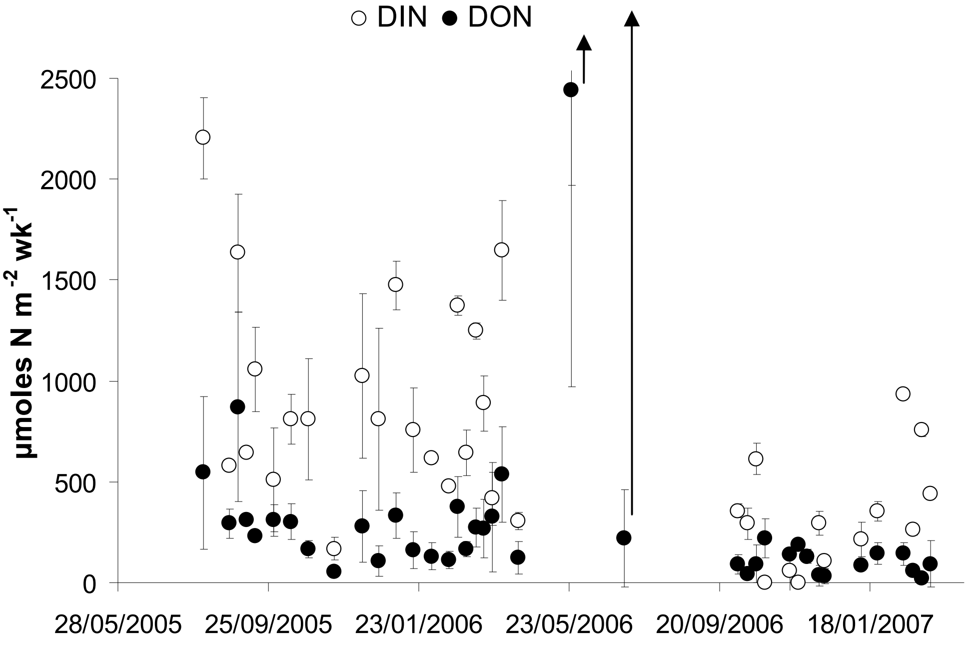


Figure 3.3: Weekly deposition of DIN and DON in μmoles N m^{-2} to standard bulk samplers. Error bar shows standard deviation of 3 replicate samplers. DIN (25/05/2006, 2870 μmoles N m^{-2}), DIN (6/07/2006, 4860 μmoles N m^{-2}).

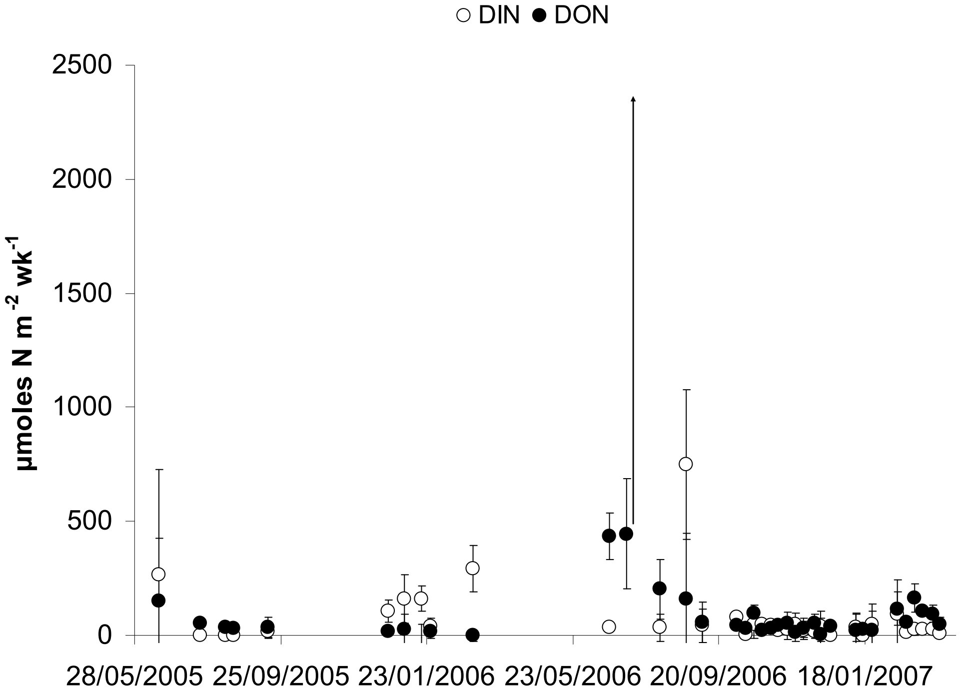


Figure 3.4: Weekly deposition of DIN and DON in µmoles N m^{-2} as wet deposition to flushing samplers. Error bar shows standard deviation of 3 replicate samplers. DIN (6/07/2006, 3020 µmoles N m^{-2}).

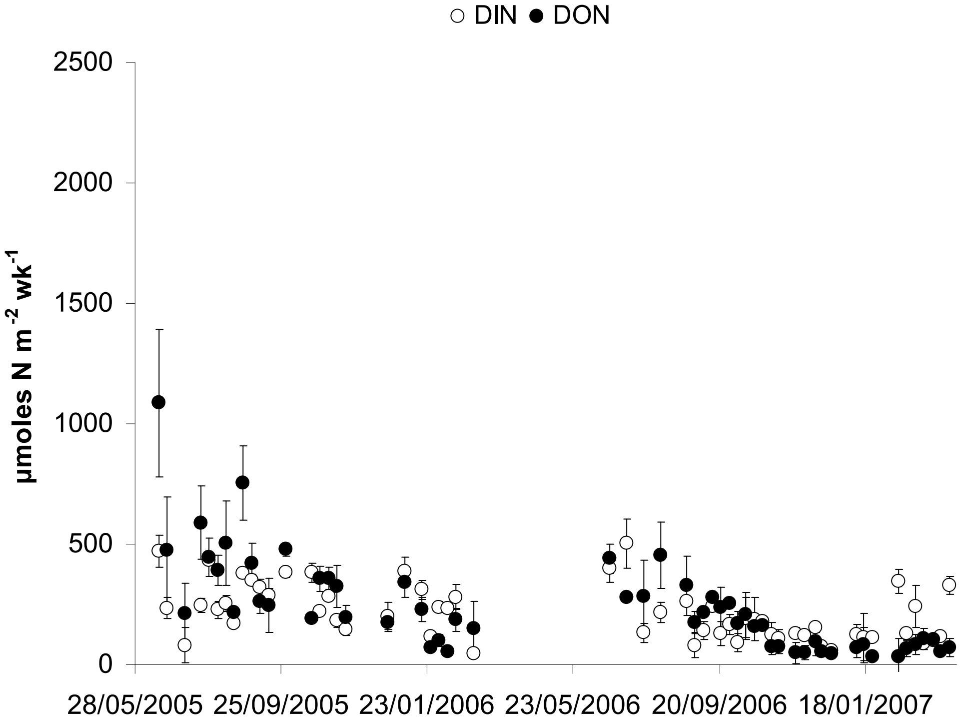


Figure 3.5: Weekly deposition of DIN and DON in µmoles N m^{-2} as dry deposition (funnel washings) to flushing samplers. Error bar shows standard deviation of 3 replicate samplers.

Figures 3.6-3.8 represent the percentage of DON relative to TDN found in each type of collector: bulk deposition, wet deposition and funnel washings, respectively. Only weeks with three valid replicates for each type of collector were included in the analysis.

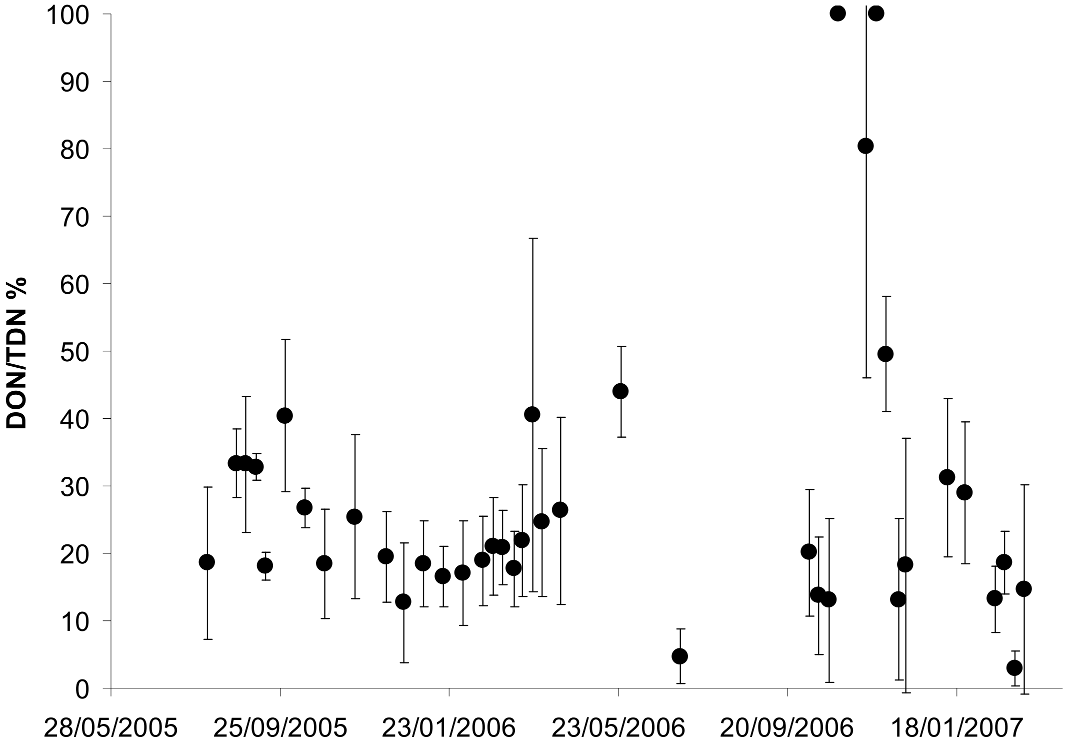


Figure 3.6: Weekly percentage of DON relative to TDN in bulk deposition. Error bar shows standard deviation of 3 replicate samplers.

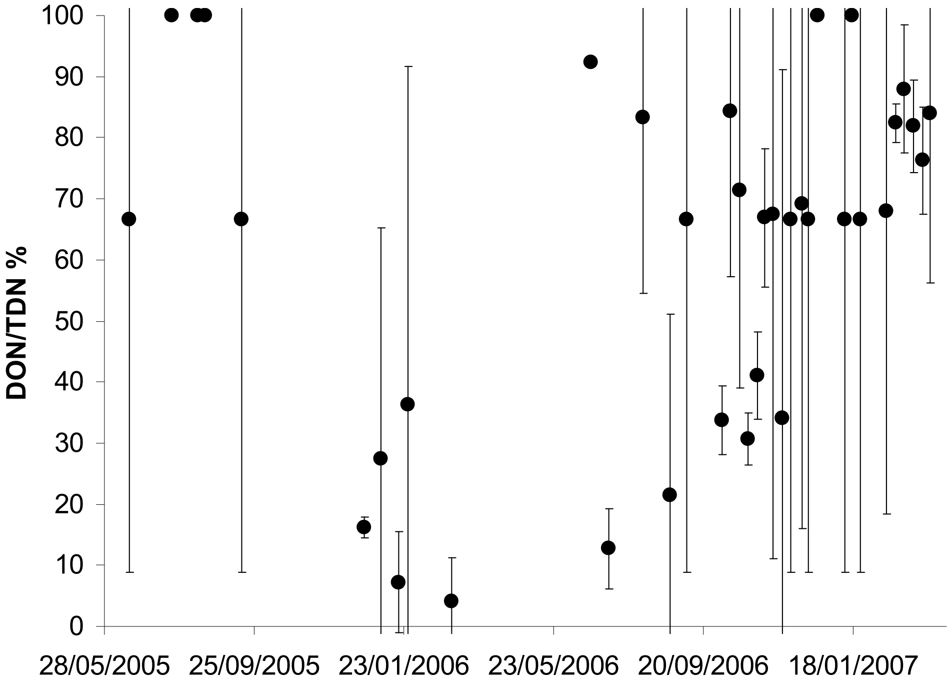


Figure 3.7: Weekly percentage of DON relative to TDN in wet deposition. Error bar shows standard deviation of 3 replicate samplers. Note that some of the DON may have been formed from transformation of DIN during sampling rather than being present originally in wet deposition (see text).

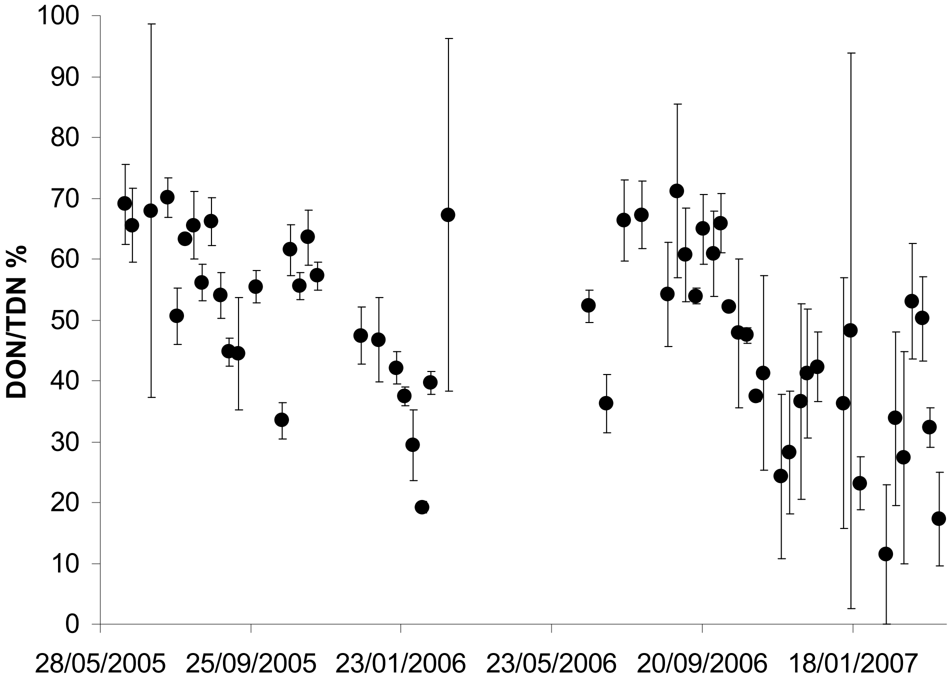


Figure 3.8: Weekly percentage of DON relative to TDN in dry deposition (funnel washings). Error bar shows standard deviation of 3 replicate samplers. Note that some of the DON may have been formed from transformation of DIN during sampling rather than being dry deposited directly (see text).

The data corresponding to the 25th of May 2006 and to the 6th of July 2006 have been included in the figures 3.3 to 3.8, but have not been included in the statistical analysis, as mineral nitrogen fertilizer was being applied to a nearby field on these dates, and may account for the large peaks in N deposition. However, 6th July 2006 is the only date in the whole period for which TDN in wet deposition was significantly higher than in dry deposition.

Table 3.1 presents the average amount of TDN and DON deposited in each type of collector, the average DON % relative to TDN, the average concentration of TDN and DON in rain, and the average volume of sample collected, either from rain (in bulk and wet deposition), or from washings (as dry deposition). The table is split into two parts: the first includes weeks with 3 valid replicates for at least one type of collector (38, 35 and 56 weekly samples for bulk, wet deposition and washings, respectively). The second part includes the 27 weekly samples with 3 valid replicates for all the 3 types of samples (bulk, wet deposition and washings). In this table, the standard deviation corresponding to the average amount deposited in the collector, the average sample volume, and the average concentration in rain refers to the differences between independent collectors of the same type. The standard deviation for the DON % relative to TDN, on the other hand, refers to the differences in the average deposition between the weeks included in that period. It has been presented in this way so the reader can have a grasp of the magnitude of deposition variability between weeks.

In theory, the addition of the washings and wet deposition together should be the same as bulk deposition. The large discrepancies found between bulk deposition and (wet + dry) deposition for N-containing solutes, but not other solutes (Cape et al., 2009), is discussed in section 3.2.3. “Standard versus flushing rain gauges”.

In a significant number of weeks, large differences were found between independent replicate samples for both types of sampler, but particularly for the wet deposition collectors. In most cases, the largest relative uncertainty in the DON:

TDN ratio is caused by low concentrations of nitrogen species in the sample, and the combined uncertainties associated with each of the species involved in the calculation of DON. The low concentration of TDN in wet deposition, compared to bulk deposition, is discussed below.

	Average Amount Deposited/ μmol N sample^{-1}		Standard Deviation of Amount Deposited in 3 replicate samplers/ μmol N sample^{-1}		Average % DON relative to TDN over all samples	Standard Deviation of %DON across all weekly samples	Rain Volume Collected/ L		Average Concentration in rain sample/ μM		Standard Deviation of Concentration across 3 replicate samplers/ μM		
	TDN	**DON**	**TDN**	**DON**	**DON**	**DON**	**Average**	**St. Dev.**	**TDN**	**DON**	**TDN**	**DON**	
Bulk Dep.	15.9	3.8	1.8	1.1	24	21	0.41	0.005	61	14	4.7	3.5	38 weeks with 3 valid replicates
Wet Dep.	2.6	1.2	0.2	0.3	47	33	0.36	0.005	9.9	5.4	0.8	0.3	35 weeks with 3 valid replicates
Washings (Dry Dep.)	8.1	4.3	0.4	0.2	53	16	0.3	0.009	N/A	N/A	N/A	N/A	56 weeks with 3 valid replicates
Bulk Dep.	14.2	3.3	1.7	0.9	23	23	0.39	0.008	56.1	11.5	3.6	2.4	27 weeks with 3 valid replicates for bulk and (wet+dry) deposition
Wet Dep.	2.3	0.8	0.2	0.2	36	35	0.36	0.012	10.8	3.7	1.8	0.3	
Washings (Dry Dep.)	7.5	3.7	0.4	0.2	49	15	0.35	0.013	N/A	N/A	N/A	N/A	
Wet+Dry Dep.	9.8	4.5	0.7	0.2	46	13	N/A	N/A	N/A	N/A	N/A	N/A	

Table 3.1: Amounts and concentrations of water-soluble nitrogen (total and organic) and rainfall amount deposited to each type of precipitation sampler (bulk, flushing) throughout the study period, for weeks in which there were valid samples from each of the 3 replicate samplers of each type.

3.2.2. Dry deposition versus wet deposition

In most of the samples, the dry deposition fraction (funnel washings) of water soluble N-containing species (both organic and inorganic) is significantly larger than the wet deposition fraction.

The weekly TDN deposition data (absolute amount, in µmoles N m^{-2} $week^{-1}$) from wet and dry deposition to the flushing gauge is shown in Figure 3.9. For comparison purposes, only the 49 weeks with 3 valid replicates for (dry + wet) deposition have been included (RSD <50% for sum of wet + dry deposition within replicates).

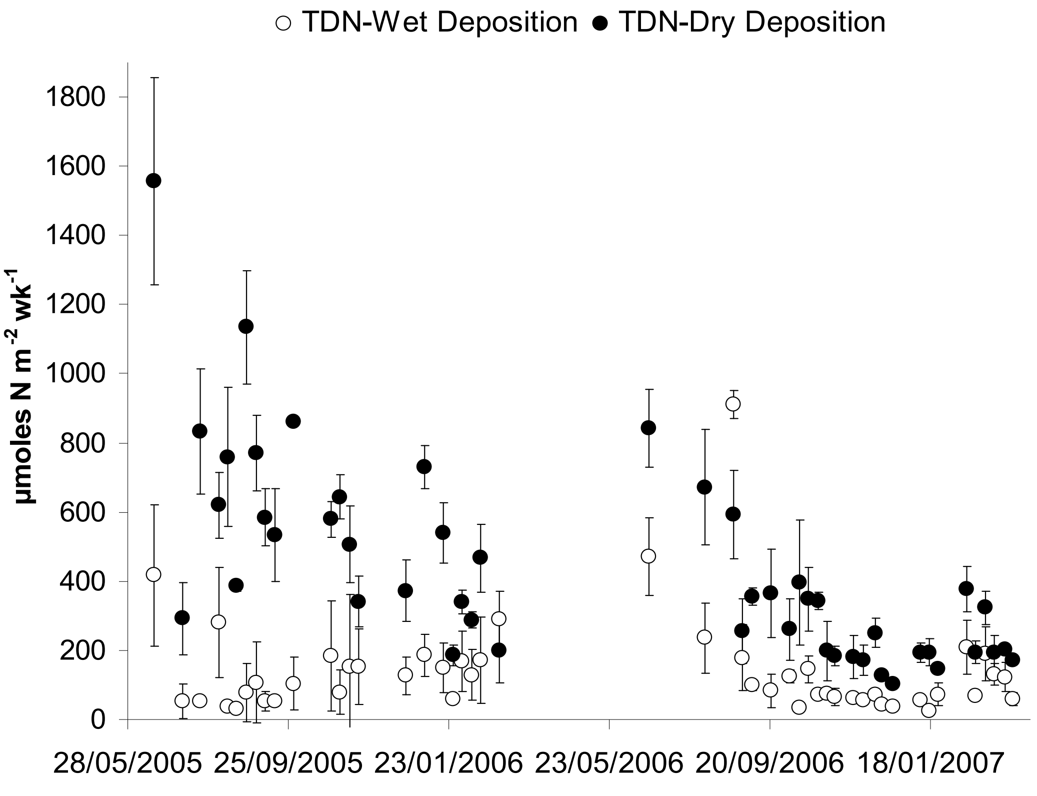


Figure 3.9: Weekly wet and dry deposition of TDN in µmoles N m^{-2} to the flushing samplers. Error bar shows standard deviation of 3 replicate samplers. Data for 6/7/2006 omitted because of likely contamination from local agricultural activity (cf. Figure 3.4).

Results from 2-way ANOVA statistical analysis for this set of data, after a Box-Cox transformation (power 0.6) was applied to the data in order to fulfil the assumptions of the model, showed highly significant ($P < 0.001$) effects of sample date and sample type (wet or dry).

The main source of variation corresponds to the variation between the two types of sample from the flushing rain gauges (dry and wet deposition). This effect is even larger than the one corresponding to sample date, which was expected to be very large. These results are in good agreement with the consistent differences between dry and wet deposition observed in Figure 3.9. The interaction term in the ANOVA was also significant ($P < 0.001$), but in only one week, out of 49 weeks with 3 valid replicates, was the amount of TDN collected from wet deposition clearly larger than from dry deposition.

3.2.3. Standard versus flushing rain gauges

3.2.3.1. Washing mechanism off: 15-week period (from 10/03/06 to 15/06/2006)

For a period of 15 weeks (from 10/03/06 to 15/06/2006) the flushing-washing mechanism of the flushing rain gauges was turned off, leaving the PTFE valve open to the rain collector. Data from this period allows direct comparison of bulk deposition between the standard rain gauges and the flushing rain gauges. For comparison purposes and statistical analysis, only 5 weeks out of the 15-week period had 3 valid replicates for both types of rain gauge. Bulk weekly TDN deposition (µmoles N m^{-2} wk^{-1}) in standard and (non-operating) flushing rain gauges is represented in Figure 3.10.

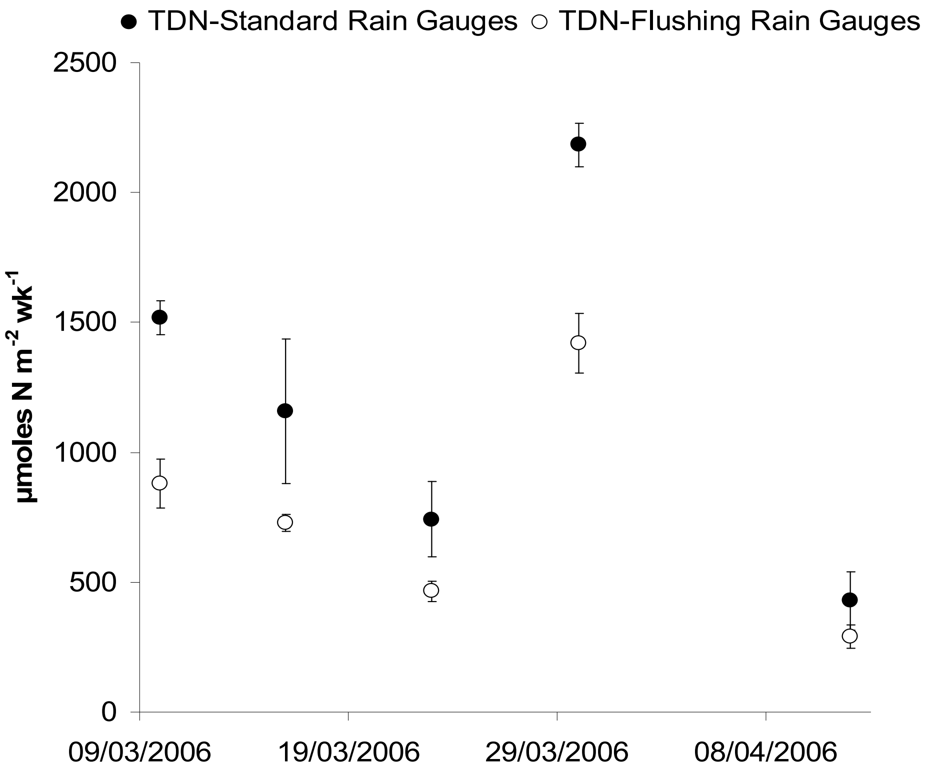


Figure 3.10: Weekly bulk deposition of TDN in µmoles N m-2 in standard and 'non-operating' flushing rain gauges. Error bar shows standard deviation of 3 replicate samplers.

Figure 3.10 clearly illustrates that the amount of TDN collected in all the 5 weeks with 3 valid replicates was larger in the standard rain gauges than in the flushing rain gauges, as confirmed by 2-way ANOVA, with $P < 0.001$ for both main effects of date and gauge type. This was an unexpected outcome, as the prior expectation was that both types of rain gauge (standard and flushing) should behave exactly the same when the flushing-washing mechanism was not in operation.

Initially, evaporation losses in standard rain gauges were contemplated as a plausible explanation for the discrepancies between standard rain gauges and flushing rain gauges. Such losses would explain the larger overall concentration of N species in standard rain gauges, as well as the lower concentrations of organic nitrogen species (see below - "DON production in flushing rain gauges"), which might include an important fraction of volatile compounds that would be lost along with water in the case of evaporation. However, this hypothesis was disproved by the experimental evidence, as no significant differences were observed between the rainfall amount between standard and flushing rain collectors (differences < 5%) or the concentrations of other solutes such as sodium, calcium, chloride and sulphate (Cape et al., 2009).

After discarding losses due to evaporation as an explanation, the most likely reason for the different behaviour of the two types of collector is losses of N-species along the 1.5m length of silicone tubing which connects the funnel to the rain collector in the flushing rain gauges, but not in the standard gauge, in which the funnel is connected directly to the sample bottle. Losses could either be due to biological activity in the tubing, which is a thymol-free area, despite being kept dark, or due to ion exchange processes between the sample and the silicone walls of the tubing. The extent of this effect is expected to be quite variable, as it would be strongly influenced by a number of factors such as temperature and rain volume. This loss of N during the sampling process has implications for estimating the relative importance of dry and wet deposition, as discussed below.

3.2.3.2. Washing mechanism on

The flushing rain gauges were performing as designed, i.e. discriminating between dry and wet deposition, for a period of 77 weeks. Figure 3.11 shows the total amount of TDN collected in standard rain gauges and in flushing rain gauges (washings + rain) each week. Only the 27 weeks with 3 valid replicates in each type of collector are included in the plot and in the statistical analysis.

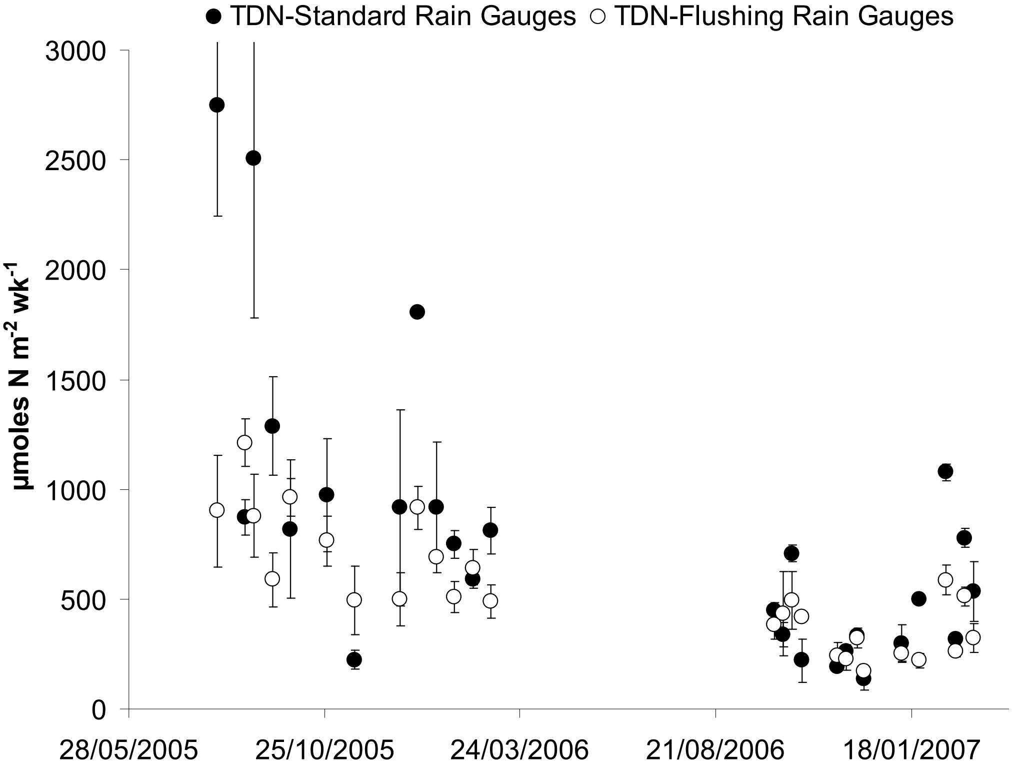


Figure 3.11: Weekly amount of TDN in µmoles N m^{-2} in standard rain gauges (bulk deposition) and flushing rain gauges (dry + wet deposition). Error bar shows standard deviation of 3 replicate samplers.

In this period of "washings on", there was also a tendency for a larger amount of N-containing species to be collected in standard rain gauges than in flushing rain gauges, but it is not so clear as in the period of "washings off", with a number of weeks with larger TDN collection in the flushing rain gauges than in the standard ones. ANOVA analysis of the dataset (after log-transformation) is consistent with these findings: variation between dates is the main source of variation, but the difference between the two types of rain gauges is still significant ($P < 0.001$).

The same reasons as during the period with washings switched off would explain results for those weeks with larger TDN collection in standard rain gauges than in flushing rain gauges, i.e. N losses along the 1.5 m long silicone tubing, either due to biological activity (as this is a biocide-free area) or due to ion exchange processes along the silicone wall surface. The results for those weeks with larger TDN amounts collected in the flushing rain gauges than in standard rain gauges could arise from one or more of the following:

i) a number of short and not very intense rain events during the collection period. (A short rain event would be enough to activate the washing mechanism in the flushing rain gauges, therefore efficiently collecting all dry deposition accumulated on the funnel surface. In the case of the standard rain gauges, on the other hand, the same short rain event might not have washed the funnel surface so efficiently and, therefore, the amount of N-species collected might be significantly smaller, at least the fraction coming from dry deposition).

ii) release of material retained on the tubing surfaces during the preceding sampling period (tubing was not cleaned each week)

iii) more efficient removal of dry-deposited material from the funnel surface by the 10% methanol wash solution than by rainfall.

3.2.3.3. DON "production" in flushing rain gauges

Summing over the 27 weeks with 3 valid independent replicates for each type of rain gauge, the total amount of TDN collected in standard rain gauges was 22 ± 3 mmoles N m^{-2}, and in the flushing ones (rain + washings) was 15 ± 1 mmoles N m^{-2}. However, the total amount of DON collected in the standard rain gauges was 5 ± 1 mmoles N m^{-2}, and in the flushing ones (rain + washings) was 7.0 ± 0.4 mmoles N m^{-2}. The type of gauge collecting smaller amounts of TDN (flushing rain gauge) collected larger amounts of DON (compare Figure 3.11 with Figure 3.12). The most likely explanation is that a portion of the 'lost' DIN is being transformed into DON inside the flushing rain gauges. Where and how this transformation occurs is a matter for further investigation.

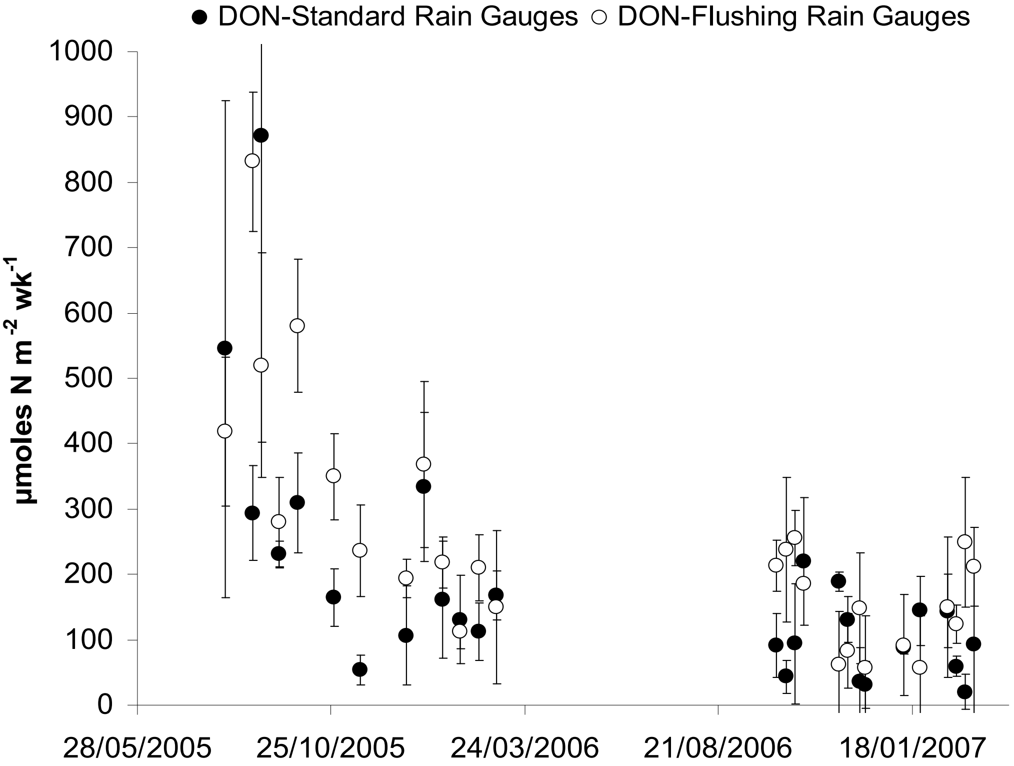


Figure 3.12: Weekly amount of DON in µmoles N m^{-2} in standard rain gauges (bulk deposition) and flushing rain gauges (dry + wet deposition). Error bar shows standard deviation of 3 replicate samplers.

3.2.4. Estimation of the relative contribution of wet and dry deposition

The lower and upper bounds to the contribution of dry deposition to the material collected by the standard rain gauge can be estimated from the above results as follows. If all transformations between different N forms are ignored (i.e. working with only the TDN data) then there are two extreme cases: (1) none of the dry deposited material was lost during sampling (a reasonable assumption as it was in 10% methanol solution), in which case the contribution of dry deposition to TDN is given by the amount collected as dry deposition as a fraction of the total collected by the standard gauge, i.e. over the 27 weeks of valid samples, 7.5/14.2 = 53% (Table 3.1); or (2) if the losses of N in the flushing gauge were entirely caused by losses from the dry deposition sample, the fraction of dry deposition would rise to (14.2-2.3)/14.2 = 84%.

For DIN, if transformations from DIN to DON are discounted and no losses from the washings occurred (case 1), the DIN deposited as dry deposition was 3.8/10.9 = 35% of the DIN in the standard sampler (Table 3.1). For case 2 (losses of DIN were all from washings) the contribution of dry deposition of DIN increases to (10.9-1.5)/10.9 = 86%. For DON, the average amount sampled as 'dry' deposition exceeded that recorded in the standard gauge (Table 3.1), implying either significant transformation from DIN to DON in the flushing sampler, or that all DON was dry deposited.

3.2.5. Estimation of the relative contribution of DON to wet and dry deposition

The loss of N from the flushing sampler leads to uncertainties in the apparent fraction of TDN contributed by DON, especially with the evidence that some transformation of DIN to DON occurred. For the standard bulk sampler, DON represented 23 ± 6% of TDN over the 27 weekly samples for which there was a complete data set, or 24 ± 7% of TDN for the 38 weekly samples for which there were 3 replicate standard bulk samples (Table 3.1). These figures should be compared with a value of 26% for 7 weekly samples at the same site in 2000 (Cape et al., 2001) or 33% for 54 weekly samples in 2000-2 (Cape et al., 2004) using steel and glass bulk samplers, rather than polyethylene funnels and bottles. The construction materials may not be important, given that the earlier study showed no significant difference between different construction materials.

The present study suggests that the contribution of DON to TDN may differ between wet and dry deposition. For wet deposition, the proportion of DON in the collected samples was 36 ± 9%, but the contribution of DON to wet deposition as measured in the standard bulk sampler is uncertain because of the losses in the flushing sampler. Because on average more DON was found in the combined (wet+dry) deposition than in the standard sampler, despite overall losses of TDN, this figure represents the upper bound to the contribution of DON to wet deposition.

The fraction could have been as low as 12%, calculated as the amount of DON measured in wet deposition relative to TDN in the standard sampler less TDN measured as dry deposition, i.e. assuming all the ‘missing’ N from the flushing sampler was originally present as DIN. However, this figure might be even lower, as it has been calculated assuming that no transformation of DIN into DON occurred in wet deposition. By similar arguments, the measured contribution of DON to dry deposition can be calculated as 49 ± 4% based on analysis of the funnel washings, but this could include at least 16 ± 15% from conversion of DIN to DON in the washings, calculated from the excess of DON measured in the flushing samplers compared with the bulk samplers (Table 3.1). The contribution of DON to dry deposition of TDN is therefore likely to be 33% or less. The lower bound can be calculated assuming all the ‘missing’ N in the flushing sampler is DIN, and that the smallest contribution from DON in the dry sampler occurs if none of the DON in the wet sampler comes from conversion of DIN, giving a value of 21%.

3.3. Conclusions

This study presents further evidence of the importance of water-soluble organic nitrogen (WSON) species in the boundary layer. On average, over the 27 weekly samples with 3 valid replicates for all the collectors, dissolved organic nitrogen (DON) represented 23 ± 6% of the total dissolved nitrogen (TDN) measured in bulk deposition, similar to the proportion of DON observed at this site previously.

The relative contribution of DON to TDN in wet and dry deposition is uncertain because of losses of N within the flushing sampler, but the upper bound to the contributions is 36 ± 9% for wet deposition and 33 ± 15% for dry deposition.

Dry deposition of particles and gas on the funnel surface, rather than deposition in rain, seems to be the main source of N-containing species (both inorganic and organic) to the bulk sampler, contributing between 53% and 84% of total N.

In general, larger amounts of N-containing species were collected in the standard bulk samplers than in the flushing samplers. This was particularly true during the period when the washings were not in operation (from 10/03/06 to 15/06/2006). This result implies chemical or biological interactions in the tubing leading from the funnel to the sampling bottle, which might be reduced by replacing silicone tubing with PTFE tubing, and by changing the tubing on each sampling occasion. This finding has implications for all types of precipitation sampler in which the funnel and the sample bottle are separated by a length of tubing – a common design.

In the flushing rain gauges, dissolved inorganic nitrogen (DIN) seems to be transformed into DON. This phenomenon requires further investigation. Biological activity transforming DIN into DON in the tubing would be a plausible explanation, despite the lack of light. It would be restricted only to the tubing, as both collecting bottles (rain and washings) are protected with thymol (a very effective biocide) against biological degradation. Another explanation might be in the rinsing solution for the washings, which contains 10% methanol to aid wetting of the funnel surface and to prevent freezing of the wash solution. Chemical reaction between DIN and methanol to produce organic material is unlikely, but the methanol wash solution may be more effective at removing dry deposited organic nitrogen from the funnel than rain water.

4. Quantification of gas and particle phase water-soluble organic and inorganic nitrogen at the CEH & Easter Bush

One of the key findings from the experimental work described in Chapter 3 was that dry deposition of particles and gas on the funnel surface, rather than wet deposition, was the main contributor of N-containing species in bulk rain samples (between 53% and 84% of total N).

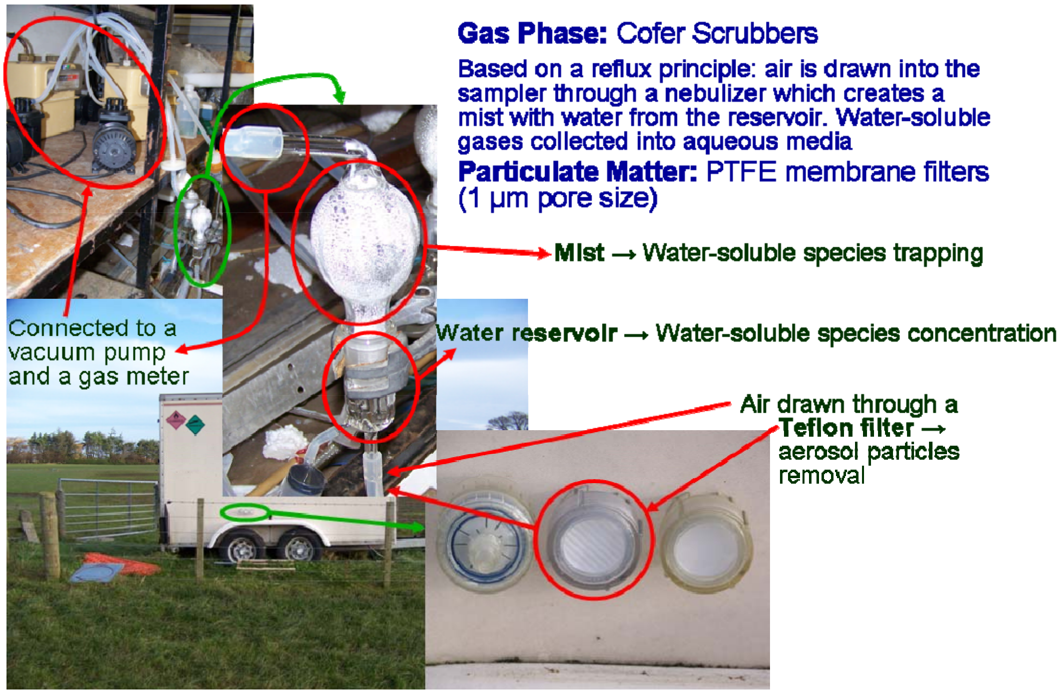
The next step in this study consisted of the experiment described in this chapter, which was designed to monitor daily atmospheric concentrations of the different water soluble nitrogen (WSN) species in the boundary layer, and to discriminate between what is in the gas phase (GP) and what is within particulate matter (PM).

4.1. Experimental

4.1.1. Collection methods

Gaseous WSN species were collected in Cofer samplers, and particulate WSN species were collected on PTFE membrane filters placed at the Cofer samplers' inlets, as illustrated in Figures 4.1 and 4.2 and described in more detail below.

Figure 4.1: View of the sampling caravan at Easter Bush sampling site.



Boundary layer water soluble species sampling

Gas Phase: Cofer Scrubbers

Based on a reflux principle: air is drawn into the sampler through a nebulizer which creates a mist with water from the reservoir. Water-soluble gases collected into aqueous media

Particulate Matter: PTFE membrane filters (1 µm pore size)

Mist → Water-soluble species trapping

Water reservoir → Water-soluble species concentration

Air drawn through a **Teflon filter** → aerosol particles removal

Connected to a vacuum pump and a gas meter

Figure 4.2: Detail of the adapted Cofer sampling set up used to collect water soluble gases and particular matter in the boundary layer.

4.1.1.1. Collection of WSN species in gas phase (Cofer samplers)

Gaseous WSN species were collected in Cofer samplers (Figure 4.3), also called Cofer scrubbers (Spaulding et al., 2002). These samplers are based on the nebulization/reflux principle: air is drawn into the sampler round the outside of a nebulizer which creates a mist from water entrained into the nebulizer from the reservoir. The fine aqueous drops provide a large interfacial surface area where water-soluble gases are quantitatively scrubbed into the mist. The mist droplets impact on the wall of the chamber, where small droplets coalesce into larger ones, consequently falling back into the reservoir to be recycled (Cofer and Edahl, 1986, Sciare and Mihalopoulos, 2000, Spaulding et al., 2002).

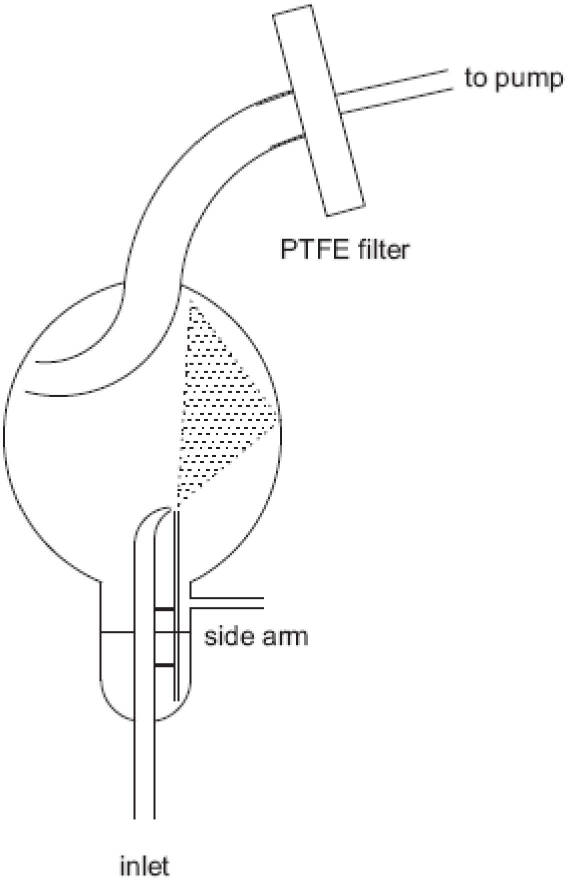


Figure 4.3: Schematic diagram of Cofer sampler used in this study. Drawing produced by Professor J. N. Cape. Source: González Benítez, J.M., Cape, J.N. and Heal, M.R., 2010. *Gaseous and particulate water-soluble organic and inorganic nitrogen in rural air in southern Scotland.* Atmospheric Environment 44 (12), 1506-1514.

Penetration of mist droplets downstream of the sampler is prevented by use of a PTFE membrane filter that excludes liquid water. The initial volume of water used in the reservoir of the Cofer sampler in this study was 10 mL, and the air flow rate through the sampler was about 5 L min^{-1}, just enough to maintain nebulization in the chamber. The total volume of air sampled was measured using a dry gas meter. A flow rate of 3 L min^{-1} was sufficient to provide efficient nebulization with the nebulizer geometry used, and high recoveries (>80%) have been reported at much higher flow rates (25-30 L min^{-1}) (Spaulding et al., 2002), but high flow rates lead to rapid evaporation of the sampling solution which limits the sampling duration. For most sampling a flow rate of 5 L min^{-1} was used as a compromise between minimizing evaporation of the sampling solution and maximising the volume of air sampled. The Cofer sampler air inlet was equipped with a PTFE membrane filter to remove aerosol particles, which were analysed separately.

Prior to sampling, all glassware was soaked overnight in 15% (v/v) dichlorodimethylsilane in toluene, and then rinsed with toluene, methanol, and dichloromethane (three times each) and dried at 150 °C (Spaulding et al., 2002). The silanization procedure makes glass surfaces hydrophobic, thereby preventing water soluble species from attaching to the glassware and improving the recirculation of nebulised droplets within the sampler.

At the end of sampling the contents of each sampler were collected into a disposable syringe attached to the water reservoir inlet. The sampler was then rinsed 3 times with a few mL of high purity water (specific resistivity > 18 MΩ cm) to collect any water-soluble material retained on its internal surfaces. The rinsings were collected into the same disposable syringe (and mixed with the rest of the sample). The syringe was then detached from the sampler and its contents placed into a pre-weighed and pre-silanized glass vial. The volume of sample was calculated from reweighing the vial. Vials were then stored at 4 °C prior to analysis. No biocide was added to preserve the samples as chemical analysis was performed a few days after collection.

4.1.1.2. Collection of WSN species in particulate matter (PTFE filters)

Particle-phase WSN species were collected on upstream PTFE membrane filters (Whatman, 1 µm pore size, 47 mm diameter) which removed aerosol particles from the air stream prior to the nebulizer. Water soluble compounds were collected from the filters into aqueous solution by immersing the filters in 10 mL of high purity water (specific resistivity > 18 MΩ cm) and then doubly extracted for 15 min each time in an ultrasonic bath (Duan et al., 2009). Samples were then filtered through a 0.2 µm pore-size inorganic membrane filter (Whatman, Anotop 10 IC) before chemical analysis. The same procedure was applied to the blank samples (high purity water doubly extracted in ultrasonic bath and filtered through a 0.2 µm pore-size inorganic membrane filter) to monitor any contamination that might have occurred during the extraction process. Aqueous samples from filter extracts were stored at 4 °C before analysis. No biocide was added to preserve the samples as chemical analyses were always performed within a few days after collection.

Three independent samplers were used: two had open-faced filter holders which gave more uniform surface coverage for aerosol capture, but could be adversely affected by rain. The third one had an enclosed filter holder, preventing rain ingress but providing a less uniform surface area for particle filtration and the possibility of losses of gaseous material (e.g. nitric acid) to the filter holder surface.

4.1.2. Study sites

Atmospheric water-soluble nitrogen species, both in the gas phase and in particulate matter, were sampled daily over a period of 4 months, from July to November 2008. The sampling campaign was divided into two different periods and locations (both in southern Scotland, less than 1 km apart). During the first sampling period, from 23rd July 2008 to 21st August 2008, the sampling site was located at the Centre for Ecology & Hydrology (N55°51’44’’, W3°12’19’’), in a ‘science park’ within 1 km of mixed farming (arable and dairy). During the second sampling period, from 26th

August 2008 to 21st November 2008, the sampling site was located at Easter Bush field site, a grassland area, mostly covered by perennial ryegrass (*Lolium perenne*), used for silage production and sheep grazing. Both sampling sites were located at 190 m above sea level, 15 km south west of Edinburgh centre and 1 km east of the Pentland Hills.

At the CEH sampling site, the air inlets of the Cofer samplers were placed at 2 m above ground, facing north-east. The main objective during this period was to evaluate the collection efficiencies of the Cofer samplers and PTFE membrane filter samplers with respect to WSN compounds. To evaluate 'breakthrough', two of the Cofer samplers were connected in series, so that any material not scrubbed by the first Cofer sampler would be collected in the second, and subsequently quantified. An additional third Cofer sampler was placed in parallel with the two in series in order to monitor reproducibility. The air inlets of the two sets of Cofer samplers were placed 10 cm apart and equipped with PTFE membrane filters (Whatman, 1 μm pore size, 47 mm diameter).

At the Easter Bush sampling site, the air inlets of the Cofer samplers were placed at 1 m above ground, facing south-west. The main aim during this period was to measure the typical concentrations of the different species under study (water soluble organic nitrogen (WSON), ammonium and nitrate) in an intensely managed grassland area. All the samples were collected in triplicate, with the three Cofer samplers running singly in parallel. At this site the air inlets of the Cofer samplers were just 1 cm apart and, as in the previous sampling site, each of them was equipped with a PTFE membrane filter (Whatman, 1 μm pore size, 47 mm diameter). Two of these were open-faced filters and one an enclosed filter.

In both studies, all Cofer aqueous samples and extracted PTFE filter samples were analysed for total dissolved nitrogen and for ammonium and nitrate using the analytical methods described in Chapter 2. Final worked-up concentrations were expressed as nmol N per m^3 of air.

4.1.3. Sample quality control

Several criteria were used to identify valid samples, both from Cofer samplers and from PTFE membrane filters.

In the case of Cofer samplers, the minimum reservoir water volume for a sample to be regarded as valid was set at 3 mL (see Section 4.2.1). The method assumes that the mist remains a sink for water-soluble species, and does not approach solution equilibrium. Samples with lower volumes might have caused the aqueous concentration of WSN species to become saturated, leading to inefficient removal, or even release back into the gas phase. Nine Cofer scrubber samples out of a total of 132 collected at Easter Bush sampling site were discarded for this reason.

The quality control test for particulate matter samples (collected on PTFE membrane filters) consisted of quantitative comparison between results from the open-face samplers and the enclosed filter sampler. In the open-face samplers most of the filter area was exposed to the atmosphere, allowing a very effective and uniform particle matter deposition across the whole membrane filter. However, the filters were vulnerable to wetting by heavy rain showers, in particular when the rain event was associated with south-west gusts of wind. In the other sampler, on the other hand, the filter was placed inside a sealed plastic holder with a small inlet of 0.5 cm diameter at the top of a 3 cm long cylinder, effectively preventing any rain from reach the PTFE membrane filter. This design provided full protection against rain, however, it might not be as efficient at collecting particulate matter as the open-face design. For this reason, the samples that yielded lower water soluble total nitrogen (WSTN) air concentrations for open-face samplers than for the enclosed sampler were discarded, in case part of the water soluble material had been removed from the PTFE membrane filters by rain. 23 filter samples collected on

PTFE membrane filters, out of a total of 168 from Easter Bush sampling site, were discarded for this reason.

For statistical analyses only those dates with three valid replicates for each type of collector were included, limiting the set of samples to 37 dates (out of 44) from the Easter Bush sampling site. Dates with three valid samples but with relative standard deviation (RSD) for air concentration of WSTN greater than 100%, for either the Cofer or filters, were regarded as "suspicious" and removed from the statistical analysis, as important discrepancies within collectors of the same type might suggest that an unnoticed problem had occurred in one or more of the samples on that particular date, either during collection or processing. Only 2 of the 37 remaining dates were discarded for this reason. An additional date (28th of August 2008) was removed from the statistical analysis, as nitrogen fertilizer (urea, 35 kg N/ha) was being applied on the field on that date. However, the data were recorded (see below).

4.2. Results

4.2.1. CEH sampling: Efficiency tests for Cofer scrubbers and PTFE filter samplers

The first sampling period (23rd July to 21st August 2008) was carried out at the CEH site, and was mainly devoted to evaluating the efficiencies of the Cofer scrubbers and the PTFE membrane filter samplers for collection of water soluble nitrogen (WSN) species in gas phase and particulate matter respectively.

4.2.1.1. Efficiency tests for Cofer samplers

The Cofer scrubbers' efficiency estimation was achieved by comparison of the derived gas phase concentrations of the different species under study obtained from the second Cofer scrubber in series versus the first Cofer scrubber in series. Figures 4.4, 4.5, 4.6 and 4.7 show these second Cofer versus first Cofer scatter plots for each of total water soluble nitrogen (TWSN), ammonium, nitrate and water soluble organic nitrogen (WSON), respectively.

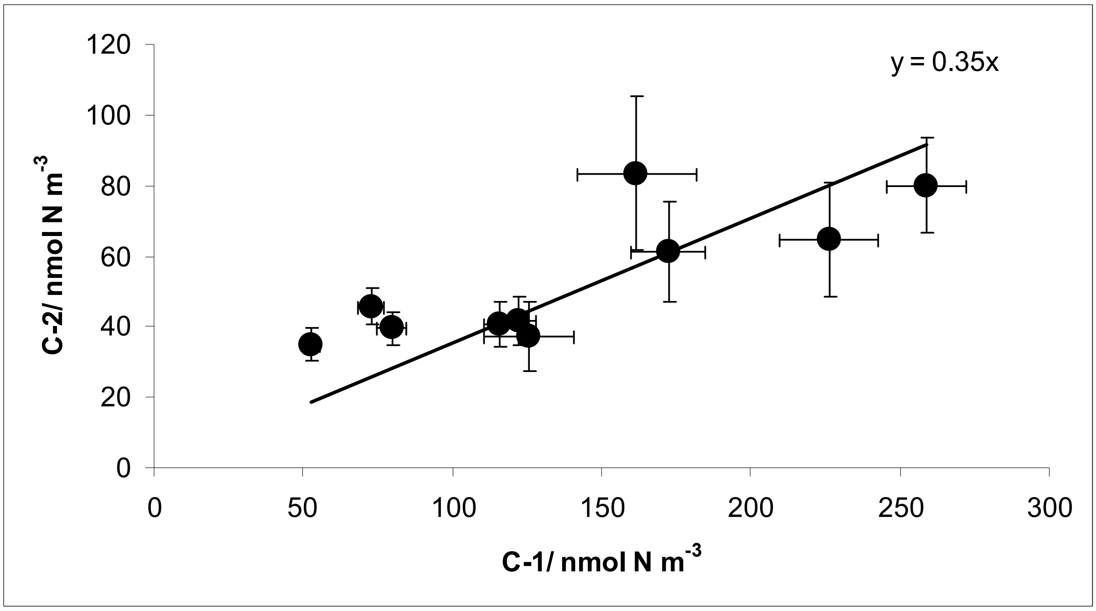


Figure 4.4: Comparison of results for the Cofer scrubbers in series: the second Cofer scrubber of the series (C-2) versus the first Cofer scrubber of the series (C-1) for gas phase (GP) total water soluble nitrogen (TWSN) concentrations in nmol N m^{-3}. Error bars show the limit of detection (LOD) of the analysis. In this context, LOD is used as an indicator of uncertainty in the concentration measurement.

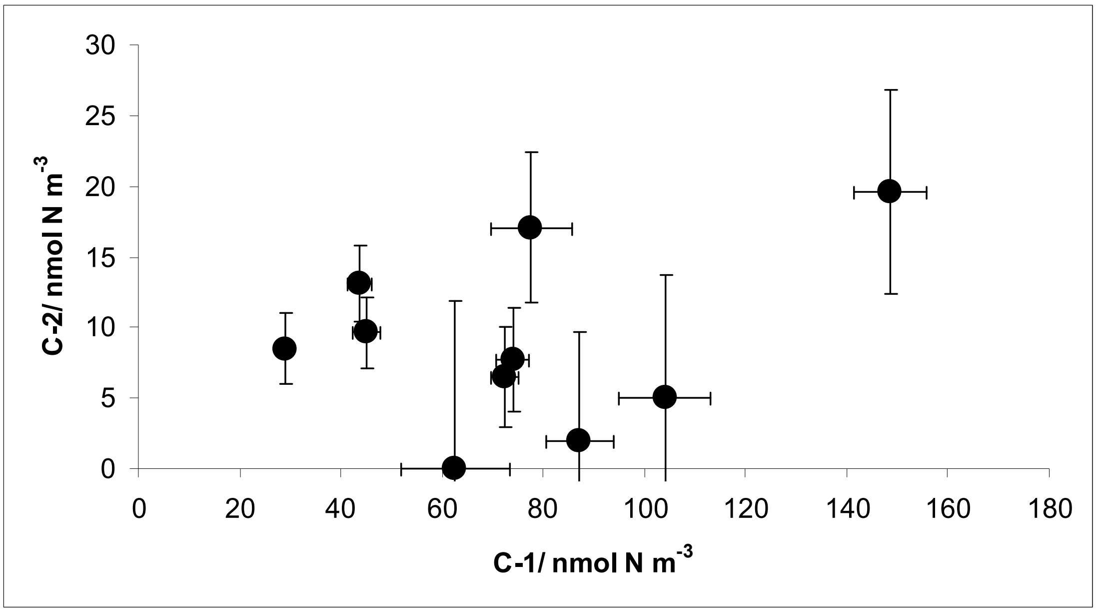


Figure 4.5: Comparison of results for the Cofer scrubbers in series: the second Cofer scrubber of the series (C-2) versus the first Cofer scrubber of the series (C-1) for gas phase (GP) ammonium concentrations in nmol N m^{-3}. Error bars show the limit of detection (LOD) of the analysis. In this context, LOD is used as an indicator of uncertainty in the concentration measurement.

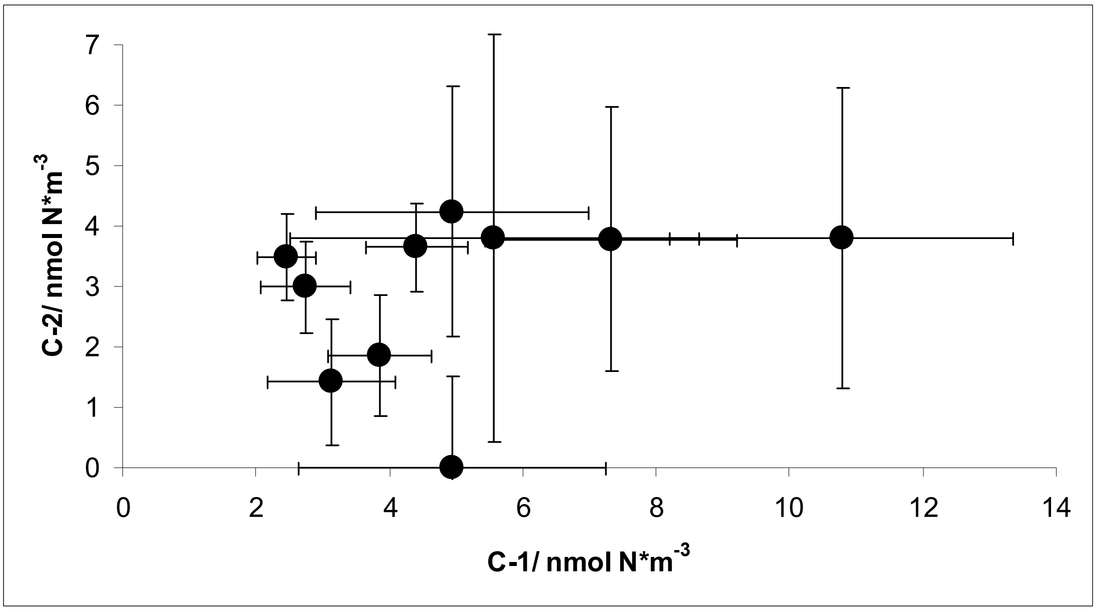


Figure 4.6: Comparison of results for the Cofer scrubbers in series: the second Cofer scrubber of the series (C-2) versus the first Cofer scrubber of the series (C-1) for gas phase (GP) nitrate concentrations in nmol N m^{-3}. Error bars show the limit of detection (LOD) of the analysis. In this context, LOD is used as an indicator of uncertainty in the concentration measurement.

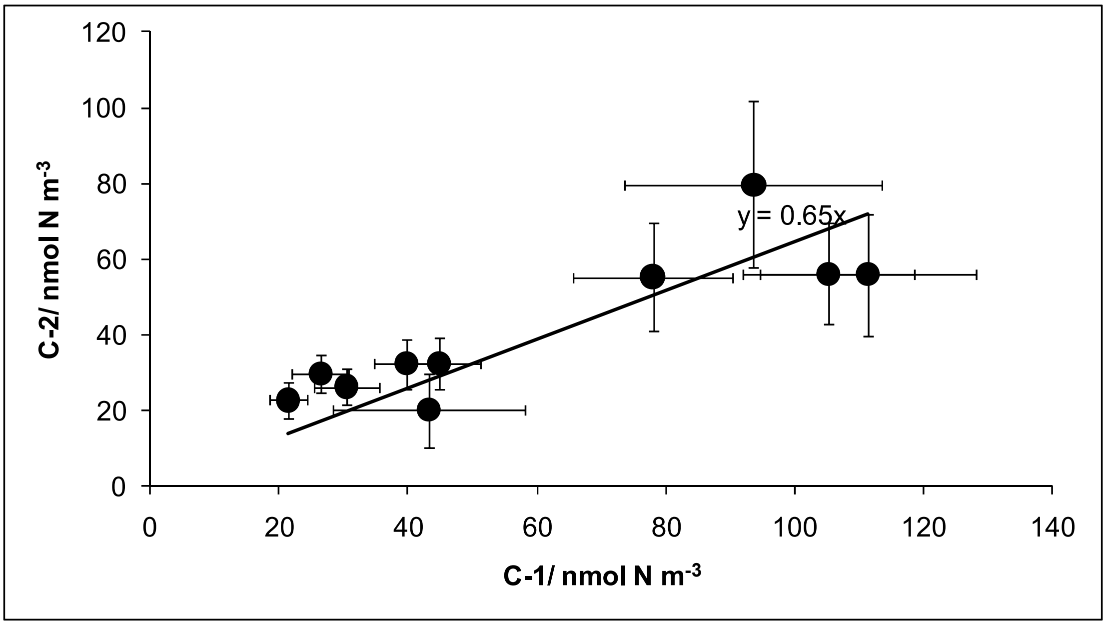


Figure 4.7: Comparison of results for the Cofer scrubbers in series: the second Cofer scrubber of the series (C-2) versus the first Cofer scrubber of the series (C-1) for gas phase (GP) water soluble organic nitrogen (WSON) species concentrations in nmol N m^{-3}. Error bars show the propagated uncertainty in the concentration measurement due to the indirect determination of WSON.

According to this test, the trapping efficiency of a single Cofer scrubber seems to vary significantly depending on the species under analysis. For TWSN, the trapping efficiency of the gas phase into the first Cofer scrubber is ~ 74 ± 4% (within a 95% confidence level), as determined from the gradient of Figure 4.4 (i.e. 0.74 = 1 – (0.35/1.35)), this regression is in the limit of statistical significance (p = 0.057), but the efficiency calculated using the average of all the valid concentrations of samples collected in the first and the second Cofer samplers (~72%) agrees well with the value of the regression.

For gas phase ammonium, collection into Cofer scrubbers is very efficient. There is very little carry over from the first to the second Cofer scrubber, and the regression corresponding to Figure 4.5 is statistically not significant. (p = 0.387). For this reason, the regression gradient was not used to calculate trapping efficiency. Calculation of trapping efficiency using the average concentration of all valid samples collected in the first and the second Cofer samplers yield a value of ~89%.

For nitrate, the trapping efficiency of the gas phase into a Cofer scrubber is low. In most of the samples, nitrate concentration is close to the limits of detection, and proportionally large carry over from the first to the second Cofer scrubber is observed. Due to proportionally large variability in the carry over from first to second Cofer scrubber, regression of nitrate concentration of samples collected into the first and second Cofer scrubber is statistically not significant ($p = 0.376$). For this reason, the regression gradient was not used to calculate trapping efficiency. As an orientation value, trapping efficiency was calculated by using the average concentration of all valid samples collected in the first and the second Cofer samplers, a value of ~63% was obtained.

For WSON, the trapping efficiency of the gas phase into a Cofer scrubber is ~ 61±5% (within a 95% confidence level), as determined from the gradient of Figure 4.7 (i.e. $0.61 = 1 – (0.65/1.65)$), this regression is statistically highly significant ($p = 0.003$), and the efficiency calculated using average concentration of all valid samples collected in the first and the second Cofer samplers (~59%) agrees well with the value of the regression. In the case of WSON, the proportion of carry over is much more constant than for nitrate, and the concentrations collected far higher. Both observations point to better trapping efficiency for WSON than for nitrate, despite the "orientation" value of ~63% efficiency for nitrate.

As already mentioned, Figure 4.5 for ammonium shows there is no significant correlation between results from the second and first Cofer sampler in the series. Which is likewise a good indicator of the excellent trapping efficiency of gas phase ammonia into Cofer samplers, as the poor correlation between both sets of results is due to the very low concentration of ammonia (in comparison with the total in the gas phase) that breaks through the first Cofer sampler. In fact, in the context of WSN species, ammonium is the only species that should be used as reference for estimating gas phase efficiency collection into Cofer scrubbers. The reason for this is that the source of ammonium in gas phase is ammonia, a very water soluble N-species (88.9 g/100 mL at 0 °C) and also a compound of major interest in this study.

In contrast to ammonium, the concentrations of nitrate collected in the two Cofer samplers in series are of the same order of magnitude (Figure 4.6). The concentrations are also close to the limit of detection. Nitrate should not be used as a reference for estimating gas phase efficiency collection into Cofer scrubbers. This is because nitrate collected into a Cofer scrubber has two main sources: nitric acid and nitrogen dioxide. Nitric acid is completely miscible in water, so if it was the only source of nitrate in the gas phase then nitrate would be an ideal reference compound for estimations of trapping efficiency of gas phase WSN material into aqueous solution inside Cofer scrubbers. On the other hand, nitrogen dioxide is only slightly water soluble. Nitrogen dioxide is trapped into aqueous solution by transformation into nitrate and nitrite through a redox reaction.

$$3H_2O + 2NO_2 \rightleftarrows NO_2^{-*} + NO_3^- + 2H_3O^+$$

*Note: any NO_2^- formed would react quickly with ambient ozone also dissolved in the aqueous phase to give NO_3^-.

This process is of course not so quick as direct solvation into water, so consequently atmospheric nitrogen dioxide is inefficiently trapped in a Cofer scrubber and most of it passes unreacted to the second Cofer scrubber to give approximately equal contributions to both Cofer scrubbers. During this study, the fraction of nitrate trapped in the second Cofer scrubber was ~ 37% on average. Assuming that all nitrate collected in this second sampler was originally in the form of nitrogen dioxide, and that the same fraction of nitrogen dioxide was collected in the first Cofer scrubber, then it can be estimated that from the total nitrate collected in aqueous solution in both samplers, an average of 74% was originally in the form of nitrogen dioxide, and an average of 26% in the form of nitric acid. In the boundary layer, nitrogen dioxide concentrations are typically 20 times larger than nitric acid concentrations (Tang et al., 2009), so if nitric acid capture efficiency is 100% then capture efficiency for nitrogen dioxide in a single Cofer scrubber is approximately 7%. This is fine for the purposes of this study, which is focused on the fraction of N species that can potentially be trapped in the rain, but confirms that nitrate cannot be used as a reference compound in the estimation of Cofer scrubber sampling efficiency. The poor correlation between nitrate results from the first and the second Cofer samplers in series (despite being of the same order of magnitude) is presumably due to fluctuations in the atmospheric ratio of nitric acid / nitrogen dioxide.

The scatter plot for WSON (Figure 4.7) shows that, as for nitrate, a large fraction of gas phase WSON breaks through the first Cofer scrubber and is collected in the second Cofer scrubber. The same explanatory comments regarding different gas phase source species can be applied to WSON as for nitrate. Some components of WSON are easily dissolved in water, and therefore would be very efficiently collected in the first Cofer scrubber, whereas the less water-soluble components would behave more like nitrogen dioxide. A proportion would therefore pass through the first Cofer scrubber to the second scrubber to give significant contributions to both samplers.

The data for TWSN (Figure 4.4) show a significant fraction of material collected in the second Cofer scrubber of the series, but this is because TWSN includes ammonium, nitrate and WSON, and as explained above there are good reasons why there is breakthrough for nitrate and WSON. For this reason TWSN also cannot be used as a reference for testing the Cofer scrubber's efficiency either.

A major cause of concern in the use of Cofer scrubbers for air sampling is their vulnerability to evaporation of the trapping solution, in particular in dry atmospheric conditions. Therefore, another aim of this test period was to assess to what extent evaporation issues might affect sample quality.

In this study, a single Cofer scrubber proved to be far more vulnerable to evaporation of the trapping solution than Cofer scrubbers in series, both first and second of the series. The most likely reason for this was the additional restriction that two Cofer scrubbers in series caused to the air flow from the vacuum pump: through the whole period of study, the volume of air that went through the Cofer scrubbers in series was approximately half of that going through the single Cofer scrubber, despite using the same vacuum pump in both settings.

In order to asses the extent to which evaporation issues might affect sample quality, refilling of Cofer scrubbers was kept to an absolute minimum, just enough for the aqueous solution in the reservoir to reach the capillary.

Comparison of ammonium recovery results in a single Cofer scrubber (SCS) and in the first of the two Cofer scrubbers in series (named "CS1") shows that trapping efficiency for SCS is on average 83 % of that in CS1 (see Figure 4.8), and the R^2 value for a linear regression between results from both samplers is relatively low: 0.80.

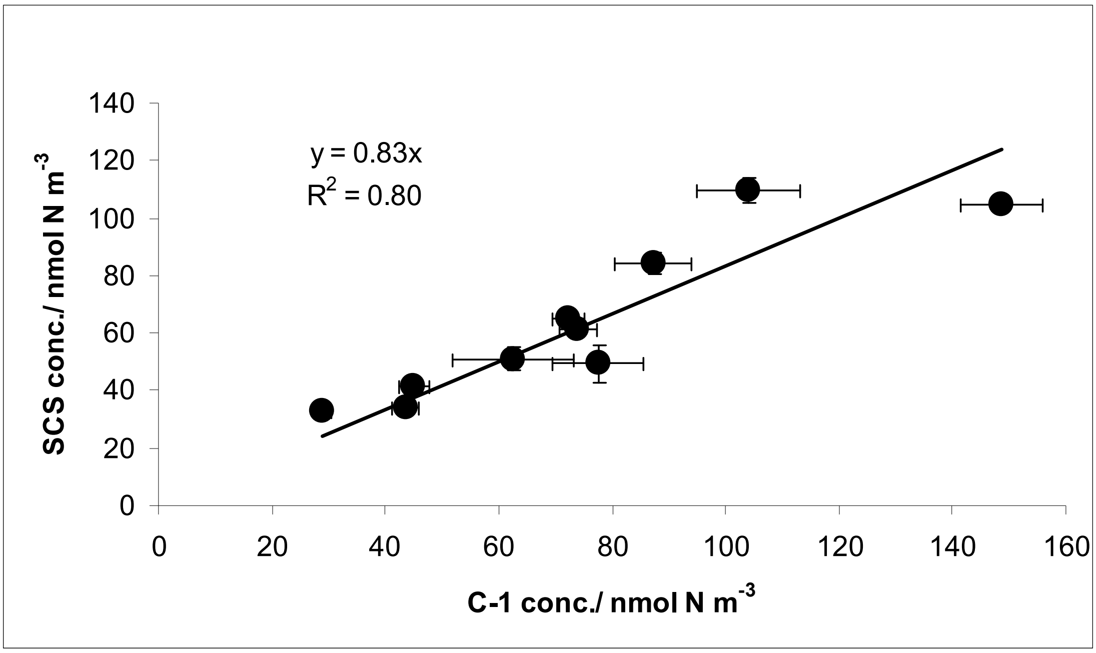


Figure 4.8: Comparison of results for a separate single Cofer scrubber (SCS) versus the first Cofer scrubber (C-1) of the two in series for gas phase ammonium concentrations in nmol N m^{-3}. Error bars show the limit of detection (LOD) of the analysis. In this context, LOD is used as an indicator of uncertainty in the concentration measurement.

However, the results for only those dates in which the single Cofer scrubber has a final water volume (in the water reservoir) larger than 3 mL, are very different:

ammonium trapping efficiency of the SCS is on average 101 % of that in CS1 (see Figure 4.9), and the R^2 value is very high: 0.98.

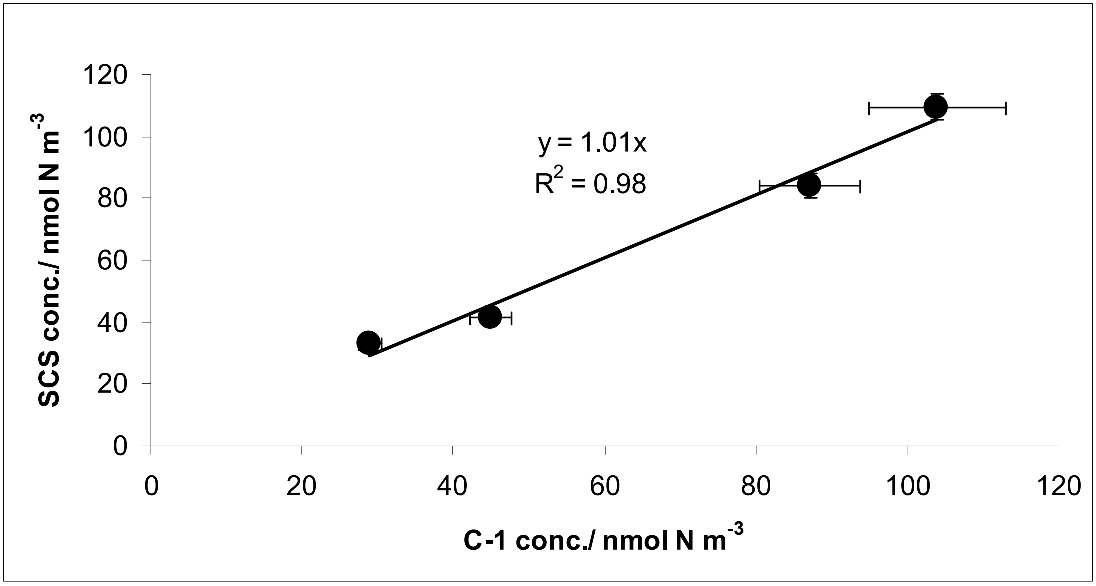


Figure 4.9: Comparison of results for a separate single Cofer scrubber (SCS) versus the first Cofer scrubber (C-1) of the two in series for gas phase ammonium concentrations in nmol N m^{-3}. Only those dates in which the single Cofer scrubber had a final water volume (in the water reservoir) larger than 3 mL are included. Error bars show the limit of detection (LOD) of the analysis. In this context, LOD is used as an indicator of uncertainty in the concentration measurement.

In contrast, for those dates on which the SCS presented a final water volume lower than 3 mL, ammonium trapping efficiency of the SCS was on average only 74% of that in the CS1, and the R^2 value of 0.90 relatively low compared to dates with more liquid present (Figure 4.10).

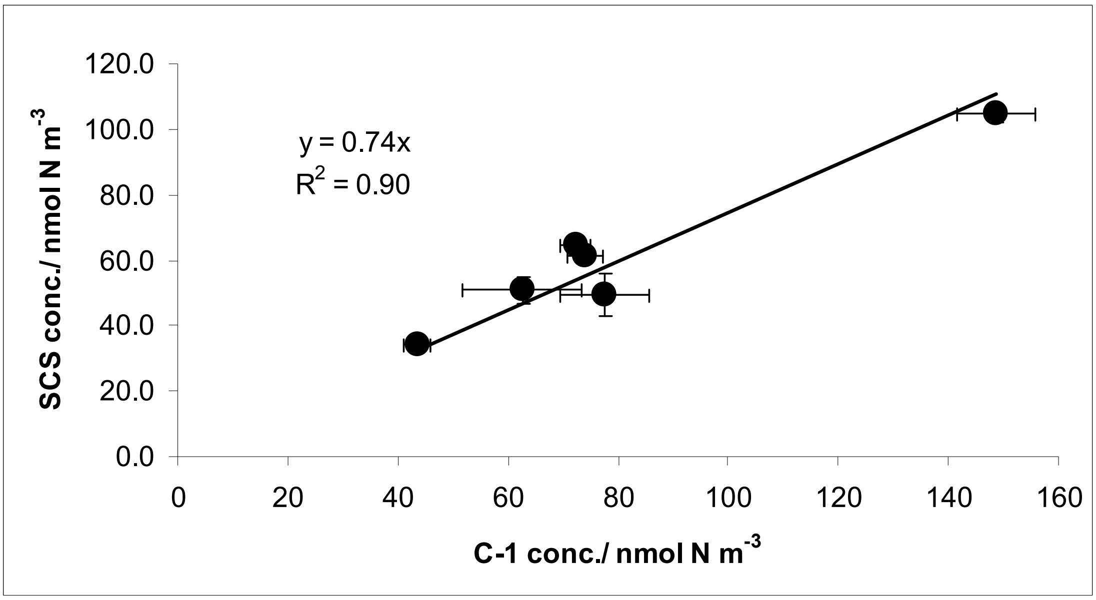


Figure 4.10: Comparison of results for a separate single Cofer scrubber (SCS) versus the first Cofer scrubber (C-1) of the two in series for gas phase ammonium concentrations in nmol N m^{-3}. Only those dates in which the single Cofer scrubber had a final water volume (in the water reservoir) smaller than 3 mL are included. Error bars show the limit of detection (LOD) of the analysis. In this context, LOD is used as an indicator of uncertainty in the concentration measurement.

These results clearly document that evaporation issues can affect the collection efficiency of Cofer scrubbers. The most likely explanation for this behaviour is that if the volume in the Cofer scrubber water reservoir drops below a certain threshold level, saturation of the trapping solution or even partial re-evaporation of material already trapped in the solution might occur, leading to underestimation of the concentration of WSN species in the gas phase. In those instances in which the water volume in the Cofer scrubber reservoir remained above 3 mL, on the other hand, no losses of material would be observed.

After careful study of the results, the "acceptable" threshold level for the water reservoir volume in a Cofer scrubber was set at 3 mL. Therefore, for the purposes of this study, Cofer samples in which water reservoir volume dropped below 3 mL during the sampling period are regarded as "suspicious", and are not included in the data analysis.

4.2.1.2. Efficiency tests for PTFE membrane filter samplers

PM collection on PTFE membrane filters was also tested during this period. Two types of filter holder were tested and compared: open-faced filter samplers and enclosed filter samplers. Comparison of results from TWSN species deposited on enclosed and open-faced filter samplers across all sampling dates shows comparable PM trapping efficiency between the enclosed filter sampler and the open-faced one (see Figure 4.11). On average, the enclosed filter sampler presents a ~103% efficiency in relation to the open-faced one with an R^2 value for the linear regression between them of 0.94.

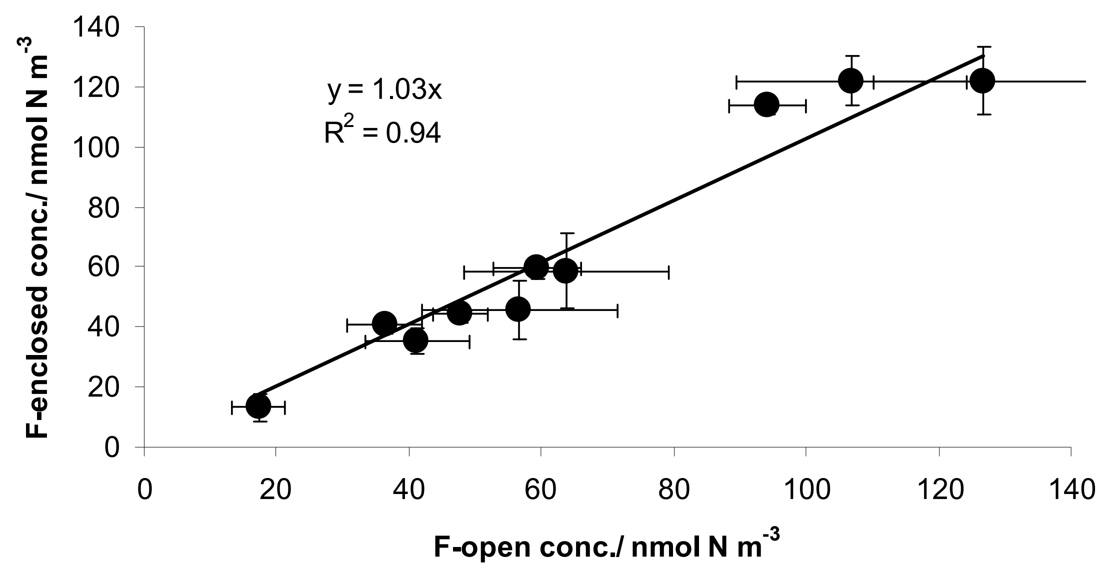


Figure 4.11: Comparison of results for an enclosed-faced PTFE membrane filter sampler (F-enclosed) versus an open PTFE membrane filter sampler (F-open) for particulate matter (PM) TWSN concentrations in nmol N m^{-3}. Error bars show the limit of detection (LOD) of the analysis. In this context, LOD is used as an indicator of uncertainty in the concentration measurement.

The next step in this study was to discriminate between dates with dry weather or light rainfall, and dates with heavy rain events: for dates with dry weather or light rainfall, the PM WSN species trapping efficiency of the enclosed filter in comparison with the open-faced one is on average ~94%, and the R^2 value of the linear regression between results from both samplers is very high (0.99) (see Figure 4.12). These results suggest that in dry weather conditions open-faced filter samplers are slightly more efficient PM collectors than the enclosed filter samplers. This is not surprising, since in the open-face samplers most of the filter area is exposed to the atmosphere, allowing a more effective and uniform particle matter deposition across the whole membrane filter than in the enclosed filters.

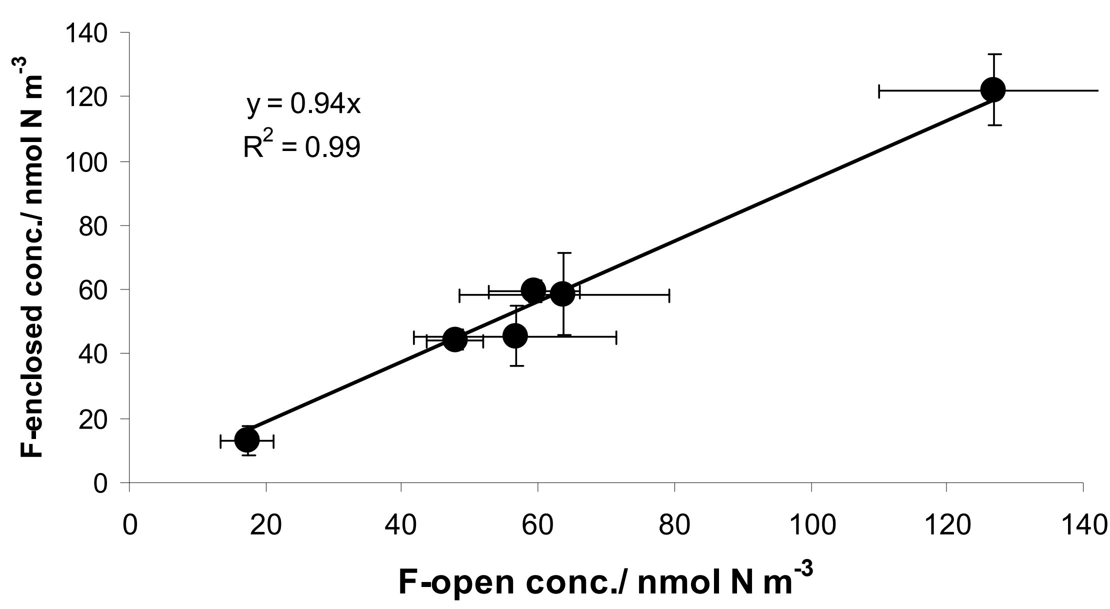


Figure 4.12: Comparison of results for an enclosed-faced PTFE membrane filter sampler (F-enclosed) versus an open PTFE membrane filter sampler (F-open) for PM TWSN concentrations in nmol N m^{-3} for only those dates classified as dry weather or light rainfall. Error bars show the limit of detection (LOD) of the analysis. In this context, LOD is used as an indicator of uncertainty in the concentration measurement.

For dates with heavy rain events, the trapping efficiency for PM WSN species on the enclosed filter sampler in comparison with the open-faced filter sampler is on average ~ 114%, and the R^2 value of the linear regression between results from both samplers is 0.97 (see Figure 4.13). Although the difference between Figures 4.12 and 4.13 is consistent with the suspected vulnerability of some material on open-faced filter samplers to being washed away during heavy rain events, the difference in the gradients of the two plots does not actually reach formal statistical significance. The upper and lower 95% confidence levels for the slope of the regression between enclosed filter samplers and open-faced filter samplers for dry or light rainfall days (Figure 4.12) are 0.94 ± 0.06, whilst for heavy rainfall days (Figure 4.13) are 1.14 ± 0.16. Thus the confidence levels for the magnitude of the two slopes overlap.

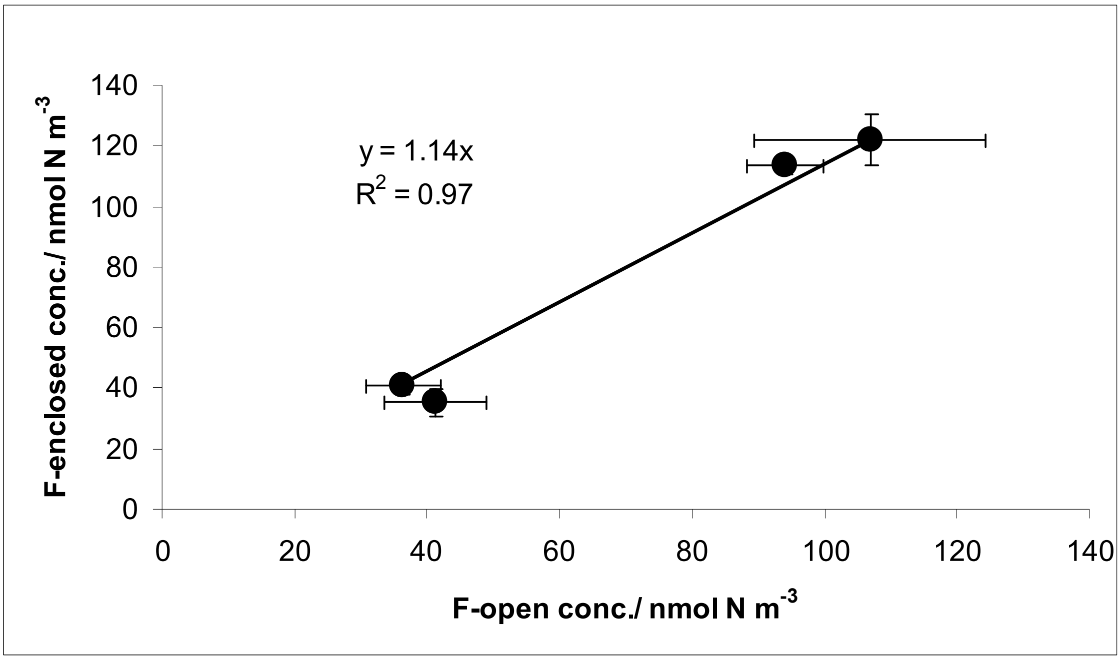


Figure 4.13: Comparison of results for an enclosed-faced PTFE membrane filter sampler (F-enclosed) versus an open PTFE membrane filter sampler (F-open) for PM TWSN concentrations in nmol N m^{-3} for only those dates classified as heavy rainfall. Error bars show the limit of detection (LOD) of the analysis. In this context, LOD is used as an indicator of uncertainty in the concentration measurement.

Both filter samplers (enclosed and open-faced) were used in the second sampling site (Easter Bush). The very small PM collection efficiency differences found between enclosed and open-faced filter samplers did not justify removing enclosed filter samplers from this study, as they are excellent tools for aerosol sampling quality control assessment, in particular if a heavy rain event occurs.

4.2.2. Easter Bush sampling: intensively managed grassland area

4.2.2.1. General overview

Over the whole sampling period, concentrations of all the species under study (ammonium, nitrate and water soluble organic nitrogen) were above the limit of detection in most of the samples. However, there were large differences in the concentrations of the different species. Overall, the dominant species was ammonium, in particular from the gas phase.

Before any further analysis is presented, it should be remembered that in the Easter Bush sampling site, gas phase samples were collected into three independent single Cofer scrubbers, which might lead to significant underestimation of gas phase WSON concentrations due to sampling inefficiencies described in the initial experiments (see section 4.2.1.1). The extent of sampling efficiency will depend on the actual composition of the material sampled, and might be as low as ~61 %. Gas phase WSON reported data have not been corrected for sampling efficiency. With regards to water soluble inorganic nitrogen (WSIN) species, the main source of ammonium collected into Cofer scrubbers (i.e. gas phase source) is ammonia, whereas the main sources of ammonium collected on PTFE membrane filters (i.e. in particulate matter) are ammonium nitrate and ammonium sulphate. The main sources of nitrate from the gas phase are nitric acid and nitrogen dioxide, and whilst nitric acid is very efficiently collected into a Cofer scrubber, only a small fraction of nitrogen dioxide in gas phase is trapped into the Cofer scrubbers. In PM, for excess ammonia gas conditions, like the ones found in Easter Bush, the main source of nitrate is ammonium nitrate, and the main source of sulphate is ammonium sulphate. Therefore, in PM, ammonium concentration should correspond to the sum of nitrate concentration plus two times sulphate concentration. For this reason sulphate was included in the chemical analysis performed on each sample, as ion balance would provide an additional quality control test for the PM collected on PTFE membrane filter samples.

Figure 4.14 shows the averaged ion balance results ($[NO_3^- + 2SO_4^{2-}]$ vs. $[NH_4^+]$) for the three independent PTFE membrane filter samplers used in this study. Only data with 3 valid replicates are included. Error bars show the standard deviation across the 3 replicate samplers. The figure shows that there is very good correlation between $[NO_3^- + 2SO_4^{2-}]$ and $[NH_4^+]$. The slope value of greater than unity is entirely consistent with an additional fraction of sulphate from marine aerosol origin. Some of the additional charge would be balanced by acidity or cations other than NH_4^+.

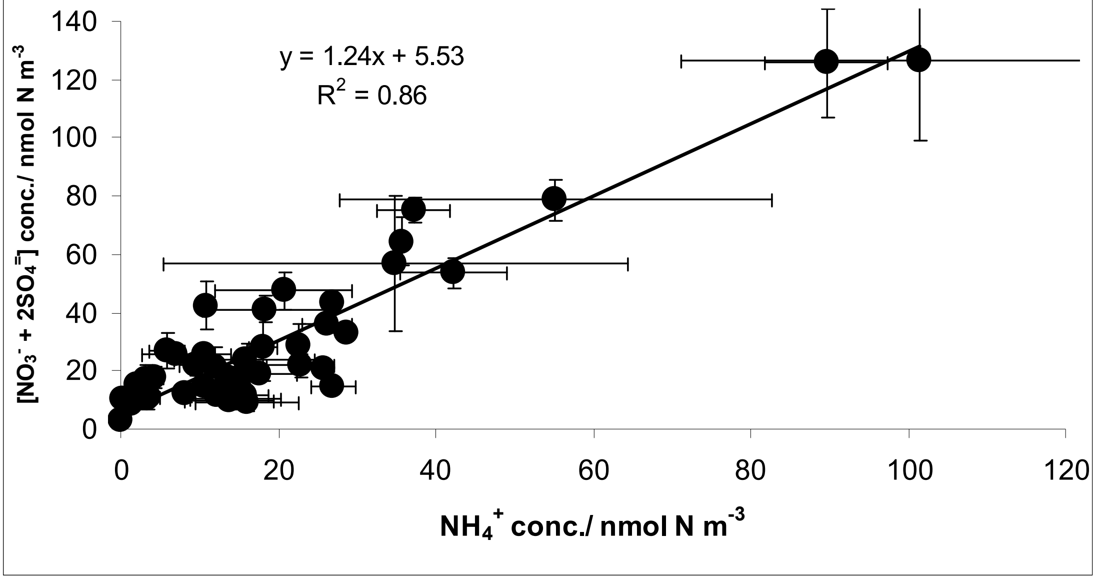


Figure 4.14: Ion balance results for PM water soluble inorganic nitrogen (WSIN) collected in PTFE membrane filter samplers in nmol N m^{-3}. Only those dates with 3 valid replicates are included. Error bar shows standard deviation of 3 replicate samplers.

Figure 4.15 shows the time series of the gas phase (GP) concentrations of ammonium, nitrate and water soluble organic nitrogen (WSON) in nmol N m^{-3}. Only those dates with 3 valid replicates are included. Error bars show standard deviation of the replicate samplers.

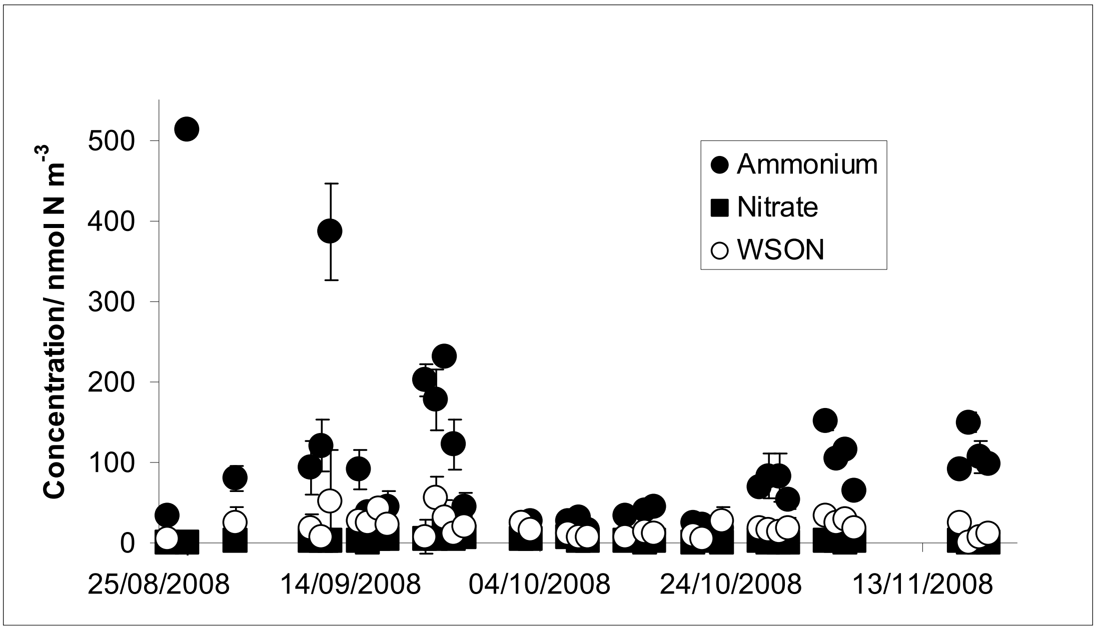


Figure 4.15: Daily gas phase concentrations of ammonium, nitrate and water soluble organic nitrogen (WSON) in nmol N m^{-3}. Only those dates with 3 valid replicates are included. Error bar shows standard deviation of 3 replicate samplers.

In order to improve scale resolution, the two obvious ammonium outliers (dates 28th August 2008 and 12th September 2008) were removed in Figure 4.16.

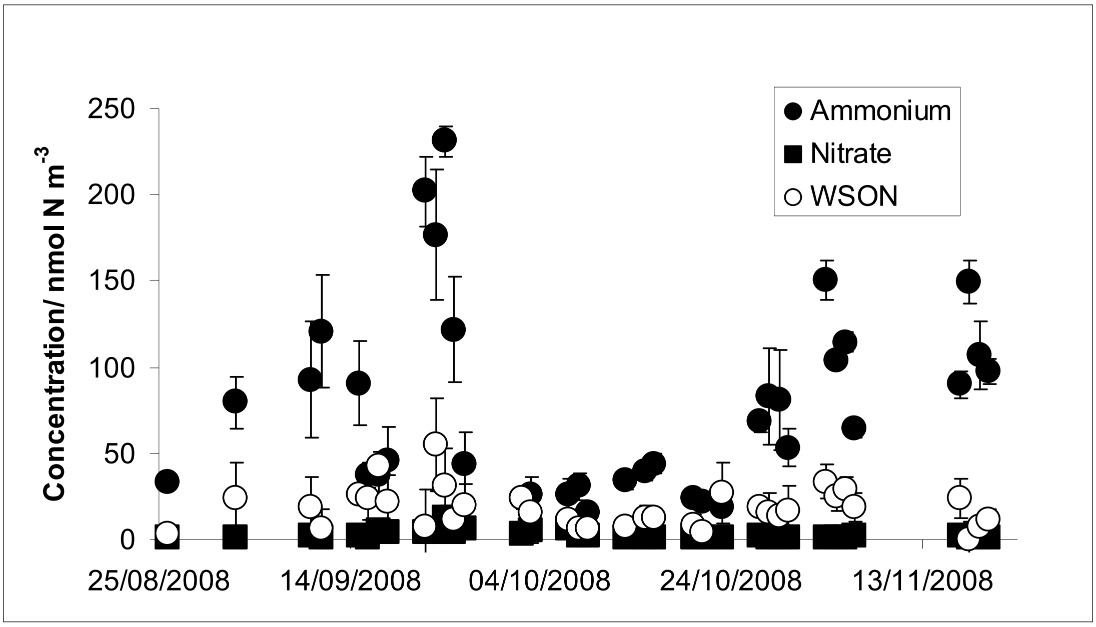


Figure 4.16: Daily gas phase concentrations of ammonium, nitrate and water soluble organic nitrogen (WSON) in nmol N m^{-3}. Two obvious outliers for ammonium concentrations have been removed. Error bar shows standard deviation of 3 replicate samplers.

Figure 4.17 shows the time series of the PM concentration of ammonium, nitrate and water soluble organic nitrogen (WSON) in nmol N m-3. Only those dates with 3 valid replicates are included. Error bars show standard deviation of the replicate samplers.

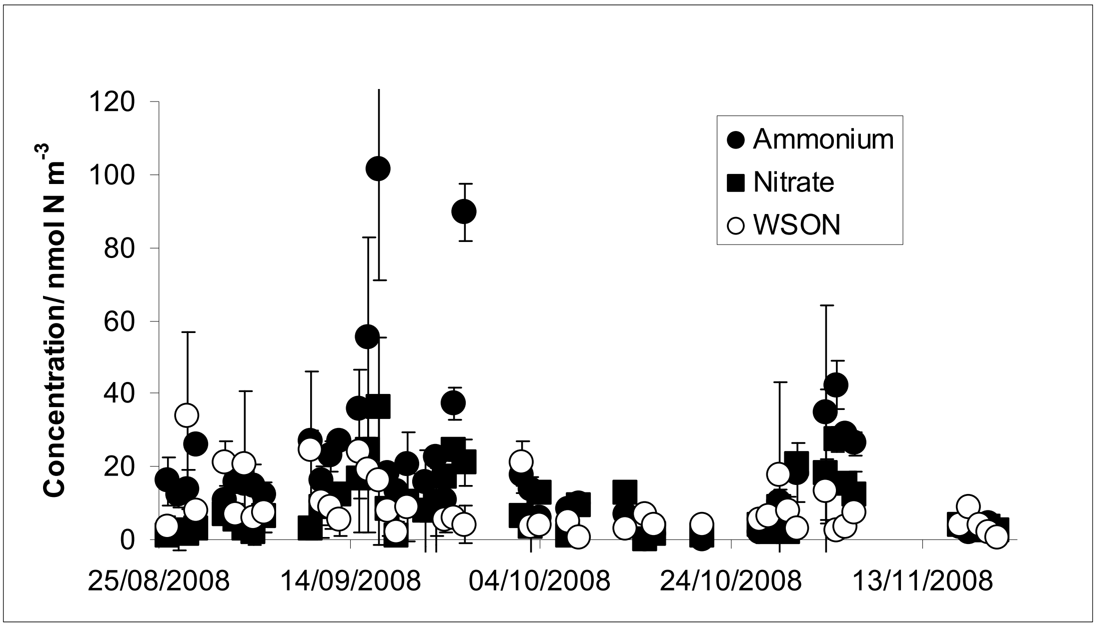


Figure 4.17: Daily particulate matter concentrations of ammonium, nitrate and water soluble organic nitrogen (WSON) in nmol N m^{-3}. Only those dates with 3 valid replicates are included. Error bar shows standard deviation of 3 replicate samplers. Vertical scale differs from gas phase (Figure 4.16).

In general, WSN species concentrations were larger in GP than in PM. Ammonium was the dominant species both in GP and in PM. Significant amounts of WSON species were found both in GP and PM. Nitrate concentrations found in this study were quite low, and it is the only species that presented lower concentrations in GP than in PM.

During the period 2nd – 21st October 2008 there seems to be a decline in the boundary layer concentrations of WSN species, both in GP and in PM. Three parameters were investigated in relation to these observations: temperature, weather conditions and wind direction. However, there was no obvious correlation between any of these and the observed drop in WSN species concentrations. A time series of daily mean temperature (in °C) and TWSN concentrations in GP and PM (in nmol N m^{-3}) is presented in Figure 4.18. The decline in TWSN concentrations does not seem to be correlated with changes in temperature: The Pearson product moment correlation coefficient (R) between temperature and TWSN in GP is -0.007, and between temperature and TWSN in PM is 0.239. Weather conditions do not seem to be related to the drop in WSN species concentrations in the period 2nd – 21st October 2008 either, as in this period 62 % of the samples were collected in dry weather, and only 38 % of the samples were collected in rainy conditions. Changes in the wind direction also does not seem a plausible explanation, as the prevailing wind direction during the period 2nd – 21st October 2008 is south-west, the same as during the rest of the period of study from 26th August 2008 to 21st November 2008. The most likely explanation for the decline in WSN species concentration is simply the relocation of livestock to a different grazing place during this short period (2nd – 21st October 2008): CCTV footage of the sampling site confirmed that all the sheep were removed from the south grazing field during a period of time spanning from the 24th September 2009 to the 20th October 2009, returning to the field on the 21st October 2009.

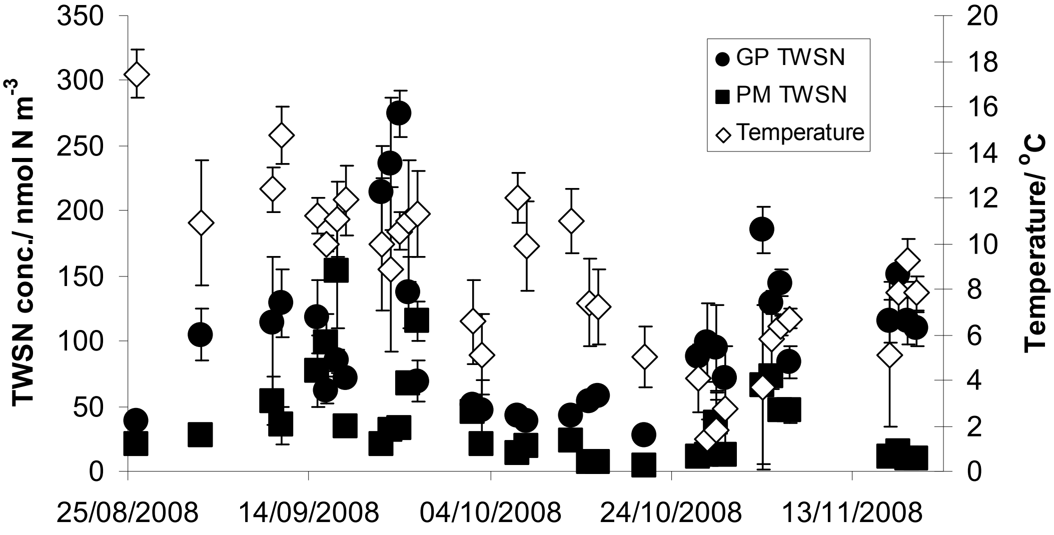


Figure 4.18: Time series of gas phase total water soluble nitrogen (GP TWSN) and particulate matter total water soluble nitrogen (PM TWSN) in nmol N m^{-3} and average temperature. Error bar for GP TWSN and PM TWSN show standard deviation of 3 replicate samplers. Error bar for temperature show standard deviation of 48 measurements across the day.

Figures 4.19, 4.20 and 4.21 plot the time series of the percentages of each of ammonium, nitrate and WSON relative to the total water soluble nitrogen (TWSN) species in the gas phase. Error bars show standard deviation of 3 replicate samplers.

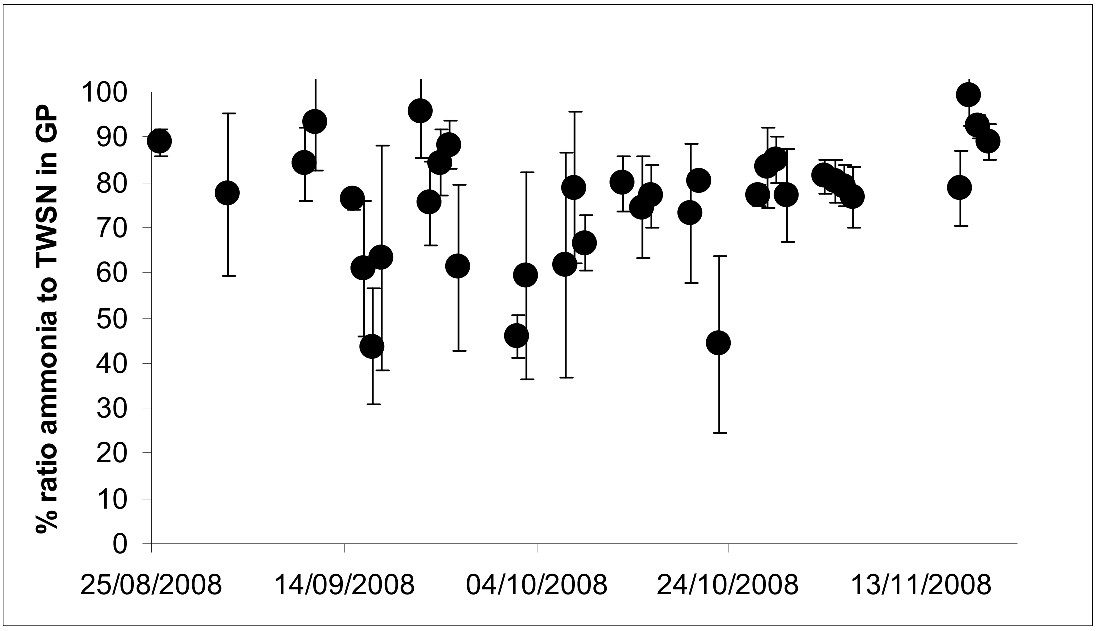


Figure 4.19: Time series of gas phase percentage of ammonia relative to the total water soluble nitrogen (TWSN) species. Error bar shows standard deviation of 3 replicate samplers.

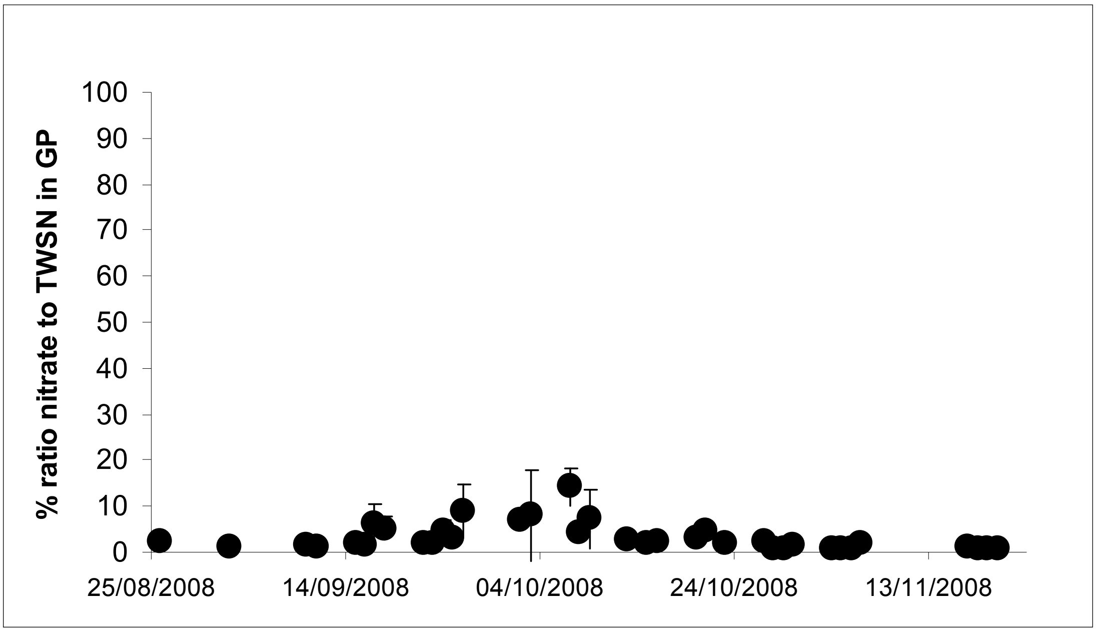


Figure 4.20: Time series of gas phase percentage of nitrate relative to the total water soluble nitrogen (TWSN) species. Error bar shows standard deviation of 3 replicate samplers.

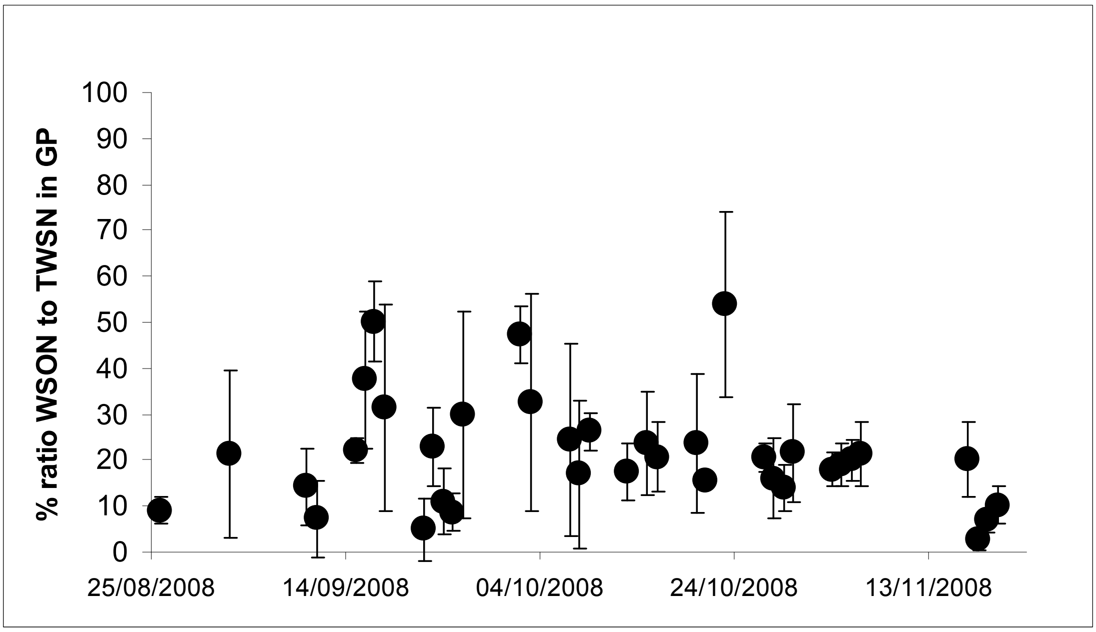


Figure 4.21: Time series of gas phase percentage of water soluble organic nitrogen (WSON) species relative to the total water soluble nitrogen (TWSN) species. Error bar shows standard deviation of 3 replicate samplers.

Similarly, Figures 4.22, 4.23 and 4.24 plot the time series of the percentages of each of ammonium, nitrate and WSON relative to the total water soluble nitrogen

(TWSN) species in particulate matter. Error bars show standard deviation of 3 replicate samplers.

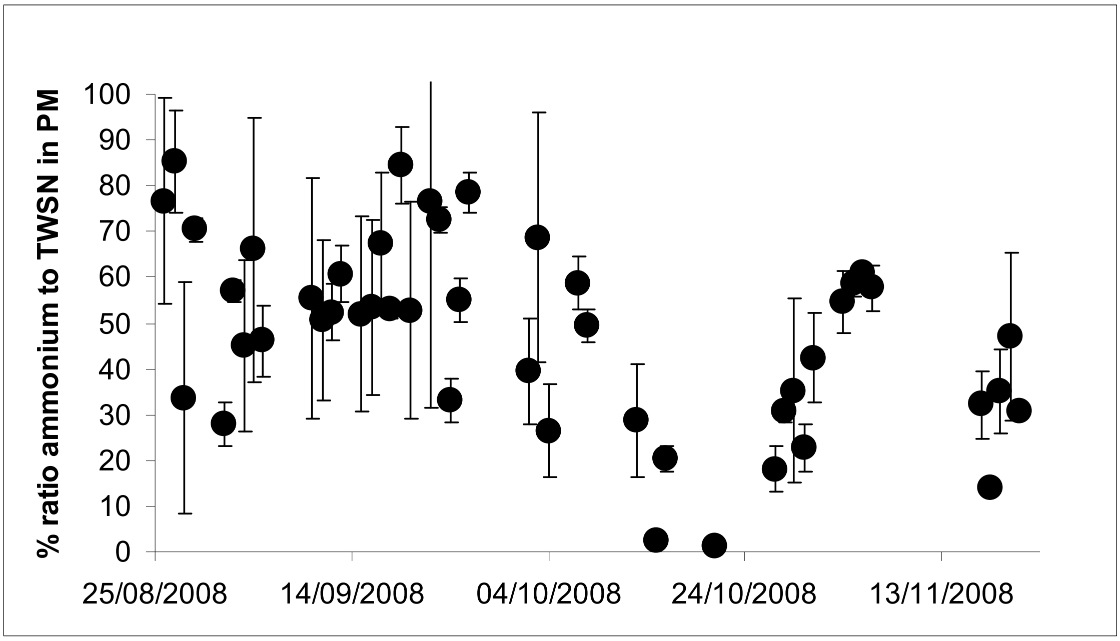


Figure 4.22: Time series of particulate matter percentage of ammonium relative to the total water soluble nitrogen (TWSN) species. Error bar shows standard deviation of 3 replicate samplers.

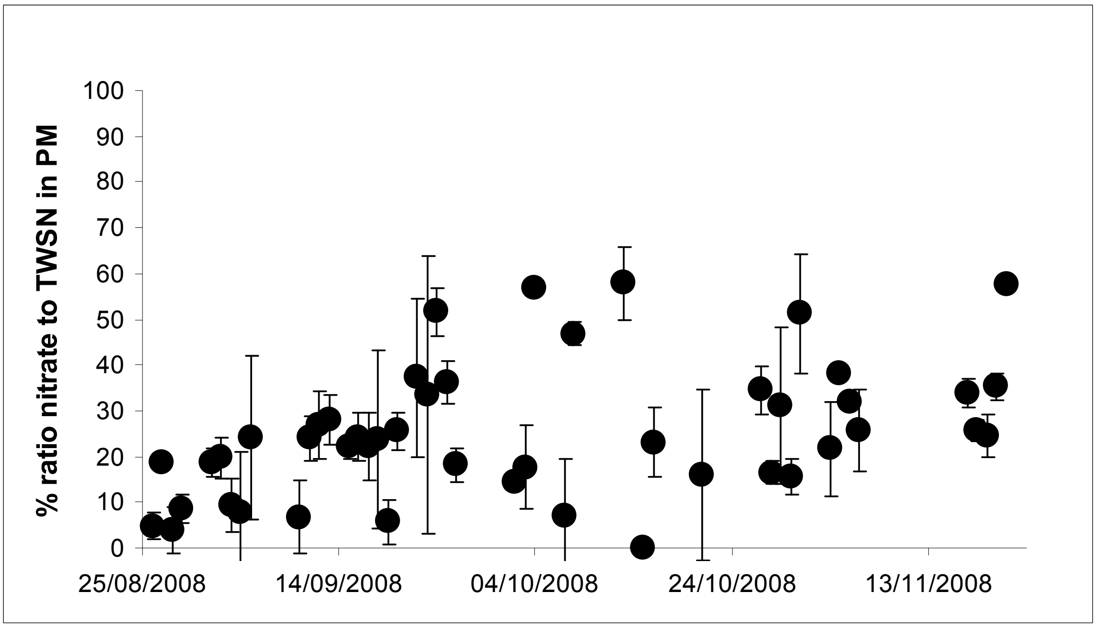


Figure 4.23: Time series of particulate matter percentage of nitrate relative to the total water soluble nitrogen (TWSN) species. Error bar shows standard deviation of 3 replicate samplers.

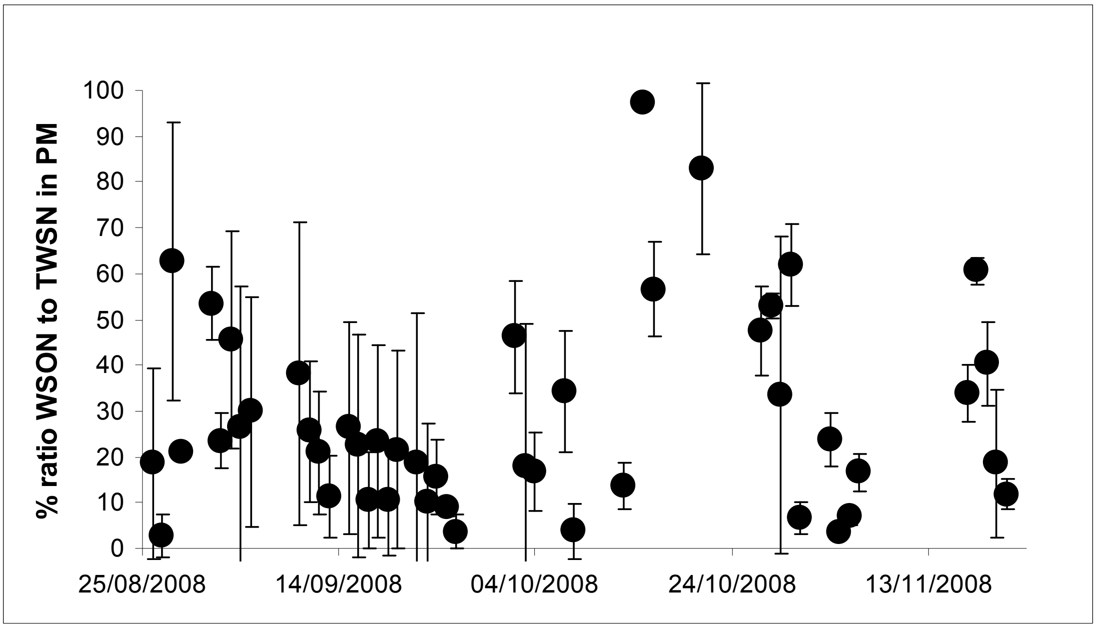


Figure 4.24: Time series of particulate matter percentage of water soluble organic nitrogen (WSON) species relative to the total water soluble nitrogen (TWSN) species. Error bar shows standard deviation of 3 replicate samplers.

Data corresponding to the 28th of August 2008 have been included in Figures 4.15 and 4.17, but have not been included in the subsequent statistical analyses, as nitrogen fertilizer (urea, 35 kg N ha^{-1}) was applied on the field surrounding the sampling location on this date. However, it is interesting to notice that ammonium concentration in the gas phase on that particular date is 512 ± 8 nmol N m^{-3}, around 6 times larger than the average concentration of the other 37 dates with 3 valid replicates (86± 6 nmol N m^{-3}); these results might suggest that an important fraction of the urea applied to the soil was lost due to volatilization into the atmosphere as ammonia gas (Ball and Ryden, 1984, Fillery et al., 1986).

Table 4.1 summarises median and average concentrations of ammonium, nitrate and WSON in the boundary layer, in nmol N m^{-3}, and percentages relative to TWSN, both in the gas phase (Cofer scrubbers) and in particulate matter (PTFE membrane filters). It includes the standard deviations (SD) of the concentrations across the 3 replicate samplers and across sampling dates. SD across replicate samplers aids to asses sampler reproducibility. SD across sampling dates is used in this context as an indicator of concentration variability for the whole period of study. The table is split into 2 parts: the first part includes all dates with 3 valid replicates for each type of collector (37 dates for Cofer scrubbers and 46 dates for PTFE membrane filters). The second part includes the 34 dates with 3 valid replicates for both Cofer scrubbers and PTFE membrane filters. In this work, gas phase nitrate and WSON reported data have not been corrected for sampling efficiency.

Full Data			**Cofer Scrubbers (Gas Phase)**	**PTFE Membrane Filters (Particulate Matter)**		**Cofer Scrubbers (Gas Phase)**	**PTFE Membrane Filters (Particulate Matter)**
Median Concentration in the Boundary Layer/ nmol N*m^{-3}		**NO_3^-**	1.5	6.4		1.5	8.0
		NH_3/NH_4^+	68.1	14.6		80.2	15.7
		WSON	16.9	5.9		17.6	5.7
Average Concentration in the Boundary Layer/ nmol N*m^{-3}		**NO_3^-**	2.5	8.9		2.6	9.8
		NH_3/NH_4^+	85.5	19.1		91.3	20.8
		WSON	18.7	8.1		19.1	7.7
Standard Deviation of Concentration in the Boundary Layer/ nmol N*m^{-3}	**Across 3 Replicate Samples**	**NO_3^-**	0.2	1.1		0.3	1.2
		NH_3/NH_4^+	6.0	0.6		6.7	0.5
		WSON	6.2	3.8		6.1	4.1
	Across all Daily Samples	**NO_3^-**	2.4	8.3		2.4	9.0
		NH_3/NH_4^+	73.8	20.3		74.2	23.4
		WSON	12.7	7.7		12.9	6.8
Average % Relative to TWSN over all Samples		**NO_3^-**	3.1	25.2		3.0	25.5
		NH_3/NH_4^+	76.2	47.6		77.5	46.1
		WSON	20.9	28.5		19.7	29.9
Standard Deviation of Average % Relative to TWSN	**Across 3 Replicate Samples**	**NO_3^-**	0.3	0.4		0.3	0.8
		NH_3/NH_4^+	3.1	6.6		2.6	6.3
		WSON	3.2	6.9		2.5	7.4
	Across all Daily Samples	**NO_3^-**	2.9	14.6		3.0	12.7
		NH_3/NH_4^+	13.6	20.4		12.9	20.5
		WSON	11.9	21.4		10.9	22.4
			37 dates with 3 valid replicates	**46 dates with 3 valid replicates**		**34 dates with 3 valid replicates for Cofer scrubbers & membrane filters**	

Table 4.1: Summary of median and average concentrations of ammonia/ammonium, nitrate and WSON in the boundary layer, in nmol N m^{-3}, and percentages relative to TWSN, both in gas phase (Cofer scrubbers) and in particulate matter (PTFE membrane filters). It includes the standard deviations (SD) of the concentrations across 3 replicate samplers and across sampling dates. All data were collected at Easter Bush sampling site over the period 26th August 2008 to 21st November 2008.

Ammonium is clearly the dominant WSN species at these sites, in particular in the gas phase. Moreover, there is a single date (12th September 2008) with a large gaseous ammonia concentration of 386 ± 61 nmol N m^{-3}, which is about 4 times the average of the 37 dates with 3 valid replicates, and approaching the concentration observed on the 28th August 2008, the fertilization day. It is known that on the 12th September 2008 no fertilizer was applied at the sampling location. However, it is not possible to know whether or not N fertilizer was applied on a nearby field on that date. To avoid any risk of ammonium overestimation, data from this date (12th September 2008) was removed from the statistical analysis and a new summary table (Table 4.2) was produced.

12/09/08 outlier not included			**Cofer Scrubbers (Gas Phase)**	**PTFE Membrane Filters (Particulate Matter)**		**Cofer Scrubbers (Gas Phase)**	**PTFE Membrane Filters (Particulate Matter)**
Median Concentration in the Boundary Layer/ nmol N*m^{-3}		**NO_3^-**	1.5	6.4		1.5	7.6
		NH_3/NH_4^+	66.1	14.2		79.4	15.7
		WSON	16.3	5.7		16.9	5.5
Average Concentration in the Boundary Layer/ nmol N*m^{-3}		**NO_3^-**	2.5	8.9		2.6	9.8
		NH_3/NH_4^+	77.1	19.0		82.4	20.7
		WSON	17.7	8.1		18.1	7.7
Standard Deviation of Concentration in the Boundary Layer/ nmol N*m^{-3}	**Across Replicate Samples**	**NO_3^-**	0.2	1.2		0.3	1.4
		NH_3/NH_4^+	6.9	0.6		7.7	0.6
		WSON	4.6	3.8		4.4	4.1
	Across a Daily Samples	**NO_3^-**	2.4	8.4		2.5	9.1
		NH_3/NH_4^+	54.3	20.5		53.7	23.7
		WSON	11.5	7.8		11.6	6.9
Average % Relative to TWSN ove all Samples		**NO_3^-**	3.1	25.2		3.0	25.5
		NH_3/NH_4^+	75.9	47.5		77.2	45.9
		WSON	21.2	28.6		20.0	30.2
Standard Deviation of Average % Relative to TWSN	**Across Replicate Samples**	**NO_3^-**	0.3	0.5		0.3	0.7
		NH_3/NH_4^+	2.8	6.6		2.3	6.3
		WSON	2.9	6.8		2.2	7.2
	Across a Daily Samples	**NO_3^-**	2.9	14.8		3.0	12.9
		NH_3/NH_4^+	13.6	20.6		12.9	20.8
		WSON	11.9	21.6		10.9	22.7
			36 dates with 3 valid replicates	**45 dates with 3 valid replicates**		**33 dates with 3 valid replicates for Cofer scrubbers & membrane filters**	

Table 4.2: Summary of median and average concentrations of ammonia/ammonium, nitrate and WSON in the boundary layer, in nmol N m^{-3}, and percentages relative to TWSN, both in gas phase (Cofer scrubbers) and in particulate matter (PTFE membrane filters). It includes the standard deviations (SD) of the concentrations across 3 replicate samplers and across sampling dates. All data were collected at Easter Bush sampling site over the period 26th August 2008 to 21st November 2008. Ammonia concentration outlier (12th September 2008) has not been included.

After removing the outlier date (12th September 2008) results remain almost unaltered for all the species in particulate matter and for nitrate and WSON in the gas phase (compare with results in Table 4.1). The average gaseous ammonia concentration, however, was slightly reduced, from 93 ± 7 nmol N m^{-3} to 82 ± 8 nmol N m^{-3} for those dates with 3 valid replicates for Cofer scrubbers and PTFE membrane filters. The only value that is significantly reduced is the SD across dates of the ammonium concentration in gas phase, from 74 nmol N m^{-3} to 54 nmolN m^{-3}.

Differences between the two parts of the table (36 & 45 dates, and 33 dates) remain within the SD values across replicate samplers for the average concentration of each species, both in the gas phase and in particulate matter. The SDs across sampling dates also remain very similar.

The results summarized in Table 4.2 indicate that, in general, the fraction of WSN species in the gas phase is larger than in particulate matter: 103 ± 12 nmol N m^{-3} and 38 ± 5 nmol N m^{-3} respectively for the 33 dates with 3 valid replicates for both Cofer scrubbers and PTFE membrane filters.

In the gas phase, ammonia is the dominant WSN species, followed by WSON, and very low nitrate concentration. An important relative concentration variability through the period of study has been observed: the ratio of SD of concentrations across dates/ average concentration is 65 %, 64 % and 96 % for ammonium, WSON and nitrate respectively. Despite the fluctuations in the absolute concentrations, the ratio of each species to the TWSN concentration remains fairly constant through the whole period of study: 77 ± 13 % for ammonia, 20 ± 11 % for WSON and 3 ± 3 % for nitrate.

As mentioned earlier, in the gas phase the main source of ammonium is ammonia, and the main sources of nitrate are nitric acid and nitrogen dioxide. Both species (ammonia and nitrogen dioxide) are mainly from anthropogenic origin. However, their sources are very different: the majority of ammonia sources are located in rural areas, farms in particular, as ammonia is mainly released into the atmosphere due to decomposition and volatilization of animal wastes. The majority of anthropogenic nitrogen dioxide sources, on the other hand, are located in urban areas, as nitrogen dioxide is mainly released into the atmosphere in high-temperature fuel combustion reactions in motor vehicles and in industrial and utility boilers. These emissions are primarily in the form of nitrogen monoxide, which is oxidized by atmospheric ozone to nitrogen dioxide. Atmospheric nitric acid is primarily formed by reaction of nitrogen dioxide with hydroxyl radicals. Therefore, at the Bush sampling locations, ammonia sources would be local, whereas nitrogen dioxide and nitric acid sources would be more distant.

The high percentage of ammonia collected from the gas phase, and the low percentage of nitrate (see Table 4.2), points to anthropogenic local sources as the main contributor of WSN species in the gas phase. It is important to remember at this point that nitrogen dioxide is very inefficiently trapped into Cofer scrubbers. However, nitrogen dioxide is the main precursor of nitric acid in the boundary layer. The highest concentrations of nitrogen dioxide would be found close to its sources. These sources are distant from the Easter Bush sampling site, so it is expected that by the time the air reaches the sampling site, a significant fraction of the nitrogen dioxide would have been transformed into nitric acid. For this reason it is anticipated that at the Easter Bush sampling site a low concentration of nitric acid in the gas phase would be associated with a low concentration of nitrogen dioxide also.

Through the whole period of study WSON accounts for an important fraction of the TWSN species in the boundary layer gas phase (20 ± 11 %). Investigation of WSON origin (natural or anthropogenic) and location of sources (local or remote) was attempted through Pearson's statistical analysis (selected p value: 0.05) and correlation plot analysis (see Table 4.3 and Figures 4.25, 4.26 and 4.27).

Table 4.3 summarises results of Pearson's statistical test for correlations of ammonium, nitrate and WSON concentrations in the gas phase. As the dataset of concentration values was not normally distributed, a log-transformation was applied to the data before statistical calculations were performed.

	Correlations (Gas Phase)		
		NO_3^-	**NH_3**
NH_3	***R***	0.128	1
	p value	0.458	
WSON	***R***	0.256	-0.033
	p value	0.132	0.849

Table 4.3: Summary of Pearson's statistical analysis for correlations of ammonia, nitrate and WSON concentrations in gas phase. Pearson product moment correlation coefficient (*R*) and p values for each pair are presented. A log-transformation was applied to the data in order to fulfil the assumptions of the model.

In Figure 4.25, GP nitrate concentrations are plotted against GP ammonia concentrations. The concentrations units are nmol N m^{-3}. Only dates with 3 valid replicates are included in this analysis and the two outlier dates discussed above remain excluded. As expected due to their different sources, no obvious correlation was found. The Pearson product moment correlation (R = 0.128) is not significant (p = 0.458), and visual inspection of the data (Figure 4.25) indicates that correlation between GP ammonia and nitrate concentrations is essentially non-existent.

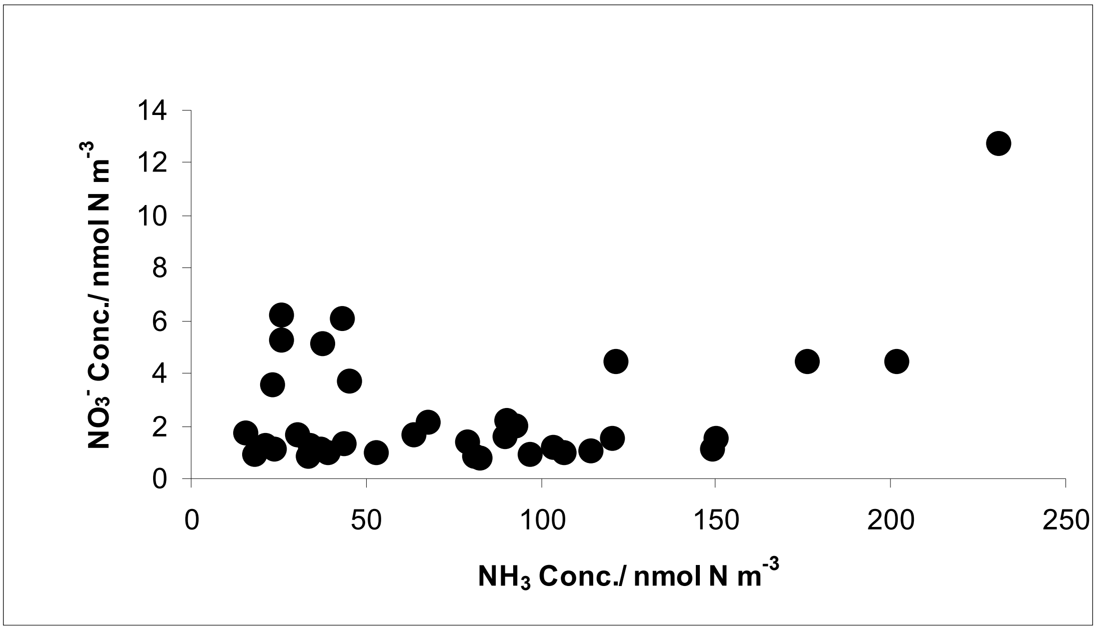


Figure 4.25: Gas phase correlation analysis: nitrate concentrations plotted against ammonia concentrations. The concentrations units are nmol N m^{-3}. Only dates with 3 valid replicates are included.

In Figure 4.26, GP WSON concentrations are plotted against GP ammonia concentrations. The concentrations units are nmol N m^{-3}. Only dates with 3 valid replicates are included in this analysis. No obvious correlation was found. These observations were confirmed by Pearson's statistical analysis of the data: the high p value (0.849) indicates no significant correlation between the two variables.

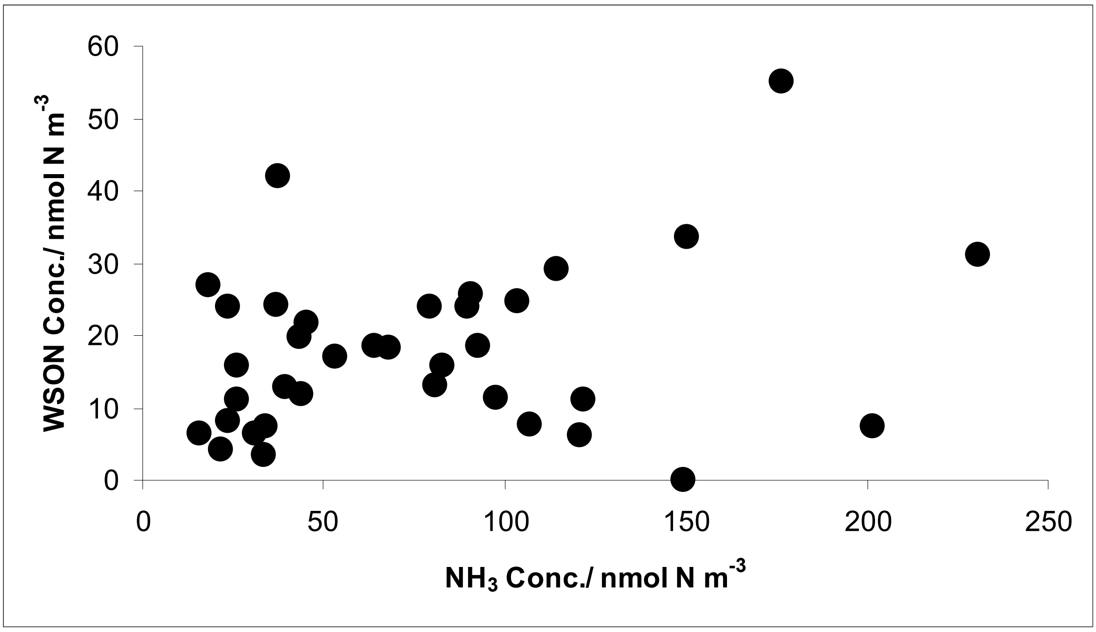


Figure 4.26: GP correlation analysis: WSON concentrations plotted against ammonia concentrations. The concentrations units are nmol N m^{-3}. Only dates with 3 valid replicates are included.

In Figure 4.27, GP WSON concentrations are plotted against GP nitrate concentrations. The concentrations units are nmol N m^{-3}. Only dates with 3 valid replicates are included in this analysis. No obvious correlation was observable from visual inspection of the data (Figure 4.27), which was confirmed by Pearson's statistical analysis of the data: the p value (0.132) indicates no significant correlation.

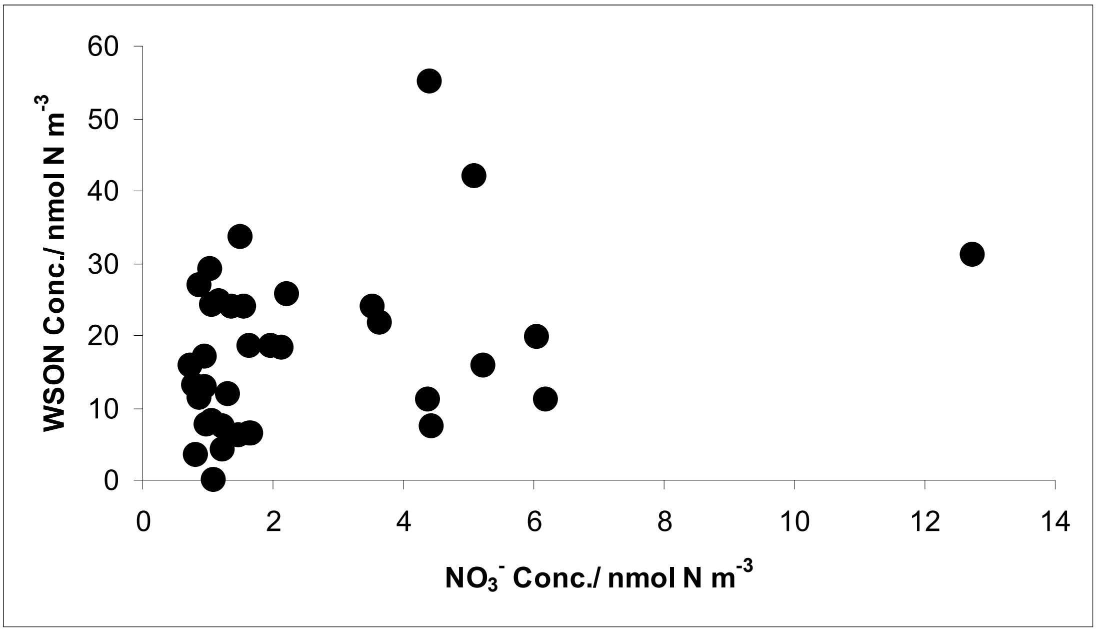


Figure 4.27: GP correlation analysis: WSON concentrations plotted against nitrate concentrations. The concentrations units are nmol N m^{-3}. Only dates with 3 valid replicates are included.

The absence of correlation between ammonium and WSON, or between nitrate and WSON, suggest that a large fraction of the WSON species in GP does not have agricultural nor combustion sources. In a rural area like the Easter Bush sampling site, these observations point to local and non-anthropogenic sources as likely sources of an important fraction of the GP-boundary layer-WSON collected during this field campaign.

In particulate matter, ammonium remains the dominant WSN species (average concentration 20.7 ± 0.6 nmol N m^{-3}, see Table 4.2), followed by nitrate (9.8 ± 1.4 nmol N m^{-3}), and WSON (7.7 ± 4.1 nmol N m^{-3}). Large concentration variability has been observed also in particulate matter: SD of concentrations across dates is 23.7, 9.1 and 6.9 nmol N m^{-3} for ammonium, nitrate and WSON respectively. Fluctuations in the ratio to the TWSN concentration across dates are larger in PM (46 ± 21 % for ammonium, 30 ± 23 % for WSON and 26 ± 13 % for nitrate) than those observed in GP (77 ± 13 % for ammonia, 20 ± 11 % for WSON and 3 ± 3 % for nitrate).

Composition of inorganic WSN species in PM (mainly ammonium nitrate and ammonium sulphate) points to a combination of local and remote sources: ammonium nitrate and ammonium sulphate are secondary particles, formed by the reaction of nitric acid and sulphuric acid with ammonia, and the main sources of ammonia in a rural area are, as mentioned earlier, local. In the absence of ammonia, nitric acid would have been the main contributor to inorganic WSN species in PM. This circumstance would have pointed to remote sources, and it would have been manifested by larger nitrate concentrations than ammonium concentrations, which is clearly not the case in this study. However, one interesting finding recorded in Table 4.2 is that the average nitrate concentration in PM is about 3 times larger than in the gas phase. This indicates that GP nitric acid reacts preferably with ammonia to produce PM ammonium nitrate, rather than remain in the gas phase, in particular when there is a large ratio ammonia / nitric acid.

WSON species concentrations in PM were found to be on average lower than in GP. However, the ratio to TWSN is larger than in GP. Again, investigation of WSON origin (natural or anthropogenic) was attempted by statistical analysis (Pearson's test) and the study of correlation plots (see Table 4.4 and Figures 4.28, 4.29 and 4.30).

	Correlations (Particulate Matter)		
		NO_3^-	**NH_4^+**
NH_4^+	***R***	0.680**	1
	p value	<0.01	
WSON	***R***	0.069	0.169
	p value	0.643	0.256

Table 4.4: Summary of Pearson's statistical analysis for correlations of ammonium, nitrate and WSON concentrations in particulate matter. Pearson product moment correlation coefficient (*R*) and p values for each pair are presented. A log-transformation was applied to the data in order to fulfil the assumptions of the model. ** indicates *R* whose correlation is significant at the 0.01 level (2-tailed).

In Figure 4.28, PM nitrate concentrations are plotted against PM ammonium concentrations. The concentrations units are nmol N m^{-3}. Only dates with 3 valid replicates are included in this analysis. As expected, since in PM the main source of nitrate anion (ammonium nitrate) is also an important source of ammonium, a strong positive correlation was found between the two ions (R = 0.68, p <0.01).

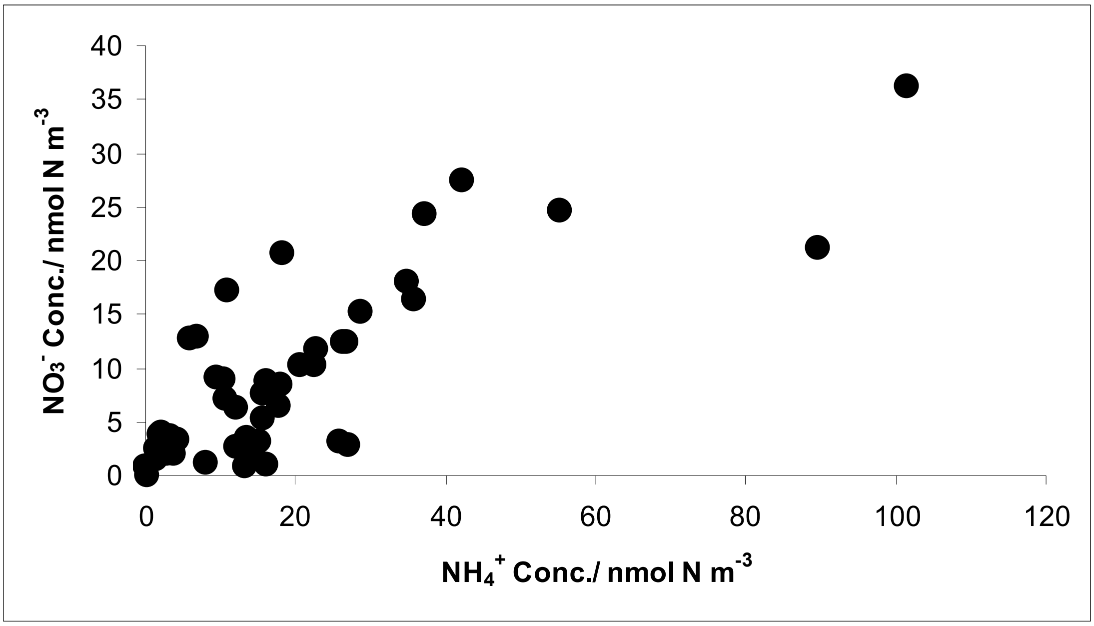


Figure 4.28: PM correlation analysis: nitrate concentrations plotted against ammonium concentrations. The concentrations units are nmol N m^{-3}. Only dates with 3 valid replicates are included.

In Figure 4.29, PM WSON concentrations are plotted against PM ammonium concentrations. The concentrations units are nmol N m^{-3}. Only dates with 3 valid replicates are included in this analysis. No obvious correlation was apparent between these two species in PM. These observations were supported by Pearson's statistical analysis of the data: the high p value (0.256) confirming no significant correlation.

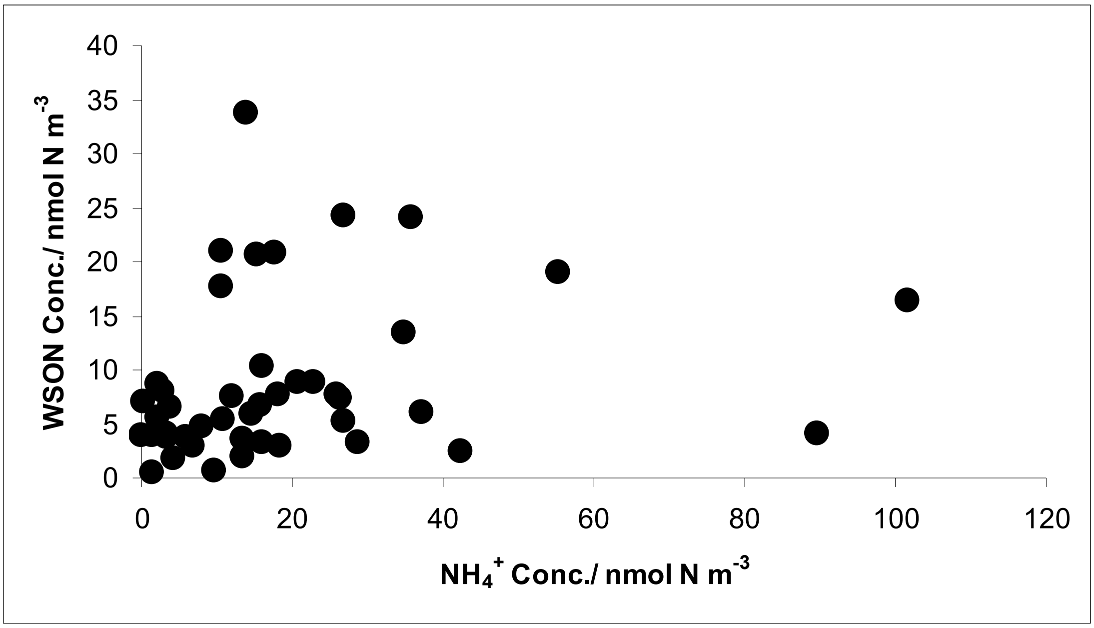


Figure 4.29: PM correlation analysis: WSON concentrations plotted against ammonium concentrations. The concentrations units are nmol N m^{-3}. Only dates with 3 valid replicates are included.

In Figure 4.30, PM WSON concentrations are plotted against PM nitrate concentrations. The concentrations units are nmol N m^{-3}. Only dates with 3 valid replicates are included in this analysis. Again, there was no significant correlation between these two species in PM ($p = 0.643$).

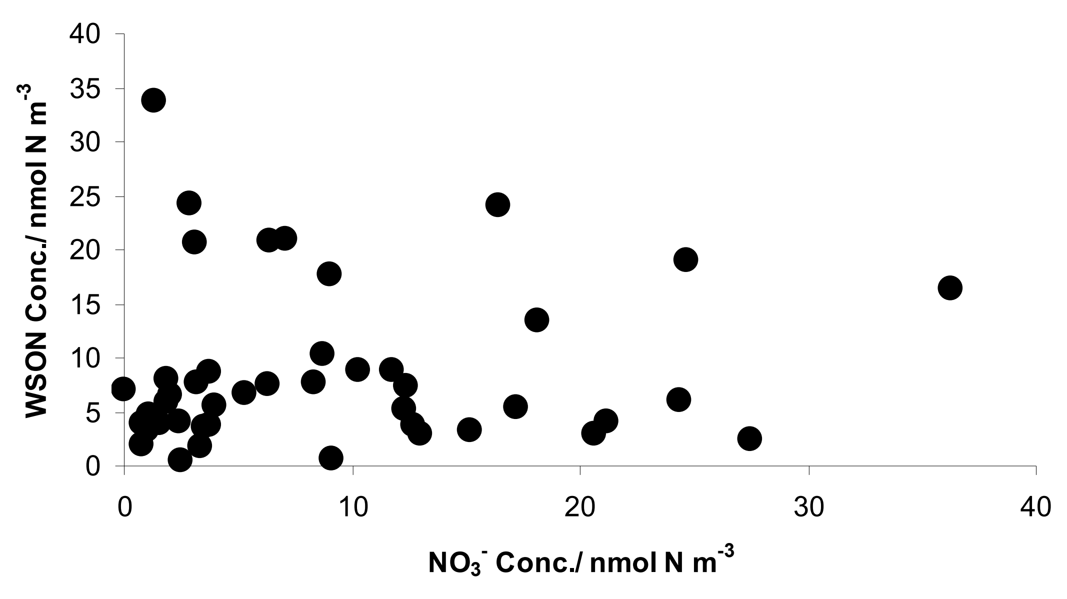


Figure 4.30: PM correlation analysis: WSON concentrations plotted against nitrate concentrations. The concentrations units are nmol N m^{-3}. Only dates with 3 valid replicates are included.

As for the gas phase, these results suggest that an important fraction of the PM-boundary layer-WSON species is not agricultural nor combustion related, pointing to a likely non-anthropogenic origin.

These results agree with a recent study carried out on marine aerosols (Facchini et al., 2008). Results from that study show higher WSON concentrations in polluted air masses than in clean air masses, however, in clean air masses, where dimethyl- and diethylammonium salts (DMA^+ and DEA^+) constitute a dominant fraction of WSON species (~35 % on average), it was found that DMA^+ and DEA^+ concentrations were always larger than in polluted air masses, concluding that DMA^+ and DEA^+ have biogenic sources and that WSON species comprises both biogenic and anthropogenic components. However, another recent study carried out in the Cape Verde islands (Muller et al., 2009) found DMA^+ and DEA^+ concentrations a factor of ten lower.

A key objective for the Cofer scrubbers and filters campaign was to investigate how WSN species are apportioned between gas phase and particulate matter. Figures

4.31, 4.32, 4.33 and 4.34 show the time series of the percentage ratios gas phase / total concentration in boundary layer (addition of gas phase and particulate matter concentrations) for each of TWSN, ammonia/ammonium, nitrate and WSON separately, respectively.

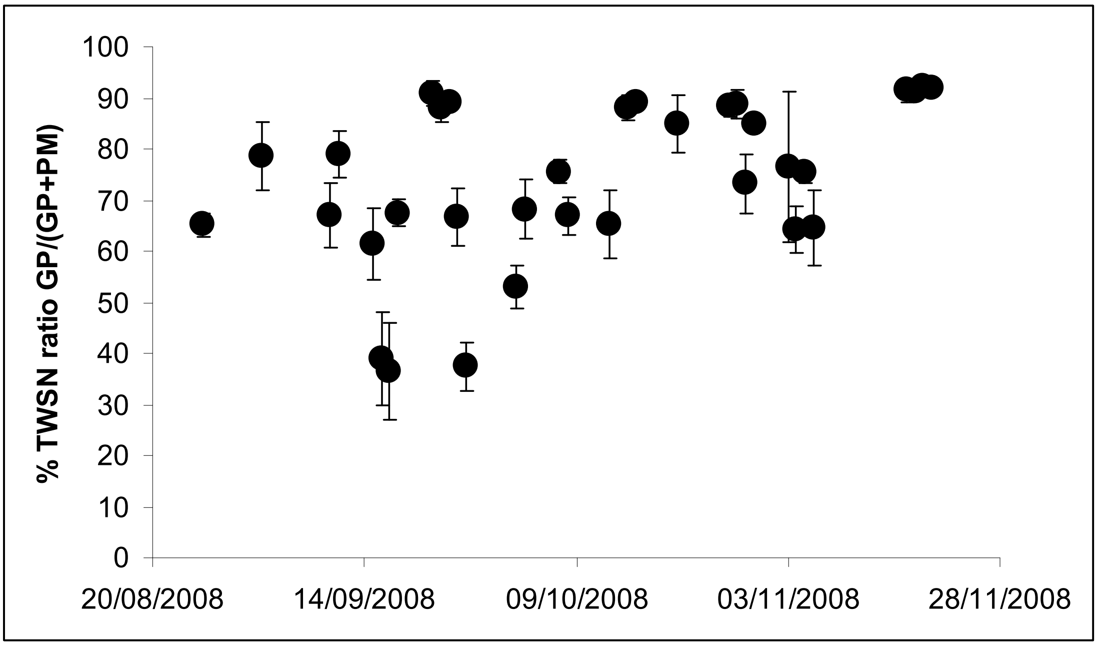


Figure 4.31: Time series of TWSN % ratio gas phase/total concentration in boundary layer (gas phase + particulate matter). Only dates with 3 valid replicates in gas phase and particulate matter are included. Error bar shows standard deviation of 3 replicates samples.

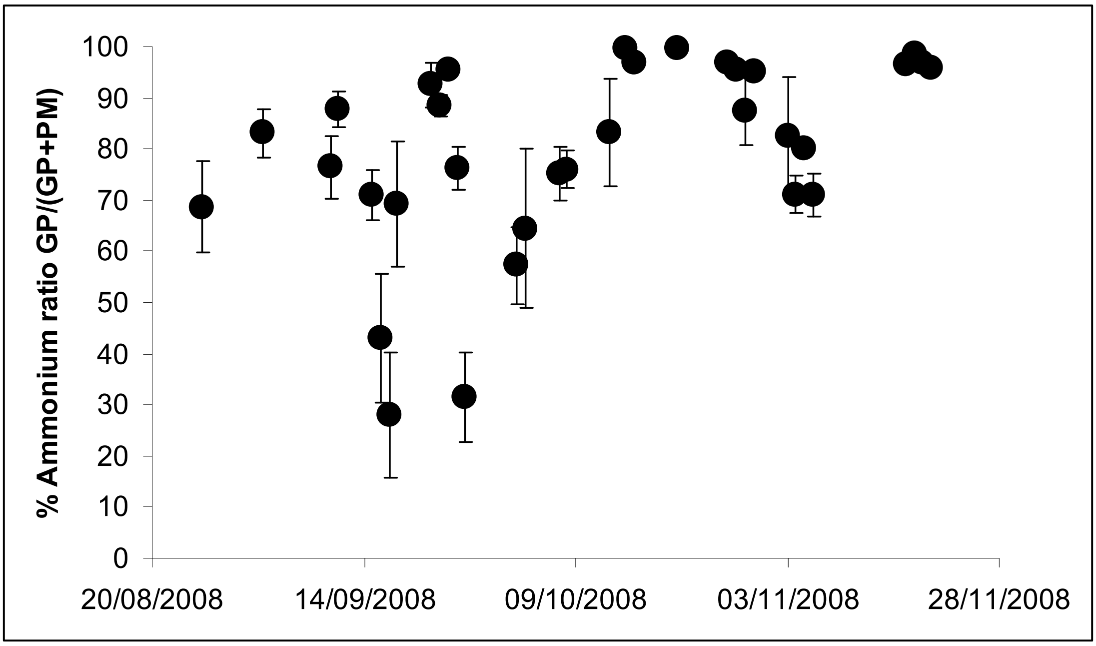


Figure 4.32: Time series of ammonia-ammonium % ratio gas phase/total concentration in boundary layer (gas phase + particulate matter). Only dates with 3 valid replicates in gas phase and particulate matter are included. Error bar shows standard deviation of 3 replicates samples.

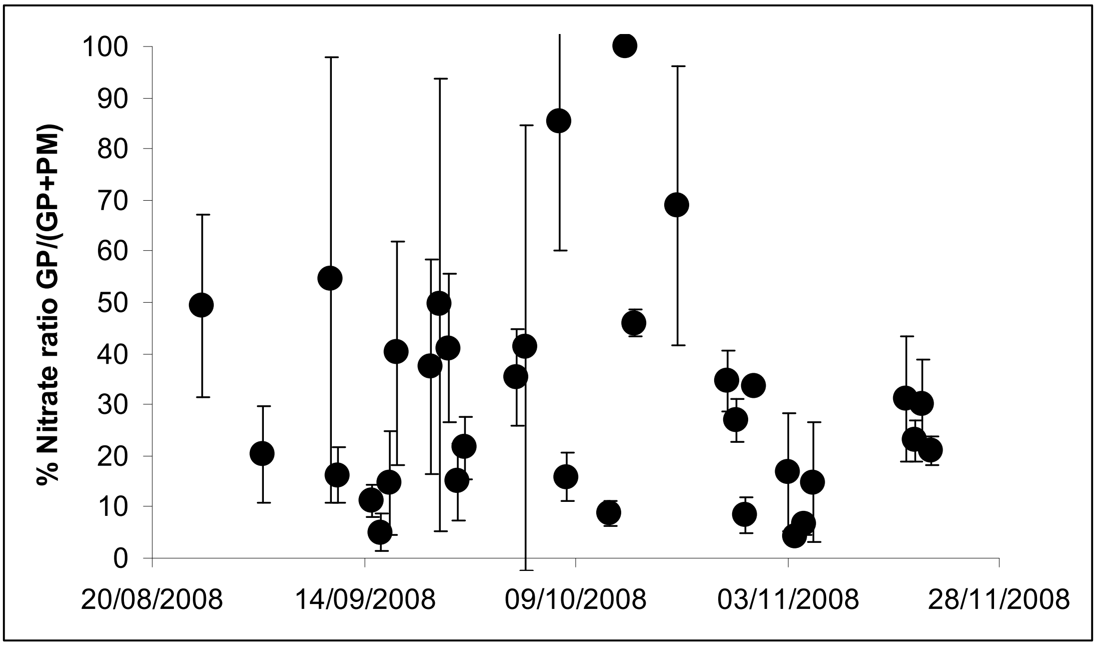


Figure 4.33: Time series of nitrate % ratio gas phase/total concentration in boundary layer (gas phase + particulate matter). Only dates with 3 valid replicates in gas phase and particulate matter are included. Error bar shows standard deviation of 3 replicates samples.

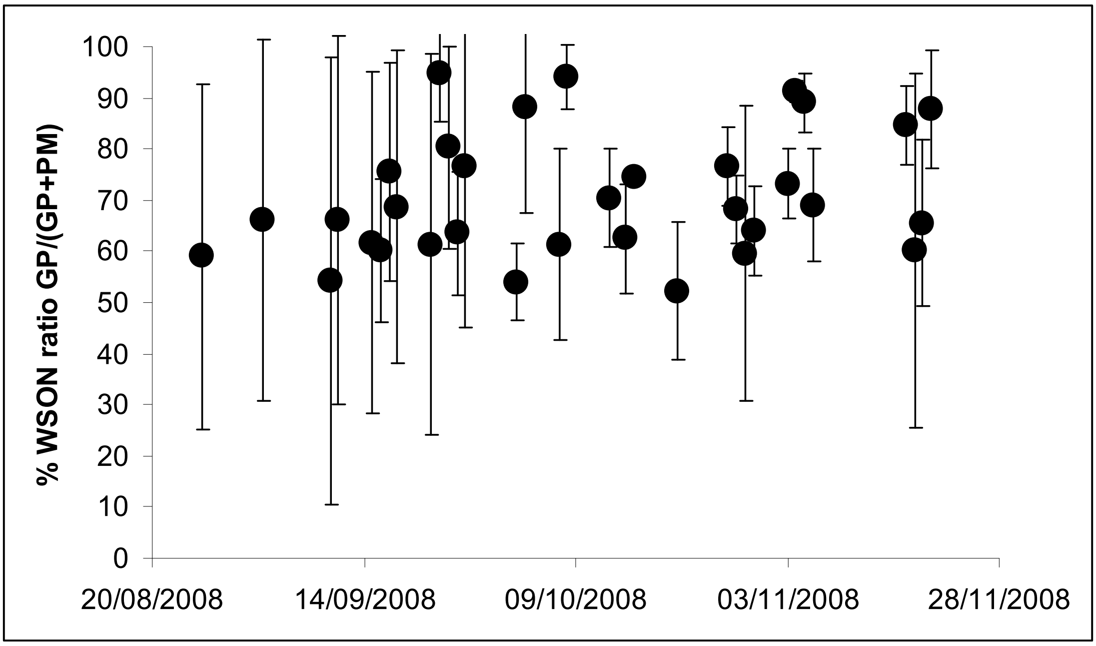


Figure 4.34: Time series of WSON % ratio gas phase/total concentration in boundary layer (gas phase + particulate matter). Only dates with 3 valid replicates in gas phase and particulate matter are included. Error bar shows standard deviation of 3 replicates samples.

Figure 4.35 summarises the averages of the ratios of the gas phase to total gas phase and PM concentrations across all the valid sampling dates for each of the WSN species under study (i.e. the averages of the ratios in each of Figures 4.31-4.34); whilst Figure 4.36 compares the average absolute concentrations of each of TWSN, ammonia/ammonium, nitrate and WSON in the gas phase and in the PM phase.

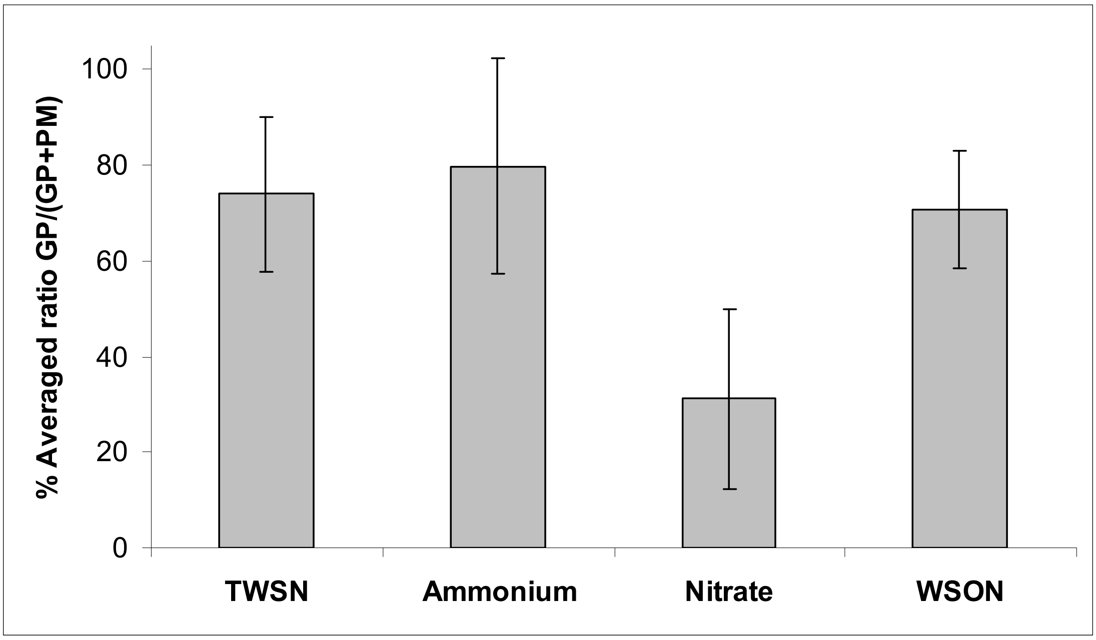


Figure 4.35: Average % concentration ratio gas phase / (gas phase + particulate matter) for TWSN, ammonia/ammonium, nitrate and WSON. Only dates with 3 valid replicates in gas phase and particulate matter are included in the statistical analysis. Ammonia concentration outliers (28th August 2008 and 12th September 2008) not included. Error bar shows standard deviation across all valid dates.

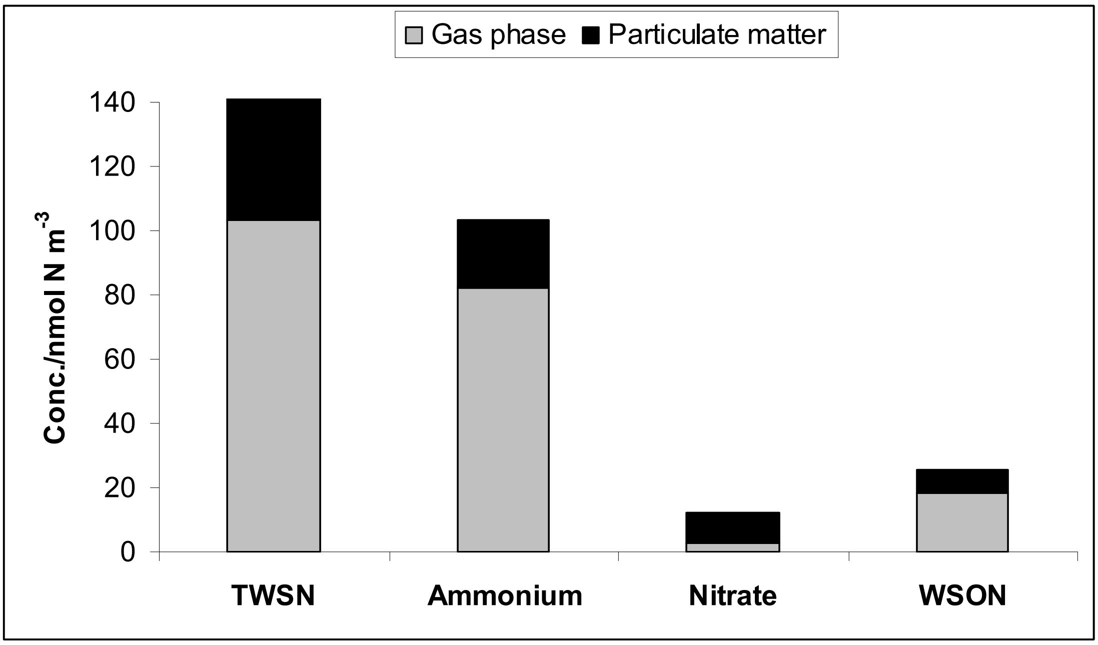


Figure 4.36: Average concentrations of TWSN, ammonia/ammonium, nitrate and WSON in gas phase and in particulate matter. The concentrations units are nmol N m^{-3}. Only dates with 3 valid replicates in gas phase and particulate matter are included in the statistical analysis. Ammonia concentration outliers (28th August 2008 and 12th September 2008) not included.

As shown in Figure 4.35, markedly larger concentrations of WSN species were found in the gas phase than in particulate matter (with the exception of nitrate). The average proportion of the total atmospheric concentration of each of the WSN species that was in the gas phase during the sampling period from 26th August 2008 to 21st November 2008 in this study was: 74 ± 16% for TWSN, 80 ± 19% for ammonia/ammonium, 31 ± 22% for nitrate, and 70 ± 12% for WSON. Figure 4.36 confirms the large difference in total atmospheric N concentrations between the three measured components of ammonia/ammonium, nitrate and WSON.

The dataset collected during this sampling campaign is very robust: Table 4.5 compares the monthly average concentrations (in nmol N m^{-3}) of ammonia / ammonium and nitric acid / nitrate in GP and in PM collected into Cofer scrubbers with those collected into a denuder for long term atmospheric sampling (Tang et al., 2009) in a nearby sampling site (CEH DELTA). The results are remarkably similar, despite the fact that, in the case of Cofer scrubbers, a number of samples were discarded due to the reasons explained in the section 4.1.3, and that consequently there are only twelve valid sampling dates for September, twelve for October and eight for November, whereas for CEH DELTA, the average concentrations comprise the whole month measurements.

	GP				**PM**			
	Cofer Easter Bush		**CEH DELTA**		**Cofer Easter Bush**		**CEH DELTA**	
	$NO_2 + HNO_3$	**NH_3**	**HNO_3**	**NH_3**	**NO_3^-**	**NH_4^+**	**NO_3^-**	**NH_4^+**
September	4.1	106	7.5	42	15.3	37	16.0	35
October	2.2	44	3.2	39	4.4	6	4.7	7
November	1.2	110	6.0	69	10.8	18	8.9	14

Table 4.5: Monthly average concentrations (in nmol N m^{-3}) of ammonia / ammonium and nitric acid / nitrate in GP and in PM collected into Cofer scrubbers in Easter Bush (Cofer Easter Bush) and into a denuder for long term atmospheric sampling in a nearby sampling site (CEH DELTA). For CEH DELTA the average concentrations comprise the whole month measurements, whereas for Cofer Easter Bush only valid sampling dates are included (twelve for September, twelve for October and eight for November).

4.2.2.2. Weather conditions

It would be expected that meteorological conditions, in particular rain events, would influence atmospheric concentrations of WSN species, both in gas phase (GP) and in particulate matter (PM). To investigate to what extent these species are affected, a subdivision discriminating between dates with rainy weather and dates with dry weather was made. Thus Table 4.6 summarises median and average concentrations of ammonium, nitrate and WSON in the boundary layer, in nmol N m^{-3}, and percentages relative to TWSN, both in the gas phase (Cofer scrubbers) and in particulate matter (PTFE membrane filters). It includes the standard deviations (SD) of the concentrations across the 3 replicate samplers and across sampling dates. The table is split into 2 parts: the first part includes the 17 dates with 3 valid replicates for Cofer scrubbers and PTFE membrane filters in dry weather. The second part includes the 16 dates with 3 valid replicates for Cofer scrubbers and PTFE membrane filters in rainy weather.

Weather Conditions			**Cofer Scrubbers (Gas Phase)**	**PTFE Membrane Filters (Particulate Matter)**		**Cofer Scrubbers (Gas Phase)**	**PTFE Membrane Filters (Particulate Matter)**
Median Concentration in the Boundary Layer/ nmol N*m^{-3}		**NO_3^-**	1.7	7.6		1.3	7.4
		NH_3/NH_4^+	97.4	9.6		58.7	17.9
		WSON	11.5	4.7		22.8	7.5
Average Concentration in the Boundary Layer/ nmol N*m^{-3}		**NO_3^-**	3.3	8.8		1.8	10.8
		NH_3/NH_4^+	100.4	16.5		63.3	25.1
		WSON	15.9	4.8		20.4	10.8
Standard Deviation of Concentration in the Boundary Layer/ nmol N*m^{-3}	**Across 3 Replicate Samples**	**NO_3^-**	0.5	2.2		0.2	1.9
		NH_3/NH_4^+	10.0	2.1		6.6	3.4
		WSON	3.8	1.6		5.3	7.0
	Across all Daily Samples	**NO_3^-**	3.1	7.5		1.2	10.7
		NH_3/NH_4^+	64.9	21.8		30.0	25.6
		WSON	13.3	4.0		9.4	8.1
Average % Relative to TWSN over all Samples		**NO_3^-**	3.5	28.7		2.6	22.1
		NH_3/NH_4^+	80.8	45.5		73.4	46.4
		WSON	16.1	29.0		24.1	31.5
Standard Deviation of Average % Relative to TWSN	**Across 3 Replicate Samples**	**NO_3^-**	0.6	2.1		0.5	3.6
		NH_3/NH_4^+	2.2	4.7		2.7	8.2
		WSON	1.7	4.3		3.1	10.7
	Across all Daily Samples	**NO_3^-**	3.7	15.2		2.0	9.2
		NH_3/NH_4^+	12.0	22.5		13.2	19.7
		WSON	8.8	24.5		11.7	21.4
			Dry weather: 17 dates with 3 valid replicates for Cofer scrubbers & membrane filters			**Rainy weather: 16 dates with 3 valid replicates for Cofer scrubbers & membrane filters**	

Table 4.6: Summary of median and average concentrations of ammonium, nitrate and WSON in the boundary layer, in nmol N m^{-3}, and percentages relative to TWSN, under different weather conditions, both in gas phase (Cofer scrubbers) and in particulate matter (PTFE membrane filters). It includes the standard deviations (SD) of the concentrations across 3 replicate samplers and across sampling dates. All data were collected at Easter Bush sampling site over the period 26th August 2008 to 21st November 2008.

In GP, the average concentrations of ammonium and nitrate are notably larger in dry weather than in rainy weather: for ammonium, the average concentration in rainy weather is about 63 % of that in dry weather; for nitrate, the average concentration in rainy weather is about 55 % of that in dry weather. ANOVA and t-test analysis of the concentrations of ammonia, nitrate and WSON are presented in Tables 4.7 and 4.8 respectively. A log-transformation was applied to the data in order to fulfil the assumptions of the model. Weather (rainy or dry) was the main effect in both analyses. Both tests confirm that the differences found between rainy and dry weather both for ammonia and nitrate concentrations in gas phase are statistically significant ($p < 0.05$). These results are not surprising, as rain would be expected to scrub water soluble material from the atmosphere.

ANOVA (gas phase concentrations)		**Sum of Squares**	**df**	**Mean Square**	**F**	***p*-value**
log-transformed TWSN conc. (GP)	**Between Groups**	0.280	1	0.280	4.521	0.036
	Within Groups	6.013	97	0.062		
	Total	6.294	98			
log- transformed ammonia conc. (GP)	**Between Groups**	0.563	1	0.563	6.513	0.012
	Within Groups	8.388	97	0.086		
	Total	8.951	98			
log- transformed nitrate conc. (GP)	**Between Groups**	0.285	1	0.285	4.972	0.028
	Within Groups	5.562	97	0.057		
	Total	5.847	98			
log- transformed WSON conc. (GP)	**Between Groups**	0.317	1	0.317	4.503	0.036
	Within Groups	6.832	97	0.070		
	Total	7.150	98			

Table 4.7: ANOVA analysis of TWSN, ammonia, nitrate and WSON concentrations in gas phase (GP). Weather type (wet or dry conditions) as main effect. Log-transformation was applied to the data in order to fulfil the assumptions of the model.

Levene's Test & T-test (gas phase concentrations)		**Levene's Test for Equality of Variances**				**T-test for Equality of Means**				
									95% Confidence Interval of the Difference	
		F	***p*-value**	**t**	**df**	***p*-value** (2-tailed)	**Mean Difference**	**Std. Error Difference**	**Lower**	**Upper**
log-transformed TWSN conc. (GP)	**Equal variances assumed**	6.527	0.012	-2.126	97	0.036	-0.106	0.050	-0.206	-0.007
	Equal variances not assumed			-2.145	92	0.035	-0.106	0.050	-0.205	-0.008
log-transformed ammonia conc. (GP)	**Equal variances assumed**	8.128	0.005	-2.552	97	0.012	-0.151	0.059	-0.268	-0.034
	Equal variances not assumed			-2.576	91	0.012	-0.151	0.059	-0.267	-0.035
log-transformed nitrate conc. (GP)	**Equal variances assumed**	13.152	0	-2.230	97	0.028	-0.107	0.048	-0.203	-0.012
	Equal variances not assumed			-2.263	82	0.026	-0.107	0.047	-0.202	-0.013
log-transformed WSON conc. (GP)	**Equal variances assumed**	1.960	0.165	2.122	97	0.036	0.113	0.053	0.007	0.219
	Equal variances not assumed			2.159	76	0.034	0.113	0.052	0.009	0.218

Table 4.8: Levene's test for equality of variances and t-test for equality of means in wet and dry weather conditions for TWSN, ammonia, nitrate and WSON concentrations in gas phase (GP). A log-transformation was applied to the data in order to fulfil the assumptions of the model.

Comparison of ammonium and nitrate concentrations in GP in dry and rainy conditions also shows that rainy conditions seem to reduce concentration variability: the coefficient of concentration variation (standard deviation of concentration across sampling dates / average concentration) drops from 0.65 in dry conditions to 0.47 in rainy conditions for ammonium, and from 0.94 in dry conditions to 0.66 in rainy conditions for nitrate, i.e. for both ammonium and nitrate rain is not only acting as a scrubber, but also as a “buffer” of their gas phase concentrations in the boundary layer. Levene's test for equality of variances presented in Table 4.8 also confirms that the differences observed in concentration variability for ammonia and nitrate in gas phase between dry and wet conditions are statistically highly-significant ($p < 0.01$). As before, a log-transformation was applied to the data in order to fulfil the assumptions of the model.

In the case of WSON species in the gas phase, the coefficient of concentration variation drops from 0.83 in dry conditions to 0.46 in rainy conditions. However, Levene's test for equality of variances (Table 4.8) shows that the differences observed in concentration variability for WSON in the gas phase between dry and wet conditions are not statistically significant ($p > 0.05$). Also, in contrast to ammonia and nitrate, WSON species in the gas phase presented larger median and average concentrations in rainy weather (23 and 20 nmol N m^{-3} respectively) than in dry weather (12 and 16 nmol N m^{-3}, respectively). ANOVA and t-test analysis of the concentrations of WSON species in gas phase (Tables 4.7 and 4.8) confirm that the differences found between rainy and dry weather conditions are statistically significant ($p < 0.05$).

It is assumed that WSON is very likely to include species that are less water soluble than ammonia and nitric acid. This would explain smaller differences between dry and wet conditions for WSON than for ammonium and nitrate. However, this assumption cannot explain a larger average concentration in the rainy days than in the dry ones. The most logical explanation for these findings would be a net production of WSON under wet conditions, possibly some chemicals released as a response to rain from the soil or the vegetation (perennial ryegrass, *Lolium perenne*) surrounding the sampling site, and the amount and intensity of precipitation not large enough to completely scrub the new material released. This explanation is, of course, highly speculative.

Another explanation for larger WSON concentrations in rainy weather might be that on those days the wind was predominantly blowing from the direction of an unidentified WSON-only source. However, this possibility seems very unlikely, as the wind direction is very variable, both for dry and wet weather, and in both cases it is predominantly from the same south-west direction.

Comparison of results in PM from dry and wet sampling dates also produced very interesting and unexpected findings: the “intuitive” expectation was that in wet weather average concentrations of WSN species would decrease, as they would be stripped from the atmosphere by rain. However, Table 4.6 shows the opposite result to this “intuitive” expectation, as average concentrations of WSN species (ammonium, nitrate and WSON) are larger in rainy weather than in dry weather (25 ± 3 nmol N m^{-3} for ammonium, 11 ± 2 nmol N m^{-3} for nitrate and 11 ± 7 nmol N m^{-3} for WSON in rainy weather, versus 17 ± 2 nmol N m-3 for ammonium, 9 ± 2 nmol N m^{-3} for nitrate and 5 ± 2 nmol N m^{-3} for WSON in dry weather). ANOVA and t-test analysis of the concentrations of ammonia, nitrate and WSON in PM are presented in Tables 4.9 and 4.10. Weather (rainy or dry) was the main effect in both analyses. A log-transformation was applied to the data in order to fulfil the assumptions of the model. According to both tests, these differences are only highly significant for WSON species ($p<0.01$), and non-significant for ammonium and nitrate ($p >0.05$), but nevertheless, none of the compounds under study met the “intuitive” expectation of lower concentrations under wet weather conditions. Due to the “cleaning” effect of rain, concentration fluctuations of PM in the boundary layer would be expected to be larger in dry weather than in wet weather. Again, experimental evidence shows no differences: Levene's test for equality of variances in PM (Table 4.10) shows that concentration variability for ammonium, nitrate and WSON in PM between dry and wet conditions are statistically non-significant ($p >0.05$).

ANOVA (particulate matter concentrations)		Sum of Squares	df	Mean Square	F	*p*-value
log-transformed TWSN conc. (PM)	**Between Groups**	0.687	1	0.687	4.58	0.035
	Within Groups	14.533	97	0.15		
	Total	15.22	98			
log-transformed ammonium conc. (PM)	**Between Groups**	0.802	1	0.802	1.62	0.206
	Within Groups	47.947	97	0.494		
	Total	48.749	98			
log-transformed nitrate conc. (PM)	**Between Groups**	0.091	1	0.091	0.47	0.496
	Within Groups	19.015	97	0.196		
	Total	19.106	98			
log-transformed WSON conc. (PM)	**Between Groups**	0.665	1	0.665	7.43	0.008
	Within Groups	8.684	97	0.09		
	Total	9.349	98			

Table 4.9: ANOVA analysis of TWSN, ammonia, nitrate and WSON concentrations in particulate matter (PM). Weather type (wet or dry conditions) as main effect. Log-transformation was applied to the data in order to fulfil the assumptions of the model.

Levene's Test & T-test (particulate matter concentrations)		Levene's Test for Equality of Variances				T-test for Equality of Means				
									95% Confidence Interval of the Difference	
		F	*p*-value	t	df	*p*-value (2-tailed)	Mean Difference	Std. Error Difference	Lower	Upper
log-transformed TWSN conc. (PM)	**Equal variances assumed**	3.233	0.075	2.141	97	0.035	0.167	0.078	0.012	0.321
	Equal variances not assumed			2.125	89	0.036	0.167	0.078	0.011	0.322
log-transformed ammonium conc. (PM)	**Equal variances assumed**	1.058	0.306	1.274	97	0.206	0.180	0.141	-0.100	0.461
	Equal variances not assumed			1.266	91	0.209	0.180	0.142	-0.103	0.463
log-transformed nitrate conc. (PM)	**Equal variances assumed**	0.533	0.467	0.683	97	0.496	0.061	0.089	-0.116	0.238
	Equal variances not assumed			0.681	95	0.497	0.061	0.089	-0.116	0.238
log-transformed WSON conc. (PM)	**Equal variances assumed**	0.453	0.503	2.725	97	0.008	0.164	0.060	0.045	0.283
	Equal variances not assumed			2.767	81	0.007	0.164	0.059	0.046	0.282

Table 4.10: Levene's test for equality of variances and t-test for equality of means in wet and dry weather conditions for TWSN, ammonia, nitrate and WSON concentrations in particulate matter (PM). A log-transformation was applied to the data in order to fulfil the assumptions of the model.

One explanation for these observations might be that the disturbance caused by the impact of rain droplets on leaves or on soil could release a fraction of the PM already settled on those surfaces back into the atmosphere, due to a mechanical action-reaction process. Of course this process would be compensated by the "cleaning" effect of rain. However, if the rain event is not intense enough, it might be possible that the first effect could dominate the second. This explanation is consistent with observations reported in previous studies (Calderón et al., 2007), in which the poor rain scavenging of fine particles of ammonium and WSON (anticipated as the main contributors to TWSN in PM in Easter Bush sampling site) was attributed to low collision efficiencies, even in the presence of a high number of big droplets. It is important to point out that the majority of the rain events included in this study had a low or medium intensity. There were a number of very intense rain events during the sampling period that could not be included in the final statistical analysis because part of the water soluble material deposited on the surface of the open-face PTFE membrane filter samplers was removed by the pouring rain.

Another explanation for these observations might be that small water droplets in light rain events could act as an interface promoting chemical reactions leading to the formation of PM.

4.3. Conclusions

Cofer scrubbers are very light, effective and inexpensive air samplers, easy to handle, to transport and to operate. They are vulnerable to evaporation issues and, for this reason, regular monitoring is required during the sampling period. These samplers might be particularly useful in sampling campaigns in remote areas, where transport logistics and environmental conditions such as high relative humidity can prove extremely challenging for heavier and more sophisticated instruments.

In the context of gas phase WSN species sampling, Cofer scrubbers present a high efficiency collection.

The use of both enclosed and open-faced filter samplers is recommended for aerosol sampling. In dry conditions enclosed filter samplers might be slightly less efficient than open-faced filter samplers, however, unlike open faced filter samplers, enclosed filter samplers are not vulnerable to heavy rain showers, therefore, in wet conditions, enclosed filter samplers are excellent tools for aerosol sampling quality control assessment.

Through the whole period of study the total amount of WSN species in the gas phase (GP) was noticeably larger than in particulate matter (PM): on average, TWSN species concentration in GP was 103 ± 12 nmol N m^{-3} (SD across dates: 59 nmol N m^{-3}) and in PM was 38 ± 5 nmol N m^{-3} (SD across dates: 34 nmol N m^{-3}). Average WSON concentration was also larger in GP (18 ± 4 nmol N m^{-3}, SD across dates: 11 nmol N m^{-3}) than in PM (8 ± 4 nmol N m^{-3}, SD across dates: 7 nmol N m^{-3}), on the other hand, in relation to the TWSN, the WSON fraction was proportionally larger in PM (~ 30 ± 7 % on average) than in GP (~ 20 ± 2 % on average), however, it is important to point out that GP samples were collected into single Cofer scrubbers, which might lead to significant underestimation of GP WSON concentrations (up to 40 %, depending on the actual composition of the material sampled), and these data have not been corrected for sampling efficiency.

A key objective in this study was to investigate how WSN species are apportioned between gas phase and particulate matter: markedly larger concentrations of WSN species were found in the gas phase than in particulate matter (with the exception of nitrate). The average proportion of the total atmospheric concentration of each of the WSN species that was in the gas phase during the sampling period from 26th August 2008 to 21st November 2008 was: 74 ± 16% for TWSN, 80 ± 19% for ammonia/ammonium, 31 ± 22% for nitrate, and 70 ± 12% for WSON.

In the gas phase the dominant WSN species by far was ammonia: on average 77 ± 2 % (SD across dates: 13 %). These results, in a rural sampling site such as Easter Bush, point to local-anthropogenic sources as the main contributor to WSN species.

WSON main potential sources, according to correlation studies with ammonium and nitrate, on the other hand, seem very unlikely to have an anthropogenic origin. In the gas phase, Pearson's statistical analysis did not show significant correlation between ammonium and WSON concentrations, and between nitrate and WSON concentrations (p values > 0.05). No significant correlations were found between ammonium & WSON concentrations and nitrate & WSON concentrations in particulate matter (p value > 0.05 in both cases). These results (no correlation of WSON with ammonium and nitrate concentrations, both in GP and PM) suggest that the major WSON sources are different than for ammonium and nitrate, i.e. at the Easter Bush sampling site, these results suggest that a large fraction of the WSON species in the boundary layer, both in the gas phase and in particulate matter, is not agricultural nor combustion related, pointing to a likely non-anthropogenic origin.

Investigations on how weather conditions influenced WSN species concentrations, both in GP and PM, yielded very interesting results. In GP, the average concentrations of ammonium and nitrate were, as expected, notably larger in dry weather than in rainy weather. However, WSON average concentration in rainy weather was significantly larger than in dry weather. A possible explanation for an increase in WSON concentrations on rainy days could be the release of certain chemicals (as a response to rain) by soil or vegetation. Another explanation for larger WSON concentrations in rainy weather might be that on those rainy days wind was predominantly blowing from the direction of an unidentified WSON source. However, this possibility seems very unlikely, as the wind direction is very variable, both for dry and wet weather, and in both cases it is predominantly from the same south-west direction.

In PM, experimental results did not meet the “intuitive” expectation that in wet weather average concentrations of WSN species would decrease, as they would be stripped from the atmosphere by rain. On the contrary, ANOVA and t-test statistical analysis of the data showed highly significant larger WSON species concentrations in wet weather conditions than in dry weather, and no significant differences for ammonium and nitrate, i.e. none of the compounds under study met the “intuitive” expectation of lower concentrations under wet weather conditions. One explanation for these observations might be that the disturbance caused by the impact of rain droplets on leaves or on soil could release back into the atmosphere part of the PM already settled on those surfaces, due to a mechanical action-reaction process. Of course this process would be compensated by the “cleaning” effect of rain. However, if the rain event is not intense enough, it might be possible that the first effect could dominate the second. This explanation is consistent with observations reported in previous studies (Calderón et al., 2007), in which the poor scavenging efficiency of fine particles by rain was attributed to low collision rates. Another explanation might be that small water droplets in light rain events could act as an interphase promoting chemical reactions leading to the formation of PM.

5. NitroEurope (NEU) Network: quantification of bulk deposition of water soluble nitrogen compounds across Europe.

In order to further investigate water-soluble nitrogen (WSN) species distribution, origin and concentrations in a wider context, rain samples from 21 different sampling sites across Europe have been analyzed for total dissolved nitrogen (TDN), and combined with other laboratories' measurements of ammonium and nitrate to provide a measure of dissolved organic nitrogen (DON). These samples were very kindly provided by 6 different institutions across Europe, all within the NitroEurope (NEU) Network framework. NEU is a project for integrated European research into the nitrogen cycle. It will run for 5 years, from February 2006 until 2011, and it is part of the European Union's Sixth Framework Programme for Research and Technological Development. Within the NEU project, rain sampling is part of Work Package 1. The study presented in this Chapter covers rain samples collected over different time periods and with different time resolutions. At the majority of the sampling sites the rain sampling technique is bulk deposition. Only at one sampling site is the collection technique wet-only deposition.

Table 5.1 summarises the main details of the sampling sites and methods included in this study: name of the sampling site, coordinates, rain collection method (bulk or wet-only deposition), sampling period, sample time resolution and name of the institution that provided the sample.

Sampling site	**Coordinates**	**Rain deposition**	**Sampling period**		**Time resolution**	**Institution**
			Start	**End**		
Fontainebleau	N48°28′35″, E02°46′48″	Bulk	Feb-08	Dec-08	Monthly	Slovak Hydrometeorological Institute, Department of Air Quality, Bratislava, Slovak Republic
Grillenburg	N50°57′00″, E13°30′45″					
Hainich	N51°04′45″, E10°27′07″					
Lägeren	N47°28′41″, E08°21′55″					
Le Bray	N44°43′02″, W00°46′09″					
Mitra III	N38°31′40″, W08°01′23″					
Polwet	N52°45′44″, E16°18′34″					
Puéchabon	N43°44′29″, E03°35′45″					
Roccarespampani	N42°24′29″, E11°55′48″					
San Rossore	N43°43′40″, E10°17′04″					
Vielsalm	N50°18′20″, E05°59′49″					
Wetzstein	N50°27′13″, E11°27′27″					
Zavižan	N44°48′53″, E14°58′32″	Bulk	Mar-08	Aug-08	Daily	Meteorological and Hydrological Service of Croatia, Air Quality Research Unit, Zagreb, Croatia
Bugac	N46°41′30″, E19°36′06″	Bulk	Oct-08	Feb-09	Daily	Hungarian Meteorological Service, Budapest, Hungary
Oensingen	N47°17′09″, E07°43′55″	Wet-only	Aug-06	May-08	Weekly	Forschungsanstalt Agroscope Reckenholz-Tänikon Research Station (ART), Zürich, Switzerland
Virolahti	N60°31′27″, E27°38′25″	Bulk	Aug-08	May-09	Weekly	Finnish Meteorological Institute, Air Quality Research
Pallas	N68°00′00″, E24°14′24″					
Wieringerwerf	N52°48′17″, E05°02′56″	Bulk	Sep-08	Dec-08	Fortnightly	Netherlands National Institute for public health and the environment (RIVM) - Laboratory for Environmental Monitoring (LVM), Bilthoven, The Netherlands
Speulderveld	N52°16′18″, E05°43′14″					
Rotterdam	N51°47′05″, E05°38′41″					
Vredepeel	N51°32′27″, E05°51′10″					

Table 5.1: Main details of all the sampling sites included in this study: name of the sampling site, coordinates, rain collection method (bulk or wet-only deposition), sampling period, sample time resolution and name of the institution that provided the sample.

In order to minimise biological changes in samples between analysis for inorganic N and shipping to CEH, empty 2 mL vials were pre-loaded with a biocide (0.1 mg thymol, 2-isopropyl-5-methylphenol) and supplied to the participating laboratories. However, it should be clarified that in all sampling sites thymol was added to collectors upon deployment. Sub-samples for analysis for TDN at CEH were sealed in the vials immediately prior to inorganic N analysis, and then shipped to the CEH laboratory where samples were immediately analyzed for determination of TDN concentrations. The technique used for TDN analysis was high-temperature catalytic oxidation (HTCO) (see Section 2.4). The DON concentration was determined indirectly, as described in preceding chapters, by subtraction of the ammonium and nitrate concentrations (provided by the originating laboratories) from the TDN concentrations determined here.

Results from the different sampling sites are presented grouped under the institution that provided the samples. The reason for this approach is that sampling periods, sampling time resolution and collection techniques are similar within all the samples provided by each institution, whereas there are variations, in particular in time resolution, between samples provided by different institutions. The shift from molar to weight units in this chapter was caused because all the inorganic data provided by the NITROEUROPE network was expressed in weight units.

5.1. Slovak Hydrometeorological Institute, Department of Air Quality, Bratislava, Slovak Republic

5.1.1. Experimental

5.1.1.1. Collection methods

Rain samples corresponding to 12 different locations across Europe (see Figure 5.1) were very kindly provided by Dr. Marta Mitosinkova, from the Slovak Hydrometeorological Institute (Department of Air Quality), Bratislava, Slovak Republic.

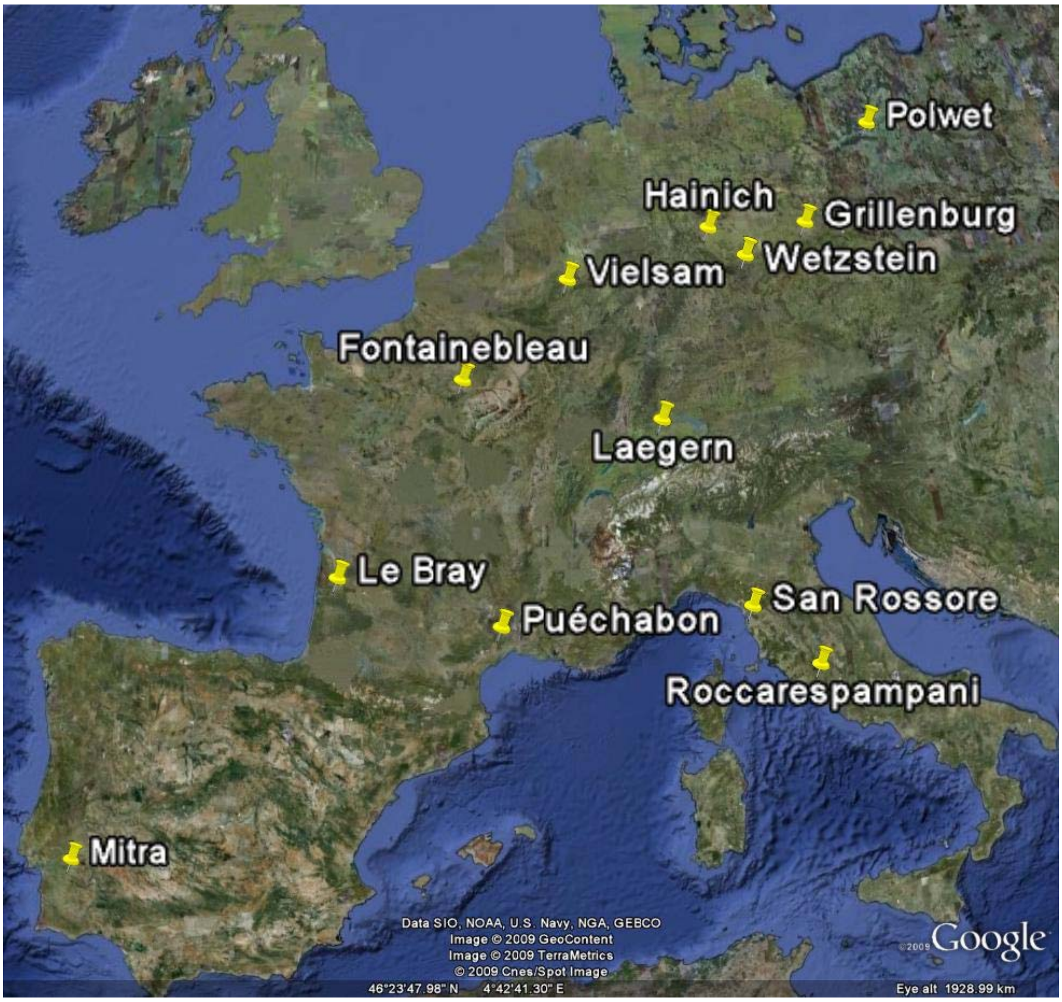


Figure 5.1: Geographical location of the 12 sampling sites of the samples provided by Dr. Marta Mitosinkova, from the Slovak Hydrometeorological Institute (Department of Air Quality), Bratislava, Slovak Republic.

Precipitation was sampled monthly over a period of 10 months, from February 2008 to December 2008, in standard rain collectors consisting of a polypropylene funnel diameter 152 mm mounted directly in a polypropylene collecting bottle (i.e. bulk deposition). Two independent bulk deposition rain collectors were placed at each sampling site.

Determination of the concentrations of the inorganic ions: ammonium, nitrate and potassium (potassium cations were used as a quality control indicator, see Section 5.1.1.3), was carried out in the Slovak Hydrometeorological Institute (Department of Air Quality), Bratislava, Slovak Republic. The analytical technique used was ion chromatography. Due to time constraints, only one of the two replicate samples was analyzed for inorganic ions.

TDN concentration of the two replicate samples was determined for all dates and for all sampling sites. DON concentration was indirectly determined by subtraction of ammonium and nitrate concentrations (provided by Dr Mintosinkova) from TDN concentrations (see Section 2.1).

5.1.1.2. Description of sampling sites

In order to monitor background and regional precipitation quality, and to detect pollution transported over long-range distances, these sites are intended to be located in relatively isolated areas, far from anthropogenic emission sources. However, in Europe, densely covered with emission sources, it is generally difficult to fulfil these criteria completely.

Fontainebleau (N48°28′35″, E02°46′48″), 92 m above sea level (a.s.l.), is a flat deciduous high oak forested area (the oak trees are 20 to 30 m tall and 60 to 150 years old), located 10 km north-east of the town of Fontainebleau (~16000 inhabitants), in the Île-de-France region, in north-central France. The temperate, mostly maritime, climate has average temperature 10.5°C, annual precipitation ~690 mm and prevailing wind direction from the north-west.

Grillenburg (N50°57′00″, E13°30′45″), 375 m a.s.l., is a flat unfertilized grassland area, with 2-4 cuts/year, surrounded by a mixed forested area. It is located in the Saxony region, east-central Germany, 14 km north-east of the city of Freiberg (~43000 inhabitants), 12 km south of the A4 highway, and 20 km south-west of the city of Dresden (~ 512000 inhabitants). The temperate continental climate has average temperature 7.2°C, annual precipitation ~853 mm and prevailing wind direction from the south-west.

Hainich (N51°04′45″, E10°27′07″), 430 m a.s.l., is a flat, forested area consisting of a mix of broad-leaved deciduous tree species (beech, *Fagus sylvatica*, is the dominant tree species). This sampling site is located 13 km north-east of the city of Eisenach (~43000 inhabitants) and of the A4 highway, and 15 km south of the city of Mühlhausen (~37000 inhabitants), in the federal state of Thuringia, in central Germany. The temperate continental climate has average temperature 6.8°C, annual precipitation ~775 mm and prevailing wind direction from the south-west.

Lägeren (N47°28′41″, E08°21′55‴), 682 m a.s.l., is a productive, managed beech forest (which also includes other tree species, mainly ash, sycamore and spruce) on the south-facing slope of the Lägeren mountain (866m a.s.l.), in the boundary of the Swiss Plateau, bordered by the Jura and the Alps, approximately 15 km north-west of Zurich (~361000 inhabitants), Switzerland. The temperate mountain climate has average temperature 8.3°C, annual precipitation ~1100 mm and prevailing wind directions from the west (maximum occurrence) and from the east (secondary maximum). This pattern in the wind direction is a consequence of the linear topography of the Lägeren mountain ridge, which leads to a channelled atmospheric flow along the slope of the ridge.

Le Bray (N44°43′2″, W0°46′9″), 72 m a.s.l., is a flat, forested area consisting of evergreen pine seeded in 1970. A maize crop receiving N fertilizers twice a year is located at 700 m upwind in the prevailing wind direction. The site is located 39 km east of the Atlantic Coast, and 20 km south-west of the city of Bordeaux (approximately 805000 inhabitants), capital of the Aquitaine region, in south-west France. The temperate Atlantic climate has average temperature 13.2°C, annual precipitation ~972 mm and prevailing wind direction from the north-west.

Mitra (N38º31′40″, W8º01′23″), 221 m a.s.l., is an evergreen broadleaf forested area covered with cork oak (*Quercus suber L.*) trees planted in 1988. The site is located in Herdade da Mitra, 12 km south-west of the city of Évora (approximately 41000 inhabitants), in the Alentejo region, in southern Portugal. The temperate Mediterranean mesothermic humid climate with hot and dry summers has average temperature 15.4°C, annual precipitation ~665 mm and prevailing wind direction from the west.

Polwet (N52°45′44″, E16°18′34″), 54 m a.s.l., is a wetland area consisting of reeds (mainly *Fragmites* communities), rushes (mainly *Carex sp*.) and mosses (*Sphangnum sp*.), with a lake on the west side, and surrounded by coniferous forest. This site is located 8 km north-west of the town of Wronki (approximately 11000 inhabitants), in the Szamotuły County, in western-central Poland. The temperate mesothermic climate has average temperature 8.5°C, annual precipitation ~526 mm and prevailing wind direction from the west.

Puéchabon (N43°44′29″, E 3°35′45″), 270 m a.s.l., is an evergreen broadleaf oak forested area (dominated by *Quercus ilex*) managed as a coppice for centuries and last cut in 1942. This site is located 35 km north-west of the Mediterranean coast and 3.5 km north-west of the Puéchabon commune in the Hérault department in the Languedoc-Roussillon region in southern France. The temperate Mediterranean mesothermic climate has average temperature 13.5°C, annual precipitation ~900 mm and prevailing wind direction from the north-west.

Roccarespampani (N42°24′29″, E11°55′48″), 172 m a.s.l., is a deciduous broadleaf oak forested area, dominated by *Quercus cerris*, *Quercus pubescens* and to a lesser extend *Quercus suber*, *Quercus ilex*, *Quercus robur*, and *Juniperus communis*. This site is located 27 km north-east of the Mediterranean coast, and 5 km south-west of the town of Tuscania (~8200 inhabitants), in the province of Viterbo, Latium Region, central Italy. The temperate Mediterranean mesothermic climate has average temperature 14.4°C, annual precipitation ~936 mm and prevailing wind direction from the north-west.

San Rossore (N43°43′40″, E10°17′04″) 11 m a.s.l., is a pine forested area, 500 m east of the Ligurian Sea, 6 km west of the A12 highway, and 9 km west from the city of Pisa (over 87500 inhabitants), in the Tuscany region, central Italy. The temperate Mediterranean mesothermic climate has average temperature 14.5°C, annual precipitation ~920 mm and prevailing wind direction from the north-west.

Vielsalm (N50°18′20″, E05°59′49″), 490 m a.s.l., is a flat (3% slope to the south) mixed forested area, 6 km west of the A27 highway and 7 km east of the town of Vielsalm (approximately 7300 inhabitants), located in the Belgian province of Luxembourg. The temperate maritime climate has average temperature 7.5°C, annual precipitation ~1000 mm and prevailing wind direction from the south-west.

Wetzstein (N50°27′13″, E11°27′27″), 785 m a.s.l., is a flat forested area consisting of evergreen conifers (*Picea abies*), 23 km south of the town of Saalfeld (approximately 28000 inhabitants), in the federal state of Thuringia, in central-east Germany. The temperate continental climate has average temperature 5.5°C, annual precipitation 880 to 1015 mm and prevailing wind direction from the south-west.

5.1.1.3. Sample quality control

Several criteria were used to identify valid precipitation samples:

(i) Good agreement in TDN concentration between the two replicate samples for each date and location: in the sending laboratory (due to time constraints) only one of the replicate samples was analysed. Dates with higher TDN concentration in the sample analyzed for inorganic ions than in the replicate sample, and with the standard deviation between replicate samples larger than the TDN concentration in the less concentrated sample were removed from the study due to strong suspicion of biological contamination. A total of 12 samples out of the 122 samples fully analyzed were discarded for that reason: 2 samples from Fontainebleau, 2 samples from Puéchabon, 1 sample from Mitra, 1 sample from Le Bray, 1 sample from Lägeren, 2 samples from Hainich and 3 samples from Vielsalm.

(ii) Samples free from obvious contamination: as K^+ is a good marker for biological contamination, samples with K^+ concentration exceeding 1 mg L^{-1} were discarded. A total of 15 samples out of 122 samples fully analyzed were removed for this reason: 2 samples from San Rossore, 1 sample from Roccarespampani, 3 samples from Puéchabon, 5 samples from Mitra, 2 samples from Lägeren and 2 samples from Hainich.

(iii) The sample must have sufficient amount of rainfall: the minimum volume was set at 50 mL. Samples with lower volumes were discarded, as they are more vulnerable to alterations in original composition, mainly due to evaporation or condensation processes. Four samples out of a total of 122 samples analyzed were discarded for this reason: 1 sample from San Rossore, 1 sample from Roccarespampani, 1 sample from Polwet and 1 sample from Mitra.

(iv) Samples with absolute value of DON negative concentration greater than 0.07 mg N L^{-1}, which represents three times the sum of the limits of detection (LOD) of TDN (LOD = 0.018mg N L^{-1}) and ammonium and nitrate (LOD = 0.003mg N L^{-1}), were regarded as not valid due to strong suspicion of alterations in sample concentration due to losses of ammonium during transport, for example, in samples with high pH: $NH_4^+ + OH^- \rightleftarrows NH_3$. Alkaline conditions, relatively high concentrations of ammonium in the sample, and increases of sample temperature during transport are all factors that would enhance losses of ammonium in the form of gas phase ammonia. Sample contamination during ammonium or nitrate analysis might be another reason for large negative concentrations of DON. A total of 13 samples out of 122 samples analyzed were discarded for this reason: 6 samples from San Rossore, 3 samples from Le Bray, 2 samples from Lägeren, 1 sample from Hainich and 1 sample from Vielsalm. Samples with negative values of DON less than 0.07 mg N L^{-1} were retained in the statistical analysis, as these negative values might be the consequence of relatively large uncertainties due to the indirect determination of DON concentrations, and therefore, the removal of these values might bias the statistical analysis towards larger average DON concentrations.

In summary, from a total of 122 samples analyzed, 36 were regarded as "not valid": 2 samples from Fontainebleau, 6 samples from San Rossore, 1 sample from Roccarespampani, 4 samples from Puechabon, 1 sample from Polwet, 5 samples from Mitra, 4 samples from Le Bray, 5 samples from Lägeren, 4 samples from Hainich and 4 samples from Vielsalm.

5.1.2. Results and discussion

Figures 5.2 to 5.13 show the time series of rain (bulk deposition) concentration of ammonium, nitrate and DON (in mg N L^{-1}) at Fontainebleau, Grillenburg, Hainich, Lägeren, Le Bray, Mitra, Polwet, Puéchabon, Roccarespampani, San Rossore, Vielsalm and Wetzstein sampling sites respectively. The vertical scale for nitrogen species concentration is constant in all the figures in order to facilitate comparison between the different sampling sites.

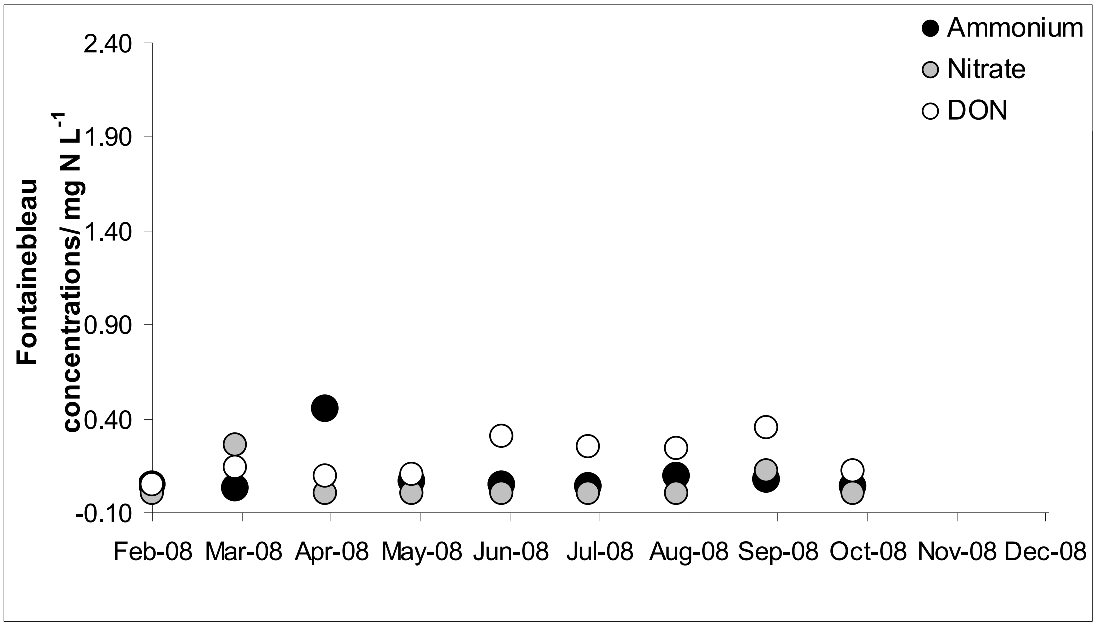


Figure 5.2: Time series of ammonium, nitrate and DON concentration in monthly rain samples (bulk deposition) in mg N L^{-1}. Fontainebleau sampling site.

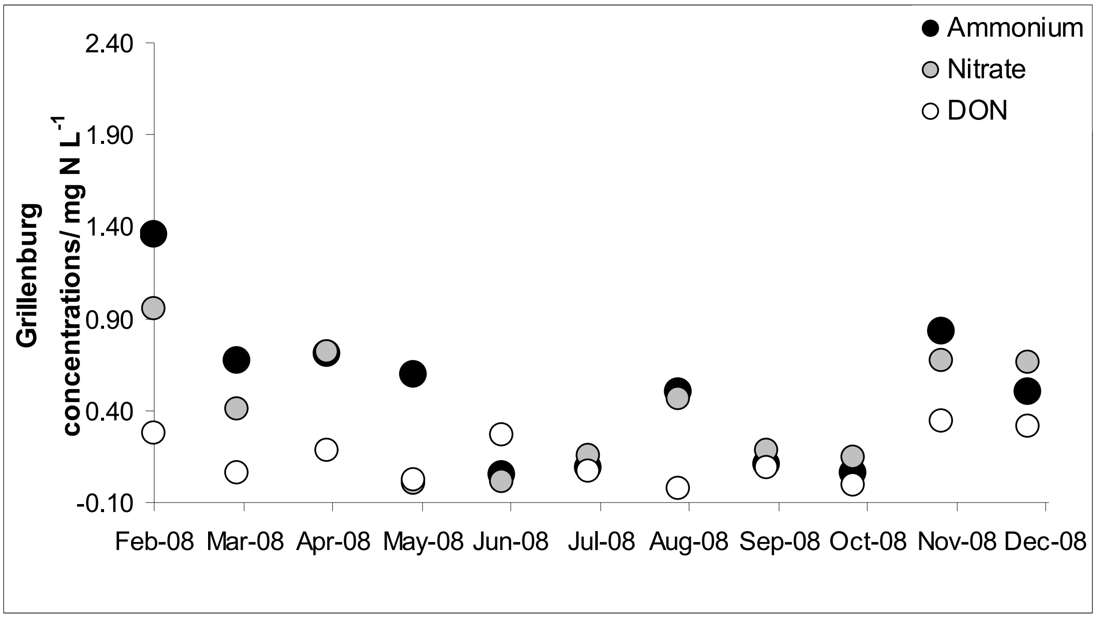


Figure 5.3: Time series of ammonium, nitrate and DON concentration in monthly rain samples (bulk deposition) in mg N L^{-1}. Grillenburg sampling site.

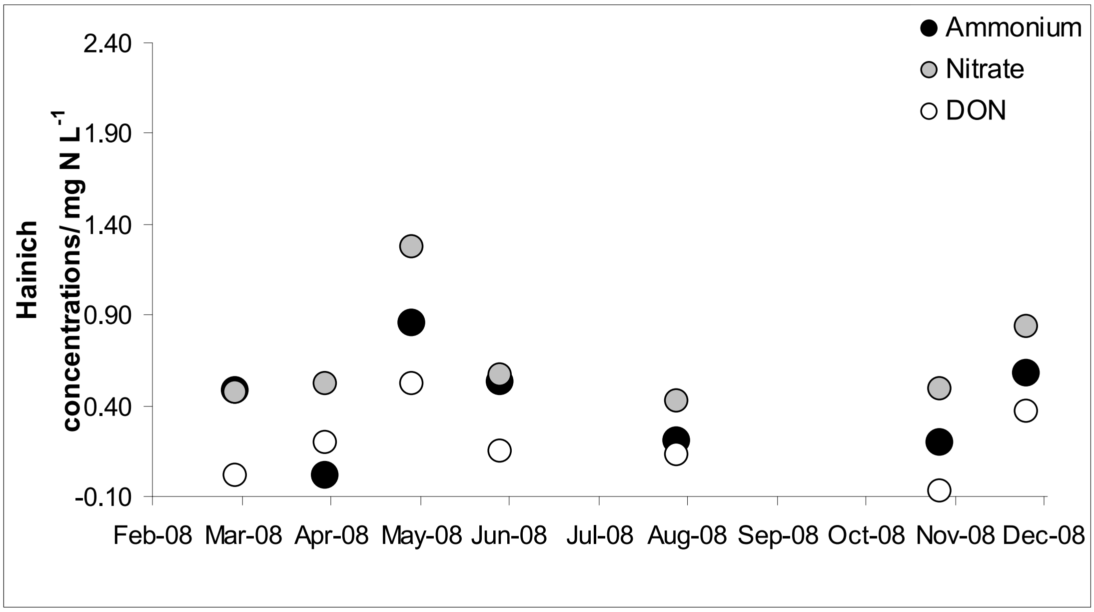


Figure 5.4: Time series of ammonium, nitrate and DON concentration in monthly rain samples (bulk deposition) in mg N L^{-1}. Hainich sampling site.

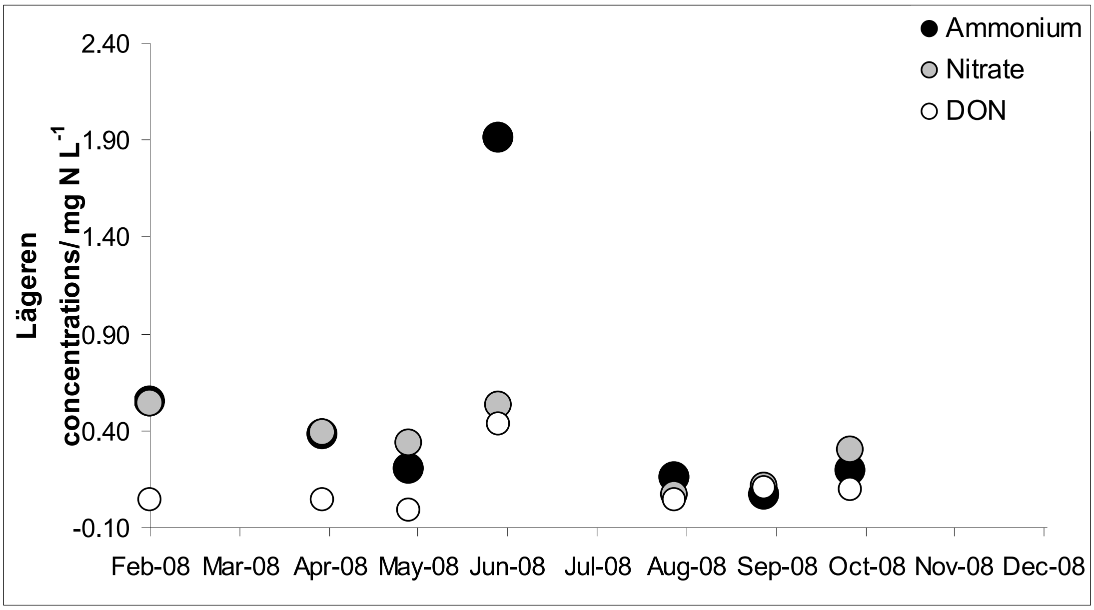


Figure 5.5: Time series of ammonium, nitrate and DON concentration in monthly rain samples (bulk deposition) in mg N L^{-1}. Lägeren sampling site.

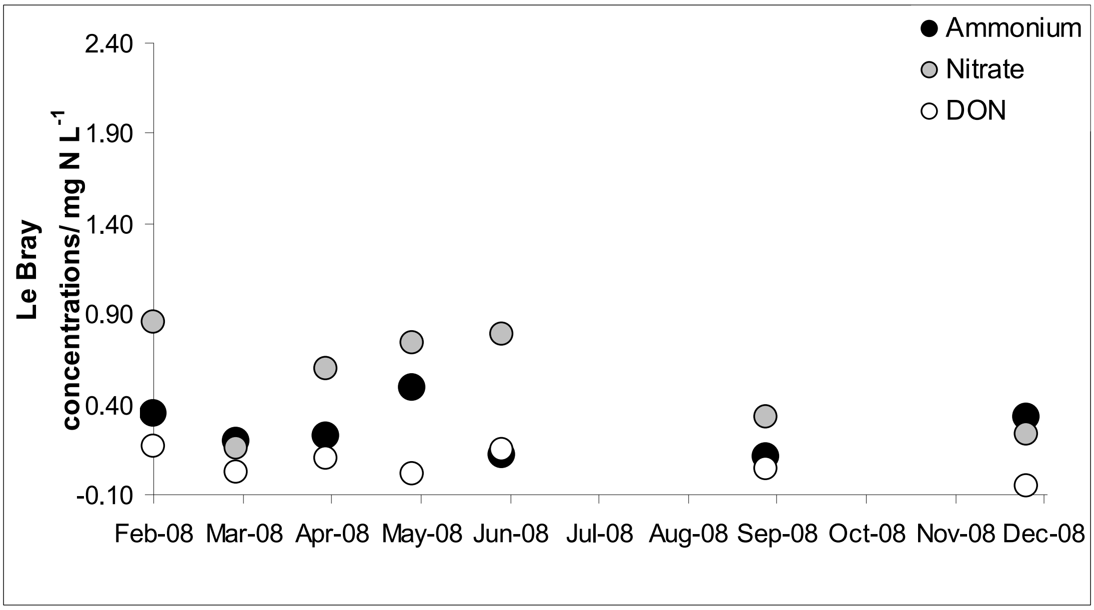


Figure 5.6: Time series of ammonium, nitrate and DON concentration in monthly rain samples (bulk deposition) in mg N L^{-1}. Le Bray sampling site.

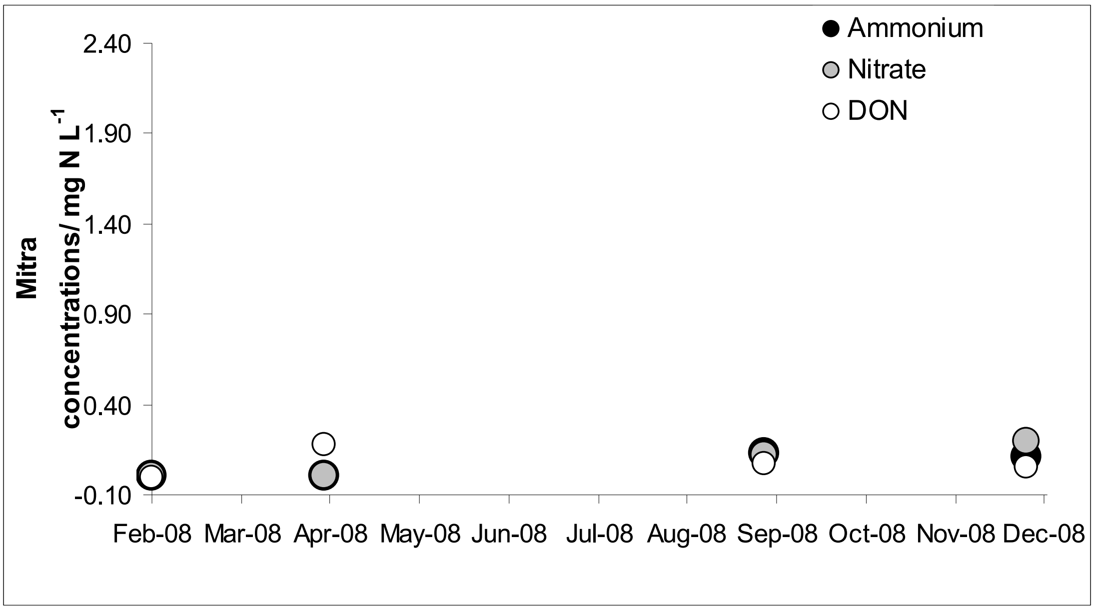


Figure 5.7: Time series of ammonium, nitrate and DON concentration in monthly rain samples (bulk deposition) in mg N L^{-1}. Mitra sampling site.

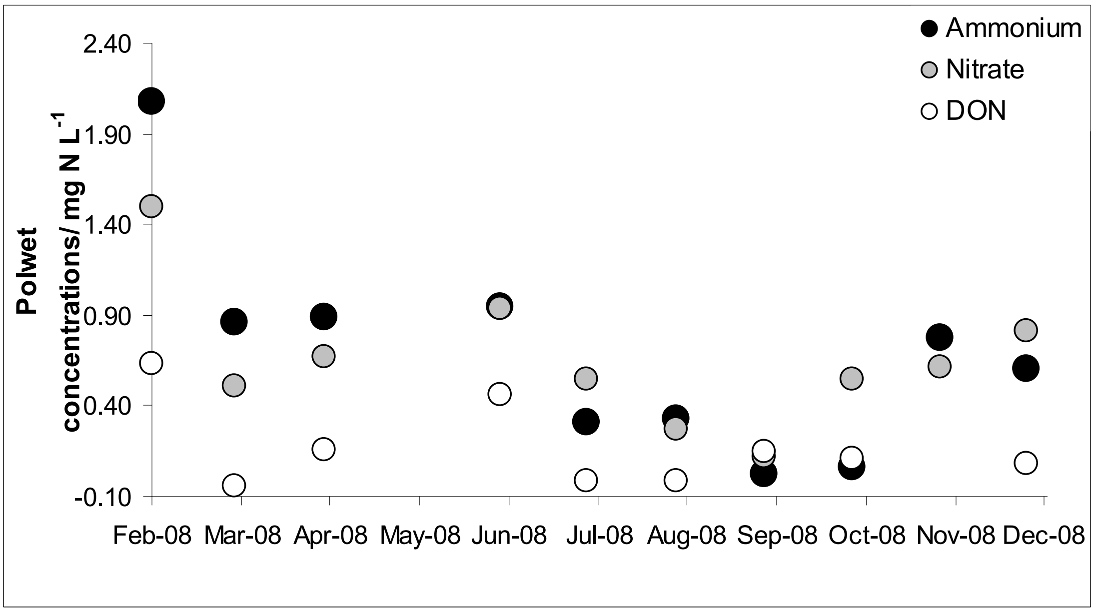


Figure 5.8: Time series of ammonium, nitrate and DON concentration in monthly rain samples (bulk deposition) in mg N L^{-1}. Polwet sampling site.

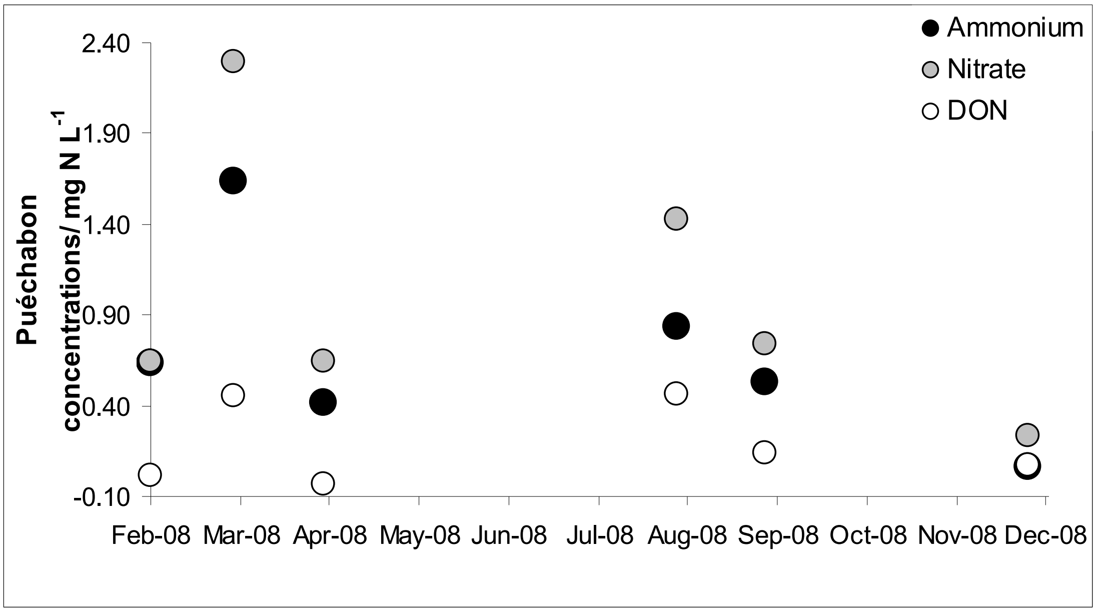


Figure 5.9: Time series of ammonium, nitrate and DON concentration in monthly rain samples (bulk deposition) in mg N L^{-1}. Puéchabon sampling site.

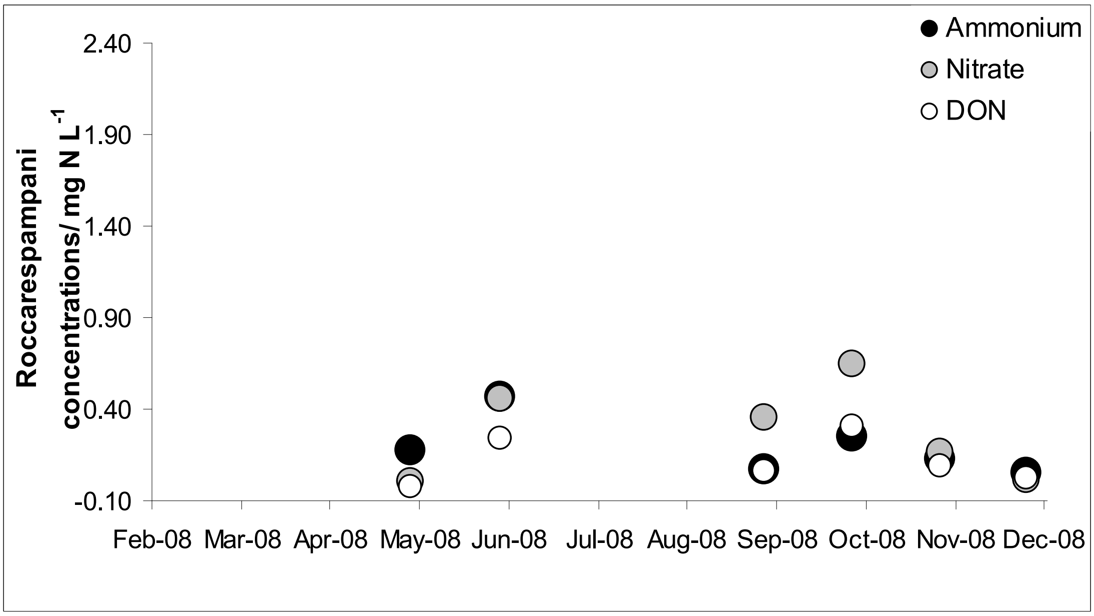


Figure 5.10: Time series of ammonium, nitrate and DON concentration in monthly rain samples (bulk deposition) in mg N L^{-1}. Roccarespampani sampling site.

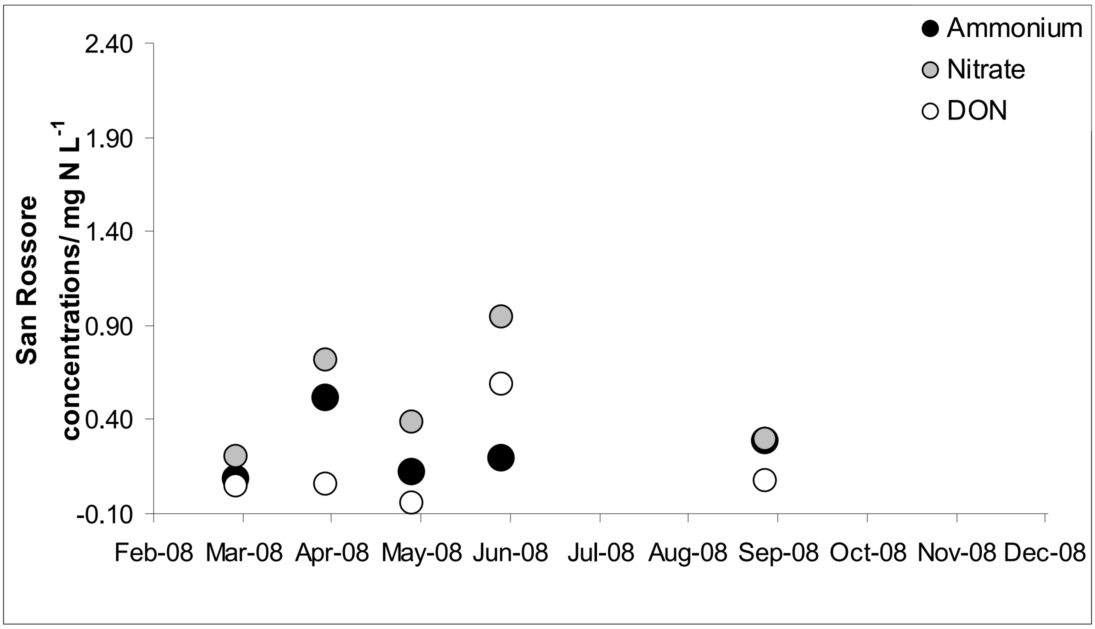


Figure 5.11: Time series of ammonium, nitrate and DON concentration in monthly rain samples (bulk deposition) in mg N L^{-1}. San Rossore sampling site.

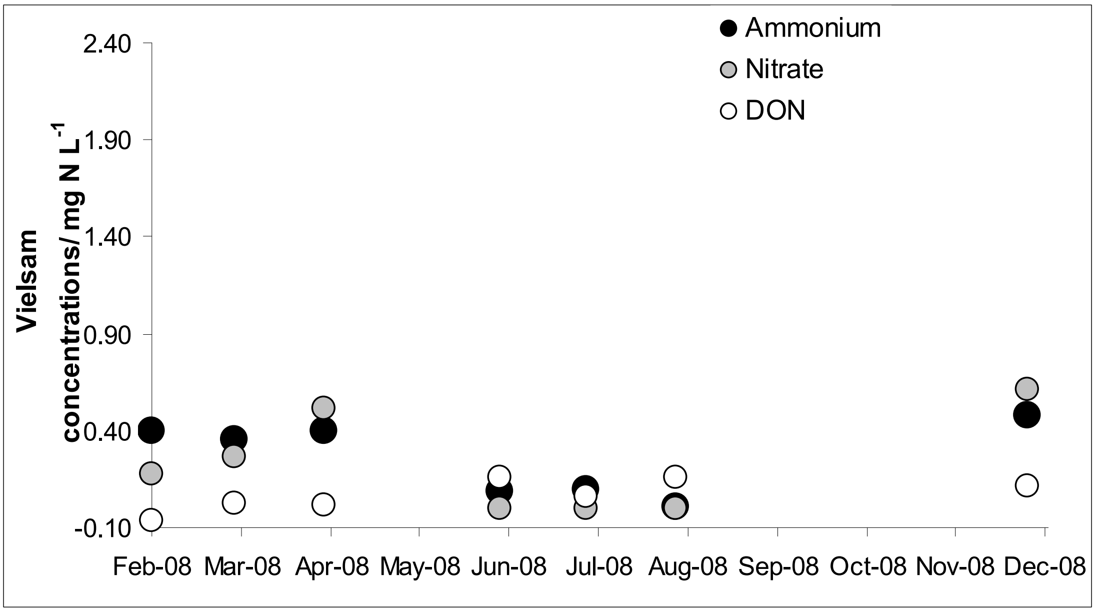


Figure 5.12: Time series of ammonium, nitrate and DON concentration in monthly rain samples (bulk deposition) in mg N L^{-1}. Vielsalm sampling site.

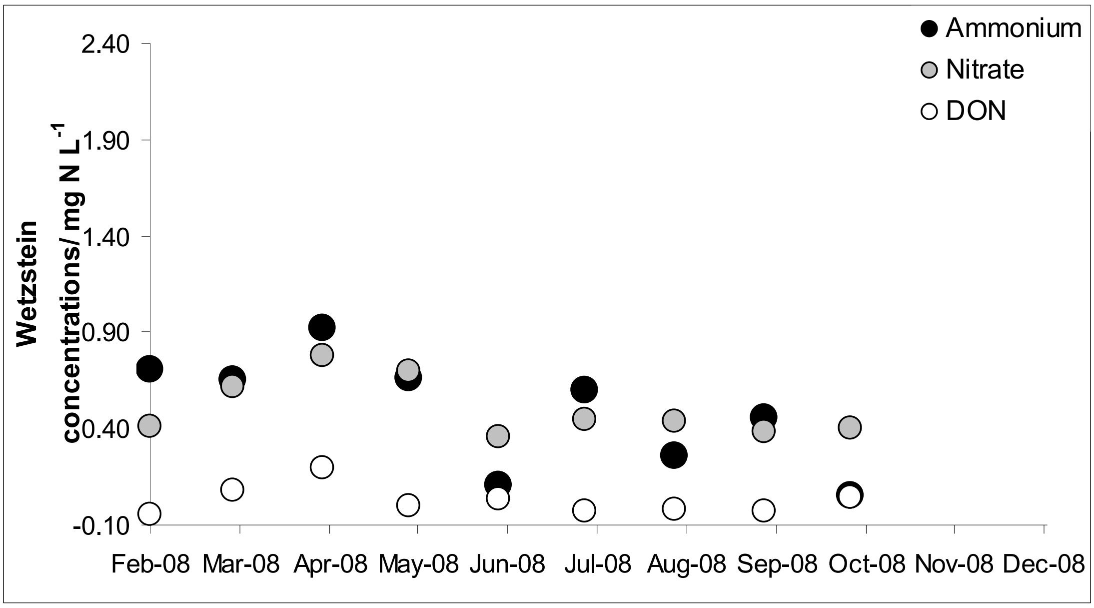


Figure 5.13: Time series of ammonium, nitrate and DON concentration in monthly rain samples (bulk deposition) in mg N L^{-1}. Wetzstein sampling site.

Concentration of total dissolved nitrogen species (TDN) in valid rain samples (bulk deposition) ranged from below the limit of detection (~0.02 mg N L^{-1}) at Mitra sampling site in February 2008, to 4.38 mg N L^{-1} at Puéchabon sampling site in March 2008.

Table 5.2 summarises average and rainfall-weighted mean concentrations (in mg N L^{-1}) of total dissolved nitrogen (TDN), ammonium, nitrate and dissolved organic nitrogen (DON) measured in the valid rain samples (bulk deposition) collected at each sampling site. Standard deviation (SD) of the concentrations across sampling dates for each sampling site has been included as an indicator of concentration variability through the period of study. Nitrogen species concentrations are normally distributed at all sampling sites according to Shapiro-Wilk normality tests, and there is good agreement between average and median concentration for most of the nitrogen species at all the sampling sites.

	Arithmetic mean concentration/ mg N L^{-1}				**Rainfall weighted mean concentration/ mg N L^{-1}**				**Standard deviation of concentrations across sampling dates/ mg N L^{-1}**			
Sampling site	**TDN**	**NH_4^+**	**NO_3^-**	**DON**	**TDN**	**NH_4^+**	**NO_3^-**	**DON**	**TDN**	**NH_4^+**	**NO_3^-**	**DON**
Fontainebleau	0.32	0.10	0.04	0.18	0.30	0.12	0.03	0.15	0.16	0.13	0.09	0.11
Grillenburg	1.04	0.50	0.40	0.14	0.99	0.46	0.41	0.11	0.77	0.41	0.32	0.13
Hainich	1.02	0.33	0.55	0.13	0.99	0.33	0.55	0.12	0.44	0.23	0.15	0.15
Lägeren	0.61	0.26	0.29	0.05	0.89	0.48	0.31	0.11	0.33	0.18	0.18	0.04
Le Bray	0.85	0.26	0.53	0.06	0.76	0.28	0.45	0.03	0.40	0.14	0.28	0.08
Mitra	0.22	0.06	0.08	0.07	0.22	0.06	0.08	0.09	0.16	0.07	0.10	0.08
Polwet	1.71	0.69	0.65	0.37	1.30	0.53	0.53	0.24	1.31	0.60	0.38	0.69
Puéchabon	1.87	0.69	1.00	0.18	1.12	0.44	0.62	0.06	1.45	0.53	0.74	0.22
Roccarespampani	0.58	0.19	0.27	0.11	0.31	0.12	0.14	0.06	0.49	0.15	0.26	0.13
San Rossore	0.89	0.24	0.51	0.14	0.69	0.21	0.41	0.06	0.60	0.17	0.31	0.25
Vielsalm	0.85	0.29	0.26	0.31	0.49	0.24	0.19	0.07	0.94	0.20	0.25	0.68
Wetzstein	1.02	0.49	0.50	0.03	1.01	0.49	0.49	0.03	0.46	0.30	0.15	0.08

Table 5.2: Summary of arithmetic mean and rainfall weighted mean concentrations of total dissolved nitrogen (TDN), ammonium, nitrate and dissolved organic nitrogen (DON) in rain (bulk deposition), in mg N L^{-1}. Also included are the standard deviations (SD) of the concentrations across sampling dates. Samples were collected monthly at each sampling site over a 10-month period from February 2008 to December 2008.

Figure 5.14 shows the rainfall-weighted mean concentrations respectively for ammonium, nitrate and dissolved organic nitrogen (DON) in mg N L^{-1} over all valid rain samples (bulk deposition) collected at each sampling site.

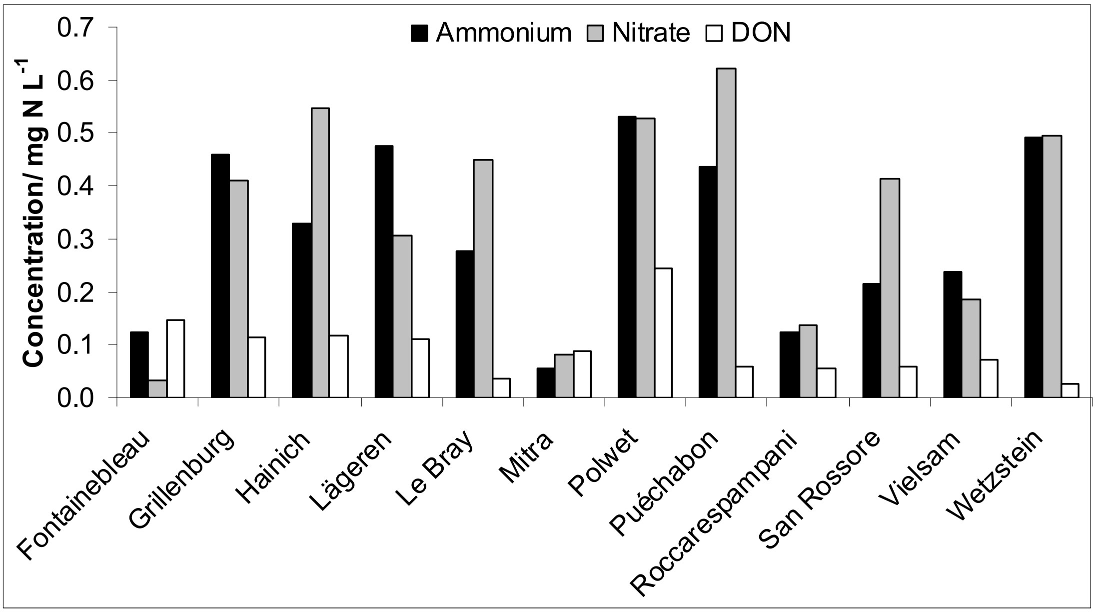


Figure 5.14: Rainfall weighted mean concentrations of ammonium, nitrate and DON in mg N L^{-1} over all valid samples for each sampling site.

Figure 5.15 shows the rainfall-weighted mean percentage respectively of ammonium, nitrate and DON concentrations relative to TDN over all valid rain samples (bulk deposition) collected at each sampling site.

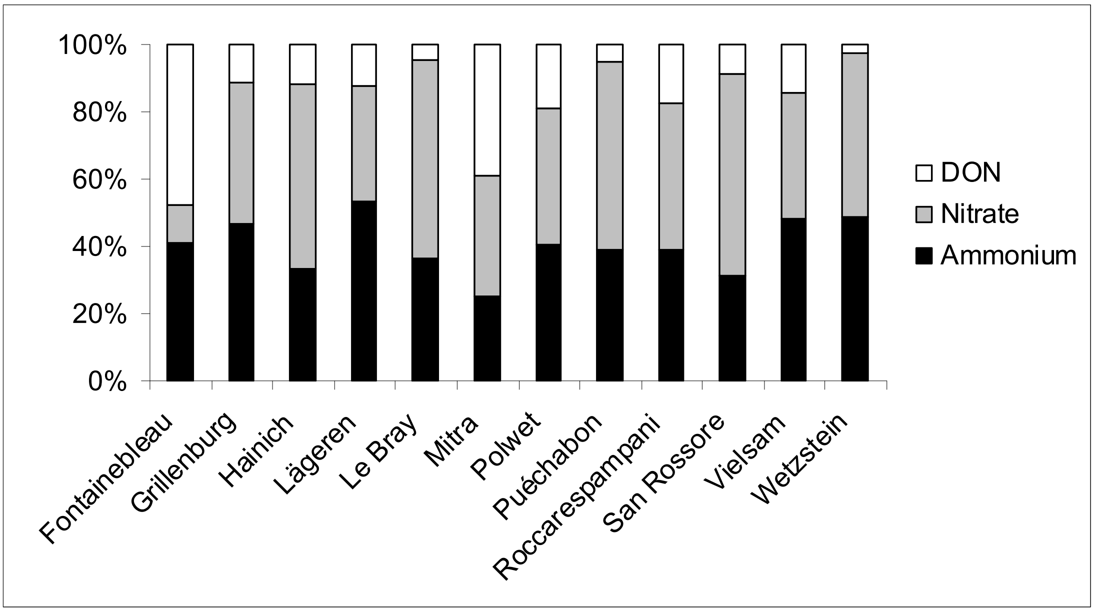


Figure 5.15: Rainfall weighted mean % of ammonium, nitrate and DON relative to TDN over all valid sampling dates for each sampling site.

On average, the sites with the highest TDN concentrations are Puéchabon and Polwet, and the sites with the lowest TDN concentrations are Mitra and Fontainebleau.

Bulk deposition might receive contributions from wet deposition (species actually dissolved in the rain) and from dry deposition (species deposited on the walls of the funnel of the rain collector and flushed inside the collector during a rain event). As discussed in Chapter 3, dry deposition might be a large contributor to bulk deposition. Species either in the gas phase or in particulate matter can contribute to wet and dry deposition, and therefore to bulk deposition as well.

It should be noted that in this study the sites with the lowest TDN concentrations (Mitra and Fontainebleau) are the sites with the largest DON fraction relative to the TDN (see Table 5.2 and Figures 5.14 and 5.15), which might point to small contributions from agricultural or combustion sources for DON, as in more pristine locations DON concentration is proportionally larger. Further investigation of DON origin was attempted by the study of correlation statistical analysis (Pearson's tests) of ammonium, nitrate and DON in all valid samples at each sampling site.

		Pearson's correlation tests		
		NH_4^+ - NO_3^-	**NH_4^+ - DON**	**NO_3^- - DON**
Fontainebleau	***R***	-0.212	-0.266	0.113
	p value	0.584	0.489	0.772
Grillenburg	***R***	0.816**	0.412	0.551
	p value	0.002	0.207	0.079
Hainich	***R***	0.577	0.312	0.791
	p value	0.231	0.548	0.061
Lägeren	***R***	0.895*	-0.25	-0.265
	p value	0.016	0.633	0.611
Le Bray	***R***	0.313	-0.268	0.75
	p value	0.495	0.562	0.052
Mitra	***R***	0.912	-0.170	-0.205
	p value	0.088	0.830	0.795
Polwet	***R***	0.891**	0.286	0.224
	p value	0.001	0.422	0.534
Puéchabon	***R***	0.974**	0.756	0.861*
	p value	0.001	0.082	0.027
Roccarespampani	***R***	0.553	0.674	0.921**
	p value	0.256	0.142	0.009
San Rossore	***R***	0.431	-0.039	0.785
	p value	0.469	0.951	0.116
Vielsalm	***R***	0.895**	0.383	0.355
	p value	0.003	0.350	0.388
Wetzstein	***R***	0.895*	-0.25	-0.265
	p value	0.016	0.633	0.611

Table 5.3: Summary of Pearson's statistical analysis for correlations of ammonium, nitrate and DON concentrations at each of the 12 locations from where rain samples were provided by Dr. Marta Mitosinkova, from the Slovak Hydrometeorological Institute (Department of Air Quality), Bratislava, Slovak Republic. ** indicates *R* whose correlation is significant at the 0.01 level (2-tailed). * indicates *R* whose correlation is significant at the 0.05 level (2-tailed).

Table 5.3 summarises the Pearson correlation coefficient data for ammonium, nitrate and DON concentrations at each of the 12 locations being discussed in this section. The results presented in this table show that (i) there is no significant correlation between ammonium (both from gas phase origin or particulate matter) and DON concentrations in any of the sampling sites under study, and (ii) only at two sampling sites (Puéchabon and Roccarespampani) is there a statistically significant correlation between nitrate and DON (Figures 5.16 and 5.17). At two further sampling sites, Hainich and Le Bray, there is an indication of a relationship between at least a fraction of DON and nitrate (Figures 5.18 and 5.19), although there is no formal statistically-significant correlation between the two species.

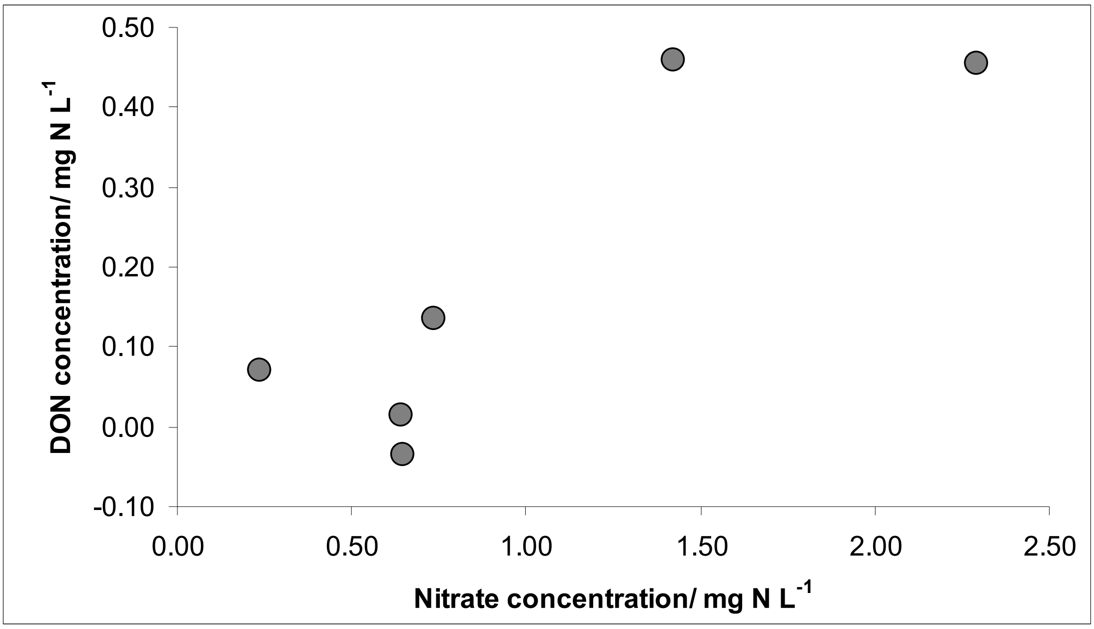


Figure 5.16: Rain samples (bulk deposition) correlation analysis for Puéchabon sampling site: DON concentrations plotted against nitrate concentrations.

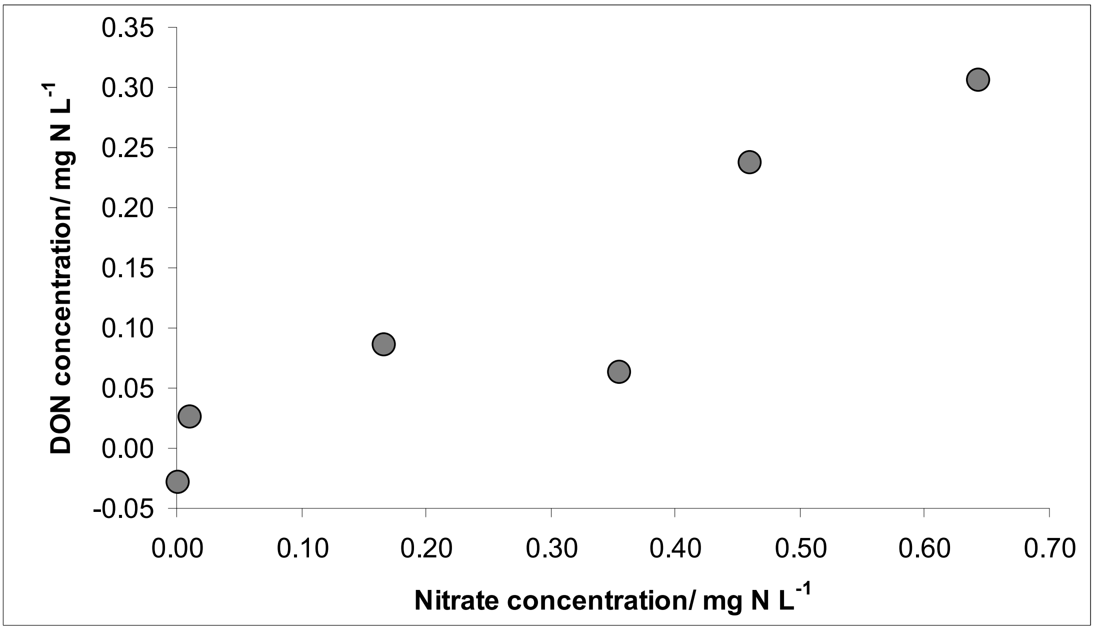


Figure 5.17: Rain samples (bulk deposition) correlation analysis for Roccarespampani sampling site: DON concentrations plotted against nitrate concentrations.

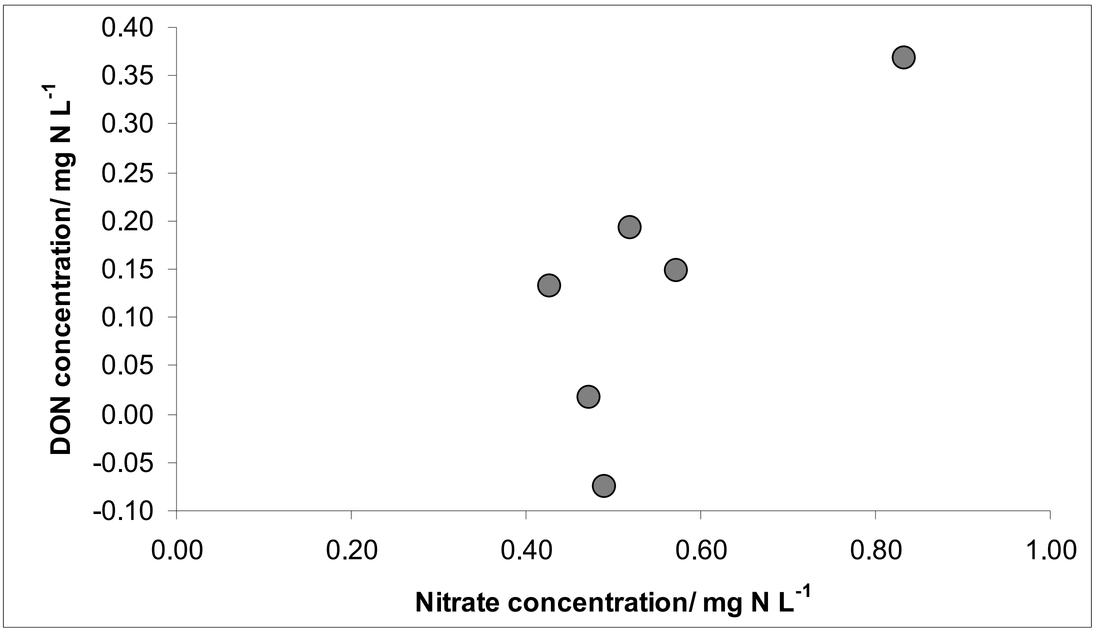


Figure 5.18: Rain samples (bulk deposition) correlation analysis for Hainich sampling site: DON concentrations plotted against nitrate concentrations.

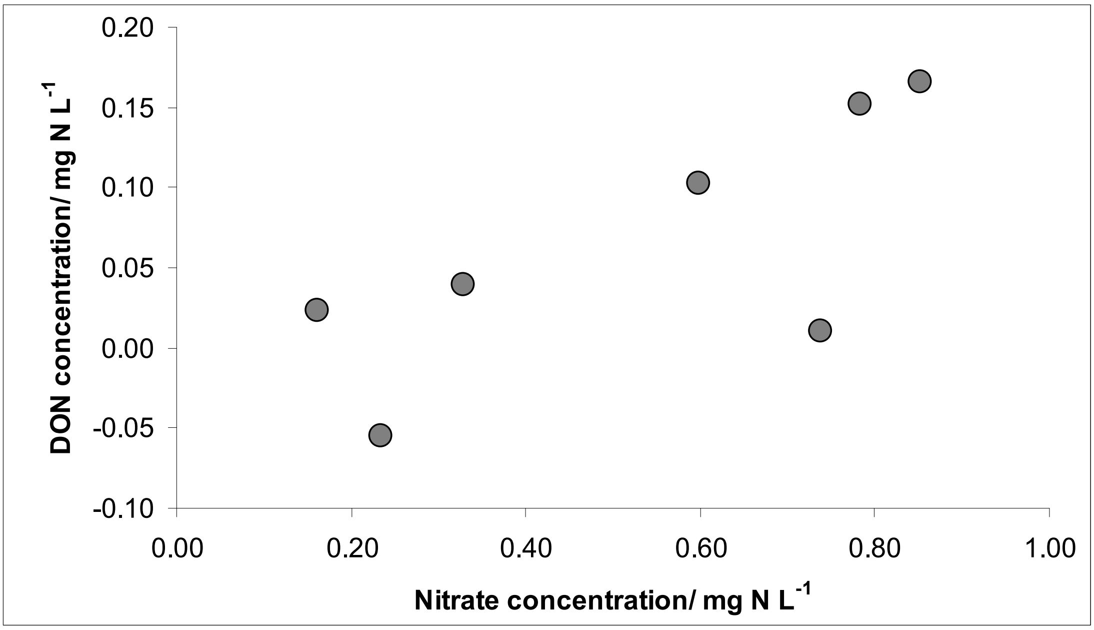


Figure 5.19: Rain samples (bulk deposition) correlation analysis for Le Bray sampling site: DON concentrations plotted against nitrate concentrations.

In the gas phase the main source of ammonium is ammonia, and the main sources of nitrate are nitric acid and nitrogen dioxide. Both species (ammonia and nitrogen dioxide) are mainly from anthropogenic origin: the majority of ammonia sources are agricultural, as ammonia is mainly released into the atmosphere due to decomposition and volatilization of animal wastes. Nitrogen dioxide is mainly released into the atmosphere in high-temperature fuel combustion reactions in motor vehicles and in industrial and utility boilers. These emissions are mainly located in urban areas and are primarily in the form of nitrogen monoxide, which is oxidized by atmospheric ozone to nitrogen dioxide. Atmospheric nitric acid is primarily formed by reaction of nitrogen dioxide with hydroxyl radicals. In particulate matter the main sources of ammonium are ammonium nitrate and ammonium sulphate. Both species are secondary particles, formed by the reaction of nitric acid and sulphuric acid with ammonia. The main sources of nitrate in particulate matter are ammonium nitrate or, in the absence of ammonia, nitric acid. The main sources of ammonium nitrate are a combination of agriculture and combustion.

According to the statistical analysis of the dataset (Pearson's test) Roccarespampani is the only sampling site that presented a highly significant correlation ($p<0.01$) between nitrate and DON (Table 5.3). At this remote location (with the lowest concentrations of nitrogen species after the Mitra and Fontainebleau sites) no correlations existed between nitrate and ammonium or between DON and ammonium. The absence of correlation between nitrate and ammonium concentrations points to gas-phase ammonia (mainly local agricultural origin) as the larger contributor to ammonium, and gas phase nitrogen dioxide (combustion origin) and nitric acid (formed by reaction of nitrogen dioxide with hydroxyl radicals) as the main contributors to nitrate at this sampling site. The absence of correlation between DON and ammonium suggests that local agricultural sources are not the main contributors to DON at this sampling site, and the highly significant correlation between DON and nitrate points to a link between an important fraction of DON and combustion sources at this sampling site.

In the case of the Puéchabon sampling site, the statistical analysis of the dataset (Pearson's test, Table 5.3) did show highly significant correlation ($p<0.01$) between nitrate and ammonium, significant correlation ($p<0.05$) between nitrate and DON, and no obvious correlation ($p = 0.08$) between ammonium and DON. The good agreement between ammonium and nitrate concentrations points to long-range transport of particulate matter (in the form of ammonium nitrate) from a combination of combustion and agricultural sources as the likely origin of most of the ammonium species and the larger fraction of nitrate species collected at this site. In all valid samples, higher concentrations of nitrate than ammonium were found, pointing to nitrogen dioxide or nitric acid as secondary contributors to nitrate concentrations in bulk deposition. At this location, the lack of correlation between DON and ammonium, and the statistically significant correlation between DON and nitrate, point to a close relation between DON and material from long-distance combustion sources (nitrogen dioxide, nitric acid or both).

For Hainich and Le Bray locations, the correlation between DON and nitrate is not, strictly speaking, statistically significant ($p = 0.061$ and 0.052 respectively in Pearson's test). However, as these p values are very close to the limit of statistical significance, it can be argued that, in both locations, at least a fraction of DON might be linked to combustion sources. In the case of Hainich, the most obvious combustion sources are located in the urban and industrial area of Eisenach (with two large manufacturing facilities, one from automobile manufacturing Opel and the other from Bosch Corporation, both located in the north-west of the town) and the A4 highway, all located at 13 km south-west of the sampling site, in the prevailing upwind direction.

In summary: the results presented in Table 5.3 suggest that an important fraction of the DON species measured in this study is not related to human activities. No evidence linking DON to agricultural activities was found at any location, but in 4 out of 12 locations at least a fraction of DON is suggested to be related to combustion sources.

5.2. Meteorological and Hydrological Service of Croatia, Air Quality Research Unit, Zagreb, Croatia

5.2.1. Experimental

5.2.1.1. Collection methods

Rain samples from the Zavižan sampling site (see Figure 5.20) were very kindly provided by Dr. Sonja Vidic, from the Meteorological and Hydrological Service of Croatia (Air Quality Research Unit), Zagreb, Croatia.

Figure 5.20: Geographical location of the sampling site (Zavižan) of the samples provided by Dr. Sonja Vidic, from the Meteorological and Hydrological Service of Croatia (Air Quality Research Unit), Zagreb, Croatia.

Precipitation was sampled daily over a period of 6 months, from March 2008 to August 2008, in a standard rain collector consisting of a polypropylene funnel diameter 152 mm mounted directly in a polypropylene collecting bottle (i.e. bulk deposition).

Determination of the concentrations of the inorganic nitrogen ions (ammonium and nitrate) was carried out in the Meteorological and Hydrological Service of Croatia (Air Quality Research Unit), Zagreb, Croatia. The analytical technique used was ion chromatography (see Sections 2.2 and 2.3).

5.2.1.2. Description of sampling site

Zavižan (N44°48′53″, E14°58′32″), 1594 m above sea level, is an isolated sampling site, located in the Lika-Senj county, the least populated in Croatia, 7 km east of the Adriatic coast, and 20 km west of the A1 highway and the town of Otočac (~4400 inhabitants). Given the moderately warm and oceanic climate under Köppen classification, most of the precipitation collected at this site is carried by air masses from south-west and west directions. This site is not influenced by local pollution and, due to its high elevation and isolation from emission sources, was selected by the European Monitoring and Evaluation Programme (EMEP) as one of the measurement sites for the detection of pollution transported over long-range distances. EMEP is a scientifically based and policy driven programme under the Convention on Long-range Transboundary Air Pollution for international co-operation to solve transboundary air pollution problems.

5.2.1.3. Sample quality control

Two criteria were used to identify valid precipitation samples:

(i) Samples were screened for obvious contamination prior to transport to the Centre for Ecology & Hydrology: samples were excluded if they had K^+ concentration greater than 1 mg L^{-1} since K^+ is a good marker for biological contamination.

(ii) Samples with value of DON concentration more negative than 0.07 mg N L^{-1}, three times the sum of the limits of detection (LOD) of TDN and ammonium and nitrate, were regarded as not valid due to strong suspicion of alterations in sample concentration due to losses of ammonium during transport. 25 samples out of a total of 67 samples analyzed were discarded for this reason. Samples with negative values of DON smaller than 0.07 mg N L^{-1} were retained in the statistical analysis, as these negative values might be the consequence of relatively large uncertainties due to the indirect determination of DON concentrations, and therefore the removal of these values might bias the statistical analysis towards larger average DON concentrations. However, due to the large number of samples discarded for failing this criterion there are concerns that the karst topography of this sampling site might have enhanced alkaline conditions in other samples too, leading to some losses of ammonium as ammonia gas during transport to the UK, and therefore to an underestimation of TDN and consequently of DON as well. pH measurements of these samples (carried out at the moment of the inorganic ions analysis) provide some evidence for this hypothesis since the average pH of 6.3 of all valid samples (range 5.3 – 7.6) was more alkaline than the pH of 5.6 for water in equilibrium with atmospheric levels of CO_2. As an improvement for future sampling campaigns, vials should be pretreated with a small amount of acid to prevent potential alkaline conditions.

5.2.2. Results and discussion

Figure 5.21 show the time series of daily rain (bulk deposition) concentration of ammonium, nitrate and DON (in mg N L^{-1}) at the Zavižan sampling site.

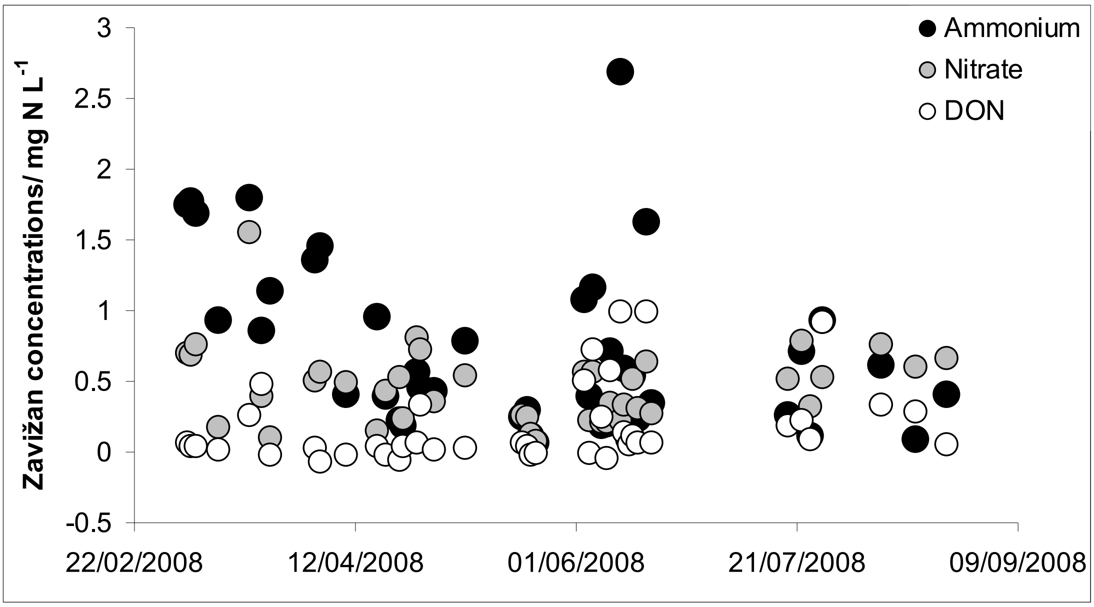


Figure 5.21: Time series of ammonium, nitrate and DON concentration in daily rain samples (bulk deposition) in mg N L^{-1}. Zavižan sampling site.

Concentration of total dissolved nitrogen species (TDN) in valid rain samples (bulk deposition) ranged from a minimum of 0.11 mg N L^{-1} on the 23rd of May 2008, to a maximum of 3.88 mg N L^{-1} on the 11th of June 2008, and the daily precipitation for valid sampling dates ranged from a minimum of 0.9 mm on the 17th of April 2008 to a maximum of 46.1 mm on the 24th of March 2008.

Table 5.4 summarises rainfall-weighted mean and median concentrations (in mg N L^{-1}) of total dissolved nitrogen (TDN), ammonium, nitrate and dissolved organic nitrogen (DON) found in the valid rain samples (bulk deposition) collected at the Zavižan sampling site. The standard deviation (SD) of the concentrations across sampling dates has been included as an indicator of concentration variability through the period of study. According to Shapiro-Wilk normality tests, nitrogen species concentrations are not normally distributed at this sampling site. Under these circumstances median concentration of the valid samples might be more representative than average concentration. For this reason Table 5.4 includes median concentrations instead of arithmetic mean concentrations.

	Zavižan sampling site	
Rainfall weighted mean concentration/ mg N L^{-1}	**TDN**	1.29
	NH_4^+	0.77
	NO_3^-	0.45
	DON	0.08
Median concentration/ mg N L^{-1}	**TDN**	1.13
	NH_4^+	0.55
	NO_3^-	0.46
	DON	0.06
Standard deviation of concentrations across sampling dates/ mg N L^{-1}	**TDN**	0.92
	NH_4^+	0.61
	NO_3^-	0.28
	DON	0.28

Table 5.4: Summary of rainfall weighted mean and median concentrations of total dissolved nitrogen (TDN), ammonium, nitrate and dissolved organic nitrogen (DON) in rain (bulk deposition), in mg N L^{-1}. It includes the standard deviations (SD) of the concentrations across sampling dates. Samples were collected daily at Zavižan sampling site over a 6-month period, from March 2008 to August 2008.

Further investigation of nitrogen species at this sampling site was performed by the study of correlation plots and correlation statistical analysis (Pearson's tests). Figures 5.22, 5.23 and 5.24 show the correlation plots of nitrate versus ammonium, DON versus ammonium and DON versus nitrate, respectively, for the Zavižan sampling site.

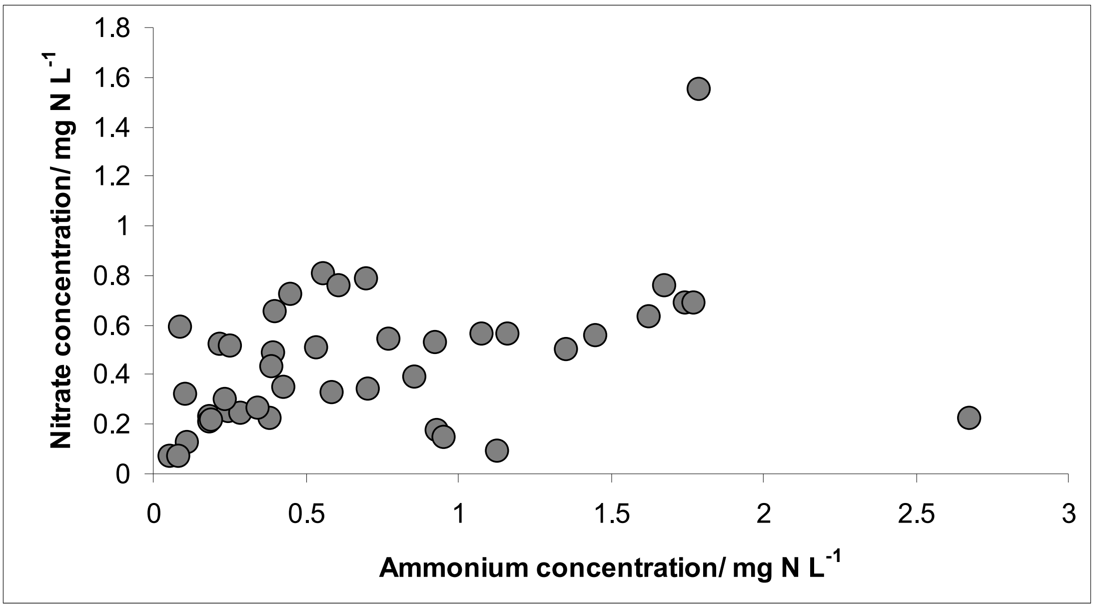


Figure 5.22: Daily rain samples (bulk deposition) correlation analysis for Zavižan sampling site: nitrate concentrations plotted against ammonium concentrations.

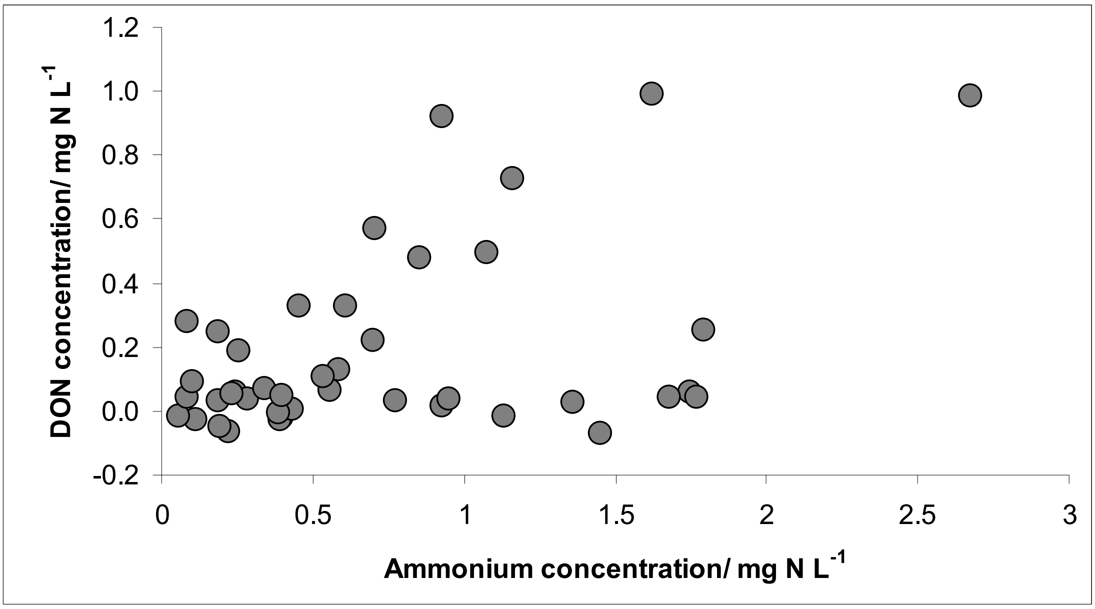


Figure 5.23: Daily rain samples (bulk deposition) correlation analysis for Zavižan sampling site: DON concentrations plotted against ammonium concentrations.

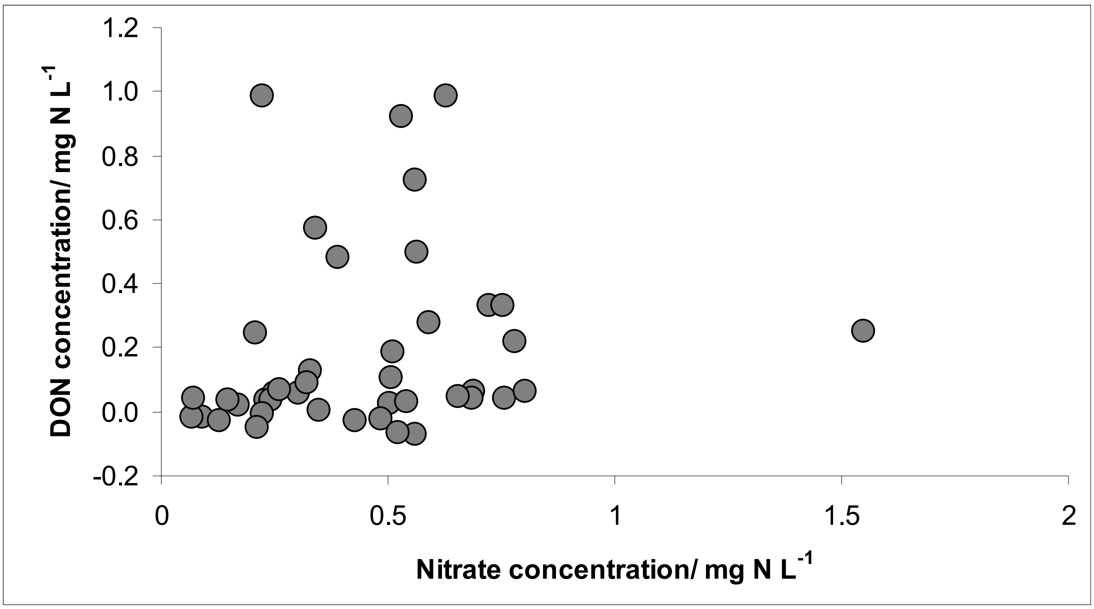


Figure 5.24: Daily rain samples (bulk deposition) correlation analysis for Zavižan sampling site: DON concentrations plotted against nitrate concentrations.

According to Pearson's test, only the correlation between nitrate and ammonium is statistically highly significant ($p<0.01$). Ammonium and nitrate datasets of concentration values were not normally distributed (Shapiro-Wilk normality test), and a square root transformation was applied to the data in order to fulfil the assumptions of the model. The good agreement between ammonium and nitrate concentrations points to particulate matter (mostly in the form of ammonium nitrate), rather than gas phase, as the main contributor to bulk deposition at this sampling site, and therefore to long-range transport from a combination of combustion and agricultural sources as the likely origin of these species. During the whole period of study ammonium concentrations are higher than nitrate concentrations. This observation can be rationalised by the presence at this sampling site of aerosol components from marine sources, for example ammonium sulphate.

In this study, the Zavižan sampling site registered low DON concentrations: in 26% of the valid samples DON concentration was below the limit of detection, and in 33% of the samples DON concentration was very close to the limit of detection. In addition, the DON dataset of concentration values was not normally distributed

(Shapiro-Wilk normality tests), and remained so even after applying a number of mathematical transformations (e.g. log and square root). For this reason Pearson's tests were not performed to analyse ammonium and DON correlations, and nitrate and DON correlations, only visual inspection of correlation plots (Figures 5.23 and 5.24). The absence of correlation between DON and ammonium and nitrate points to sources other than agricultural or combustion as the main contributors to DON at this sampling site.

5.3. Hungarian Meteorological Service (Országos Meteorológiai Szolgálat), Budapest, Hungary

5.3.1. Experimental

5.3.1.1. Collection methods

Rain samples from the Bugac sampling site (see Figure 5.25) were very kindly provided by Dr. László Horváth, from the Hungarian Meteorological Service (Országos Meteorológiai Szolgálat), Budapest, Hungary.

Precipitation was sampled daily over a period of 5 months, from October 2008 to February 2009, in a standard rain collector consisting of a polypropylene funnel diameter 152 mm mounted directly in a polypropylene collecting bottle (i.e. bulk deposition).

Determination of the concentration of the inorganic nitrogen ions (ammonium and nitrate) was carried out in the laboratories of the Hungarian Meteorological Service (Országos Meteorológiai Szolgálat), Budapest, Hungary. The analytical technique used was ion chromatography (see Sections 2.2 and 2.3).

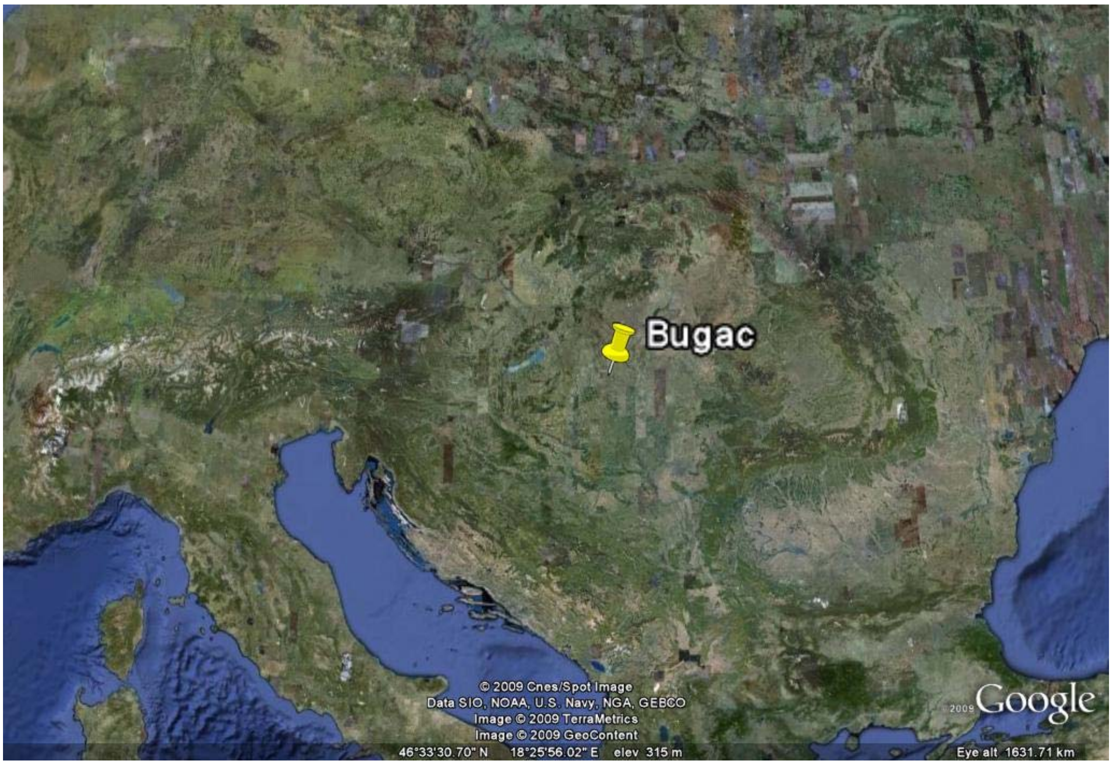


Figure 5.25: Geographical location of the sampling site (Bugac) of the samples provided by Dr. László Horváth, from the Hungarian Meteorological Service (Országos Meteorológiai Szolgálat), Budapest, Hungary.

5.3.1.2. Description of sampling site

Bugac (N46°41′30″, E19°36′06″), 111 m above sea level, is a flat and semi-arid sandy grassland managed area (dominant species: *Festuca pseudovina, Carex stenophylla, Salvia pratensis*) in the Kiskunság National Park (between the rivers Danube and Tisza). This site is located 15 km west of the M5 highway and 5 km west of the village of Bugac (~ 1600 inhabitants), in the Bács-Kiskun county, in the Pannonian Plain, in southern Hungary. The region has a semi-arid continental climate, with an average temperature of 10.4°C and average annual precipitation of 562 mm, and a prevailing wind direction from the north-east.

5.3.1.3. Sample quality control

Several criteria were used to identify valid precipitation samples:

(i) Samples were screened from obvious contamination previous to transport to the Centre for Ecology & Hydrology: samples were excluded if they had K^+ concentration greater than 1 mg L^{-1} since K^+ is a good marker for biological contamination.

(ii) The sample must have sufficient amount of rainfall: the minimum volume for daily samples was set at 5 mL. Samples with lower volumes were discarded, as they are more vulnerable to alterations in original composition, and very close to the minimum amount of sample required for the analytical techniques used in this study. 3 samples out of a total of 33 samples analyzed were discarded for this reason.

(iii) Samples with negative values of DON larger than 0.07 mg N L^{-1}, three times the sum of the limits of detection (LOD) of TDN and ammonium and nitrate, were regarded as not valid due to strong suspicion of alterations in sample concentration due to losses of ammonium during transport. 3 samples out of a total of 33 samples analyzed were discarded for this reason.

In summary, from a total of 33 samples analyzed, 6 were regarded as “not valid”.

5.3.2. Results and discussion

Figure 5.26 show the time series of daily rain (bulk deposition) concentration of ammonium, nitrate and DON (in mg N L^{-1}) at the Bugac sampling site.

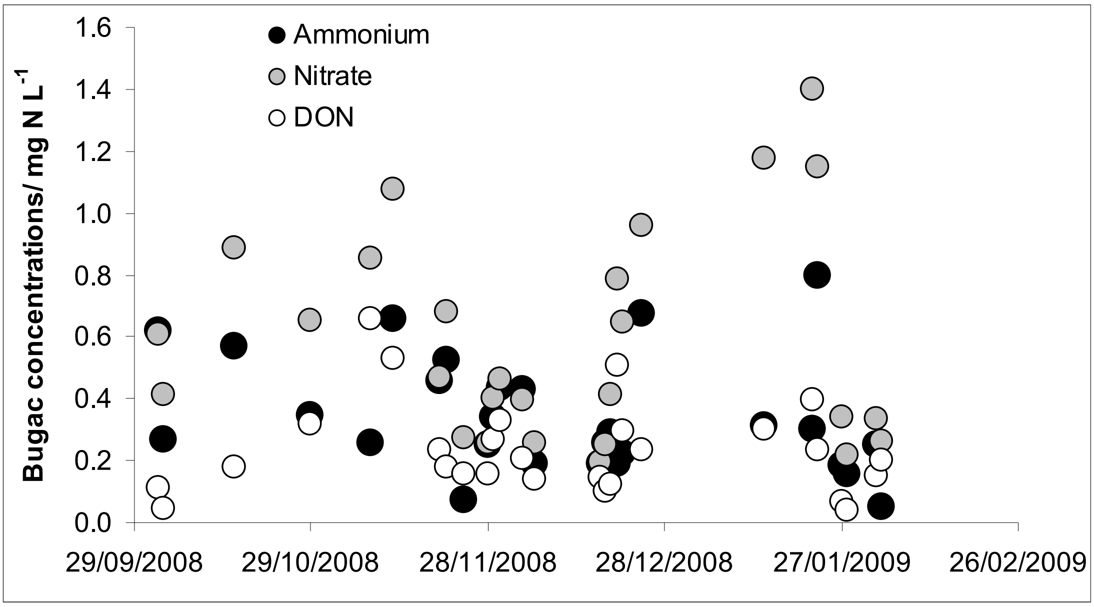


Figure 5.26: Time series of ammonium, nitrate and DON concentration in daily rain samples (bulk deposition) in mg N L^{-1}. Bugac sampling site.

Concentration of total dissolved nitrogen species (TDN) in valid rain samples (bulk deposition) ranged from 0.41 mg N L^{-1} on the 28th of January 2009, to 2.26 mg N L^{-1} on the 12th of November 2008.

Table 5.5 summarises average and median concentrations (in mg N L^{-1}) of total dissolved nitrogen (TDN), ammonium, nitrate and dissolved organic nitrogen (DON) found in the valid rain samples (bulk deposition) collected at the Bugac sampling site. The standard deviation (SD) of the concentrations across sampling dates has been included as an indicator of concentration variability through the period of study. At this sampling site nitrogen species concentrations are normally distributed according to the Shapiro-Wilk normality test, and there is good agreement between average and median concentration for all nitrogen species, in particular for DON. Note that rainfall-weighted concentrations could not be calculated because no precipitation data were supplied for these samples.

	Bugac sampling site	
Average concentration/ mg N L^{-1}	**TDN**	1.16
	NH_4^+	0.39
	NO_3^-	0.56
	DON	0.23
Median concentration/ mg N L^{-1}	**TDN**	1.16
	NH_4^+	0.29
	NO_3^-	0.46
	DON	0.2
Standard deviation of concentrations across sampling dates/ mg N L^{-1}	**TDN**	0.57
	NH_4^+	0.19
	NO_3^-	0.34
	DON	0.15

Table 5.5: Summary of average (not rainfall-weighted) and median concentrations of total dissolved nitrogen (TDN), ammonium, nitrate and dissolved organic nitrogen (DON) in rain (bulk deposition), in mg N L^{-1}. It includes the standard deviations (SD) of the concentrations across sampling dates. Samples were collected daily at Bugac sampling site over a 5-month period, from October 2008 to February 2009.

Further investigation of nitrogen species in this sampling site was undertaken through the study of correlation statistical analysis (Pearson's tests). Table 5.6 summarises correlation Pearson's test of ammonium, nitrate and DON at the Bugac sampling site.

	Pearson's correlations (Bugac)		
		NH_4^+	**NO_3^-**
NO_3^-	*R*	0.571**	1
	p value	0.002	
DON	*R*	0.155	0.612**
	p value	0.441	0.001

Table 5.6: Summary of Pearson's statistical analysis for correlations of ammonium, nitrate and DON concentrations in Bugac sampling site. ** indicates *R* whose correlation is significant at the 0.01 level (2-tailed).

Statistical analysis of the dataset (Pearson's test) showed highly significant correlation ($p<0.01$) between nitrate and ammonium and between nitrate and DON, but no obvious correlation ($p = 0.44$) between ammonium and DON.

Good agreement between ammonium and nitrate concentrations points to long-range transport of particulate matter (in the form of ammonium nitrate) from a combination of combustion and agricultural sources as the likely origin of most of the ammonium species and the larger fraction of nitrate species collected in this site. In the majority of valid samples (24 samples out of a total of 27), higher concentrations of nitrate than ammonium were present, pointing to gas-phase nitrogen dioxide as a secondary contributor to nitrate concentrations in bulk deposition. The absence of correlation between DON and ammonium, and the statistically highly significant correlation between DON and nitrate in this sampling site, point to a close relation between DON and material from long-distance combustion sources (nitrogen dioxide or nitric acid), but not to a relation between DON species and agricultural sources.

5.4. Agroscope Reckenholz-Tänikon Research Station (ART), Zürich, Switzerland

5.4.1. Experimental

5.4.1.1. Collection methods

Rain samples from the Oensingen sampling site (see Figure 5.27) were very kindly provided by Dr. Markus Jocher, from the Agroscope Reckenholz-Tänikon Research Station (ART), Zürich, Switzerland.

Precipitation (wet-only deposition) was sampled weekly over a period of 21 months, from August 2006 to May 2008, in a rain collector consisting of a polypropylene funnel mounted directly into a polypropylene collecting bottle. The funnel was equipped with an automated lid which was removed when a rain event was detected by a wetness grid (i.e. this sampler collected wet deposition only).

However, it should be noted that this design is different from the “flushing rain gauges” used at CEH as described in Chapter 3.

Determination of the concentrations of nitrogen inorganic ions (ammonium and nitrate) was carried out in the laboratories of the Agroscope Reckenholz-Tänikon Research Station (ART), Zürich, Switzerland. The analytical technique used was ion chromatography (see Sections 2.2 and 2.3).

Figure 5.27: Geographical location of the sampling site (Oensingen) of the samples provided by Dr. Markus Jocher, from the Agroscope Reckenholz-Tänikon Research Station (ART), Zürich, Switzerland.

5.4.1.2. Description of sampling site

Oensingen (N47°17′09″, E07°43′55″), 450 m above sea level, is an intensively managed flat grassland area (no grazing), 4-5 cuts/year receiving 150-200 kg N ha^{-1} year^{-1} in the form of cattle slurry and mineral fertiliser. Average cover fractions of grass, legume, and herb species are 90:30:7. The site is located 100 m south of the

A1 highway between Zürich and Bern, the busiest highway in Switzerland, and 1 km south-east of the town of Oensingen (~ 4600 inhabitants), in the district of Gäu, canton of Solothurn in the central Plateau of Switzerland. It has a temperate continental climate, with average annual temperature of 9.5°C and annual precipitation of ~1100 mm, and prevailing wind direction from the north-east.

5.4.1.3. Sample quality control

Two criteria were used to identify valid precipitation samples:

(i) Samples free from obvious contamination: samples were excluded if they had K^+ concentration greater than 1 mg L^{-1} since K^+ is a good marker for biological contamination. 3 samples out of a total of 47 were discarded for this reason.

(ii) Samples with negative values of DON larger than 0.07 mg N L^{-1}, three times the sum of the limits of detection (LOD) of TDN and ammonium and nitrate, were regarded as not valid due to strong suspicion of alterations in sample concentration due to losses of ammonium during transport. 6 samples out of a total of 47 samples analyzed were discarded for this reason.

In summary, from a total of 47 samples analyzed, 9 were regarded as “not valid”.

5.4.2. Results and discussion

Figure 5.28 show the time series of weekly rain (wet deposition) concentration of ammonium, nitrate and DON (in mg N L^{-1}) at the Oensingen sampling site.

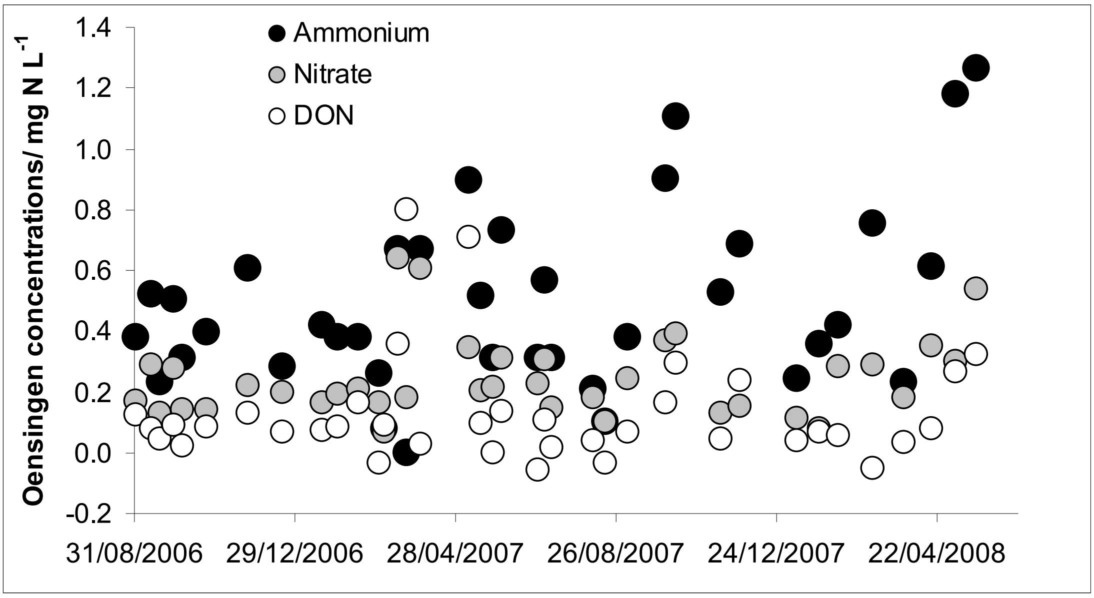


Figure 5.28: Time series of ammonium, nitrate and DON concentration in weekly rain samples (wet deposition) in mg N L^{-1}. Oensingen sampling site.

Concentration of total dissolved nitrogen species (TDN) in valid rain samples (wet deposition) ranged from a minimum of 0.17 mg N L^{-1} on the 8th of August 2008, to a maximum of 2.13 mg N L^{-1} on the 5th of May 2008.

Table 5.7 summarises average and median concentrations (in mg N L^{-1}) of total dissolved nitrogen (TDN), ammonium, nitrate and dissolved organic nitrogen (DON) found in the valid rain samples (wet deposition) collected at the Oensingen sampling site. The standard deviation (SD) of the concentrations across sampling dates has been included as an indicator of concentration variability through the period of study. According to the Shapiro-Wilk normality test, nitrogen species concentrations are not normally distributed in this sampling site. However, there is fairly good agreement between median and average concentrations in all nitrogen species in this sampling site. Note that rainfall-weighted concentrations could not be calculated because no precipitation data were supplied for these samples.

	Oensingen sampling site	
Average concentration/ mg N L^{-1}	**TDN**	0.86
	NH_4^+	0.49
	NO_3^-	0.24
	DON	0.13
Median concentration/ mg N L^{-1}	**TDN**	0.73
	NH_4^+	0.41
	NO_3^-	0.21
	DON	0.08
Standard deviation of concentrations across sampling dates/ mg N L^{-1}	**TDN**	0.49
	NH_4^+	0.29
	NO_3^-	0.13
	DON	0.18

Table 5.7: Summary of average (not rainfall-weighted) and median concentrations of total dissolved nitrogen (TDN), ammonium, nitrate and dissolved organic nitrogen (DON) in rain (wet deposition), in mg N L^{-1}. It includes the standard deviations (SD) of the concentrations across sampling dates. Samples were collected weekly at Oensingen sampling site over a 21-month period, from August 2006 to May 2008.

This sampling site is located close to anthropogenic nitrogen sources, both agricultural and combustion. During the period of study, ammonium concentrations were higher than nitrate concentrations in 37 out of 38 valid samples. Further investigation of nitrogen species at this sampling site was undertaken by the study of correlation plots and correlation statistical analysis (Pearson's test). Figures 5.29, 5.30 and 5.31 show the correlation plots of nitrate versus ammonium, DON versus ammonium and DON versus nitrate respectively for the Oensingen sampling site.

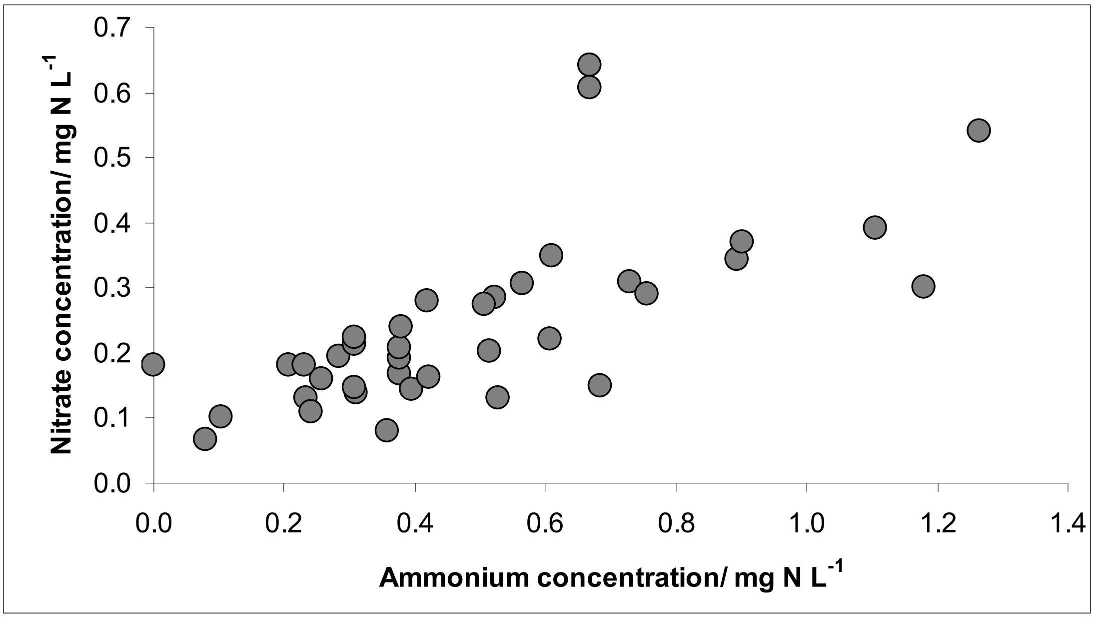


Figure 5.29: Weekly rain samples (wet deposition) correlation analysis for Oensingen sampling site: nitrate concentrations plotted against ammonium concentrations.

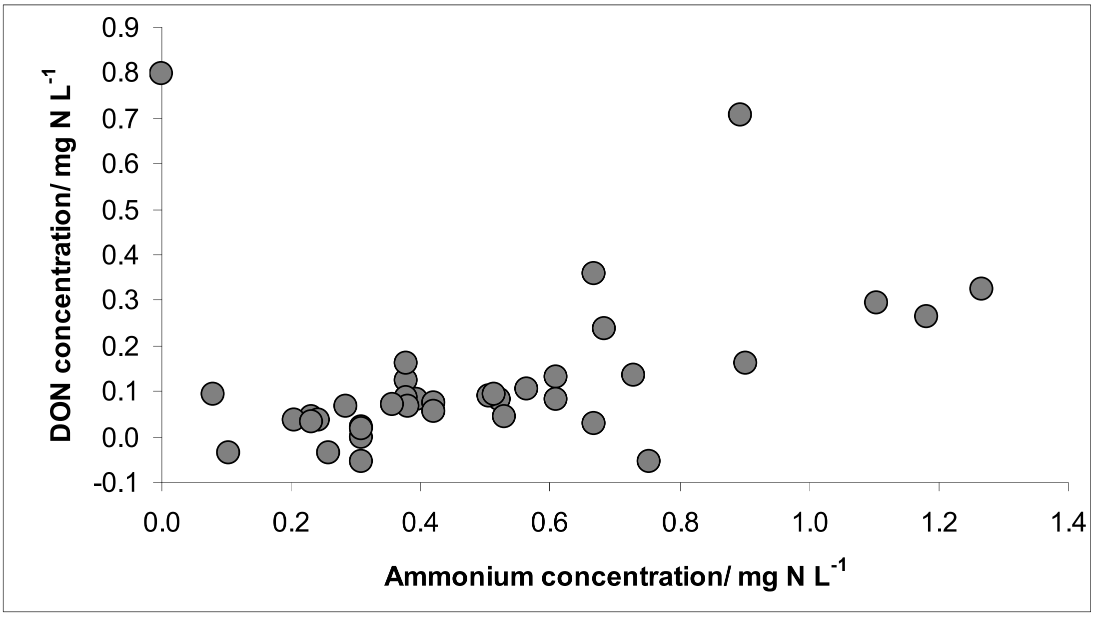


Figure 5.30: Weekly rain samples (wet deposition) correlation analysis for Oensingen sampling site: DON concentrations plotted against ammonium concentrations.

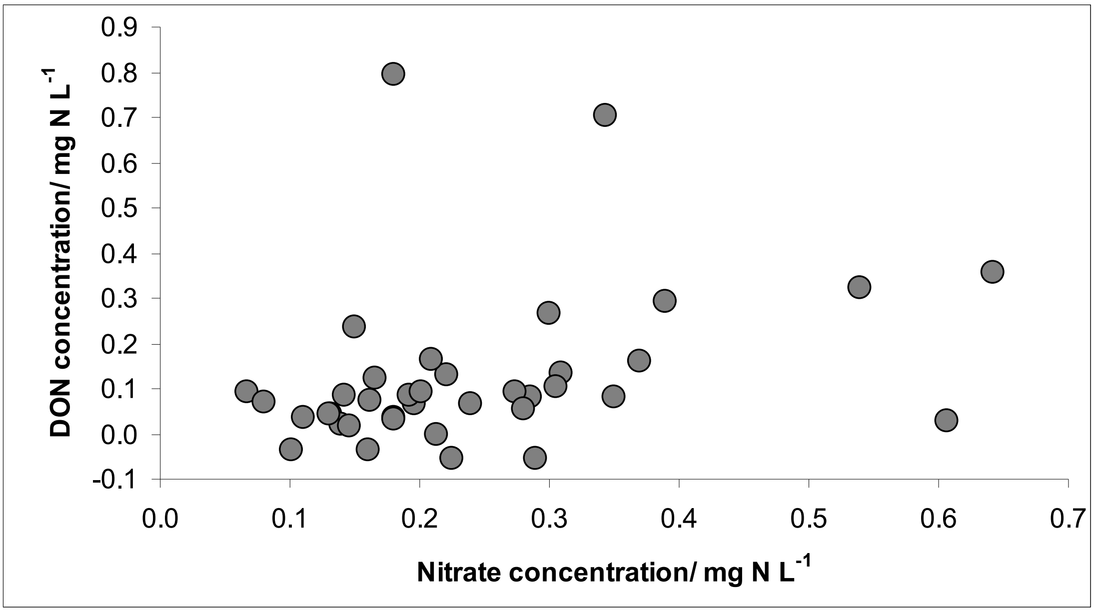


Figure 5.31: Weekly rain samples (wet deposition) correlation analysis for Oensingen sampling site: DON concentrations plotted against nitrate concentrations.

According to Pearson's test, correlation between nitrate and ammonium is statistically highly significant ($p<0.01$). Ammonium and nitrate datasets of concentration values were not normally distributed (Shapiro-Wilk normality tests), and a square root transformation was applied to the data in order to fulfil the assumptions of the model. The statistically highly significant correlation between ammonium and nitrate concentrations points to particulate matter (in the form of ammonium nitrate) from a combination of combustion and agricultural sources (and possibly including long-range transported material) as the likely origin of most of the nitrate species and the larger fraction of ammonium species collected in this site. As mentioned already, in nearly 100% of valid samples higher concentrations of ammonium than nitrate were found. Therefore at the Oensingen sampling site, strongly influenced by local agricultural sources, these findings point to gas-phase ammonia as a secondary contributor to ammonium concentrations in wet deposition.

The DON dataset of concentration values was not normally distributed (Shapiro-Wilk normality test), and remained so after trying several transformations (log and square root). Visual inspection of the Figures 5.30 and 5.31 did not show obvious correlation between DON and ammonium or between DON and nitrate. DON concentrations remained fairly constant and low through the whole period of study (17% of the valid samples were below the limit of detection). However, there seems to be some correlation between ammonium and DON on those dates with the highest concentrations of ammonium. This observation is very likely related to cattle slurry fertilization events. The absence of correlation between DON and nitrate implies that particulate matter from combustion sources was an unlikely contributor to DON at this sampling site.

5.5. Finnish Meteorological Institute, Air Quality Research

5.5.1. Experimental

5.5.1.1. Collection methods

Rain samples corresponding to 2 different locations in Finland (Virolahti and Pallas, Figure 5.32) were very kindly provided by Dr. Ulla Makkonen, from the Finnish Meteorological Institute, Air Quality Research Department, Helsinki, Finland.

Precipitation was sampled weekly over a period of 10 months, from August 2008 to May 2009, in standard rain collectors consisting of a polypropylene funnel mounted directly in a polypropylene collecting bottle (i.e. bulk deposition).

Determination of the concentration of the inorganic nitrogen (ammonium and nitrate) was carried out at the Finnish Meteorological Institute, Air Quality Research Department, Helsinki, Finland. The analytical technique used was ion chromatography (see Sections 2.2 and 2.3).

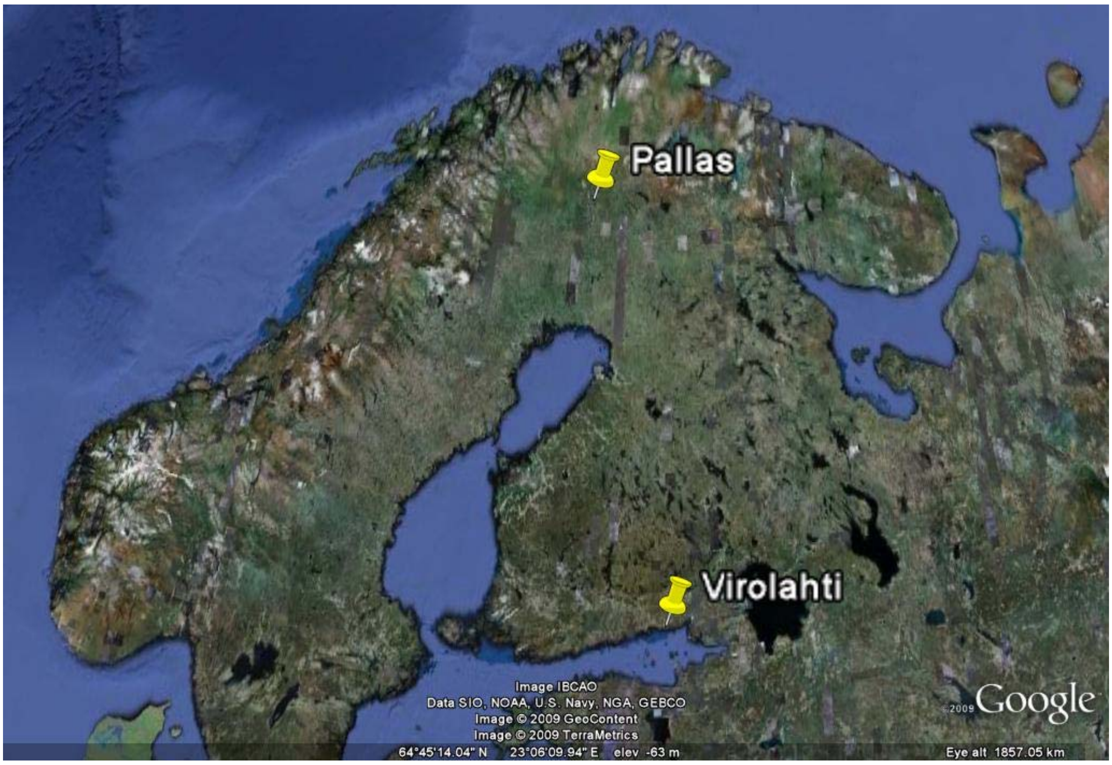


Figure 5.32: Geographical location of the 2 sampling sites of the samples provided by Dr. Ulla Makkonen, from the Finish Meteorological Institute, Air Quality Research Department, Helsinki, Finland.

5.5.1.2. Description of sampling sites

Both sampling sites (Virolahti and Pallas) are part of the NITROEUROPE network, but they were also selected by the European Monitoring and Evaluation Programme (EMEP) for monitoring pollution transported over long-range distances.

Virolahti (N60°31′27″, E27°38′25″), 20 m above sea level, is located in south-east Finland, about 6 km west of the Finnish-Russian border, 2 km north of the Gulf of Finland and 5 km south of the E18 highway. The traffic flow on this highway is about 3000 vehicles per day, but long truck queues (up to tens of kilometres long) often form as drivers wait along the road to cross the border into Russia. Helsinki metropolitan area (population ~1 million) is located 160 km to the south-west and the Russian metropolis of St. Petersburg (~4.7 million inhabitants) 160 km to the south-east. Across the Gulf of Finland, about 130 km south of Virolahti, several significant particle emission sources, e.g. oil shale utilizing power plants and cement plants (Anttila et al., 2008), are to be found. This sampling site has a northern maritime temperate climate, average temperature 5.6°C, annual precipitation ~640 mm, and prevailing wind directions from the south-west (maximum occurrence) and from the south-east (secondary maximum).

Pallas (N68°00′00″, E24°14′24″), 340 m above sea level, is located in a very remote area, at the northernmost limit of the northern boreal forest, in the subarctic region, on the top of a small hill covered by coniferous forest, in the middle of a circa 100 m × 100 m clearing. The area has no significant local or regional anthropogenic pollution sources (Hatakka et al., 2003). This sampling site has a subarctic climate with an average temperature of -1.1°C and annual precipitation of ~500 mm, and prevailing wind direction from the west. The ground is covered in snow from the middle of October to late May and there is a three and a half week long polar night in winter and a seven week long polar day in summer.

5.5.1.3. Sample quality control

Two criteria were used to identify valid precipitation samples:

(i) Previous to transport to the Centre for Ecology & Hydrology samples were screened for possible biological contamination (samples with K^+ concentration greater than 1 mg L^{-1} were discarded). 1 sample out of a total of 29 from the Pallas sampling site, and 3 samples out of a total of 33 from the Virolahti sampling site, were discarded for this reason.

(ii) Samples with negative values of DON larger than 0.07 mg N L^{-1}, three times the sum of the limits of detection (LOD) of TDN and ammonium and nitrate, were regarded as not valid due to strong suspicion of alterations in sample concentration due to either losses of ammonium during transport or to sample contamination during ammonium or nitrate analysis. 5 samples out of a total of 29 from the Pallas sampling site were discarded for this reason. No sample from the Virolahti sampling site was discarded for this reason.

In summary, from a total of 29 samples analyzed in Pallas sampling site, 6 were discarded, and from a total of 33 samples analyzed in Virolahti sampling site 3 were discarded.

5.5.2. Results and discussion

Figures 5.33 and 5.34 show the time series of rain (bulk deposition) concentration of ammonium, nitrate and DON (in mg N L^{-1}) at the Virolahti and Pallas sampling sites respectively. The vertical scale for nitrogen species concentration is the same in both figures in order to facilitate comparison between the two sampling sites.

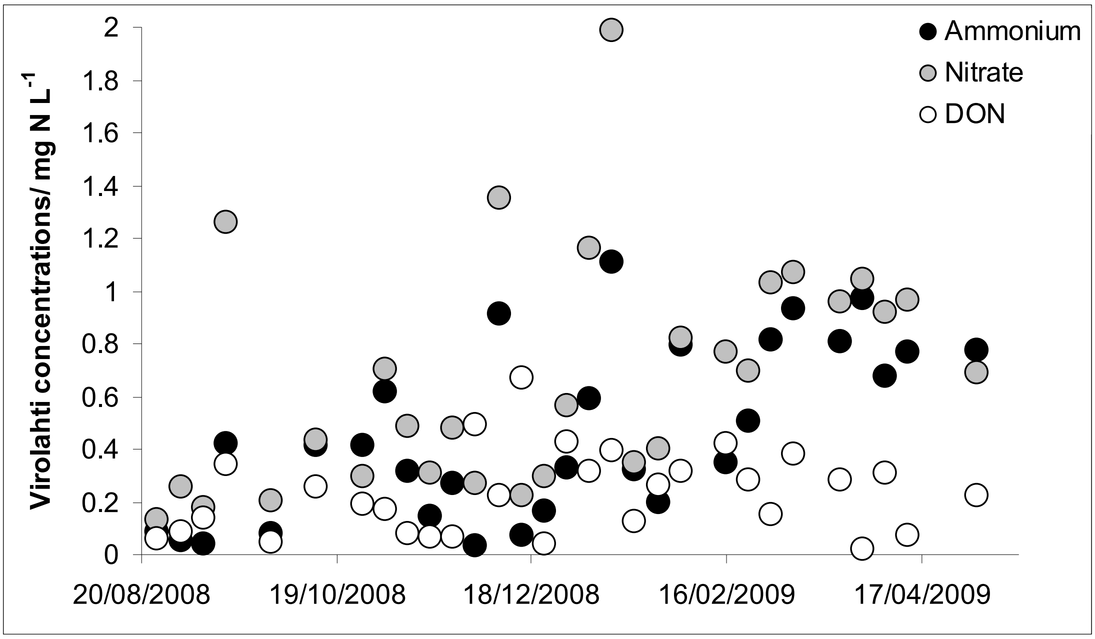


Figure 5.33: Time series of ammonium, nitrate and DON concentration in weekly rain samples (bulk deposition) in mg N L^{-1}. Virolahti sampling site.

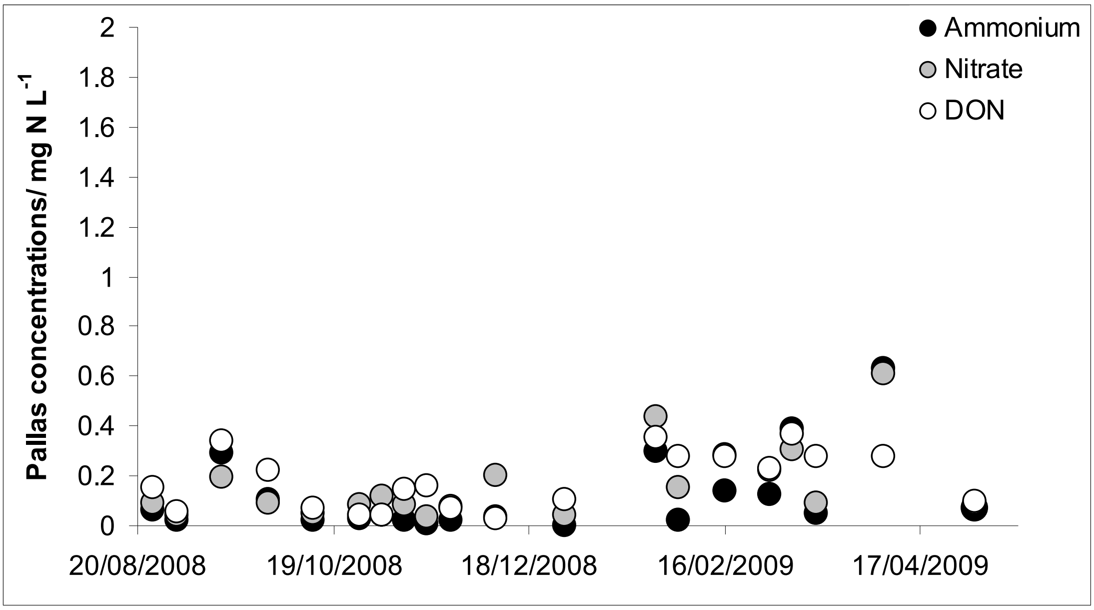


Figure 5.34: Time series of ammonium, nitrate and DON concentration in weekly rain samples (bulk deposition) in mg N L^{-1}. Pallas sampling site.

Table 5.8 summarises rainfall-weighted mean and median concentrations (in mg N L^{-1}) of total dissolved nitrogen (TDN), ammonium, nitrate and dissolved organic nitrogen (DON) found in the valid rain samples (bulk deposition) collected at the Virolahti and Pallas sampling sites. The standard deviation (SD) of the concentrations across sampling dates for each sampling site has been included as an indicator of concentration variability through the period of study. All nitrogen species concentrations are normally distributed at the Virolahti sampling site according to Shapiro-Wilk normality test, but none of the nitrogen species at the Pallas sampling site are normally distributed.

		Site	
		Virolahti	**Pallas**
Rainfall weighted mean concentration/ mg N L^{-1}	**TDN**	0.95	0.28
	NH_4^+	0.33	0.05
	NO_3^-	0.44	0.12
	DON	0.17	0.11
Median concentration/ mg N L^{-1}	**TDN**	1.4	0.27
	NH_4^+	0.41	0.04
	NO_3^-	0.63	0.09
	DON	0.22	0.14
Standard deviation of concentrations across sampling dates/ mg N L^{-1}	**TDN**	0.78	0.37
	NH_4^+	0.33	0.16
	NO_3^-	0.43	0.15
	DON	0.16	0.11

Table 5.8: Summary of rainfall weighted mean and median concentrations of total dissolved nitrogen (TDN), ammonium, nitrate and dissolved organic nitrogen (DON) in rain (bulk deposition), in mg N L^{-1}. It includes the standard deviations (SD) of the concentrations across sampling dates. All samples were collected weekly at Virolahti and Pallas sampling sites over a 10-month period, from August 2008 to May 2009.

Figure 5.35 shows the rainfall-weighted mean concentrations for ammonium, nitrate and dissolved organic nitrogen (DON) in mg N L^{-1} over all valid rain samples (bulk deposition) collected at Virolahti and Pallas.

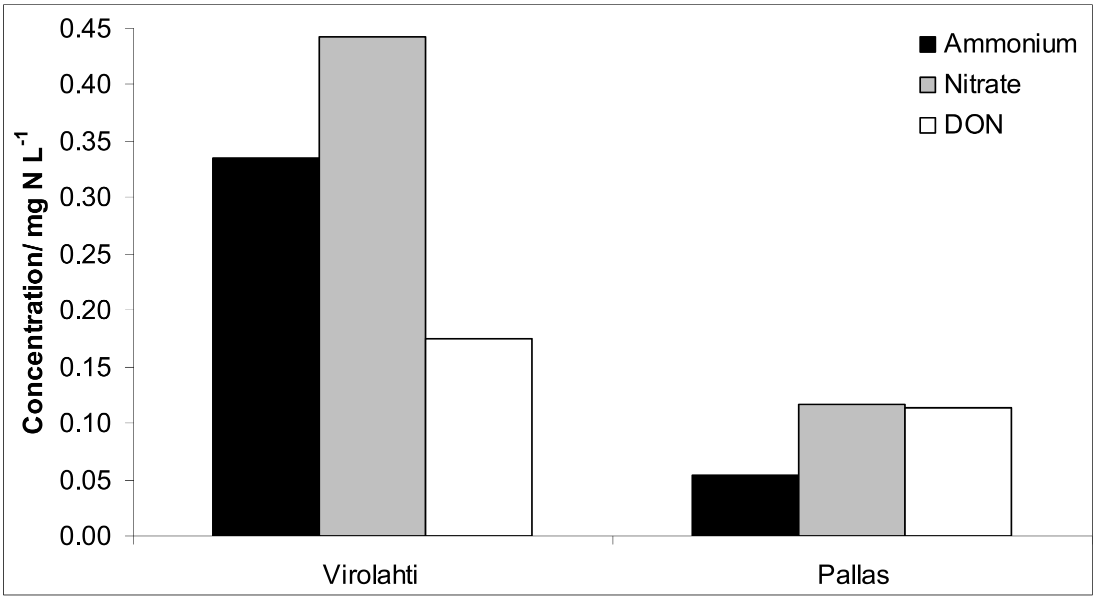


Figure 5.35: Rainfall weighted mean concentrations of ammonium, nitrate and DON in mg N L^{-1} over all valid samples for Virolahti and Pallas sampling sites.

Figure 5.36 shows the rainfall-weighted mean percentage of ammonium, nitrate and DON concentrations relative to TDN over all valid rain samples (bulk deposition) collected at both sampling sites.

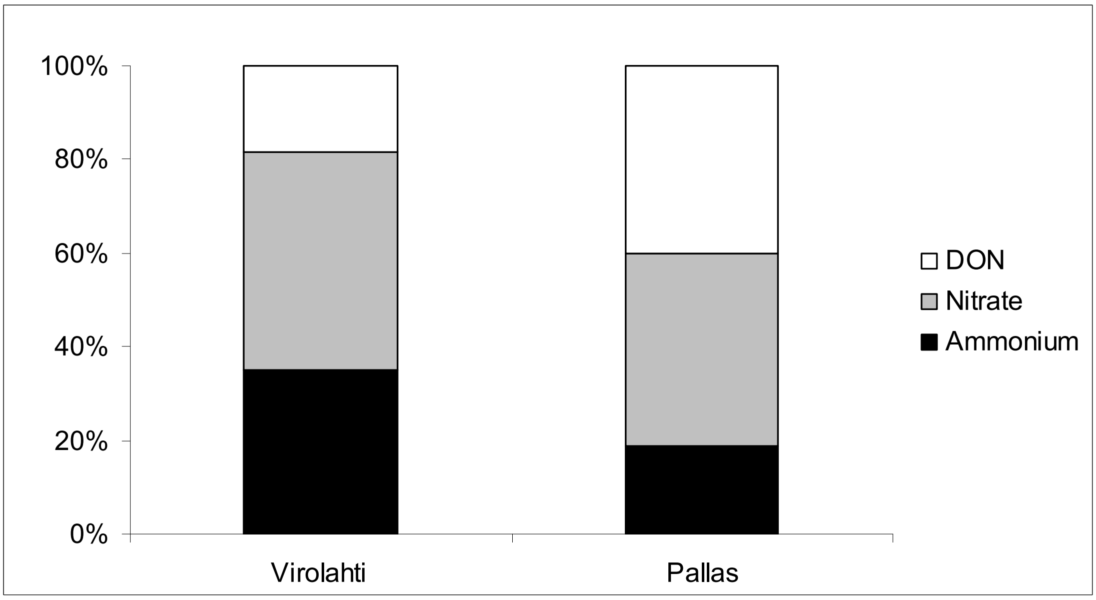


Figure 5.36: Rainfall weighted mean % of ammonium, nitrate and DON relative to TDN over all valid sampling dates for Virolahti and Pallas locations.

The sampling site closer to anthropogenic emission sources (Virolahti) presents higher concentrations of nitrogen species, in particular for ammonium and nitrate. DON concentrations are also higher at Virolahti than at Pallas sampling site, but the differences are not so large as for ammonium and nitrate. The DON fraction relative to TDN is notably larger at the Pallas sampling site (percentage of DON relative to TDN ~40%) than at the Virolahti sampling site (percentage of DON relative to TDN ~18%), which might point to a general absence of anthropogenic sources for DON, as in a more pristine location DON concentration is proportionally larger. However, higher absolute DON concentrations at Virolahti than at Pallas sampling site suggest that at least a fraction of the total DON material collected in bulk deposition might have anthropogenic sources, either agricultural or combustion. It is also possible that the lower DON concentrations found at the Pallas sampling site might be a consequence of reduced biogenic activity in a subarctic climate, making the case for non-anthropogenic sources of DON. Further investigation of DON origin was undertaken by the study of correlation statistical analysis (Pearson's test) of ammonium, nitrate and DON in all valid samples at both sampling sites.

Table 5.9 summarises Pearson's correlation test of ammonium, nitrate and DON at the Virolahti and Pallas sampling sites.

		Pearson's correlation tests		
		NH_4^+ - NO_3^-	**NH_4^+ - DON**	**NO_3^- - DON**
Virolahti	***R***	0.864**	0.078	0.233
	p value	7.76E-10	0.682	0.214
Pallas	***R***	0.835**	0.494*	0.392
	p value	0.001	0.016	0.064

Table 5.9: Summary of Pearson's statistical analysis for correlations of ammonium, nitrate and DON concentrations at Virolahti and Pallas sampling sites. ** indicates *R* whose correlation is significant at the 0.01 level (2-tailed). * indicates *R* whose correlation is significant at the 0.05 level (2-tailed).

Statistical analysis of the dataset (Pearson's test) at Virolahti showed highly significant correlation ($p<0.01$) between nitrate and ammonium, and no obvious correlation between nitrate and DON ($p = 0.21$), nor between ammonium and DON ($p = 0.68$). The good correlation between ammonium and nitrate concentrations points to long-range transport of particulate matter (in the form of ammonium nitrate) from a combination of combustion and agricultural sources as the likely origin of most of the ammonium species and the larger fraction of nitrate species collected in this site. In most valid samples (28 samples out of a total of 30), higher concentrations of nitrate than ammonium were found; the E18 highway, 5 km north of Virolahti sampling site, might be a likely source for NOx, however, it can be argued that it is too close to have an important effect on rain chemistry of this site. Possibly nearby industry and cities upwind (e.g. Helsinki) would be the most likely sources for this material. The absence of correlation between DON and ammonium and nitrate suggests that at this sampling site a large fraction of DON material is not linked either to agricultural or to combustion sources.

In the case of Pallas, statistical analysis of the dataset (Pearson’s test) showed a highly significant correlation ($p<0.01$) between nitrate and ammonium, a significant correlation ($p<0.05$) between DON and ammonium, and no obvious correlation between nitrate and DON ($p = 0.064$). Ammonium, nitrate and DON datasets of concentration values in Pallas sampling site were not normally distributed (Shapiro-Wilk normality test), and a logarithm transformation was applied to the data in order to fulfil the assumptions of the model. The good agreement (both in terms of correlation and in order of magnitude) between ammonium and nitrate concentrations points to long-range transport of particulate matter (in the form of ammonium nitrate) from a combination of combustion and agricultural sources as the likely origin of most of the nitrate and ammonium species collected in this site. The significant correlation between DON and ammonium but not between DON and nitrate might be related to biogenic (but not agricultural) sources of ammonium/ammonia. At this sampling site, with little influence from anthropogenic emissions, ammonium/ammonia from biogenic origin might make up an important fraction of the total ammonium collected in bulk deposition. DON species would be correlated with this biogenic fraction of ammonium (as DON is not correlated with nitrate in this sampling site), making a strong argument for biogenic sources as the main contributors to DON species in this sampling site.

In summary, the results obtained at both the Virolahti and Pallas sampling sites show no evidence of DON compounds linked to agricultural or combustion sources here.

5.6. Netherlands National Institute for public health and the environment (RIVM), Laboratory for Environmental Monitoring (LVM), Bilthoven, The Netherlands.

5.6. 1. Experimental

5.6.1.1. Collection methods

Rain samples collected from 4 different locations in The Netherlands (Figure 5.37) (Wieringerwerf, Speulderveld, Huisseling and Vredepeel) were very kindly provided by Dr. Ariën Stolk, from the National Institute for Public Health and the Environment (RIVM), Laboratory for Environmental Monitoring (LVM), Bilthoven, the Netherlands.

Figure 5.37: Geographical location of the 4 sampling sites (Wieringerwerf, Speulderveld, Huisseling and Vredepeel) of the samples provided by Dr. Ariën Stolk, from the National Institute for public health and the environment (RIVM), Laboratory for Environmental Monitoring (LVM), Bilthoven, the Netherlands.

Precipitation was sampled at fortnight resolution over a period of 4 months, from September 2008 to December 2008, in standard rain collectors consisting of a polypropylene funnel mounted directly in a polypropylene collecting bottle (i.e. bulk deposition).

Determination of the concentrations of the inorganic nitrogen (ammonium and nitrate) was carried out in the Laboratory for Environmental Monitoring (LVM), at the National Institute for Public Health and the Environment (RIVM), Bilthoven, The Netherlands. The analytical technique used was ion chromatography (Sections 2.2 and 2.3).

5.6.1.2. Description of sampling sites

The locations of the 4 sampling sites provided by RIVM are approximately evenly spaced along a diagonal line from the north-west to the south-east of the Netherlands (Figure 5.37). The sampling sites are listed from north to south.

Wieringerwerf (N52°48′17″, E05°02′56″), 4 m below sea level, is located in an agricultural area within a polder, below sea level (dikes and pumping engines keep the land dry), 4 km west of the Ijsselmeer, 2.6 km east of the E22 highway, 25 km east of the North Sea coast, and 5 km south of the town Wieringerwerf (~6000 inhabitants), in the Dutch province of North Holland. The temperate Atlantic climate has average annual temperature 9.8°C, annual precipitation ~960 mm and prevailing wind direction from the west.

Speulderveld (N52°16′18″, E05°43′14″), 23 m above sea level, is located in a slightly undulating forested area (dominant tree species: Japanese Lark, Beech, Scots Pine and Hemlock), in the Veluwe forest-rich ridge of hills in the province of Gelderland, in the central eastern part of the Netherlands. The site is 10 km south-east of the E232 highway and the small city of Harderwijk (~42000 inhabitants), 9 km north of the E30 highway, 16 km north-west of the city of Apeldoorn (approximately 136000 inhabitants), and 8 km east of the town of Putten (approximately 23000 inhabitants). The temperate Atlantic climate has average annual temperature 9.8°C, annual precipitation ~966 mm and prevailing wind direction from the south-west.

Huisseling (N51°47′05″, E05°38′41″), 5 m above sea level, is located in a flat agricultural area, 1 km south-west of the city of Ravenstein (~8400 inhabitants) and 50 m north of the A50 highway, in the province of North Brabant in the south of the Netherlands. The temperate Atlantic climate has annual average temperature 9.9°C, annual precipitation ~925 mm and prevailing wind direction from the south-west.

Vredepeel (N51°32′27″, E05°51′10″), 26 m above sea level, is located in a relatively isolated flat agricultural area (included in the EMEP measurement network), 1 km west of the small village of Vredepeel (~270 inhabitants), and 1 km north of a military air base, in the province of Limburg, in the south-east of the Netherlands. The temperate Atlantic climate has annual average temperature 9.9°C, annual precipitation ~915 mm and prevailing wind direction from the south-west.

5.6.2. Results and discussion

5.6.2.1. Nitrogen species in Wieringerwerf, Speulderveld, Huisseling and Vredepeel sampling sites

Figures 5.38 to 5.41 show the time series of rain (bulk deposition) concentration of ammonium, nitrate and DON (in mg N L^{-1}) at the Wieringerwerf, Speulderveld, Huisseling and Vredepeel sampling sites, respectively. The vertical scale for nitrogen species concentration is the same in all figures in order to facilitate comparison between the four sampling sites.

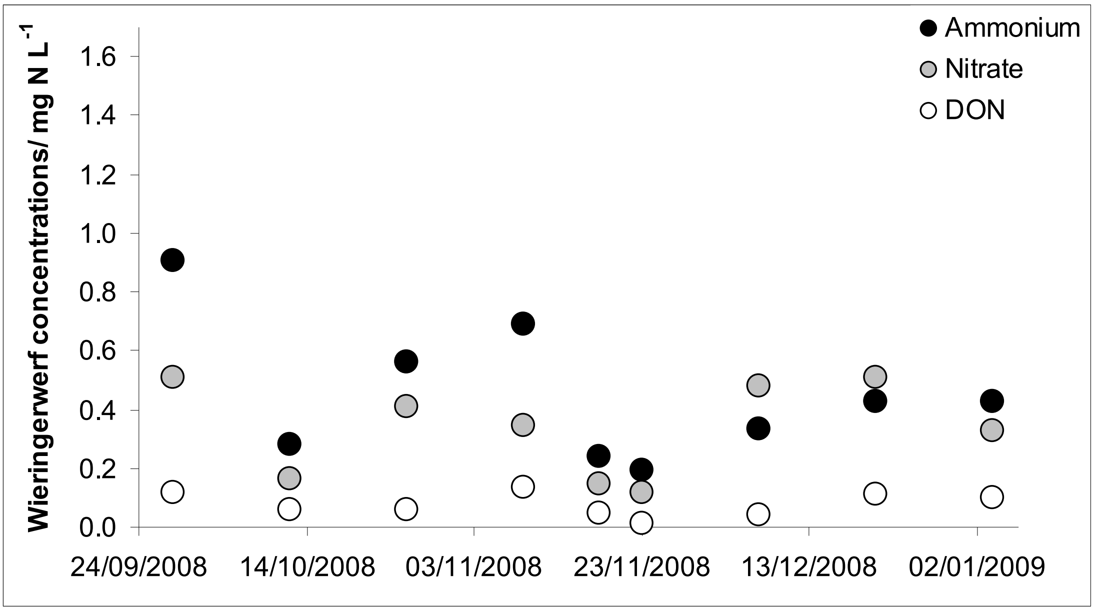


Figure 5.38: Time series of ammonium, nitrate and DON concentration in fortnightly rain samples (bulk deposition) in mg N L^{-1}. Wieringerwerf sampling site.

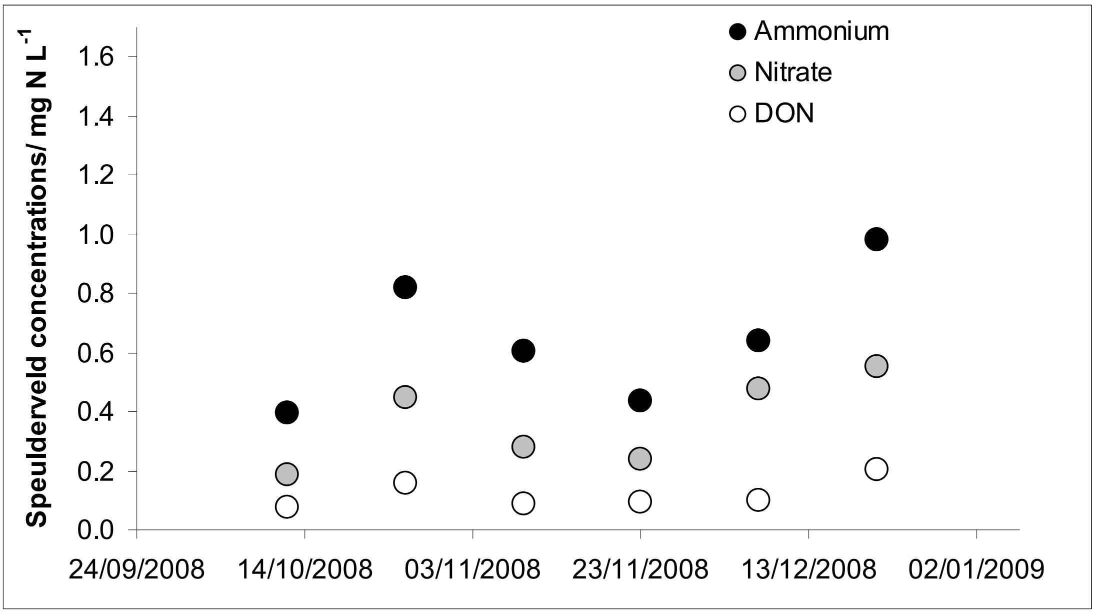


Figure 5.39: Time series of ammonium, nitrate and DON concentration in fortnightly rain samples (bulk deposition) in mg N L^{-1}. Speulderveld sampling site.

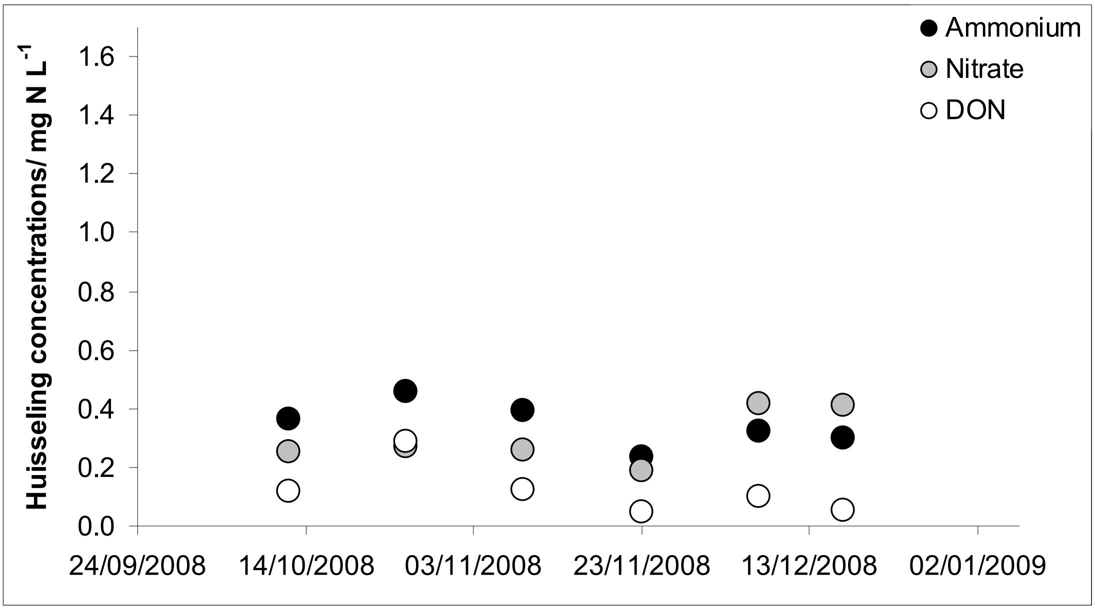


Figure 5.40: Time series of ammonium, nitrate and DON concentration in fortnightly rain samples (bulk deposition) in mg N L^{-1}. Huisseling sampling site.

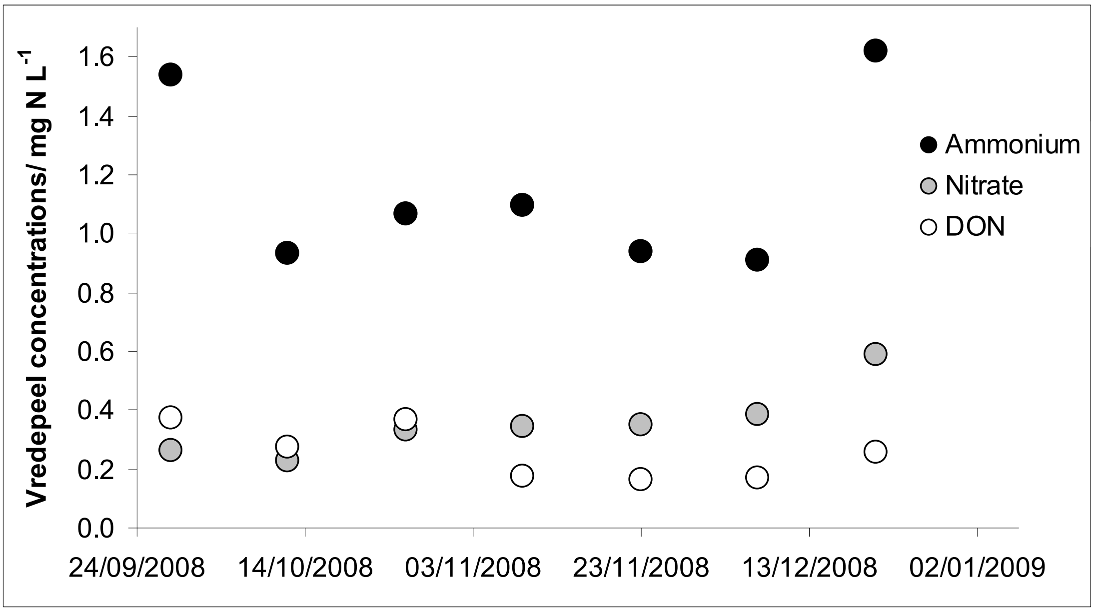


Figure 5.41: Time series of ammonium, nitrate and DON concentration in fortnightly rain samples (bulk deposition) in mg N L^{-1}. Vredepeel sampling site.

Concentration of total dissolved nitrogen species (TDN) in valid rain samples (bulk deposition) ranged from a minimum 0.32 mg N L^{-1} in Wieringerwerf sampling site in the 2nd fortnight of November 2008, to a maximum 2.46 mg N L^{-1} in Vredepeel sampling site in the 2nd fortnight of December 2008.

Table 5.10 summarises average (not rainfall weighted) and median concentrations (in mg N L-1) of total dissolved nitrogen (TDN), ammonium, nitrate and dissolved organic nitrogen (DON) measured in the valid rain samples (bulk deposition) collected fortnightly at the Wieringerwerf, Speulderveld, Huisseling and Vredepeel sampling sites. The standard deviation (SD) of the concentrations across sampling dates for each sampling site has been included as an indicator of concentration variability through the period of study. All nitrogen species concentrations are normally distributed at all sampling sites according to the Shapiro-Wilk normality test, and results from average and median concentrations for all nitrogen species at all the four locations are remarkably similar.

	Average concentration/ mg N L^{-1}				**Median concentration/ mg N L^{-1}**				**Standard deviation of concentrations across sampling dates/ mg N L^{-1}**			
Sampling site	**TDN**	**NH_4^+**	**NO_3^-**	**DON**	**TDN**	**NH_4^+**	**NO_3^-**	**DON**	**TDN**	**NH_4^+**	**NO_3^-**	**DON**
Wieringerwerf	0.86	0.45	0.33	0.08	0.86	0.42	0.35	0.06	0.39	0.23	0.16	0.04
Speulderveld	1.13	0.64	0.36	0.12	1.09	0.62	0.36	0.10	0.41	0.22	0.15	0.05
Huisseling	0.77	0.35	0.30	0.12	0.77	0.34	0.26	0.11	0.18	0.08	0.09	0.09
Vredepeel	1.77	1.16	0.36	0.25	1.61	1.07	0.34	0.26	0.41	0.30	0.12	0.09

Table 5.10: Summary of average (not rainfall weighted) and median concentrations of total dissolved nitrogen (TDN), ammonium, nitrate and dissolved organic nitrogen (DON) in rain (bulk deposition), in mg N L^{-1}. Also included are the standard deviations (SD) of the concentrations across sampling dates. Samples were collected fortnightly at each sampling site over a 4-month period, from September 2008 to December 2008.

Figure 5.42 shows the median concentrations for ammonium, nitrate and dissolved organic nitrogen (DON) in mg N L^{-1} over all valid rain samples (bulk deposition) collected at the four sampling sites.

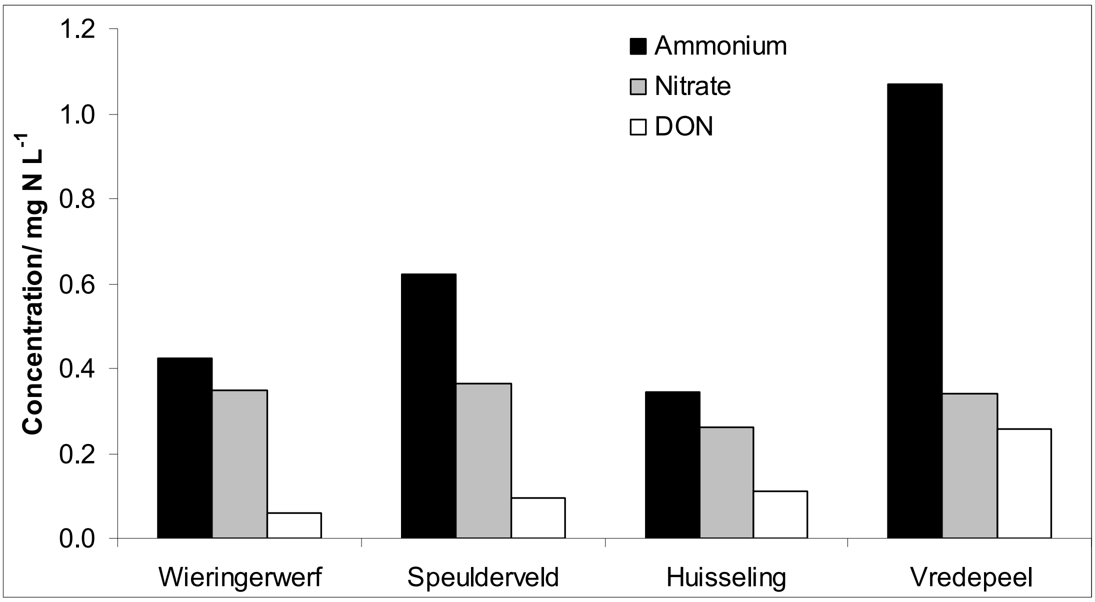


Figure 5.42: Median concentrations of ammonium, nitrate and DON in mg N L^{-1} over all valid samples for each sampling site.

Figure 5.43 shows the median percentage of ammonium, nitrate and DON concentrations relative to TDN over all valid rain samples (bulk deposition) collected at the four sampling sites.

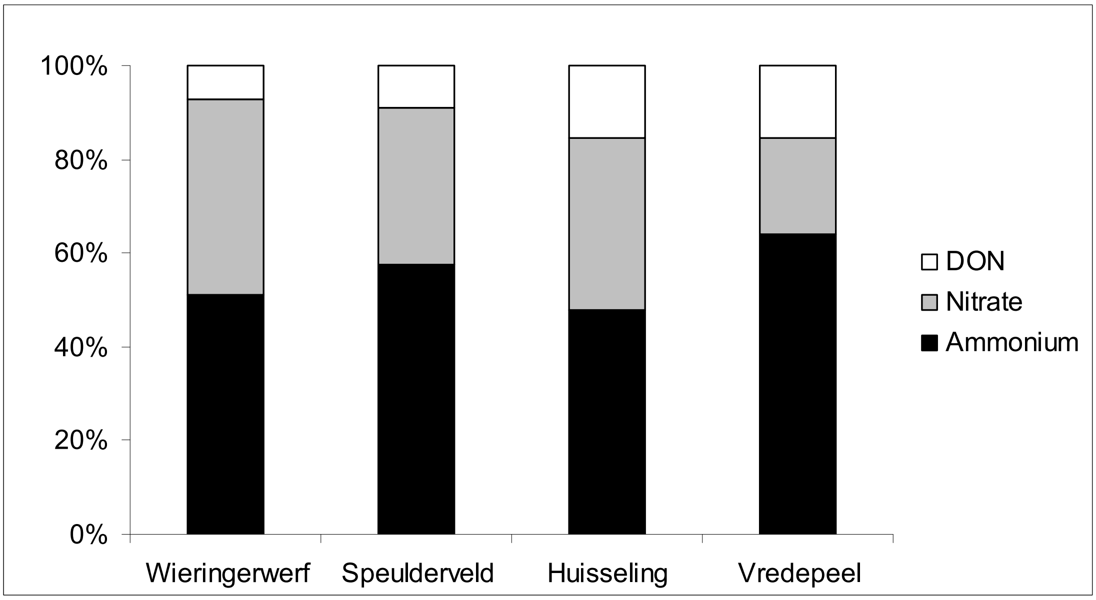


Figure 5.43: Median % of ammonium, nitrate and DON relative to TDN over all valid sampling dates for each sampling site.

Nitrate concentrations are on average very similar at all four of these sampling sites and also quite constant over time. Ammonium is the nitrogen species whose average concentration presents larger differences across the four sampling sites, possibly related to different degrees of agricultural influence at each sampling site. DON does not appear to be proportionally larger at those sites with lower TDN concentrations (in contrast to other sampling sites already commented on in sections 5.1.2 and 5.5.2). Although the largest average proportion of DON is observed at the Huisseling sampling site (~16%), which is the sampling site with the lowest TDN concentrations on average, this proportion is very similar to the average DON proportion at Vredepeel (~14%), which is the sampling site with the highest TDN concentrations on average. This suggests some extent of agricultural influence in DON species; comparing the four sampling sites, DON average concentration seems to increase with ammonium average concentration, whereas nitrate average concentrations remain quite similar at all four sampling sites. As with data obtained for sampling sites elsewhere, further investigation of DON origin was undertaken by the study of correlation statistical analysis (Pearson's test) of ammonium, nitrate and DON in all valid samples.

Table 5.11 summarises Pearson's correlation coefficient data for ammonium, nitrate and DON concentrations at each of the 4 locations. The results presented in this table show remarkable differences in the correlations found in each location.

		Pearson's correlation tests		
		NH_4^+ - NO_3^-	**NH_4^+ - DON**	**NO_3^- - DON**
Wieringerwerf	***R***	0.658	0.756*	0.583
	p value	0.054	0.019	0.1
Speulderveld	***R***	0.910*	0.945**	0.823*
	p value	0.012	0.004	0.044
Huisseling	***R***	-0.054	0.903*	-0.153
	p value	0.918	0.014	0.772
Vredepeel	***R***	0.475	0.494	-0.25
	p value	0.282	0.26	0.589

Table 5.11: Summary of Pearson's statistical analysis for correlations of ammonium, nitrate and DON concentrations in Wieringerwerf, Speulderveld, Huisseling and Vredepeel sampling sites. ** indicates *R* whose correlation is significant at the 0.01 level (2-tailed). * indicates *R* whose correlation is significant at the 0.05 level (2-tailed).

Statistical analysis of the dataset (Table 5.11) for the Wieringerwerf sampling site showed significant correlation ($p<0.05$) between DON and ammonium, a p value very close to the threshold of statistical significance ($p = 0.054$) for the correlation between nitrate and ammonium, and no correlation between nitrate and DON ($p = 0.10$). Visual inspection of correlation plots (Figures 5.44 and 5.45) suggest that, although there is a tendency for DON concentrations to increase with ammonium concentrations, there is a closer correlation between nitrate and ammonium than between DON and ammonium.

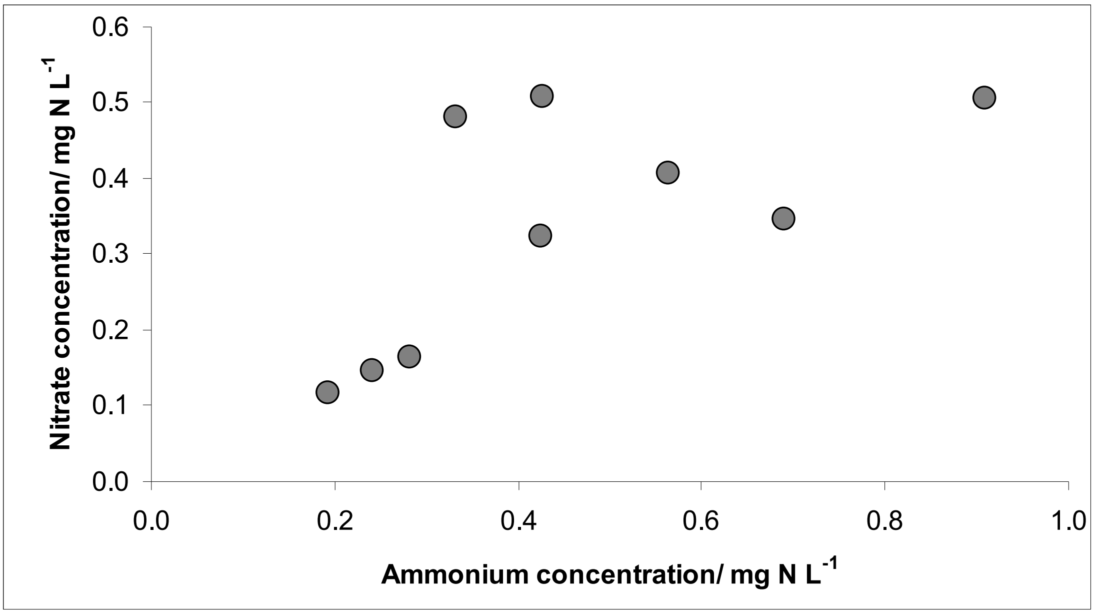


Figure 5.44: Fortnight rain samples (bulk deposition) correlation analysis for Wieringerwerf sampling site: nitrate concentrations plotted against ammonium concentrations.

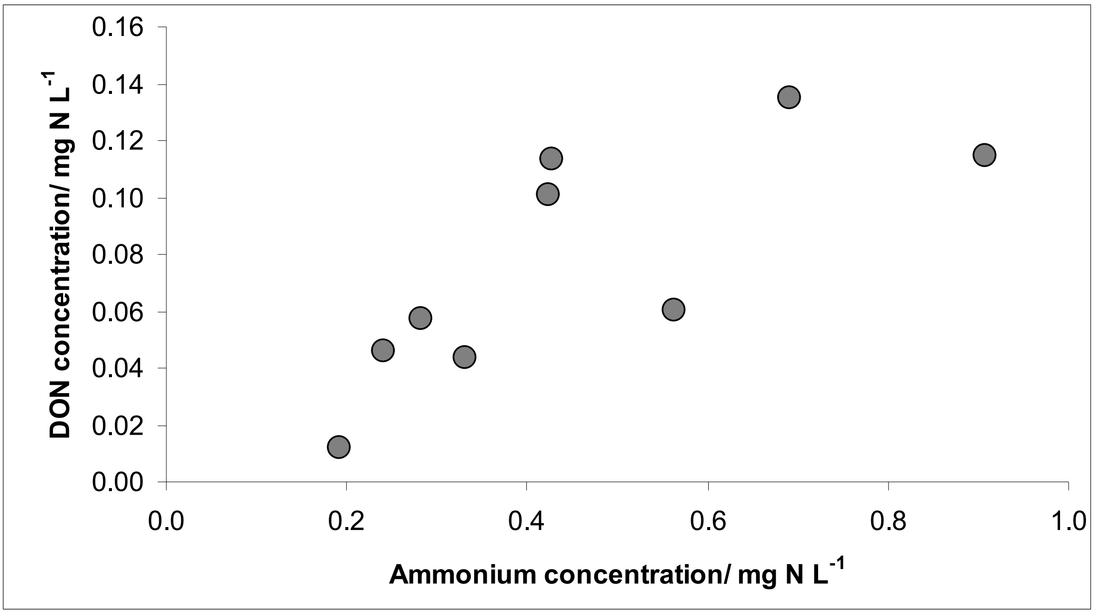


Figure 5.45: Fortnight rain samples (bulk deposition) correlation analysis for Wieringerwerf sampling site: DON concentrations plotted against ammonium concentrations.

The good correlation between ammonium and nitrate suggests that a large fraction of the total inorganic nitrogen species collected in bulk deposition were in the form of ammonium nitrate, i.e. long-range particulate matter from a combination of agricultural and combustion sources. The two obvious outliers to the otherwise good fit in the nitrate-ammonium correlation (corresponding to the two samples from December 2008) might be explained by an increased contribution from combustion sources (in the form of nitrogen dioxide or nitric acid) to the nitrate collected in the bulk deposition during that period. The larger concentration of ammonium than nitrate in most of the samples might be explained by an additional contribution to ammonium, either from gas phase ammonia, likely from local agricultural sources, or from ammonium sulphate aerosol, either from more distant agricultural sources than for ammonia or from marine origin (this sampling site is located 25 km east of the North Sea coast, in the prevailing wind direction). Due to the agricultural activity at this sampling site, locally produced gas-phase ammonia is the most likely contributor to the additional ammonium concentration. These results suggest that DON is possibly not related to particulate ammonium nitrate, but at least a fraction of the DON collected in this sampling site is expected to be linked to a secondary source of ammonium (local ammonia gas) and therefore to local agricultural sources. This relation with ammonium sources, but not with ammonium nitrate, would explain both the significant correlation between DON and ammonium concentrations and the lack of correlation between DON and nitrate concentrations.

Statistical analysis of the dataset (Table 5.11) at the Speulderveld sampling site showed a highly significant correlation ($p<0.01$) between DON and ammonium, and significant correlations ($p<0.05$) between DON and nitrate, and between nitrate and ammonium.

The location of the Speulderveld sampling site, surrounded by forest, with no local agricultural or combustion sources, and the significant correlation between ammonium and nitrate concentrations, points to long-range transport of particulate matter, in the form of ammonium nitrate, from a combination of combustion and agricultural sources, as the likely origin of most of the nitrate species and the largest fraction of the ammonium species collected in this site. In all valid samples ammonium concentration is higher than nitrate concentration, pointing to ammonium sulphate (long range agricultural sources) as a secondary contributor to ammonium concentration in bulk deposition at this sampling site. The highly significant correlation between DON and ammonium, and the significant correlation between DON and nitrate, suggests a link between DON and particulate ammonium (both ammonium nitrate and ammonium sulphate), and therefore to remote agricultural sources. At this sampling site, it can be argued that combustion sources are possibly not an important contributor to DON in bulk deposition, as correlation between DON and nitrate is not as good as between DON and ammonium. As already mentioned, the highly significant correlation between DON and ammonium points to a link between particulate matter ammonium and DON. The significant correlation between nitrate and both ammonium and DON might be due to a large contribution of particulate matter ammonium nitrate to the total concentration of nitrate in bulk deposition at this sampling site (combination of remote agricultural and combustion sources). The additional nitrate contribution from purely combustion sources, likely in the form of nitrogen dioxide or nitric acid, would not correlate with agricultural sources, therefore, this fraction would not be correlated with ammonium and, if in this case DON species are linked to ammonium, then the nitrogen dioxide or nitric acid fraction would not be correlated with DON species either. If this is the case, then the overall correlation between DON species and ammonium should be better than between DON species and nitrate. As this is case, then it can be argued that DON species are not linked to the combustion sources (at this sampling site).

Statistical analysis of the data (Table 5.11) from the Huisseling sampling site showed significant correlation ($p<0.05$) only between DON and ammonium. The location of this sampling site, in an agricultural area and close to the A50 highway, and the lack of correlation between ammonium and nitrate, points to gas-phase ammonia (from local agricultural sources) and nitrogen dioxide or nitric acid (from combustion sources) as the most likely main contributors to bulk deposition ammonium and nitrate concentrations respectively. At this sampling site, the significant correlation between DON and ammonium points to a link between local agricultural sources and DON species.

Statistical analysis of the data (Table 5.11) from the Vredepeel sampling site showed no significant correlation ($p>0.05$) between any of the nitrogen species under study (ammonium, nitrate and DON). The location of the Vredepeel sampling site, in an agricultural area, and the lack of correlation between ammonium and nitrate points to gas-phase ammonia (from local agricultural sources) and nitrogen dioxide or nitric acid (from local or remote combustion sources) as the most likely main contributors to bulk deposition of ammonium and nitrate concentrations, respectively. At this sampling site, agricultural activity is clearly the dominant anthropogenic source of N species, and the lack of correlation between DON and ammonium, and between DON and nitrate suggests that the main sources of DON are different from either agricultural or combustion.

In summary, at the sampling sites operated by RIVM, DON species collected in bulk deposition do not seem to be related to combustion sources, either local or remote. On the other hand, at three out of four sampling sites at least some fraction of the DON species collected in bulk deposition seems to be related to agricultural activities, either local (at the Wieringerwerf and Huisseling sampling sites) or remote (at the Speulderveld sampling site). However, this possible connection between DON species and agricultural activity should be taken cautiously, since analysis of the data at the Vredepeel sampling site suggests that DON species are not linked to anthropogenic sources (either agricultural or combustion). It is important to highlight that Vredepeel is the sampling site with seemingly the largest anthropogenic influence (consistently the highest concentrations of ammonium through the whole period of study in comparison with the rest of the sites), i.e. at sampling sites with low concentrations of ammonium, a significant correlation between DON and ammonium was found, whereas at higher concentrations of ammonium such correlation was not found.

5.6.2.2. Persulphate wet oxidation vs. high-temperature catalytic oxidation methods in TDN determination

Determination of TDN in all bulk deposition samples from all four Dutch sites was independently carried out at the Laboratory for Environmental Monitoring (LVM), Bilthoven, the Netherlands. Determination of TDN at the LVM was performed using the persulphate wet oxidation method (Section 1.3). This method achieves chemical oxidation of DON to nitrate under alkaline conditions using persulphate as the oxidant. The oxidation step is followed by colorimetric determination of nitrate. In contrast, as described in Chapter 2, the TDN determination method used in this work at CEH was high-temperature catalytic oxidation followed by chemiluminescence detection of nitric oxide. This allowed direct comparison of results from both methods and Figure 5.46 plots the persulphate wet oxidation data against the high-temperature catalytic oxidation data for the same batch of samples.

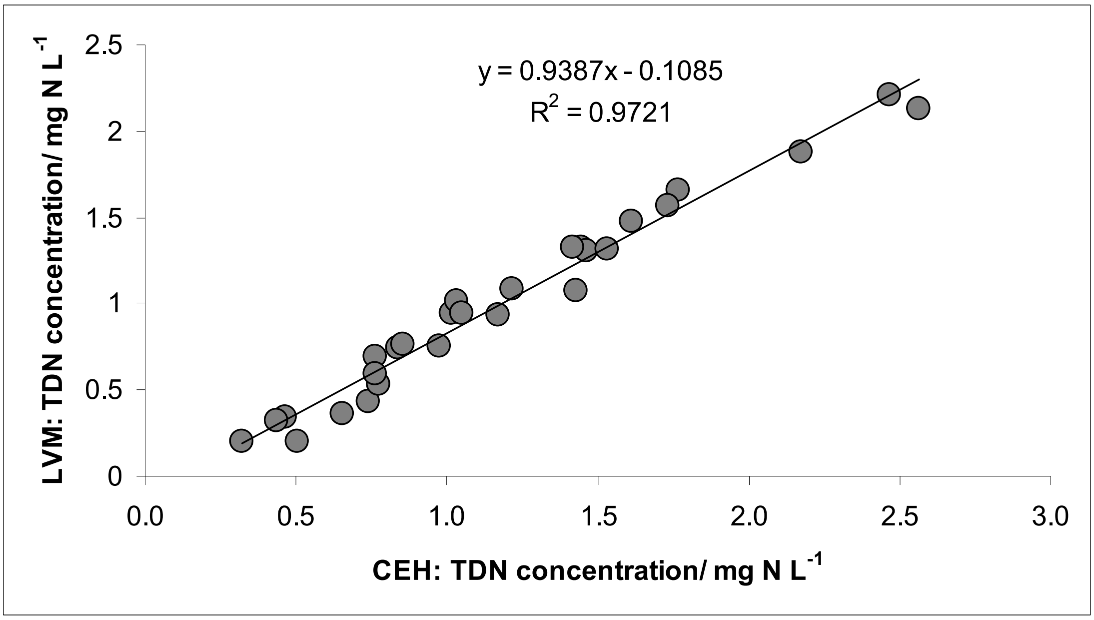


Figure 5.46: Comparison of results for TDN determination using 2 different methods: results from a persulphate wet oxidation method (carried out at the LVM, Bilthoven, the Netherlands) are plotted against results from a high temperature oxidation method (carried out at the CEH, Edinburgh, UK). All valid samples from all four sampling sites (Wieringerwerf, Speulderveld, Huisseling and Vredepeel) are included in this plot.

The plot shows a very good agreement between both sets of data (R^2 = 0.972). However, there is an offset of ~10% between results from both methods. The two possible explanations for this offset are either underestimation of TDN concentrations in the persulphate wet oxidation method, or overestimation of TDN concentrations in the high-temperature catalytic oxidation method. According to the dataset, underestimation of TDN concentrations in the persulphate wet oxidation method is the most likely explanation as using the results from the persulphate wet oxidation method for TDN determination would produce negative DON concentration values in 57% of the valid samples.

In summary, this study found good agreement between persulphate wet oxidation and high-temperature catalytic oxidation methods for TDN determination. However, an offset of ~10% between results from both methods was encountered which was attributed to a likely underestimation of TDN concentrations by the persulphate wet oxidation method (at least in the batch of samples under study).

5.7. Conclusions

A number of samples with relatively large negative DON concentrations were encountered. These samples were removed from the statistical analysis, but it raises concerns regarding the integrity of the samples during transport, in particular possible alterations due to losses of ammonium in the form of gas-phase ammonia. Alkaline conditions, relatively high concentrations of ammonium in the sample, and increases of sample temperature during transport are all factors that would enhance such losses. As an improvement for future sampling campaigns, vials should be pretreated with thymol to avoid biological degradation, but also with a small amount of acid to prevent alkaline conditions which might lead to a potential loss of ammonium in the form of gaseous ammonia.

According to the data gathered in this study, DON species seem to be largely not related to anthropogenic nitrogen sources, either agricultural or combustion. At 11 out of 21 sampling sites no significant correlation was found either between DON and ammonium or between DON and nitrate.

Only at 1 sampling site (Speulderveld), did DON present significant correlations with both ammonium and nitrate (highly significant correlation between DON and ammonium). At this sampling site it is suspected that at least a fraction of the DON species is linked to remote agricultural sources.

Different magnitudes of DON and nitrate correlation (but no DON and ammonium correlation) were found at a number of sites: highly significant correlation at 2 sampling sites (Roccarespampani and Bugac), significant correlation at 1 sampling site (Puéchabon), and visual (but not statistically significant) correlation at 2 sampling sites (Hainich and Le Bray). At all these sites the interpretation is that DON is influenced to different extents by combustion sources.

At 4 sampling sites (Oensingen, Pallas, Wieringerwerf and Huisseling) there was a significant correlation between DON and ammonium (although not between DON and nitrate). At Oensingen, Wieringerwerf and Huisseling the interpretation is that at least a fraction of the DON species might be related to local agricultural sources, possibly in the shape of slurry fertilization. However, at the Pallas sampling site, located in a remote subarctic area, the DON-ammonium correlation cannot be attributed to local agricultural sources. At this sampling site ammonium sources are expected to be biogenic, which is consistent with the low concentrations of ammonia present (lower than nitrate and DON concentrations).

An analytical method comparison study found very good linear agreement between persulphate wet oxidation and high-temperature catalytic oxidation methods for TDN determination. However, an offset of ~10% between results from both methods was noted which is attributed to a very likely underestimation of TDN concentrations by the persulphate wet oxidation method.

6. Final discussion & future work

Some technical difficulties regarding TDN determination using a high-temperature catalytic oxidation (HTCO) method were encountered in the early stages of this project. These difficulties consisted of slightly different responses for the ammonium standard and for the other N-containing standards in the nitrogen-specific HPLC detector (ANTEK 8060-M). As explained in chapter 2, these difficulties were finally overcome, and in fact the methodology was optimized to the extent that in an independent comparison with the persulphate wet oxidation method, the HTCO method produced more reliable responses for TDN: this comparison found good agreement between both methods for TDN determination. However, an offset of ~10% between results from both methods was observed. This offset was attributed to a likely underestimation of TDN concentrations by the persulphate wet oxidation method because, according to the persulphate wet oxidation method, a number of samples would present "negative" DON concentrations after subtracting DIN concentrations to TDN concentrations.

With regards to the atmospheric concentrations and deposition behaviour of water-soluble reactive nitrogen compounds (RNCs), the use of novel flushing rain gauges (for wet-only precipitation sampling) and Cofer scrubbers combined with PTFE filters (for air sampling) yielded very interesting results.

Results from flushing rain gauges at the Centre for Ecology & Hydrology (CEH) field site showed that, during the period of study, dry deposition of particles and gas on the funnel surface, rather than deposition in rain, was the main source of water soluble RNCs (both inorganic and organic species) to the bulk sampler, contributing between 53% and 84% of total water soluble RNC deposition. These findings have important implications in terms of potential overestimation of wet deposition rates, in particular for some studies assuming small contributions of dry deposition to bulk rainfall collectors (Goller et al., 2006) and for the commonly-used "non-flushing" designs for wet deposition sampling (such as those with lids on the rain collectors which open automatically when a rain event is detected).

Results from the Cofer samplers/ PTFE filters sampling campaign carried out at the Easter Bush field site showed that, during the period of study, the proportion of water soluble RNCs in the gas phase was larger than in particulate matter, on average 74 ± 16% of the total RNCs collected in this study were in the gas phase.

These results accomplished one of the key objectives in this study: to investigate how water-soluble RNC species were apportioned between wet and dry deposition, and, within the atmosphere, the partitioning of RNC species between gas phase and particulate matter. According to these results, it is possible to conclude that during the period of study, dry, rather than wet, deposition was the main contributor to bulk deposition, and that gas phase comprised a far larger contribution to boundary layer water-soluble RNC species than particulate matter.

Another key objective in this study was to quantify as accurately as possible the contribution of WSON to precipitation and air samples collected at the CEH and Easter Bush sites. The experimental results showed that WSON species represented an important fraction of the total water soluble RNCs in all types of deposition: ~23 ± 6% on average in bulk deposition, ~36 ± 9% on average in wet deposition and ~33 ± 15% on average in dry deposition (although, in this study, due to the documented losses of water-soluble RNCs within the flushing sampler, the relative contribution of WSON species to the total water soluble RNCs in wet and dry deposition lacks the same degree of confidence as for bulk deposition). Within the atmosphere, WSON species represented ~20 ± 2 % of water soluble total nitrogen (WSTN) on average in gas phase and ~30 ± 7 % of WSTN on average in particulate matter. However, it should be pointed out that the actual WSON contribution to gas phase might have been underestimated due to sampling efficiency issues of volatile organic material into single Cofer scrubbers.

Rain samples (bulk deposition) collected across Europe showed large variations in water-soluble RNC species concentration across different locations: from as little as 0.32 mg N L^{-1} on average at the Fontainebleau sampling site, to 1.87 mg N L^{-1} on average at the Puéchabon sampling site. The relative contribution of DON species to the TDN in bulk deposition also varied significantly across the different sampling sites, from less than 4% on average at Wetzstein, to more than 50% on average at Fontainebleau. However, in general, at most sampling sites WSON species were found to be an important contribution to the total water-soluble RNC deposition. The average and median DON contribution across the 21 sampling sites was ~ 19% and ~ 11% respectively.

The final objective of this project was to investigate WSON origin and potential sources. Correlation studies of atmospheric WSON with ammonia/ammonium and nitrate at the main sampling site (Easter Bush, UK) pointed to non-anthropogenic sources as the main contributors to WSON in the boundary layer at this location, both in the gas phase and in particulate matter.

Correlation studies of DON with ammonium and nitrate in bulk deposition samples from different sites across Europe led to interesting conclusions: at 5 sampling sites the WSON species are suspected to be influenced to different extent by anthropogenic combustion sources (due to different levels of DON and nitrate correlation in the samples); at 3 sampling sites a significant fraction of the WSON species might be related to local agricultural sources (significant correlation between DON and ammonium), possibly due to slurry fertilization; and at 1 sampling site it is suspected that at least a fraction of the WSON species are linked to remote agricultural sources. However, at the majority of the European sampling sites (12 out of 21), correlation studies led to similar conclusions as at the UK Easter Bush sampling site, i.e. WSON species seem to be largely unrelated to anthropogenic sources, of either agricultural or combustion origin. Summary of correlation tests in table 6.1.

		Pearson's correlation tests		
		NH_4^+ - NO_3^-	NH_4^+ - DON	NO_3^- - DON
Edinburgh	***R***	0.128	-0.03	0.256
	p value	0.458	0.849	0.132
Fontainebleau	***R***	-0.212	-0.266	0.113
	p value	0.584	0.489	0.772
Grillenburg	***R***	0.816**	0.412	0.551
	p value	0.002	0.207	0.079
Hainich	***R***	0.577	0.312	0.791
	p value	0.231	0.548	0.061
Lägeren	***R***	0.895*	-0.25	-0.265
	p value	0.016	0.633	0.611
Le Bray	***R***	0.313	-0.268	0.75
	p value	0.495	0.562	0.052
Mitra	***R***	0.912	-0.17	-0.205
	p value	0.088	0.83	0.795
Polwet	***R***	0.891**	0.286	0.224
	p value	0.001	0.422	0.534
Puéchabon	***R***	0.974**	0.756	0.861*
	p value	0.001	0.082	0.027
Roccarespampani	***R***	0.553	0.674	0.921**
	p value	0.256	0.142	0.009
San Rossore	***R***	0.431	-0.039	0.785
	p value	0.469	0.951	0.116
Vielsalm	***R***	0.895**	0.383	0.355
	p value	0.003	0.35	0.388
Wetzstein	***R***	0.895*	-0.25	-0.265
	p value	0.016	0.633	0.611
Bugac	***R***	0.571**	0.155	0.612**
	p value	0.002	0.441	0.001
Virolahti	***R***	0.864**	0.078	0.233
	p value	7.76E-10	0.682	0.214
Pallas	***R***	0.835**	0.494*	0.392
	p value	0.001	0.016	0.064
Wieringerwerf	***R***	0.658	0.756*	0.583
	p value	0.054	0.019	0.1
Speulderveld	***R***	0.910*	0.945**	0.823*
	p value	0.012	0.004	0.044
Huisseling	***R***	-0.054	0.903*	-0.153
	p value	0.918	0.014	0.772
Vredepeel	***R***	0.475	0.494	-0.25
	p value	0.282	0.26	0.589

Table 6.1: Summary of Pearson's statistical analysis for correlations of ammonium, nitrate and DON concentrations at each location studied during this project. ** indicates *R* whose correlation is significant at the 0.01 level (2-tailed). * indicates *R* whose correlation is significant at the 0.05 level (2-tailed).

The information and conclusions presented in this study should be complemented with a more detailed picture of the deposition patterns of RNC at different locations (apportionment between wet and dry deposition, apportionment between gas phase and particulate matter, contribution of WSON species, main sources of WSON species). For this reason future work should include the deployment of standard and flushing rain gauges, as well as Cofer samplers (equipped with PTFE filters) at additional sampling sites (possibly within the NITROEUROPE framework). Ideally the set of sampling sites should include different latitudes, climates and weather conditions, as well as different orography, ecosystems and distances to anthropogenic sources of RNCs. In a subsequent stage, future work should also include the identification of the individual compounds included within the bulk WSON species. Development of a reliable HPLC separation method for WSON will be essential in order to accomplish such objective.

In this project, the main drawback of the use of flushing rain gauges was that larger amounts of water-soluble RNCs were collected in standard bulk samplers than in the flushing samplers (but not larger volume of rain). This result very likely implies chemical or biological interactions in the tubing leading from the funnel to the sampling bottle, and must be addressed previous to the deployment phase. It is expected that these interactions might be reduced by replacing silicone tubing with PTFE tubing, and by changing the tubing on each sampling occasion. This finding also has implications for all types of precipitation sampler in which the funnel and the sample bottle are separated by a length of tubing.

The main advantages of the deployment of Cofer scrubbers combined with PTFE filters for air monitoring are their high efficiency of collection and simplicity of operation. The main drawbacks, on the other hand, are low time resolution and high vulnerability to evaporation issues (which requires frequent monitoring during the sampling period).

As a final recommendation for the improvement of sample preservation in future sampling campaigns, and in addition to thymol pretreatment, vials should be pretreated with a small amount of acid to prevent alkaline conditions which might lead to potential losses of ammonium in the form of gaseous ammonia. Alkaline conditions, relatively high concentrations of ammonium in the sample, and increases of sample temperature during transport are all factors that would enhance ammonium losses in the form of gas phase ammonia.

References

Akse J.R., Thompson J.O., Sauer R.L., Atwater J.E., 1998. "Reagentless" flow injection determination of ammonia and urea using membrane separation and solid phase basification. Microchemical Journal 59, 372-382.

Ambonguilat S., Gallard H., Garron A., Epron F., Philippe Croue J., 2006. Evaluation of the catalytic reduction of nitrate for the determination of dissolved organic nitrogen in natural waters. Water Research 40, 675-682.

Aneja V.P., Blunden J., Roelle P.A., Schlesinger W.H., Knighton R., Niyogi D., Gilliam W., Jennings G., Duke C.S., 2008. Workshop on Agricultural Air Quality: State of the science. Atmospheric Environment 42, 3195-3208.

Anttila P., Makkonen U., Hellén H., Kyllönen K., Leppänen S., Saari H., Hakola H., 2008. Impact of the open biomass fires in spring and summer of 2006 on the chemical composition of background air in south-eastern Finland. Atmospheric Environment 42, 6472-6486.

Atkinson R., 2000. Atmospheric chemistry of VOCs and NOx. Atmospheric Environment 34, 2063-2101.

Ball P., Ryden J., 1984. Nitrogen relationships in intensively managed temperate grasslands. Plant and Soil 76, 23-33.

Beman M.J., Arrigo K.R., Matson P.A., 2005. Agricultural runoff fuels large phytoplankton blooms in vulnerable areas of the ocean. Nature 434, 211-214.

Bronk D.A., Lomas M.W., Glibert P.M., Schukert K.J., Sanderson M.P., 2000. Total dissolved nitrogen analysis: comparisons between the persulfate, UV and high temperature oxidation methods. Marine Chemistry 69, 163-178.

Burns D.A., 2004. The effects of atmospheric nitrogen deposition in the Rocky Mountains of Colorado and southern Wyoming, USA-a critical review. Environmental Pollution 127, 257-269.

Calderón S.M., Poor N.D., Campbell S.W., 2007. Estimation of the particle and gas scavenging contributions to wet deposition of organic nitrogen. Atmospheric Environment 41, 4281-4290.

Campbell N.A., Reece J.B., 2002. Biology, Benjamin / Cummings Publishing Company, Inc.

Cape J.N., Anderson M., Rowland A.P., Wilson D.R., 2004. Organic nitrogen in precipitation across the United Kingdom. Water, Air, and Soil Pollution Focus 4, 25-35.

Cape J.N., Dijk N.v., Tang Y.S., 2009. Measurement of dry deposition to bulk precipitation collectors using a novel flushing sampler. Journal of Environmental Monitoring, 11, 353-358.

Cape J.N., Kirika A., Rowland A.P., Wilson D.R., Jickells T.D., Cornell S., 2001. Organic nitrogen in precipitation: Real problem or sampling artefact? The Scientific World Journal 1, 230-237.

Cape J.N., Leith I.D., 2002. The contribution of dry deposited ammonia and sulphur dioxide to the composition of precipitation from continuously open gauges. Atmospheric Environment 36, 5983-5992.

Christou M., Avramides E.J., Jones D.L., 2006. Dissolved organic nitrogen dynamics in a Mediterranean vineyard soil. Soil Biology and Biochemistry 38, 2265-2277.

Christou M., Avramides E.J., Roberts J.P., Jones D.L., 2005. Dissolved organic nitrogen in contrasting agricultural ecosystems. Soil Biology and Biochemistry 37, 1560-1563.

Cofer W.R., Edahl R.A., 1986. A new technique for collection, concentration and determination of gaseous tropospheric formaldehide. Atmospheric Environment 20, 979-984.

Cornell S., Randell A., Jickells T., 1995. Atmospheric inputs of dissolved organic nitrogen to the oceans. Nature 376, 243-246.

Cornell S.E., Jickells T.D., 1999. Water-soluble organic nitrogen in atmospheric aerosol: a comparison of UV and persulfate oxidation methods. Atmospheric Environment 33, 833-840.

Cornell S.E., Jickells T.D., Cape J.N., Rowland A.P., Duce R.A., 2003. Organic nitrogen deposition on land and coastal environments: a review of methods and data. Atmospheric Environment 37, 2173-2191.

Cuesta D., Taboada A., Calvo L., Salgado J.M., 2008. Short- and medium-term effects of experimental nitrogen fertilization on arthropods associated with Calluna vulgaris heathlands in north-west Spain. Environmental Pollution 152, 394-402.

Dämmgen U., Erisman J.W., Cape J.N., Grunhage L., Fowler D., 2005. Practical considerations for addressing uncertainties in monitoring bulk deposition. Environmental Pollution 134, 535-548.

Dittman J.A., Driscoll C.T., Groffman P.M., Fahey T.J., 2007. Dynamics of nitrogen and dissolved organic carbon at the Hubbard Brook Experimental Forest. Ecology 88, 1153-1166.

Doval M.D., Fraga F., Perez F.F., 1997. Determination of dissolved organic nitrogen in seawater using Kjeldahl digestion after inorganic nitrogen removal. Oceanologica Acta 20, 713-720.

Duan F., Liu X., He K., Dong S., 2009. Measurements and characteristics of nitrogen-containing compounds in atmospheric particulate matter in Beijing, China. Bulletin of Environmental Contamination and Toxicology 82, 332-337.

Dwyer J., Kavanagh L., Lant P., 2008. The degradation of dissolved organic nitrogen associated with melanoidin using a UV/H2O2 AOP. Chemosphere 71, 1745-1753.

Erisman J.W., 2004. The Nanjing Declaration on Management of Reactive Nitrogen. BioScience 54, 286-287.

EU, 2001. Directive 2001/81/EC of the European Parliament and of the Council of 23 October 2001 on national emission ceilings for certain atmospheric pollutants. EU Official Journal L 309, 22-30.

Facchini M.C., Decesari S., Rinaldi M., Carbone C., Finessi E., Mircea M., Fuzzi S., Moretti F., Tagliavini E., Ceburnis D., O'Dowd C.D., 2008. Important source of marine secondary organic aerosol from biogenic amines. Environmental Science & Technology 42, 9116-9121.

Fillery I.R.P., Simpson J.R., De Datta S.K., 1986. Contribution of ammonia volatilization to total nitrogen loss after applications of urea to wetland rice fields. Nutrient Cycling in Agroecosystems 8, 193-202.

Forsum A., Dahlman L., Nasholm T., Nordin A., 2006. Nitrogen utilization by Hylocomium splendens in a boreal forest fertilization experiment. Functional Ecology 20, 421-426.

Fryzuk M.D., 2004. Inorganic chemistry: Ammonia transformed. Nature 427, 498.

Galloway J.N., Schlesinger W.H., Levy H., Michaels A., Schnoor J.L., 1995. Nitrogen fixation: Anthropogenic enhancement-environmental response. Global Biogeochemical Cycles 9, 235-252.

Galloway J.N., Townsend A.R., Erisman J.W., Bekunda M., Cai Z., Freney J.R., Martinelli L.A., Seitzinger S.P., Sutton M.A., 2008. Transformation of the nitrogen cycle: recent trends, questions, and potential solutions. Science 320, 889-892.

Giffen R., 1899. The wheat problem. Nature 61, 169-171.

Goller R., Wilcke W., Fleischbein K., Valarezo C., Zech W., 2006. Dissolved nitrogen, phosphorus, and sulfur forms in the ecosystem fluxes of a montane forest in Ecuador. Biogeochemistry 77, 57-89.

Graedel T.E., Crutzen P.J., 1993. Atmospheric Change: An Earth System Perspective, W. H. Freeman and Company, New York

Hadi D.A., Cape J.N., 1995. Preservation of throughfall samples by chloroform and thymol. International Journal of Environmental Analytical Chemistry 61, 103 - 116.

Ham Y.S., Tamiya S., 2007. Contribution of dissolved organic nitrogen deposition to total dissolved nitrogen deposition under intensive agricultural activities. Water, Air & Soil Pollution 178, 5-13.

Ham Y.S., Tamiya S., Choi I.S., 2007. Contribution of dissolved organic nitrogen deposition to nitrogen saturation in a forested mountainous watershed in Tsukui, Central Japan. Water, Air & Soil Pollution 178, 113-120.

Hatakka J., Aalto T., Aaltonen V., Aurela M., Hakola H., Komppula M., Laurila T., Lihavainen H., Paatero J., Salminen K., Viisanen Y., 2003. Overview of the atmospheric research activities and results at Pallas GAW station. Boreal Environment Research 8, 365–383.

Heeb N.V., Saxer C.J., Forss A.-M., Bruhlmann S., 2008. Trends of NO-, NO2-, and NH3-emissions from gasoline-fueled Euro-3- to Euro-4-passenger cars. Atmospheric Environment 42, 2543-2554.

Hooper R., 2006. Something in the air. NewScientist 190, 40-43.

Hopkinson C., Cifuentes L., Burdige D., Fitzwater S., Hansell D., Henrichs S., Kahler P., Koike I., Walsh T., Bergamaschi B., 1993. Measurement of Dissolved Organic-Carbon and Nitrogen in Natural-Waters - DON Subgroup Report. Marine Chemistry 41, 23-36.

Houghton J.T., 2004. Global Warming: The Complete Briefing Cambridge University Press, Cambridge

Jones D.L., Healey J.R., Willett V.B., Farrar J.F., Hodge A., 2005. Dissolved organic nitrogen uptake by plants--an important N uptake pathway? Soil Biology and Biochemistry 37, 413-423.

Jones D.L., Kielland K., 2002. Soil amino acid turnover dominates the nitrogen flux in permafrost-dominated taiga forest soils. Soil Biology & Biochemistry 34, 209-219.

Jones D.L., Willett V.B., 2006. Experimental evaluation of methods to quantify dissolved organic nitrogen (DON) and dissolved organic carbon (DOC) in soil. Soil Biology and Biochemistry 38, 991-999.

Juretschko S., Timmermann G., Schmid M., Schleifer K.-H., Pommerening-Roser A., Koops H.-P., Wagner M., 1998. Combined molecular and conventional analyses of nitrifying bacterium diversity in activated sludge: Nitrosococcus mobilis and Nitrospira-like bacteria as dominant populations. Applied and Environmental Microbiology 64, 3042-3051.

Keene W.C., Montag J.A., Maben J.R., Southwell M., Leonard J., Church T.M., Moody J.L., Galloway J.N., 2002. Organic nitrogen in precipitation over Eastern North America. Atmospheric Environment 36, 4529-4540.

Kelly S.D., Stein C., Jickells T.D., 2005. Carbon and nitrogen isotopic analysis of atmospheric organic matter. Atmospheric Environment 39, 6007-6011.

Kinzig A.P., Socolow R.H., 1994. Human impacts on the nitrogen cycle. Physics Today 47, 24-31.

Krab E., Cornelissen J., Lang S., van Logtestijn R., 2008. Amino acid uptake among wide-ranging moss species may contribute to their strong position in higher-latitude ecosystems. Plant and Soil 304, 199-208.

Kranabetter J.M., Dawson C.R., Dunn D.E., 2007. Indices of dissolved organic nitrogen, ammonium and nitrate across productivity gradients of boreal forests. Soil Biology and Biochemistry 39, 3147-3158.

Lee D.S., Longhurst J.W.S., 1992. A comparison between wet and bulk deposition at an urban site in the UK. Water Air and Soil Pollution 64, 635-648.

Lee W., Westerhoff P., 2005. Dissolved organic nitrogen measurement using dialysis pretreatment. Environmental Science & Technology 39, 879-884.

Luttke J., Scheer V., Levsen K., Wunsch G., Cape J.N., Hargreaves K.J., StoretonWest R.L., Acker K., Wieprecht W., Jones B., 1997. Occurrence and formation of nitrated phenols in and out of cloud. Atmospheric Environment 31, 2637-2648.

Maie N., Parish K.J., Watanabe A., Knicker H., Benner R., Abe T., Kaiser K., Jaffe R., 2006. Chemical characteristics of dissolved organic nitrogen in an oligotrophic subtropical coastal ecosystem. Geochimica et Cosmochimica Acta 70, 4491-4506.

Matsumoto K., Uematsu M., 2005. Free amino acids in marine aerosols over the western North Pacific Ocean. Atmospheric Environment 39, 2163-2170.

Muller C., Iinuma Y., Karstensen J., van Pinxteren D., Lehmann S., Gnauk T., Herrmann H., 2009. Seasonal variation of aliphatic amines in marine sub-micrometer particles at the Cape Verde islands. Atmospheric Chemistry and Physics 9, 9587–9597.

Nakamura T., Ogawa H., Maripi D.K., Uematsu M., 2006. Contribution of water soluble organic nitrogen to total nitrogen in marine aerosols over the East China Sea and western North Pacific. Atmospheric Environment 40, 7259-7264.

Neff J.C., Holland E.A., Dentener F.J., McDowell W.H., Russell K.M., 2002. The origin, composition and rates of organic nitrogen deposition: A missing piece of the nitrogen cycle? Biogeochemistry 57, 99-136.

NERC, 2008. Anthropocene: a new epoch. Planet Earth, Natural Environment Research Council, 3.

Nozawa S., Hakoda A., Sakaida K., Suzuki T., Yasui A., 2005. Method performance study of the determination of total nitrogen in soy sauce by the Kjeldahl method. Analytical Sciences 21, 1129-1132.

Pacheco M., Donoso L., Sanhueza E., 2004. Soluble organic nitrogen in Venezuelan rains. Tellus B 56, 393-395.

Paul J.P., Williams B.L., 2005. Contribution of [alpha]-amino N to extractable organic nitrogen (DON) in three soil types from the Scottish uplands. Soil Biology and Biochemistry 37, 801-803.

Persson J., Nasholm T., 2001. Amino acid uptake: a widespread ability among boreal forest plants. Ecology Letters 4, 434-438.

Petit C., Bandosz T.J., 2008. Removal of ammonia from air on molybdenum and tungsten oxide modified activated carbons. Environmental Science & Technology 42, 3033-3039.

Pool J.A., Lobkovsky E., Chirik P.J., 2004. Hydrogenation and cleavage of dinitrogen to ammonia with a zirconium complex. Nature 427, 527-530.

Raven J.A., Smith F.A., 1976. Nitrogen Assimilation and Transport in Vascular Land Plants in Relation to Intracellular pH Regulation. New Phytologist 76, 415-431.

Rowland A.P., 1983. An Automated-Method for the Determination of Ammonium-N in Ecological Materials. Communications in Soil Science and Plant Analysis 14, 49-63.

Russell K.M., Galloway J.N., Macko S.A., Moody J.L., Scudlark J.R., 1998. Sources of nitrogen in wet deposition to the Chesapeake Bay region. Atmospheric Environment 32, 2453-2465.

Schäfer H., Läubli M., Dörig R., 2003. Ion Chromatography, Metrohm AG, Herisau, Switzerland

Scharenbroch B.C., Lloyd J.E., 2004 A literature review of nitrogen availability indices for use in urban landscapes. Journal of Arboriculture 30, 214-230.

Schwendenmann L., Veldkamp E., 2005. The role of dissolved organic carbon, dissolved organic nitrogen, and dissolved inorganic nitrogen in a tropical wet forest ecosystem. Ecosystems 8, 339-351.

Sciare J., Mihalopoulos N., 2000. A new technique for sampling and analysis of atmospheric dimethylsulfoxide (DMSO). Atmospheric Environment 34, 151-156.

Scudlark J.R., Russell K.M., Galloway J.N., Church T.M., Keene W.C., 1998. Organic nitrogen in precipitation at the mid-Atlantic US coast - Methods evaluation and preliminary measurements. Atmospheric Environment 32, 1719-1728.

Seitzinger S.P., Sanders R.W., 1999. Atmospheric Inputs of Dissolved Organic Nitrogen Stimulate Estuarine Bacteria and Phytoplankton. Limnology and Oceanography 44, 721-730.

Sharp J.H., Rinker K.R., Savidge K.B., Abell J., Benaim J.Y., Bronk D., Burdige D.J., Cauwet G., Chen W.H., Doval M.D., Hansell D., Hopkinson C., Kattner G., Kaumeyer N., McGlathery K.J., Merriam J., Morley N., Nagel K., Ogawa H., Pollard C., Pujo-Pay M., Raimbault P., Sambrotto R., Seitzinger S., Spyres G., Tirendi F., Walsh T.W., Wong C.S., 2002. A preliminary methods comparison for measurement of dissolved organic nitrogen in seawater. Marine Chemistry 78, 171-184.

Smil V., 1999. Nitrogen in crop production: An account of global flows Global Biogeochemical Cycles 13 647-662.

Spaulding R.S., Talbot R.W., Charles M.J., 2002. Optimization of a mist chamber (Cofer scrubber) for sampling water-soluble organics in air. Environmental Science and Technology 36, 1798-1808.

Stevenson F.J., Cole M.A., 1999. Cycles of Soil: Carbon, Nitrogen, Phosphorus, Sulfur, Micronutrients, John Wiley & Sons, Inc., New York

Stoltzenberg D., 2005. Fritz Haber: Chemist, Nobel Laureate, German, Jew: A Biography, Chemical Heritage Foundation

Tang Y.S., Braban C., Sutton M.A., Anderson M., Simmons I., Dijk N.v., Cape J.N., Smith R.I., Lawrence H., 2009. Monitoring of nitric acid, particulate nitrate and other species in the UK-2008. Centre for Ecology and Hydrology (Edinburgh Research Station) Annual Summary Data for DEFRA.

UN-ECE, 1999. Convention on long-range transboundary air pollution to abate acidification, eutrophication and ground-level ozone. United Nations Economic Commission for Europe.

Vandenbruwane J., Neve S.D., Qualls R.G., Salomez J., Hofman G., 2007. Optimization of dissolved organic nitrogen (DON) measurements in aqueous samples with high inorganic nitrogen concentrations. Science of The Total Environment 386, 103-113.

Vitousek P.M., Aber J., Howarth R.W., Likens G.E., Matson P.A., Schinder D.W., Schlesinger W.H., Tilman D., 1997. Human alteration of the global nitrogen cycle: causes and consequences. Ecological Applications 7, 737-750.

Westerhoff P., Mash H., 2002. Dissolved organic nitrogen in drinking water supplies: a review. Journal of Water Supply Research and Technology-Aqua 51, 415-448.

Whitehead J.D., Twigg M., Famulari D., Nemitz E., Sutton M.A., Gallagher M.W., Fowler D., 2008. Evaluation of laser absorption spectroscopic techniques for Eddy covariance flux measurements of ammonia. Environmental Science & Technology 42, 2041-2046.

Wood E.C., Herndon S.C., Timko M.T., Yelvington P.E., Miake-Lye R.C., 2008. Speciation and chemical evolution of nitrogen oxides in aircraft exhaust near airports. Environmental Science & Technology 42, 1884-1891.

Wu Y., Dittmar T., Ludwichowski K.-U., Kattner G., Zhang J., Zhu Z.Y., Koch B.P., 2007. Tracing suspended organic nitrogen from the Yangtze River catchment into the East China Sea. Marine Chemistry 107, 367-377.

Yasuhara T., Nokihara K., 2001. High-throughput analysis of total nitrogen content that replaces the classic Kjeldahl method. Journal of Agricultural and Food Chemistry 49, 4581-4583.

Zhang Y., Zheng L., Liu X., Jickells T., Neil Cape J., Goulding K., Fangmeier A., Zhang F., 2008. Evidence for organic N deposition and its anthropogenic sources in China. Atmospheric Environment 42, 1035-1041.

Publications

González Benítez J.M., Cape J.N., Heal M.R., van Dijk N., Díez A.V., 2009. Atmospheric nitrogen deposition in south-east Scotland: Quantification of the organic nitrogen fraction in wet, dry and bulk deposition. Atmospheric Environment 43 (26), 4087-4094.

González Benítez J.M., Cape J.N., Heal M.R., 2010. Gaseous and particulate water-soluble organic and inorganic nitrogen in rural air in southern Scotland. Atmospheric Environment 44 (12), 1506-1514.