Nitrogen fluxes at the landscape scale: A case study in Scotland

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Abstract

Nitrogen (N) fluxes show a substantial variability at the landscape scale. Emissions are transferred by atmospheric, hydrological and anthropogenic dispersion between different landscape elements or ecosystems, e.g. farms, fields, forests or moorland. These landscape N fluxes can cause impacts to the environment, such as loss of biodiversity. The aim of this study is to illustrate how landscape N fluxes can be quantified by integrating atmospheric and fluvial fluxes in a Scottish landscape of 6 km x 6 km that contains intensively managed poultry farming, extensively managed beef and sheep farming, semi-natural moorland and woodland.

Atmospheric ammonia (NH_3) emissions of two deep pit free range layer poultry houses were estimated by high time-resolution measurements of NH_3 concentrations and meteorological variables downwind of layer poultry houses and the application of an inverse Gaussian plume model. Atmospheric NH_3 concentrations and deposition fluxes across the study landscape were studied at a resolution of 25 m x 25 m. The approach combined a detailed landscape inventory of all farm activities providing high resolution NH_3 emission estimates for atmospheric dispersion modelling and an intensive measurement programme of spatial NH_3 concentrations for verifying modelled NH_3 concentrations. The spatially diverse emission pattern resulted in a high spatial variability of modelled mean annual NH_3 concentrations (0.3 to 77.9 μg NH_3 m^{-3}) and dry deposition fluxes (0.1 to >100 kg NH_3-N ha^{-1} yr^{-1}) within the landscape.

Annual downstream fluxes and variation in spatial concentration of dissolved inorganic nitrogen (NH_4^+ and NO_3^-) and dissolved organic nitrogen (DON) were studied in the two main catchments within the study landscape (agricultural grassland vs. semi-natural moorland catchment). The grassland catchment was associated with an annual downstream total dissolved nitrogen (TDN) flux of 14.4 kg N ha^{-1} yr^{-1}, which was 66% higher than the flux of 8.7 kg ha^{-1} yr^{-1} from the moorland catchment. This difference was largely due to the NO_3^- flux being one order of magnitude higher in the grassland catchment. The contribution of DON to the TDN flux varied between the catchments with 49% in the grassland and 81% in the moorland catchment.

Fluvial and atmospheric N fluxes were combined to derive N budgets of the two catchments. Agricultural activities accounted for the majority of N input to the catchments, with atmospheric deposition also playing a significant role, especially in the moorland catchment. Both catchments showed large stream export fluxes compared to their net import which suggests that their capacity of N storage is limited.

This thesis quantifies major N fluxes in a study landscape and shows their large spatial variability. Agricultural activities dominate landscape N dynamics. The work demonstrates the importance of considering landscape N variability when attempting to reduce the environmental impact of agricultural activities.

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Author’s contribution to the papers

Paper I: The application of a Gaussian plume model to quantify ammonia emissions from poultry housing
E. Vogt took part in planning the field experiment and was responsible for setting it up and equipment maintance. She processed the data, run the model and wrote the manuscript in cooperation with the coauthors.

Paper II: Environmental impact assessment of atmospheric ammonia at the landscape scale: Local vs. national scale modelling
E. Vogt took part in planning and setting up the field experiment. She was responsible for the field and laboratory work of the monitoring programme. She processed the data, run the local atmospheric dispersion model and wrote the manuscript in cooperation with the coauthors.

Paper III: Effect of land use on fluxes and concentrations of organic and inorganic nitrogen in streams
E. Vogt took part in planning the experiment and setting up the equipment. She was responsible for field and most of the laboratory work. She processed the data and wrote the manuscript in cooperation with the coauthors.

Paper IV: Estimation of nitrogen budgets for contrasting catchments at the landscape scale
E. Vogt developed the idea of this paper in cooperation with the coauthors. She wrote the manuscript with contributions from the coauthors.

1 Introduction

1.1 Why nitrogen fluxes at the landscape scale?

Landscape ecology describes an interdiciplinary field studying ecological effects of the spatial patterning of ecosystems (e.g. Turner, 1989). The exact definition and spatial dimension of a landscape can vary depending on the research objectives (Liu and Taylor, 2002). However, *landscape* commonly refers to a spatially heterogeneous area at scales of hectares to many square kilometres (Turner and Gardner, 1994). The concept of landscape ecology emphasises the interactions and exchanges across relatively homogeneous landscape components, such as agricultural fields or woodland patches (Forman and Godron, 1981). Landscape scale interactions or processes include fluxes of energy and mineral nutrients as well as species (Forman, 1995).

Nitrogen (N) is a nutrient transported by atmospheric, hydrological and anthropogenic dispersion between landscape components (Cellier et al., 2011). Nitrogen is a key nutritional element of any form of life on earth. Although the atmosphere consists to about 78% of diatomic nitrogen (N_2), this form of N is unreactive and thus unavailable to most organisms (Galloway et al., 2004). Reactive nitrogen (N_r) consists of all biologically, photochemically and radiatively active N compounds in the earth's atmosphere and biosphere (Galloway et al., 2004). Thus, it includes reduced (e.g. NH_3, NH_4^+), oxidised (e.g. NO_2, N_2O, NO_3^-) and organic forms of N (e.g. urea). The limited availability of N_r restrains the primary production in many terrestrial and aquatic ecosystems (Vitousek and Howarth, 1991). However, industrial production of N_r made large scale agricultural production possible and led to a significant alteration of the N cycle (Galloway et al., 2008; Sutton et al., 2009). Particularly in oligotrophic ecosystems, which are characterised by low nutrient levels, N input can cause environmental impacts, such as loss of biodiversity, through eutrophication and acidification (Vitousek et al., 1997).

Today, in most European rural landscapes, agricultural activities determine the majority of N_r fluxes (Cellier et al., 2011). Farms represent the operational units at which the management decisions are made which determine the extent of N_r transferred into the atmosphere and water (Jarvis et al., 2011). Thus, the landscape scale is the scale where both N is managed (by farm activities) and the impact to the environment occurs (Sutton et al., 2007). This makes determining landscape N_r fluxes important for environmental protection and policy makers. A good understanding of the quantities and dynamics of N fluxes at the landscape scale is essential for designing effective regulations aiming to reduce the environmental impact of nitrogen.

The following subchapters introduce the main farm, atmospheric and hydrological N_r fluxes relevant at the landscape scale (sections 1.2 1.3 and 1.4), the study landscape and its characteristics regarding N_r fluxes (section 1.5) and the aims and objectives of the present study (section 1.6).

1.2 Farm nitrogen fluxes

The main farm N_r fluxes discussed in this subsection are summarised after Jarvis et al. (2011) (Figure 1.1). Nitrogen is often imported to the farm from outside the landscape by products such as livestock, feed, bedding, synthetic fertiliser and manure. Fluxes within the farm are e.g. movements of livestock between houses and fields, and movements of manure between livestock houses, manure storage and fields. Farm export N_r fluxes include sold manure, crop products (e.g. cereals) and animal products (e.g. meat, milk and eggs).

Those N_r fluxes represent farm operations and not all of those processes have a direct impact to the landscape environment. For example, some imports and exports to and from the landscape, e.g. through imported feed or exported manure, take place on roads and are thus decoupled from the landscape environment. The main N losses from a farm to the environment occur through atmospheric and hydrological fluxes from farm buildings and agricultural fields.

Animal housing and manure storage represent N_r emission sources, mainly of ammonia (NH_3), which is volatilised from urine and excreta (see also section 1.3). These emissions are influenced by differences in type and number of livestock, housing system (e.g. ventilation type) and manure management (e.g. frequency of manure removal). Cropped or grazed fields represent emission sources of NH_3, nitrous oxide (N_2O) and nitric oxide (NO) and sources of N_r losses of nitrate (NO_3^-), ammonium (NH_4^+) and dissolved organic nitrogen (DON) through surface runoff and leaching into stream- and groundwater (section 1.4). These fluxes from agricultural fields are strongly influenced by the type and amount of N applied to the field and the type and number of grazing livestock. Ammonia is directly emitted through volatilisation from urine and excreta patches and from manure applied to the field. Emissions of N_2O and NO are largely due to increased soil microbial activity after N input through grazing livestock, synthetic fertiliser and manure (section 1.3). Thereby, not only the N application rate plays a significant role, grazing livestock also contribute to these emissions, particularly to N_2O, by soil compaction caused by trampling (Oenema et al., 1997).

The magnitude by which farm processes cause losses to the environment, depends largely on the N efficiency of the specific farm, i.e. the more effectively a farm uses its N the fewer the environmental impacts. For example, crops need to be supplied with the correct amount of N at the correct time to allow successful growth, otherwise this leads either to a restricted crop productivity or to an N surplus which may be lost to the environment. However, not all N losses to the environment can be avoided by optimal farm management. A farm represents a local, intensive concentration of various N_r forms resulting in a greater probability of N loss than in natural ecosystems.

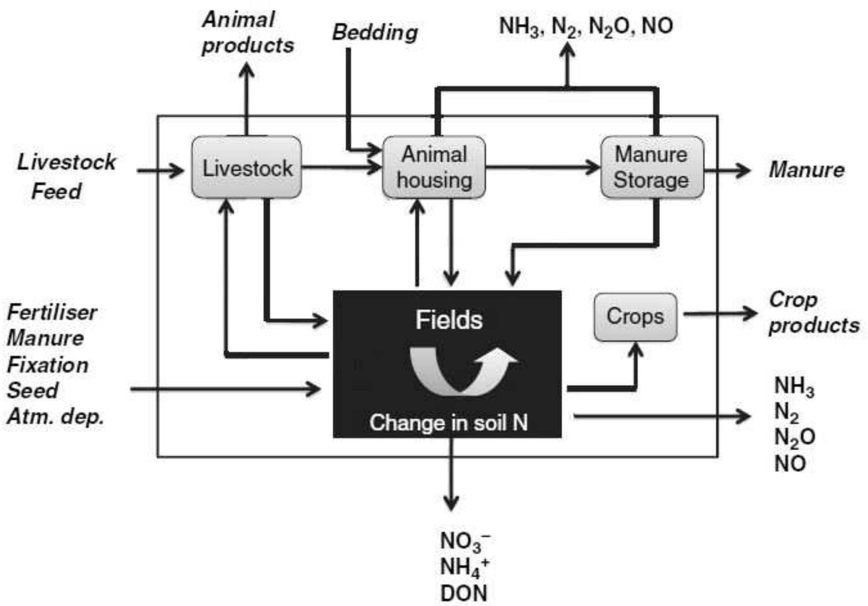


Figure 1.1: Nitrogen fluxes on a farm (Atm. dep. = atmospheric deposition). Source: Jarvis et al. (2011)

1.3 Atmospheric nitrogen fluxes

The main atmospheric N flows are illustrated in Figure 1.2, i.e. not all N species are included. For atmospheric processes at the landscape scale not all of the atmospheric N compounds are equally important. For example, although nitric oxide (NO) and nitrogen dioxide (NO_2) play an important role in atmospheric chemistry, especially in the production and destruction of ozone (Crutzen, 1979), they have little impact close to their sources due to their low dry deposition rates (Finlayson-Pitts and Pitts, 2000). The main sources of NO and NO_2 are combustion processes of fossil fuel, however soil emissions of NO also make a significant contribution to global totals, particularly in connection with agricultural land use (Davidson and Kingerlee, 1997; Fowler et al., 1998a). Another atmospheric process involving NO_2 is the conversion to nitric acid (HNO_3) which has an efficient deposition rate (Finlayson-Pitts and Pitts, 2000). However, the conversion rate is slow (Hertel et al., 2011) and thus less relevant for landscape scale processes.

In contrast, many processes involving ammonia (NH_3) occur within the landscape scale. The main sources of NH_3 are agricultural activities (EEA, 2007; Van der Hoek, 1998). Most of the agricultural NH_3 emissions originate from livestock farming, i.e. from livestock houses, manure storage, manure spreading and grazing animals (Beusen et al., 2008). Ammonia volatilises from those sources at rates which depend on water content, pH and temperature (e.g. Ferm, 1998). After emission, NH_3 is subject to high dry deposition rates which leads to a large spatial variability of NH_3 at the landscape scale (Cellier et al., 2011).

Gaseous NH_3 also neutralises atmospheric acids such as HNO_3 to form aerosol ammonium (NH_4^+) and nitrate (NO_3^-) which are mainly removed from the atmosphere by wet deposition (van Pul et al., 2009). However, those processes occur over larger scales than landscapes as aerosols can travel long distance before being deposited.

Nitrous oxide (N_2O) (which is not included in Figure 1.2 as it plays an important role only in the upper layer of the atmosphere) is one of the major greenhouse gases with a high global warming potential (IPCC, 2007). At the global scale, the largest source of N_2O are emissions from soils, particularly agricultural soils (Butterbach-Bahl et al., 2011). The microbial soil processes nitrification (oxidation of NH_4^+ to

NO_3^-) and denitrification (reduction of NO_3^- to N_2) can release N_2O (as well as NO) as intermediate products (e.g. Davidson et al., 2000). Those processes are affected by soil conditions, such as soil moisture, temperature, soil pH and availability of carbon (C) and N in the soil (Bouwman, 1996). However, at the landscape scale N_2O has no significant interactions after its emission, thus it is only of importance as a potential loss of N (Cellier et al., 2011).

Although the potential importance of organic N compounds in the atmosphere has been recognised (Neff et al., 2002), their sources and composition remain largely unknown (Hertel et al., 2011).

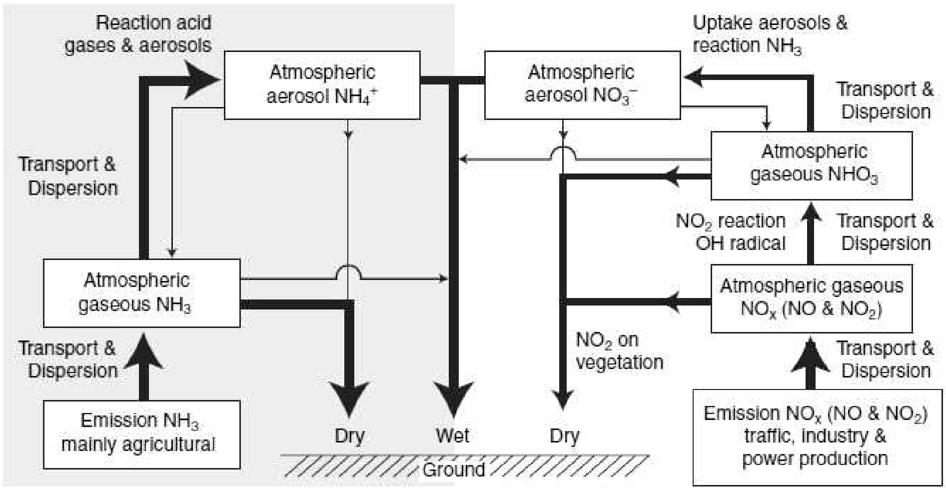


Figure 1.2: Atmospheric processes of reduced N (NH_x, left) and oxidised N (NO_y, right). Source: Hertel et al. (2011)

1.4 Hydrological nitrogen fluxes

The main forms of N in aquatic ecosystems are dissolved inorganic N (NH_4^+, NO_3^-) and dissolved and particulate organic N (DON, PON) (Durand et al., 2011). Surface water runoff and leaching from terrestrial ecosystems to stream- and groundwater represent an important hydrological N_r flux at the landscape scale. The amount of N leached from soils depends on the availablity of dissolved N (NH_4^+, NO_3^- and DON) in the soil and the mobility of the different N forms (Butterbach-Bahl et al., 2011). While NH_4^+ is usually quite immobile in the soil, NO_3^- is very mobile and thus subject to leaching. Some forms of DON may also leach from soils, despite a high plant demand (Neff et al., 2003). The magnitude of N leached is influenced by soil microbial processes providing different forms of N and the N input to the soil, e.g. due to grazing, fertiliser applications and atmospheric deposition (Jarvis, 2000).

Streamwater N downstream fluxes are largely the result of N sources within the catchment. However, the N_r flux to the stream also depends on catchment specific hydrological processes, particularly the relative importance of surface water and deep water pathways in the N_r transfer from terrestrial ecosystems to the stream (Durand et al., 2011). As surface flows have a time scale of minutes to days and deep flows a time scale of months to decades, the downstream N_r flux may contain waters with contrasting histories (Cellier et al., 2011; Durand and Torres, 1996).

1.5 Study landscape

As part of the NitroEurope Integrated Project (Sutton et al., 2007), a study landscape was established in southern Scotland. The climate of the region is oceanic temperate with predominantly southwesterly winds. The location of the study landscape as well as land cover and soil types within the 6 km x 6 km study area are shown in Figure 1.3.

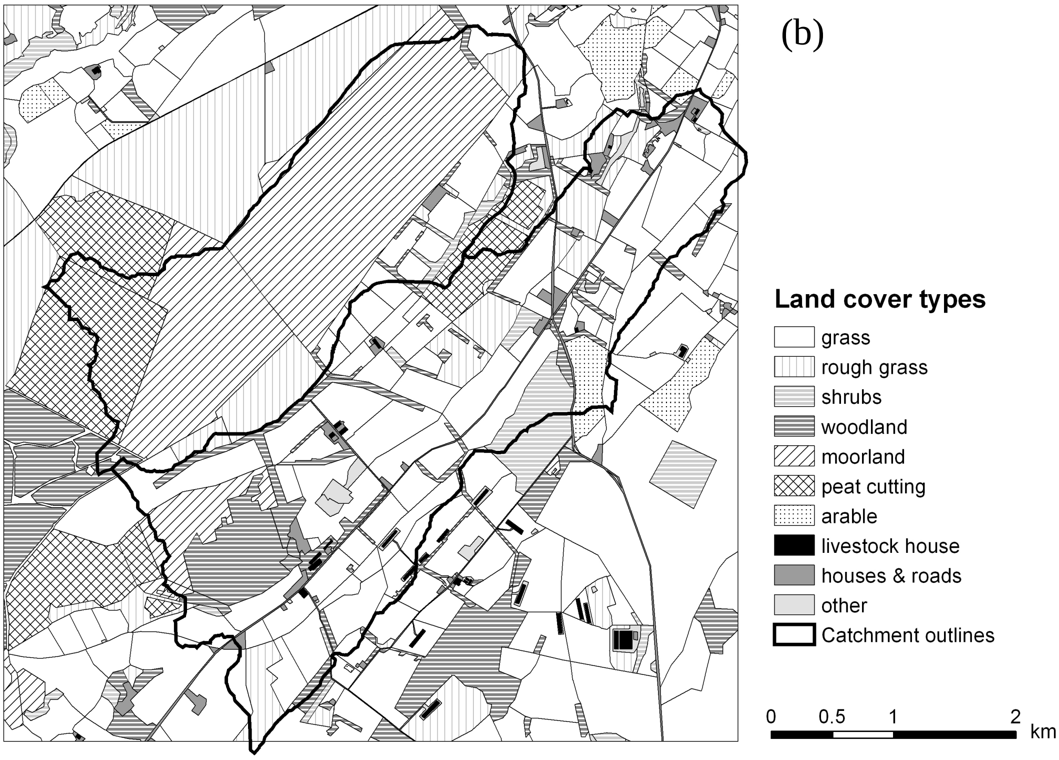
Semi-natural moorland and rough grass areas dominate the northwestern part of the landscape. The peat-dominated moorland area is partially grazed by sheep at low stocking densities, and is partly designated as a Site of Special Scientific Interest (SSSI) and partly undergoing peat cutting. The moorland was partly drained approximately 50 years ago which is indicated by parallel, overgrown ditches throughout the moorland, each up to one metre deep (Flechard and Fowler, 1998). However, the ground is permanently damp or waterlogged during all seasons except summer (Flechard and Fowler, 1998). Peat pH measured in the moorland area ranged from 2.5 to 2.8 at 10 cm depth and from 2.5 to 3.0 at 150 cm depth (Billett et al., 2004). With the high water content, low pH and only small amount of available N, microbial processes are usually quite low in moorlands. Moorlands are known to be vulnerable to enhanced N deposition with regards to changes in biodiversity, microbial activity and leaching rates (Pilkington et al., 2005).

The southeast of the study landscape is dominated by agricultural land, such as pastures grazed by beef cattle and sheep. The agriculturally improved grassland receives additional nitrogen input, through e.g. grazing livestock and/or applications of manure/synthetic fertiliser. Thus, the potential for N losses is increased both through gaseous losses and through leaching into surface waters or groundwaters (e.g. Davies, 2000). The magnitude of these losses is dependent on the soil type, weather conditions and on management practices (e.g. Clayton et al., 1994; Velthof et al., 1996). For instance, the type and stocking density of grazing animals, the type and amount of fertiliser applied, timing of fertiliser application and soil drainage are important factors influencing N loss (Bouwman, 1996; Vinten et al., 2002). Thus, different magnitudes of loss can be expected for different fields in the landscape, depending on the listed factors.

The agricultural land in the southeast of the study landscape is also interspersed with intensive poultry farming. The study area contains 24 poultry houses, containing nearly 1.5 million laying hens which are partly kept in cages and partly as free-range birds. Those livestock houses represent large point sources of NH_3 emissions (e.g. Fowler et al., 1998b). Ammonia emissions can vary substantially depending on the number of birds, type and age of birds, the housing system and climatic conditions (e.g. Groot Koerkamp et al., 1998). These large emission fluxes of the poultry houses also cause large NH_3 dry deposition fluxes, which can have negative effects on sensitive ecosystems, such as semi-natural moorland.

Two main catchments are situated within the study area, representing the contrasting land uses of the landscape: one catchment is dominated by moorland, the other by grazed grassland (Figure 1.3). As land use, land management and atmospheric deposition determine the nitrogen sources in catchments (Wade et al., 2005), N dynamics between the two catchments are expected to differ and may consequently lead to different N budgets.

For this study, fluxes of N_r due to farm management were derived from a detailed local survey of all farms and fields in the study landscape, which was carried out by the Scottish Agricultural College (SAC). Farm activities were recorded for each farm building and each agricultural field through 2008, including e.g. type and numbers of livestock housed and grazed, crop type and the application of synthetic and organic fertiliser. To some of the farm activity data, a typical N content was applied to derive N_r fluxes, e.g. to different manure types (DEFRA, 2010).



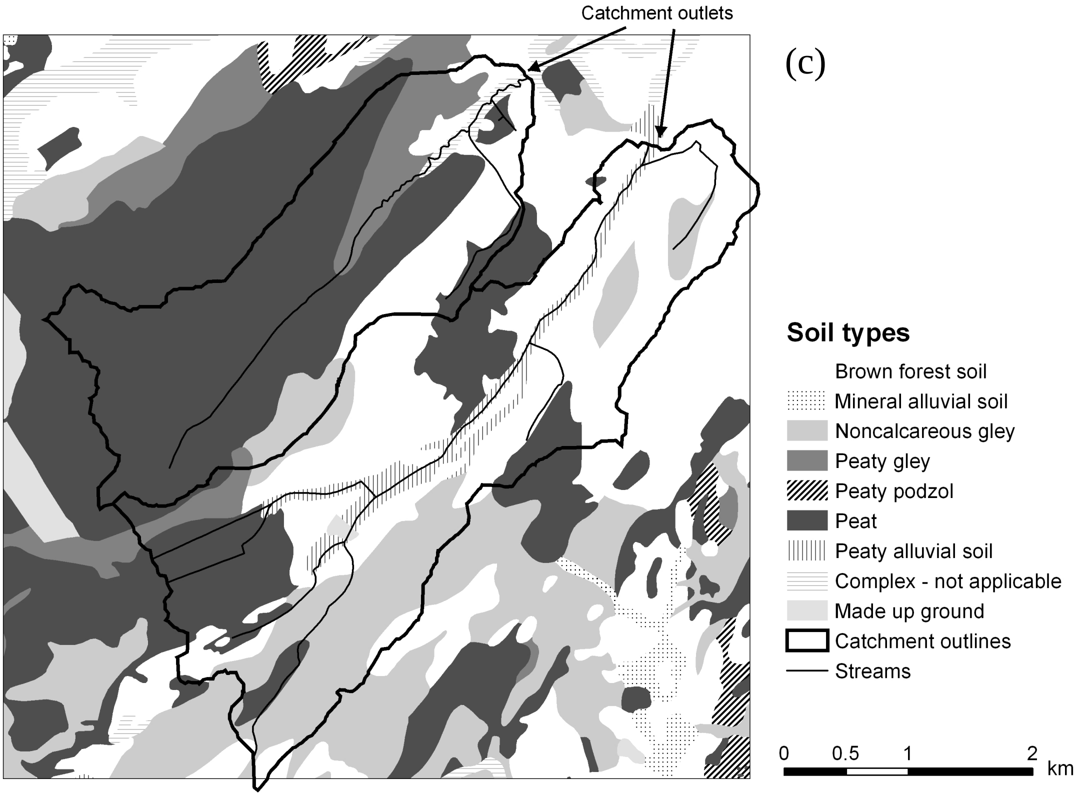


Figure 1.3: Maps of (a) the approximate location of the study landscape in the UK, (b) land cover, and (c) soil types within the study landscape with outlines of the two studied catchments.

1.6 Aims and objectives

This study aims to understand the magnitude of N fluxes in a particular study landscape in southern Scotland (section 1.5). By doing so, this study aims to contribute to knowledge about landscape N fluxes in general, especially those within areas including both natural ecosystems and agricultural land. This is important to be able to protect the environment from harmful effects of landscape N fluxes.

Quantifying all atmospheric and hydrological fluxes of multiple N_r species within the study landscape is beyond current practical capabilities. Thus, this project focuses on main known N_r fluxes particular to this study area (section 1.5). The specific aims and objectives were:

a) To establish the magnitude of NH_3 emission fluxes from significant point sources (poultry houses) within the landscape by using campaign-based, high time-resolution measurements of atmospheric NH_3 concentrations downwind of several poultry houses and an inverse Gaussian plume model (Paper I).

b) To quantify NH_3 dry deposition fluxes within the landscape at high spatial resolution (25 m) by using a spatial network of continuous, monthly atmospheric NH_3 measurements across the landscape verifying concentrations modelled by a local dispersion model (Paper II).

c) To analyse catchment downstream fluxes of NH_4^+, NO_3^- and DON and the influence of farm and atmospheric deposition N_r fluxes on streamwater concentrations by discharge and concentration measurements, combined with campaigns of spatial concentration measurements across the catchments (Paper III).

d) To estimate catchment N budgets by combining the derived atmospheric, hydrological and farm N_r fluxes with gap filling from literature (Paper IV).

The following four chapters (chapters 2, 3, 4 and 5) consist of separate research papers containing results, discussion and conclusions from the above described approaches. The thesis concludes with an overall thesis discussion (chapter 6) and conclusions (chapter 7).

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2 Paper I: The application of a Gaussian plume model to quantify ammonia emissions from poultry housing

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Abstract

High time-resolution measurements of atmospheric ammonia concentrations and meteorological variables were made in the plume downwind of layer poultry houses. The application of an inverse Gaussian plume model was used to estimate the ammonia emission strengths, and ammonia emission factors per bird place were established for two deep pit free range poultry houses. Results of daily emission rates observed in May 2007 and June/July 2008, suggest annual average emission factors ranging from 0.16 to 0.40 kg NH_3 bird^{-1} yr^{-1}, with an average of 0.27 ± 0.07 (standard deviation) kg NH_3 bird^{-1} yr^{-1}. This is 35% higher than housing emissions from free range systems used in the UK national inventory. Overall, the emission rates from this system are in line with figures found in the literature and highlight the use of the inverse plume method as a relevant technique for verifying inventory estimates of ammonia emission rates from point sources.

Keywords: ammonia, atmospheric dispersion, Gaussian plume, emission factor, poultry, point source

2.1 Introduction

2.1.1 Atmospheric ammonia (NH_3)

Agriculture is the major source of atmospheric NH_3, contributing 80-90% to the total NH_3 emissions in Europe (EEA, 2007). Around 65% of agricultural NH_3 emissions originate from livestock production to which livestock houses and manure storage contribute 42% (Beusen et al., 2008). From an environmental perspective, NH_3 has two significant properties. Firstly, as the primary basic gas in the atmosphere, it reacts with acids leading to the formation of particulate matter (Seinfeld and Pandis, 1998). Particles have a wide range of impacts including effects on climate and human health (Davidson et al., 2005). Secondly, NH_3 deposits onto surfaces such as plants, soil and water (Asman, 2001). Dry and wet deposition of NH_3 both in the gas and particulate phase can lead to eutrophication of ecosystems. In agricultural systems this can be beneficial as NH_3 acts as a fertiliser. In semi-natural terrestrial or aquatic ecosystems, NH_3 deposition can lead to changes in biodiversity and be directly toxic to plants (Sutton et al., 2009).

2.1.2 NH_3 emission factors (EFs) for layer poultry in literature

The large contribution of livestock to NH_3 emissions has motivated many studies aimed at establishing livestock type specific emission factors. An emission factor (EF) is the average emission rate of a pollutant per emitting entity. Ammonia EFs for animal housing are well-documented (e.g. Faulkner and Shaw, 2008; Groot Koerkamp et al., 1998; Misselbrook et al., 2000). However, only some of the published values are based on new experimental data and, of those, many studies were only conducted over a short time period. Hence, there remains a considerable uncertainty in NH_3 EFs for animal housing.

Table 2.1 summarises the published NH_3 EFs for laying hens. The wide range of EFs is mainly due to factors such as housing management, climate and seasonal variations that influence the NH_3 emission rates considerably (European Commission, 2003). Reported EFs for layers from studies shown in Table 2.1 range from 0.04 to 0.52 kg NH_3 bird^{-1} yr^{-1} with an average of 0.23 ± 0.12 (53%). Emissions are smallest for systems where the manure is dried quickly and effectively, as this reduces the hydrolysis of excreted uric acid to form NH_3.

Table 2.1: NH_3 emission factors (EF) for layer poultry in literature (if not stated otherwise a layer weight of 2.2 kg (Misselbrook et al., 2009) is assumed for conversion from an EF per lw (500 kg live body weight) or lu (live unit = lw) to an EF per bird)

NH_3 housing EF [kg NH_3 bird^{-1} year^{-1}]	Original reference	Housing system	EF type	Region	Source
0.27	0.22 kg NH_3-N bird^{-1} year^{-1}	Poultry, unspecified	Regional estimate	UK	Sutton et al. (1995)
0.19	0.19 kg NH_3 bird^{-1} year^{-1}	-	Regional estimate	Europe	McInnes (1996)
0.24*	0.20 kg NH_3-N bird^{-1} year^{-1} *	Poultry, unspecified	Regional estimate	Global	Bouwman et al. (1997)
0.19	0.19 kg NH_3 bird^{-1} year^{-1}	-	Regional estimate	Europe	Van der Hoek (1998)
0.27	136.6 g NH_3-N lu^{-1} day^{-1}	Average layer (32% perchery and 68% cages)	Regional estimate	UK	Misselbrook at al. (2000)
0.37*	0.37 kg NH_3 bird^{-1} year^{-1} *	-	Regional estimate	Europe	Battye et al. (2003)
0.26	132.5 g NH_3-N lu^{-1} day^{-1}	-	Regional estimate	Ireland	Hyde et al. (2003)
0.17	0.14 kg NH_3-N bird^{-1} year^{-1}	-	Regional estimate	UK	Misselbrook et al. (2009)
0.33	9.2 g NH_3 500 kg lw^{-1} h^{-1} and average body weight of 2.06 kg	Belt system	Experimental	UK	Wathes et al. (1997)
0.12	13.9 mg NH_3 bird^{-1} h^{-1} (average across countries)	Belt system	Experimental	Northern Europe	Groot Koerkamp et al. (1998)
0.16	0.13 kg NH_3-N bird^{-1} year^{-1} (average across seasons)	Belt system	Experimental	USA	Keener et al. (2001)
0.06	1.3 g NH_3-N 500 kg lw^{-1} h^{-1}	Daily scraped belt system	Experimental	UK	Nicholson et al. (2004)
0.15	3.3 g NH_3-N 500 kg lw^{-1} h^{-1}	Weekly scraped belt system	Experimental	UK	Nicholson et al. (2004)
0.04	0.1 g NH_3 bird^{-1} day^{-1}	Weekly scraped belt system	Experimental	Ireland	Hayes et al. (2006)
0.06	0.06 kg NH_3 bird^{-1} year^{-1}	Ventilated belt system	Experimental	Italy	Fabbri et al. (2007)
0.33	9.2 g NH_3 500 kg lw^{-1} h^{-1} and average body weight of 2.06 kg	Perchery	Experimental	UK	Wathes et al. (1997)
0.31	35.1 mg NH_3 bird^{-1} h^{-1} (average across countries)	Perchery / deep pit	Experimental	Northern Europe	Groot Koerkamp et al. (1998)
0.52	0.42 kg NH_3-N bird^{-1} year^{-1} (average across seasons)	Caged, deep pit	Experimental	USA	Keener et al. (2001)
0.38	8.2 g NH_3-N 500 kg lw^{-1} h^{-1}	Caged, deep pit	Experimental	UK	Nicholson et al. (2004)
0.18	0.5 g NH_3 bird^{-1} day^{-1}	Deep pit	Experimental	Ireland	Hayes et al. (2006)
0.16	0.16 kg NH_3 bird^{-1} year^{-1}	Caged, deep pit	Experimental	Italy	Fabbri et al. (2007)

* EF includes storage outside stable and surface spreading of waste

2.1.3 Techniques to determine NH_3 emissions from livestock houses

Most previous studies to determine NH_3 emissions from livestock houses have measured NH_3 concentrations inside the building, close to the air outlets, and combined these with the ventilation rate measured by anemometers or by tracer gas method (e.g. Demmers et al., 1999; Phillips et al., 2001). However, it remains a challenge to estimate the ventilation rate correctly, especially in naturally ventilated buildings (Demmers et al., 1998). Another method, although less used, is to calculate NH_3 losses from livestock houses as the difference between nitrogen input and output, but the accuracy of this method has been criticised (Groot Koerkamp et al., 1998; Phillips et al., 2000). There have also been efforts to measure the NH_3 flux from buildings directly with passive flux samplers (e.g. Schjoerring et al., 1992). However, a problem with this method is the NH_3 recovery, which validation tests revealed either to be irregular or low, at ~66% (Scholtens et al., 2004).

A different approach to measure emissions from complex sources involves applying dispersion models together with concentration measurements downwind of the source. Several studies applied a backward Lagrangian stochastic (bLS) model to calculate backward trajectories from the measurement site to estimate emissions from livestock houses (Flesch et al., 2005) and feedlots (Flesch et al., 2007; McGinn et al., 2007). A simpler alternative to the bLS is the inverse application of a Gaussian plume model (GPM). For example, Siefert et al. (2004) and Siefert and Scudlark (2008) applied a sampling grid of passive ammonia samplers downwind of a poultry house and used a GPM to estimate emissions from the building. A criticism of the approach used in these two studies is that the temporal resolution of the passive samplers, applied for up to half a day, may be too low to account for meteorological fluctuations in dispersion rates, providing errors in the calculated fluxes. By contrast, Hensen et al. (2009) recently analysed plume data measured with fast sensors downwind of a farm with cattle and pig housing. They compared the results of two different dispersion models (GPM and analytical model) and found a reasonable agreement of derived values which equated to 94% and 63%, respectively, with emissions calculated from inventory estimates for the study farm, based on published emission factors. While the comparison between the two models is encouraging, such deviations from the inventory estimates are not unexpected given the potential for farm level and seasonal variation in emission.

In the current study, the inverse modelling approach was used to determine NH_3 emissions from poultry houses. Atmospheric NH_3 concentrations and meteorological variables were measured at a high time-resolution (5 minutes) within 1 km of several layer poultry houses. By applying a GPM, the source strength of individual buildings, and therefore an emission factor per bird place, was derived. This study investigates the extent to which it is possible to assess the variability of livestock housing emissions and the possibility of capturing emissions of multiple livestock houses at a single measurement point. Both of these contribute to improving methodologies for estimating NH_3 fluxes at the landscape scale.

2.2 Site and methods

2.2.1 Site

The study was carried out in southern Scotland, an area with a mild, oceanic climate. Predominantly southwesterly winds bring cloudy and changeable weather with an annual rainfall of around 1000 mm. The site is situated in a rural landscape with slightly undulating terrain. Most surrounding land is used as extensive grassland for grazing sheep and, to a lesser extent, beef cattle. The measurement site is located close to several large poultry houses (Figure 2.1). All birds are laying hens; most of them are kept in cages (7 sheds), some in a free range system (11 sheds). Within a radius of 1.5 km of the measurement site, more than 1 million layers are kept in the 18 poultry houses.

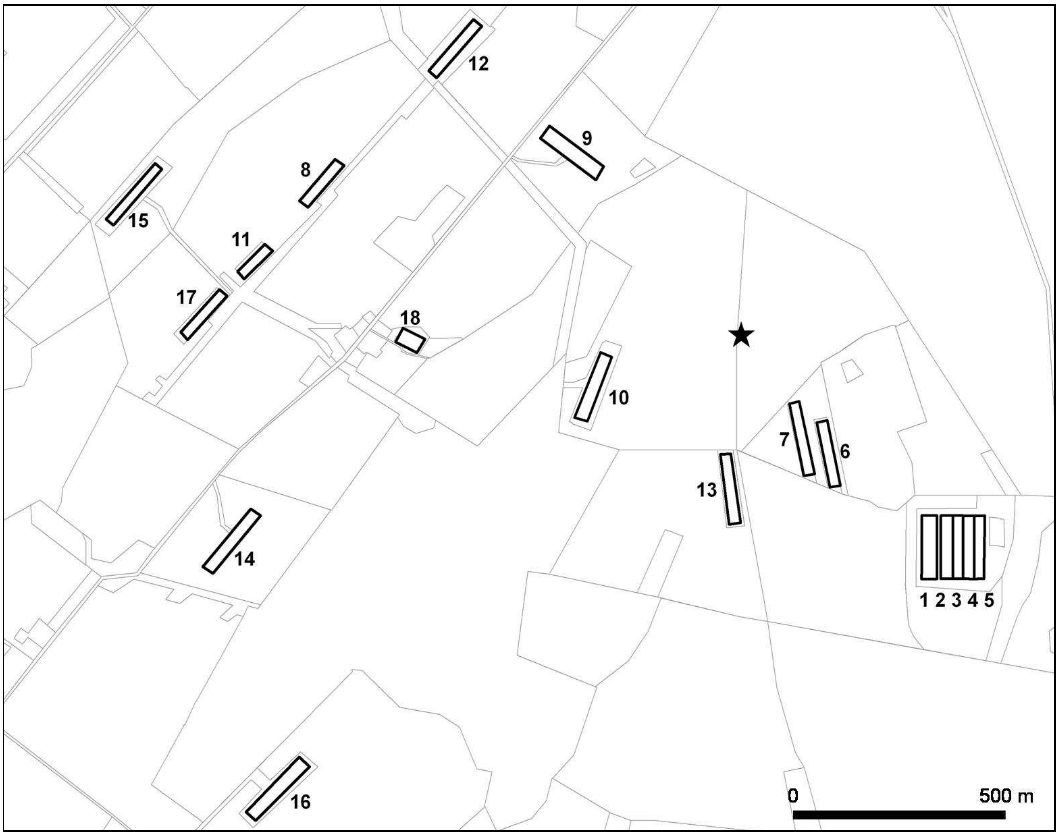

Figure 2.1: Map of measurement site (star) with surrounding poultry houses

2.2.2 Laying hen houses

This study focuses on the emission rates for two free range laying hen houses (sheds 10 and 13 in Figure 2.1) which are approximately 300 m from the measurement site. The houses are of deep pit type with a bird capacity of 32,000 birds each. Wood shavings are supplied for dust bathing and the manure is removed after each production cycle. The sheds are ventilated continuously, 24 hours a day and all year around, by gable vents. As the doors for the birds are open during the day, the sheds are also naturally ventilated. The indoor temperature is maintained, as far as possible, to 21 °C, although this can vary when the doors are open. Hy-Line Variety Brown laying hens are kept at both sites and are free to graze on the pastures around the buildings during the day. However, it was observed during this study that only a small fraction of birds are outside the building at any time, which is in agreement with previous studies (e.g. Misselbrook et al., 2000). It can therefore be assumed that the overall emissions are dominated by the manure excreted and accumulated in the house itself. During the measurement campaigns both poultry houses were occupied by birds reaching the end of their productive cycle, at around 70 to 80 weeks of age.

2.2.3 *NH_3 and meteorological measurements*

Atmospheric NH_3 concentrations and meteorological data were collected during two campaigns. Campaign 1 took place from 22 May to 1 June 2007 and campaign 2 from 28 May to 9 July 2008. Measurements were made continuously throughout both campaigns, with data gaps due only to instrument maintenance. NH_3 concentrations were measured with a photoacoustic analyser (Nitrolux™-100, Pranalytica Inc.) which samples at a rate of ~1.5 l min^{-1}. The instrument operates by optically exciting NH_3 molecules and measuring acoustic waves resulting from increased inter-molecular collision rates. The calibrated measurement range is 0 to 300 ppb, with a published sensitivity of 0.1 ppb (Pranalytica Inc.). However, calibration tests showed a linear response up to 500 ppb. In a recent study, the accuracy was shown to be ± 4% (von Bobrutzki et al., 2010). Data were logged every 12 seconds and averaged over periods of 15 minutes. A 10 m long, heated polyethylene inlet line was attached to a pump-up mast with a rain-protected inlet at 4.5 m height from the ground. The response time of the set-up was in the order of 5 minutes.

An ultrasonic 3D anemometer (WindMaster, Gill Intruments) operating at 20 Hz was mounted at a height of 5 m to measure wind speed, direction, turbulence and atmospheric stability parameters. Data were logged, processed and averaged over 15 minutes to match the NH_3 data intervals using an analysis programme implemented in LabVIEW (National Instruments, Inc.). Pasquill atmospheric stability classes were calculated according to Golder (1972) using the Monin-Obukhov length (L) and an estimated roughness length (z_0) of 2 cm. Temperature, relative humidity and precipitation data were recorded at a measurement site located 3 km to the northwest.

2.2.4 *Gaussian plume model (GPM)*

Gaussian plume models (GPMs) are commonly used to model atmospheric dispersion (Mosquera et al., 2005). GPMs can be used to estimate gas concentrations within a few kilometers downwind of a source (e.g. Barratt, 2001). The GPM used in this study was implemented in Microsoft Excel and requires meteorological input parameters including wind speed, wind direction and atmospheric stability class. Information is also needed on source locations, emission height and roughness length (z_0) of the surface between the source and the measurement site. The poultry houses are described as matrices of point sources on a 10 m grid. The GPM then simulates NH_3 concentrations at the measurement site assuming a given emission strength for each specified source. Daily emission factors can be calculated by changing the emission strengths to fit the modelled concentrations (plus an added background concentration, derived as the running minimum concentration of ± 12 hours) to the daily time-series of measured concentrations. In this study, different methods for optimising the model to measurement fit were tested (see Section 2.2.5).

The concentration χ (g m^{-3}) at the downwind distance *x*, the crosswind distance *y* and the height *z* (m) is obtained by the Gaussian distribution equation:

$$X(x,y,z)=\frac{Q}{2\pi u\sigma_y\sigma_z}\exp\left[\frac{-(y)^2}{2\sigma_y^2}\right]\left\{\exp\left[\frac{-(z+H)^2}{2\sigma_z^2}\right]+\exp\left[\frac{-(z-H)^2}{2\sigma_z^2}\right]\right\}$$

where *Q* is the emission rate (g s^{-1}), *u* the wind speed (m s^{-1}), σ_y and σ_z are the dispersion parameters for the crosswind and vertical direction (m) and *H* is the emission height (m). The dispersion parameter σ_z was set to the source building height to reflect the enhanced dispersion at emission release. The concentration χ increases with emission rate *Q* and decreases with wind speed (*u*) or plume spreading in the crosswind (σ_y) or vertical directions (σ_z). Further descriptions of the model can be found in Hensen and Scharff (2001) and Hensen et al. (2009).

When using the Gaussian dispersion equation, several theoretical assumptions are made (Turner, 1994). For instance, turbulent mixing is assumed to be random and the time-averaged concentration profiles in both the crosswind and vertical directions can be described by the Gaussian distribution. For this reason GPMs are uncertain close to a source (0-100 m) or when buildings have a dominant influence on the dispersion processes (Mosquera et al., 2005). For this study, these criteria were met, since the closest source was more than 200 m away and there were no complex terrain or large obstacles nearby. In addition, the emission rate is assumed to be constant and there is insignificant plume depletion due to chemical reactions or deposition between source and measurement point. Finally, meteorological conditions, such as wind speed, wind direction and atmospheric stability, should be constant over the travel time from source to measurement point. This assumption is not met when wind speeds are below 1 m s^{-1} (European Process Safety Centre, 1999), and those data were thus discarded from this study. These assumptions are not always true in field conditions and the implications of this are discussed in Section 2.3.3 in the context of uncertainty analysis.

2.2.5 GPM optimisation methods

Measured 15 minute NH_3 concentration data were modelled with the GPM separately for each day. Modelled 15 minute concentrations were optimised to fit measured 15 minute concentrations over one day. Daily emission rates were determined assuming a constant source strength over one day. The best fit was derived using method 1 (“Linear Fit”) and method 2 (“Log Fit”). In Linear Fit, the sum of the squared differences between measured and modelled data is minimised by changing the emission strengths of the contributing poultry houses. This was done by using the solver function in Microsoft Excel. In Log Fit, the natural logarithm was taken of measured and modelled concentrations and the difference of the two minimised as in Linear Fit. This approach gives less weight to outlier points.

2.2.6 GPM performance assessment

The GPM performance was assessed both statistically and visually. Where statistics provide a quantitative assessment, a visual evaluation has the advantage of identifying data artefacts e.g. if the timing is off between measurements and model simulations.

The statistical metrics used in this study are those recommended by Derwent et al. (2009) for evaluating air quality model performance. The data points on a scatter plot of modelled versus measured concentrations that lie between the 1:2 and 1:0.5 correspondence lines are those model estimates (M_i) that lie within a factor of two of the observations (O_i). The proportion of data points that satisfy the condition $0.5 \leq M_i/O_i \leq 2.0$ is called FAC2. If FAC2 is larger than 50% the model performance is considered acceptable.

The normalised mean bias (NMB) is a measure of the relative difference between the model simulations and observations and gives information on over- or underestimation by the model. The NMB is defined as follows:

$$NMB = \frac{\sum_{i=1}^{N} M_i - O_i}{\sum_{i=1}^{N} O_i}$$

According to the recommendations of Derwent et al. (2009), model performance is deemed acceptable if the NMB lies between -0.2 (-20%) and +0.2 (+20%)

The visual assessment of model performance was done by plotting measured and modelled data on a daily basis. It was then evaluated by eye to check if the evolution of the measured concentrations could be reproduced by the GPM. Data were used to calculate emission factors if two of the three performance measures suggested acceptable performance.

2.3 Results and discussion

2.3.1 NH_3 and meteorological data

Measured NH_3 concentrations during the campaigns ranged from below 1 to greater than 500 ppb, with a mean concentration of 27 ppb (Table 2.2). Temporal variability was mainly due to local meteorology affecting wind direction and turbulent mixing of the emitted NH_3. In addition, weather conditions may have influenced NH_3 volatilisation, although temperatures in the layer houses were generally around 21°C.

In both campaigns, the lowest NH_3 concentration was measured in rainy conditions under neutral atmospheric stratification and the maximum NH_3 concentration was measured at night time, under stable stratification and low mean wind speed. In stable atmospheric conditions, dispersion of the released NH_3 is restricted; therefore NH_3 concentrations at the site are increased. Rainy periods were considered separately in the calculation of NH_3 emission rates due to the influence of rain scavenging NH_3 from the plume.

Table 2.2: Overview of NH_3 and meteorological data collected during campaign 1 and 2.

	Campaign 1 (22 May – 1 June 2007)	**Campaign 2** (28 May – 9 July 2008)
NH_3 [ppb] (15 min mean values)		
Minimum	0.8	0.8
Maximum	542	387
Mean	27.1	27.4
Median	17.6	15.7
Data coverage	79%	34%
Meteorology		
Mean T [°C]	9.1	12.1
Mean RH [%]	78	79
Total rainfall [mm]	43	94
Time raining	15%	9%
Mean wind speed [m s^{-1}]	4.3	3.8
Main atmospheric stability class	D (neutral) (55% of time)	D (neutral) (57% of time)

As expected, a temperature driven diurnal cycle for NH_3 concentrations with higher concentrations during the day was not observed in this study, suggesting that the occurence of local NH_3 plumes were the main driver of the measured NH_3 concentrations. In contrast, as noted above, high NH_3 concentrations were often observed at night time during stable atmospheric stratification.

The prevailing wind direction during both measurement campaigns was southwest (Figure 2.2). However, in campaign 2 the prevailing wind sector was shifted towards the south compared with campaign 1. This means that more plumes from shed 13 could be observed in campaign 2, whereas shed 10 is well represented in both datasets. Though other sheds contributed to the measurements at times throughout each campaign, there were only sufficient data to quantify the emissions from shed 10 and 13. However, the influence of nearby poultry houses located to the south, west and northwest on NH_3 concentrations at the measurement site is illustrated in the windroses.

As the wind rarely came from the southeast, data for poultry houses in this direction are sparse. In both campaigns, northeasterly winds brought relatively little atmospheric NH_3 to the measurement site as there were no large point sources nearby. The largest NH_3 concentration in campaign 2 from the east was due to one data point which was measured under stable night time conditions, with a wind speed of 1.6 m s^{-1} and a high standard deviation in wind direction. The associated air mass origin is therefore highly uncertain and this spike can, therefore, be ignored.

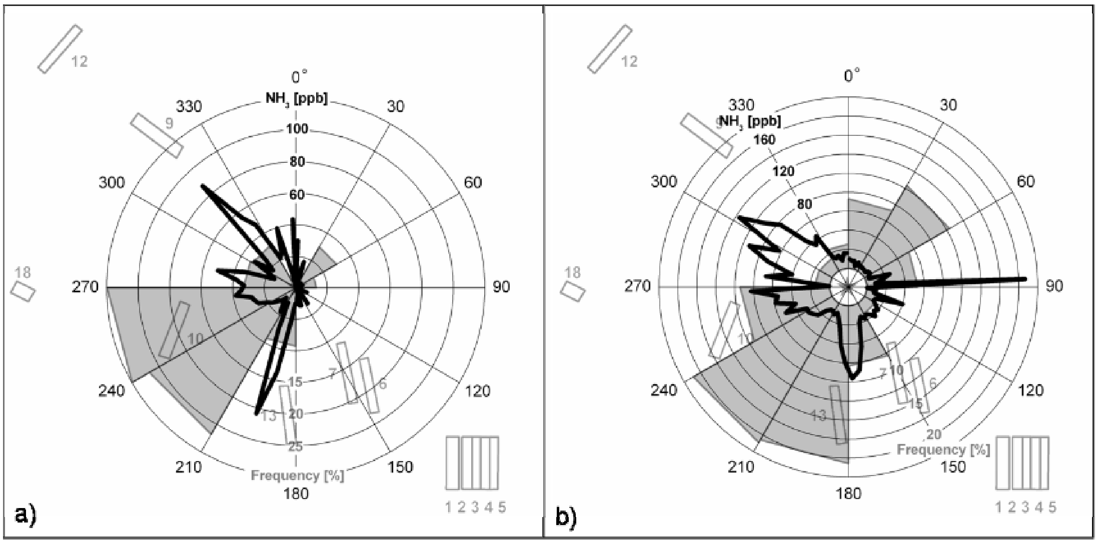

Figure 2.2: Windroses of campaign 1 (a) and campaign 2 (b) with underlying map of poultry houses. NH_3 concentrations (15 minute means, black line) averaged for each 5° wind sector and wind direction frequency (grey sectors) for each 30° sector. Data with wind speeds below 1 m s^{-1} are excluded.

Even though the windroses of both campaigns look similar, the directions in which the highest emissions were observed are slightly different. In campaign 1 the highest mean concentrations were detected for wind directions of 200°, 280° and 320°, whereas in campaign 2, these directions were shifted anticlockwise, with the highest values for wind directions of 180°, 270° and 300°. This may reflect variation in emissions and dispersion between the measurement campaigns.

2.3.2 Choice of GPM optimisation approach

Overall, Log Fit estimated larger emissions than Linear Fit, as shown in Figure 2.3. For campaign 1, this difference was 35% with Log Fit = 1.35 x Linear Fit + 0.09 (R^2 = 0.76), for campaign 2 it was 23% with Log Fit = 1.23 x Linear Fit + 0.05 (R^2 = 0.79). It was found that Linear Fit gave a closer fit to the peak concentrations, whereas Log Fit fitted closer to background concentration, but overestimated peak concentrations (not shown). As the plumes are associated with the peak concentrations, Linear Fit was chosen as the optimisation method for this study. The uncertainty associated with this decision is considered later.

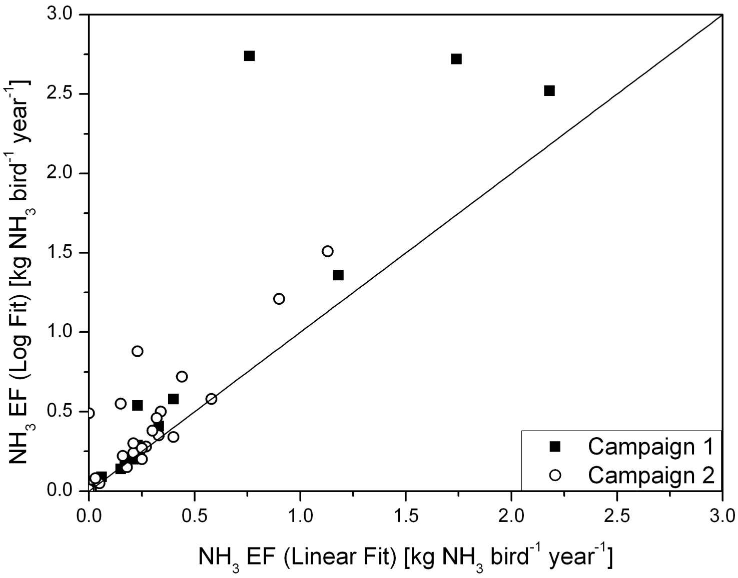

Figure 2.3: Scatter plot of daily emission estimates of Linear Fit against Log Fit with the 1:1 correspondence line.

2.3.3 GPM performance

The performance of the GPM using Linear Fit in simulating the measured concentrations was assessed both statistically and visually. Table 2.3 gives an overview of the assessment for each day and a statistical average for each campaign. Both the fraction of model simulations which lie within a factor of two of the observations (FAC2) and the normalised mean bias (NMB) vary from day to day. FAC2 ranges from 37% to 100% on individual days and the mean values are 68% and 70% for campaigns 1 and 2, respectively. As the mean FAC2 values are greater than 50%, this suggests that the optimisation method worked acceptable and the GPM could simulate temporal plume dynamics.

The NMB varies between -6% and -62% for individual days indicating that the GPM is biased towards underestimating concentrations. The NMB average is -33% ±

15 (standard deviation) over both campaigns. One reason for this may be that background concentrations, derived as the running minimum concentration of ± 12 hours, are underestimated. As Linear Fit is optimised to fit peak concentrations, this results in negative NMB values.

Table 2.3: Statistical and visual assessment of daily model performance of campaigns 1 and 2

	FAC2* [%]	NMB** [%]	Visual assessment
Campaign 1 (2007)			
22 May	93	-7	Results usable
23 May	43	-30	Results usable
24 May	50	-29	Results usable
25 May	65	-25	Results usable
26 May	73	-29	Results usable
27 May	76	-37	Too few emission data
28 May	92	-29	Too few emission data
29 May	39	-56	Poor curve reproduction
30 May	81	-19	Results usable
31 May	64	-61	Poor curve reproduction
1 June	73	-43	Poor curve reproduction
Average	68	-33	
Standard deviation	18	15	
Campaign 2 (2008)			
28 May	-	-	Background emissions
29 May	66	-30	Poor curve reproduction
30 May	67	-59	Too few emission data
31 May	69	-17	Too few emission data
16 June	84	-12	Results usable
17 June	84	-31	Results usable
18 June	87	-21	Poor curve reproduction
24 June	61	-37	Poor curve reproduction
25 June	66	-42	Poor curve reproduction
26 June	65	-30	Results usable
27 June	57	-38	Results partly usable (for shed 13)
28 June	100	-6	Results usable
2 July	37	-57	Poor curve reproduction
3 July	54	-62	Poor curve reproduction
4 July	52	-31	Poor curve reproduction
5 July	88	-37	Too few emission data
6 July	-	-	Background emissions
7 July	77	-36	Results usable
8 July	77	-19	Results usable
Average	70	-33	
Standard deviation	16	16	

*FAC2: Fraction of model estimates within a factor of two of the measurements (see Section 2.2.6)

**NMB: Normalised mean bias (see Section 2.2.6)

The days for which results were suitable for estimating emission source strengths are shown in Figure 2.4 and Figure 2.5. For example, during 25 May 2007 (Figure 2.4), high and low periods of NH_3 concentration are simulated well by the GPM, both temporally and in magnitude. It appears, however, that NH_3 concentrations are modelled better during the day than under stable night time conditions. In stable conditions, a clear plume may not develop and instead emissions accumulate around the farm without being dispersed. This situation is difficult to model accurately and the dispersion parameters (σ_y, σ_z) are highly uncertain. Between plumes, many of the modelled concentrations, particularly at night, decrease to a lower level than those measured, which may be partly due to reasons unrelated to the emission factors, such as an underestimation of background concentrations or the instrument not responding rapidly enough. Shed 10 was the main contributor to NH_3 concentrations measured on 25 May 2007 (17 hours).

For 26 June 2008 (Figure 2.5) the numbered peaks 1, 2 and 3 were all attributed to the same source (shed 13). Peaks 1 and 3 are overestimated while peak 2 is underestimated by the GPM. This is thought to be mostly because modelled data are optimised to fit measured data for a whole day and the source strength may vary throughout the day, for instance if the building ventilation rate changes. However, changing wind conditions may also contribute to the discrepancy.

The effect of changing wind speed on measured NH_3 concentrations can be oberved on several days, e.g. on 17 June 2008 (Figure 2.5), when an increase in wind speed causes an increased dilution of NH_3 emissions. By contrast, no significant relationship could be found between daily emission rates and average wind speeds.

Although not all discrepancies between measurements and model outputs can be explained simply, there do seem to be some common conditions when the GPM performs poorly. In some cases, sudden changes in the atmospheric stability class were observed. Another factor is a rapidly changing wind direction which makes detection of plumes from a single house difficult. Also, plumes from clustered sources are difficult to simulate using the GPM (see e.g. sheds 1 to 7 or sheds 9 and 12).

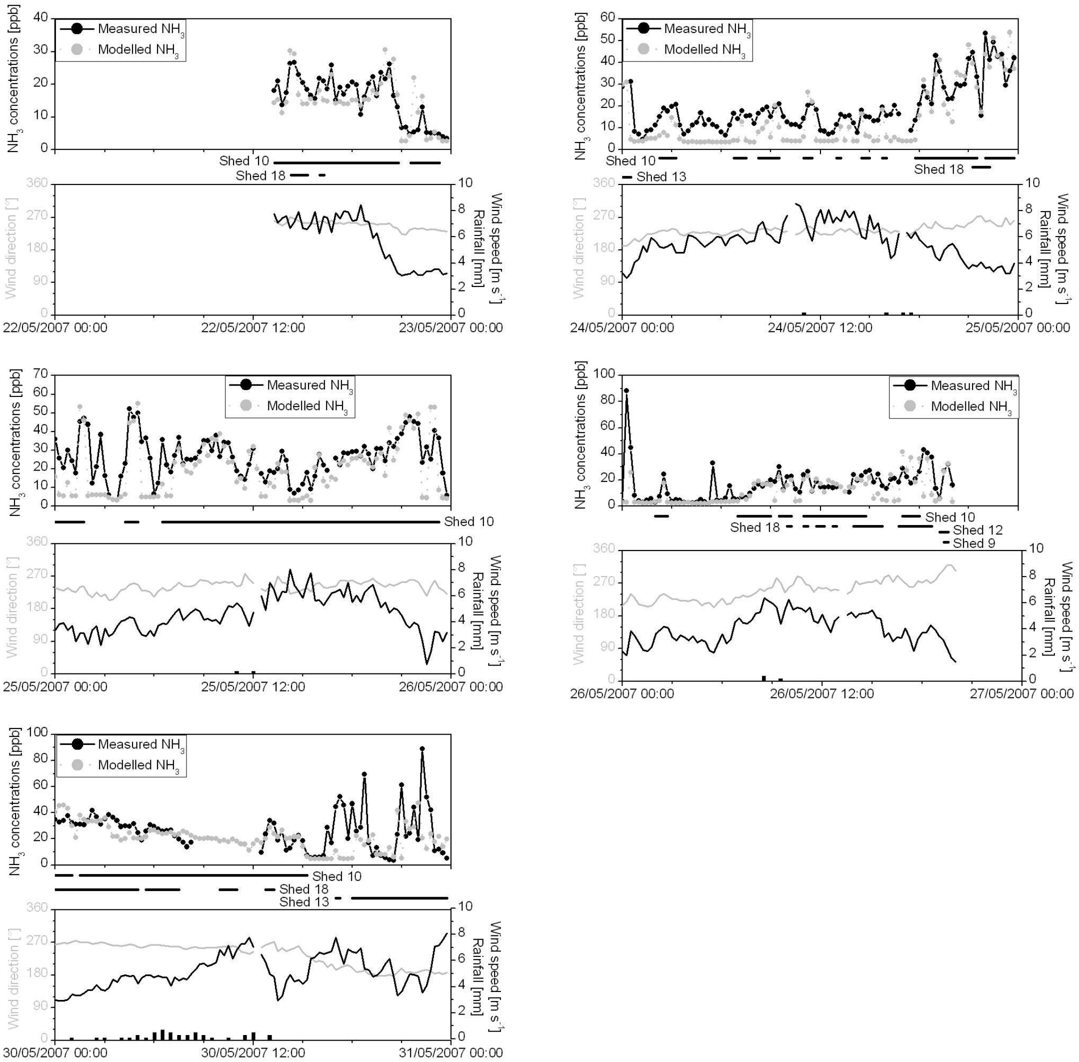

Figure 2.4: Daily plots of measured and modelled NH_3 concentrations with source contributions, wind direction, wind speed and rainfall of campaign 1. Modelled NH_3 data for these five days were used to calculate emission factors (the six other days of campaign 1 were not used).

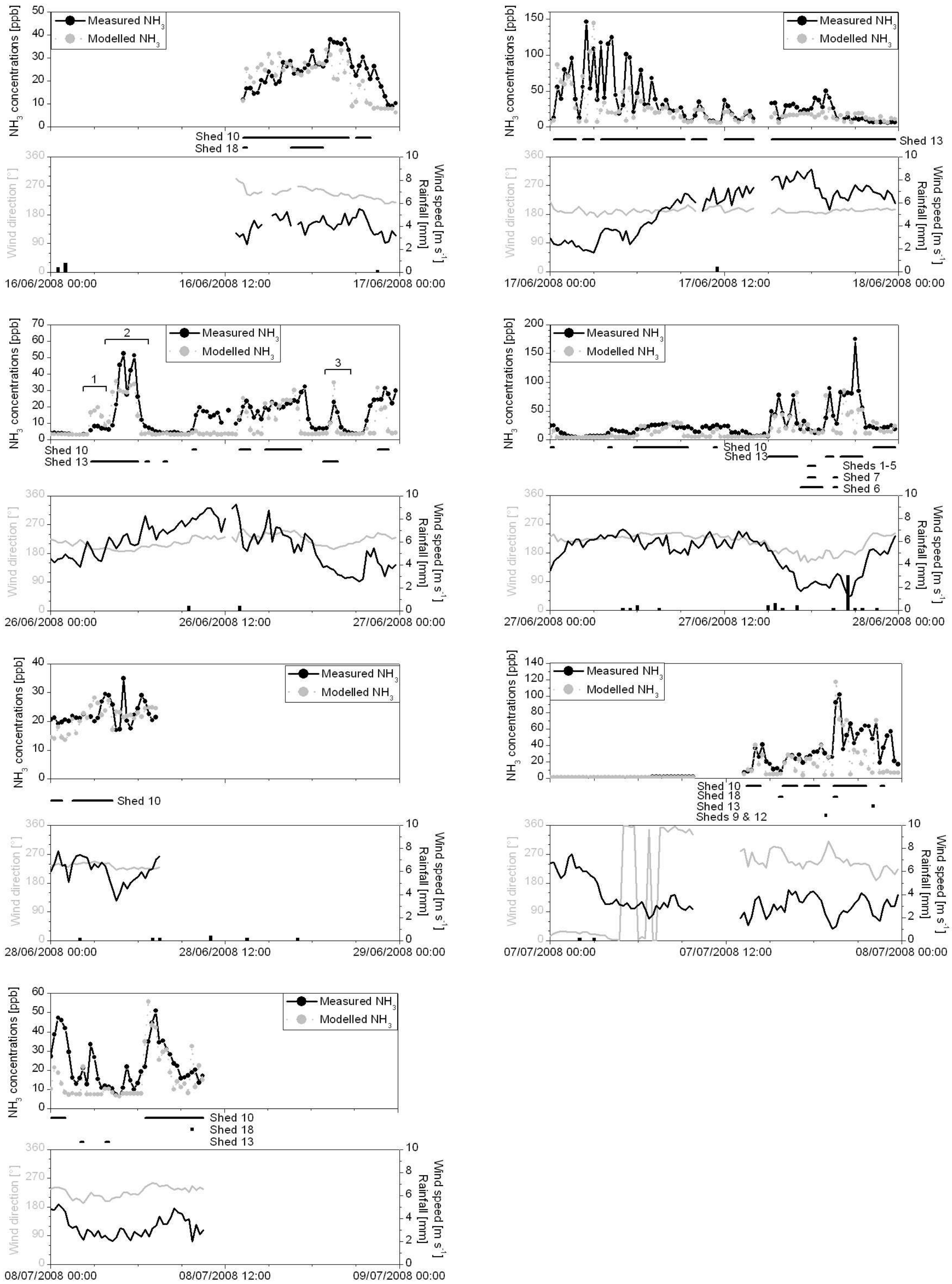

Figure 2.5: Daily plots of measured and modelled NH_3 concentrations with source contribution, wind direction, wind speed and rainfall of campaign 2. Modelled NH_3 data for these seven days were used to calculate emission factors (the 10 other days of campaign 2 were not used).

The GPM can only perform well when taking into account the model's theoretical assumptions (see Section 2.2.4) in the practical design of the study. It is assumed that NH_3 remains in the atmosphere between the source and measurement site. NH_3 is a reactive gas, therefore dry and wet deposition as well as gas-to-particle conversion occur soon after its release. To limit the effect of those removal processes, no emission strengths were derived for point sources more than 1000 m from the site. Sheds for which emission rates have been established are at 300 m distance to the measurement site. The dry deposition has been estimated for similar distances to the source in other studies. Fowler et al. (1998) quantified dry deposition within 300 m of the source to be in the order of 3-10% of emissions for a forested area, and the values here for agricultural grassland can be expected to be substantially less. In contrast, Loubet et al. (2006) estimated the amount of NH_3 dry deposited within 200 m of three example sources to vary between 4-34% depending on turbulent mixing (e.g. source height, roughness length) and surface exchange parameters (e.g. NH_3 compensation point). In the case of elevated emissions from a poultry building and short agricultural grassland with significant compensation point, it is expected that recapture will be towards the lower end of this range.

Loubet et al. (2009) calculated a NH_3 wet deposition rate of 5% at 1 km downwind of the source for a wind speed of 2 m s^{-1} and rainfall of 1 mm h^{-1}. Hence, periods with significant rain may be affected by rain scavenging and are therefore considered separately in Section 2.3.4.

As the measurement site in this study is situated within agricultural grassland, secondary NH_3 sources, such as grazing animals, may be present between the source and the site. This was however considered to have a minor effect on NH_3 concentrations at the site, because the effect is incorporated into the background concentration rather than the peak concentrations generated by plumes downwind of the poultry houses. The observed high temporal variability in NH_3 concentrations is thus characteristic of plumes from point sources.

2.3.4 NH_3 emission factors (EF)

Emission strengths of individual poultry houses have been calculated from modelled fit to measurements according to Linear Fit shown in Figure 2.4 and Figure 2.5. The total emission strength of each house is converted into kg NH_3 $bird^{-1}$ yr^{-1}

using the number of hen places. As this annual value is calculated by simple scaling from emissions observed for measurements during spring 2007 and spring/summer 2008, it should be noted that actual annual emissions may be different (see discussion of uncertainties below).

Table 2.4 shows EFs for sheds 10 and 13 estimated from the data of both campaigns. Data from campaign 1 were suitable to estimate EFs for shed 10. In the dataset, there were five days with a minimum of six hours of detected plumes from this shed per day. The EF range equates to 0.17 to 0.40 kg NH_3 bird^{-1} yr^{-1}assuming a constant source strength throughout the year. The lowest EF (0.17 kg NH_3 bird^{-1} yr^{-1}) was observed on 30 May 2007. On that day, emissions from the shed were measured until 15:00, and during most of this time there was continuous light rainfall, which may explain the slightly lower EF. The average EF for shed 10 calculated from these five days of campaign 1 is 0.27 ± 0.10 kg NH_3 bird^{-1} yr^{-1}, or, excluding 30 May 2007, 0.29 ± 0.09 kg NH_3 bird^{-1} yr^{-1}.

During campaign 2, sufficient data were obtained to estimate NH_3 EFs for two poultry houses, sheds 10 and 13. Seven days provided good plume data, of which five days included plumes from shed 10 and three days plumes from shed 13. For shed 10, EFs range from 0.25 to 0.34 kg NH_3 bird^{-1} yr^{-1}, with an average of 0.29 ± 0.04 kg NH_3 bird^{-1} yr^{-1}. Shed 13 EFs range from 0.16 to 0.25 kg NH_3 bird^{-1} yr^{-1}, with an average of 0.20 ± 0.04 kg NH_3 bird^{-1} yr^{-1}.

Table 2.4: Calculated daily NH_3 emission factors (EFs), daily meteorological and NH_3 concentration data for campaigns 1 and 2

		NH_3 EF [kg NH_3 bird^{-1} yr^{-1}]	Rainfall [mm]	Time raining [h]	Mean T [°C]	Mean wind speed [m s^{-1}]	Mean NH_3 conc. [ppb]	Mean NH_3 background conc. [ppb]
Campaign 1 (2007)								
Shed 10								
	22 May	0.24	0.0	0.0	9.9	5.8	15.6	2.6
	24 May	0.40	1.2	2.5	12.0	5.6	19.5	4.0
	25 May	0.33	0.4	1.0	7.5	4.6	26.3	4.6
	26 May	0.21	0.8	1.5	6.8	3.5	29.6	3.4
	30 May	0.17	7.5	10.0	9.1	5.2	26.4	6.5
Campaign 2 (2008)								
Shed 10								
	16 June	0.27	1.6	2.0	10.1	4.1	23.9	8.5
	26 June	0.34	1.0	1.5	11.8	5.8	14.1	3.3
	28 June	0.25	1.6	3.5	13.1	6.1	22.6	13.9
	7 July	0.32	0.4	1.0	12.2	3.5	19.2	3.1
	8 July	0.30	0.0	0.0	13.0	2.9	21.7	7.6
Shed 13								
	17 June	0.16	1.2	1.0	10.6	5.6	32.0	6.3
	26 June	0.25	1.0	1.5	11.8	5.8	14.1	3.3
	27 June	0.21	6.5	7.0	11.8	5.0	25.9	6.6

Sheds 10 and 13 are layer houses of the same type with the same management practice. Their plumes were observed during the same season of the year, and they were occupied by birds of similar age. Therefore, their NH_3 EFs should be very similar. Overall, EFs in this study ranged from 0.16 to 0.40 kg NH_3 bird^{-1} yr^{-1}, which is within the range of values found in the literature (see Table 2.1). Nevertheless, the highest estimated emission is 2.5 times larger than the lowest estimate. Excluding emission rates significantly affected by rain, the mean estimated EF in this study is 0.27 ± 0.07 (standard deviation) kg NH_3 bird^{-1} yr^{-1}. The average NH_3 housing EF used in the UK inventory for an average layer (including all types of systems) is 0.17 kg NH_3 bird^{-1} yr^{-1}, and for a free range layer it is 0.20 kg NH_3 bird^{-1} yr^{-1} (Misselbrook et al., 2009). Results of this study, therefore, provide a mean value which is 35% higher than the official UK emission estimate of Misselbrook et al. (2009). In contrast, the Scottish Environment Protection Agency (SEPA) use an EF of 0.29 kg NH_3 bird^{-1} yr^{-1} for caged (i.e. not free range) layers in deep pit houses (SEPA, 2010). This value is close to the findings of this study.

The main uncertainties within results of this study are in relation to: a) the choice of optimisation method, b) seasonal representation, c) representativity in relation to the bird production cycle and d) the potential role of dry deposition or other background emissions.

The two optimisation methods for the GPM provided daily emission rates which differed by about 30% (Figure 2.3). Based on a better characterisation of the plume peak concentrations, results have been calculated using the linear optimisation method (Linear Fit). If Log Fit were used, the present estimates would be rather larger than shown above. Hence, the uncertainty associated with this methodological difference suggests that Linear Fit provides a conservative estimate of the emissions, so that this cannot explain the difference with the UK inventory values of Misselbrook et al. (2009).

Secondly, it should be considered whether the present measurements are seasonally representative. At a nearby measurement site, the mean temperature ranges from 4°C in the winter to 13°C in summer. Therefore, the mean temperature during measurements of 11°C (Table 2.4) is in the higher end of this range. Although the regression of daily estimated emission rates of shed 10 with outdoor temperature was not significant (Temperature [°C] = 13.7 x Emission rate [kg NH_3 bird^{-1} yr^{-1}] + 6.7; R^2 = 0.18), a relationship may be found over a larger temperature range (i.e. including cold winter months).

Another factor which may lead to an overestimation of annual emissions calculated in this study is that measurements were conducted towards the end of the production cycle. As manure gets removed from deep pit houses after each cycle, the emissions are likely to be higher at the end than at the beginning of the cycle. Fabbri et al. (2007) observed the difference in emissions of a deep pit layer house between the beginning and the end of the cycle to be 28%. However, this value was not constant throughout the year.

Lastly, dry deposition of NH_3 between source and measurement site may lead to an underestimation of source emission strengths, while background emissions, such as from grazing cattle, could lead to overestimate the emissions. In practice, both processes are expected to occur: firstly, dry deposition close to the source under conditions of high concentrations, and secondly, emissions from agricutural grassland. Overall, considering the characterisation of plumes measured (Figure 2.4 and Figure 2.5), the relatively small background concentrations (Table 2.4) and the typically small fraction of the source which is dry deposited in the first 300 m (<10%, see Section 2.3.3), these factors are considered to provide less than ± 10% effect on the estimated emissions in this study.

2.4 Conclusions

Livestock housing emissions can be determined by making stationary measurements of atmospheric concentrations downwind of sources and applying a Gaussian plume model (GPM), as used in this study. However, to establish reliable emission factors (EFs), certain requirements have to be met. The study has to be designed such that theoretical Gaussian dispersion assumptions are fulfilled as much as is possible under field conditions. This inverse modelling approach is, however, more difficult to apply for clustered sources. A distance of more than 100 m between sources and less than 1 km distance between source and measurement site is considered best for this method, to avoid building turbulence effects and to minimise the influence of plume depletion. As the GPM did not perform well for all periods, only well modelled data were selected for estimating emission factors.

NH_3 EFs for two deep pit free range layer houses were estimated from two measurement campaigns conducted in spring 2007 and spring/summer 2008. Daily estimated EFs were extrapolated to annual values, which range from 0.16 to 0.40 kg NH_3 bird^{-1} yr^{-1}. This range reflects the wide range found in the literature. Although the average annual EF calculated in this study of 0.27 ± 0.07 (standard deviation) kg NH_3 bird^{-1} yr^{-1} is 35% higher than the current estimate in the national emission inventory for the UK, it lies within the range of emission estimates of studies used to calculate this national average. However, there are a number of factors contributing to the uncertainty of the estimated EFs in this study. These factors include: a) optimisation method for fitting GPM results to measurements (with the method used providing conservative estimates of emissions), b) possible temperature dependence of emissions, c) timing of the measurements in relation to production cycle (which might lead to larger than typical values), and d) the role of surface exchange processes (emissions and dry deposition) with the grassland between the farm and the measurement point.

Long term stationary NH_3 measurements downwind of layer houses, covering all seasons and an entire production cycle, would offer valuable information about both short term and long term variations in NH_3 source strengths.

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3 Paper II: Environmental impact assessment of atmospheric ammonia at the landscape scale: Local vs. national scale modelling

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Abstract

Atmospheric ammonia (NH_3) concentrations and deposition fluxes were studied at a resolution of 25 m x 25 m in a 6 km x 6 km landscape containing intensive poultry farming, agricultural grassland, woodland and a large semi-natural moorland. The approach combined a detailed landscape inventory of all farm activities providing high resolution NH_3 emission estimates for atmospheric dispersion modelling and an intensive measurement programme of spatial NH_3 concentrations for verifying modelled NH_3 concentrations. The spatially diverse emission pattern resulted in a high spatial variability of modelled mean annual NH_3 concentrations (0.3 to 77.9 µg NH_3 m^{-3}) and dry deposition fluxes (0.1 to > 100 kg NH_3-N ha^{-1} yr^{-1}) within the landscape. Largest impacts were predicted for woodland and shrub patches within the agricultural area, while larger moorland areas located northwest of the poultry houses were only at minor risk due to atmospheric dilution and the prevailing southwesterly winds. The large spatial variability of NH_3 within the

landscape could not be resolved by a national model at 1 km resolution, emphasising the need for high resolution NH_3 assessment incorporating farm and field specific emissions. The case study illustrates how spatial arrangement of sources and sinks at the landscape scale is critical to the level of risk that NH_3 represents to semi-natural ecosystems. This provides a basis for the use of spatial planning to minimise environmental impacts of atmospheric NH_3.

Keywords: ammonia, critical level, landscape scale, dispersion modelling, spatial planning

3.1 Introduction

Most atmospheric ammonia (NH_3) originates from agricultural activities (Misselbrook et al., 2000; Van der Hoek, 1998). Intensive livestock farming, especially pig and poultry houses due to their high stocking density, represent large NH_3 point sources (e.g. Dragosits et al., 2006). High NH_3 concentrations are directly toxic to plants and its deposition can lead to eutrophication and acidification of ecosystems which cause changes in biodiversity of sensitive ecosystems (Cape et al., 2009b; Cellier et al., 2009; Krupa, 2003; Pitcairn et al., 2009). A number of studies have been conducted to quantify the effect of NH_3 emission sources on surrounding ecosystems. For example, Fowler et al. (1998) quantified concentrations and deposition fluxes within 300 m of a poultry farm site in Scotland using measurements and deposition modelling. Similarly, Pitcairn et al. (1998; 2002) analysed the impact of deposition fluxes on woodland flora in the immediate surroundings of large sources. Frati et al. (2007) studied the effect of NH_3 emission on sensitive vegetation (lichens) within 2500 m of an Italian pig farm. Sutton et al. (1998) compared deposition estimates based on different scales, ranging from field to landscape to national scale. They concluded that, due to the spatial variability of NH_3, the quality of environmental impact assessment is dependent on the resolution of the deposition data. A more detailed analysis of the landscape study in Sutton et al. (1998) is provided by Dragosits et al. (2002). Emission transport and deposition were modelled within a 5 km x 5 km landscape in England at 50 m resolution; however, no measurements were conducted in the study area. Other studies focused on strategies to reduce the effect of emission hotspots on ecosystems by locating tree belts around the sources; indicating the importance of relative spatial location of sources and sinks, and assessing possible landscape planning measures to decrease effects on sensitive habitats (Dragosits et al., 2006; Theobald et al., 2001).

To assess the environmental impact of pollutants, the United Nations Economic Commission for Europe (UNECE) developed critical thresholds of pollutant concentrations and deposition fluxes, so called Critical Levels (CLEs) and Critical Loads (CLOs). A CLE is a pollutant concentration in the atmosphere above which plants or ecosystems may be directly negatively affected (Posthumus, 1988). Recently, long term CLEs of NH_3 were reviewed and new, lower values proposed (Cape et al., 2009a): 1 μg NH_3 m^{-3} for the most sensitive vegetation types, i.e. lichens and bryophytes, and 3 ± 1 μg NH_3 m^{-3} for higher plants in natural vegetation. A CLO is a pollutant deposition below which no significant harmful effects on the environment are expected to occur according to current knowledge (Posthumus, 1988). Nitrogen (N) CLOs are defined for specific ecosystem types (UNECE, 2010). In contrast to the CLE approach, which is specifically defined for NH_3, the CLO integrates all forms of reactive N and therefore requires estimates of total N deposition. According to Sutton et al. (2009) these estimates are uncertain and as it is much easier to measure NH_3 concentrations, the CLE has the advantage of being a more practical approach. However, up to now, exceedance of CLOs is the more commonly used tool for impact assessment. For atmospheric NH_3, this may reflect that previous long term NH_3 CLEs were set at much less precautious level than associated values of N CLOs (e.g. Burkhardt et al., 1998), which was one reason for the revision of new long term NH_3 CLEs (Sutton et al., 2009).

For assessing the environmental impact of NH_3 concentrations and deposition, it is also essential to estimate NH_3 emissions accurately (Hellsten et al., 2008). Hallsworth et al. (2010) highlighted the problem of modelling NH_3 dispersion at relatively coarse scales, such as 5 km resolution, due to the high spatial variability of NH_3 emissions. Thus, they expect 5 km modelling to underestimate the impact of NH_3 concentrations on semi-natural areas close to intensive agricultural areas. However, at UK national scale, deposition fluxes and their impact assessment are based on 5 km resolution modelling (Dore et al., 2007; Matejko et al., 2009).

The current study is part of landscape scale studies conducted within the NitroEurope Integrated Project (NEU) (Sutton et al., 2007). Landscape scale is understood as a spatially heterogeneous area covering several square kilometres that contain interacting ecosystems (Forman and Godron, 1981). In rural landscapes, anthropogenic processes in the form of farm management determine to a large extent N dynamics and much of its environmental impact within the landscape (Cellier et al., 2011). The aim of the NEU landscape analysis is to quantify N flows at the landscape scale using a range of measurement and modelling approaches. In this study, we analyse the NH_3 dispersion and its environmental impact in a rural landscape of 6 km x 6 km in southern Scotland. The landscape is characterised by a diverse emission pattern with a large number of NH_3 emission hotspots as well as large areas of sensitive ecosystems as potential sinks. In this study, a detailed landscape inventory of all farms and fields was carried out to coincide with an intensive spatial monitoring programme of NH_3 concentrations. The NH_3 dispersion and deposition has been modelled at 25 m resolution and with this dataset we can assess the environmental impact of local NH_3 sources within this landscape. The results have implications for the sustainable management of landscapes that combine both intensive livestock agriculture and areas needing environmental protection.

3.2 Site and methods

3.2.1 Study area

The study landscape is situated in southern Scotland. The climate of the region is temperate with an annual mean temperature of ~8°C, a typical rainfall of around 1000 mm and predominantly southwesterly wind. The area covers 6 km x 6 km (Figure 3.1) and is dominated by agricultural grassland (48%), followed by moorland (21%), rough grass (13%) and woodland (10%). The moorland is located in the northwestern part of the study landscape and is partially grazed by sheep at low stocking densities, partly designated as Site of Special Scientific Interest (SSSI) and partly undergoing peat cutting. In contrast to this area with relatively low NH_3 emissions, the southeastern part is dominated by agricultural land, such as pastures grazed by beef cattle and sheep interspersed with poultry farming within 24 poultry houses, which contain nearly 1.5 million laying hens. Most of the layers are kept in caged houses with belt systems from which manure is removed two to three times a week (circled poultry houses in Figure 3.1). However, the majority of the houses are deep-pit houses, and in most of those layers are kept as free-range birds.

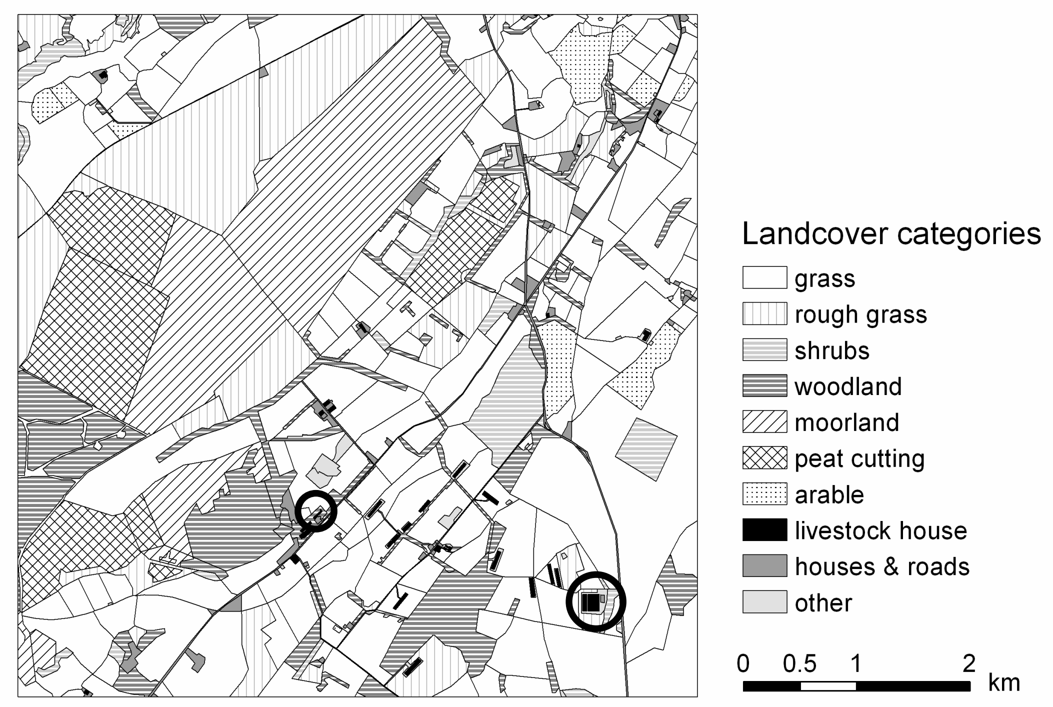

Figure 3.1: Land cover types in the 6 km x 6 km study landscape in southern Scotland. Manure is cleared at least two times per week from the circled poultry houses (see section 3.3.3).

3.2.2 Landscape inventory and emissions

Detailed land cover and farm activity data were obtained by a local survey carried out by the Scottish Agricultural College (SAC). Farm activities were recorded for each farm building and each agricultural field through 2008, including type and numbers of livestock housed and grazed, manure management, ventilation type and emission height, crop type and the application of mineral and organic fertiliser. Land cover and farm activity data were processed with a Geographical Information System (ESRI, ArcGIS) and emissions were calculated for each individual field and livestock house. Emissions were initally calculated by applying the average NH_3 emission factors (EFs) of the UK emission inventory (Misselbrook et al., 2009) to the farm activity data. After analysing initial results, EFs were partly adjusted to account for specific management practices in the landscape (see section 3.3.3). All data were converted to a 25 m grid resolution for atmospheric dispersion modelling (see section 3.2.4).

3.2.3 Spatial NH_3 measurements

To capture the high spatial variability of atmospheric NH_3 in the study landscape, ALPHA passive diffusion samplers (Tang et al. 2001) were deployed at 31 locations from April 2007 to December 2008 to measure monthly average concentrations at a sampling height of 1.5 m above ground. Measurement locations were distributed across the study area with more sites in NH_3 emitting areas to capture the concentration gradients around the sources. To assess measurement precision and uncertainty, samplers were exposed in triplicate at each location. The sampling rate of the ALPHA samplers was calibrated against the DELTA denuder reference system (NAMN, Sutton et al., 2001b) as it is carried out in the UK National Ammonia Monitoring Network (Sutton et al., 2001a). ALPHA samplers were stored in a cold room (4°C) until analysis in the laboratory with an NH_3 flow injection analyser (AMFIA, ECN), based on analysis by selective ion membrane transfer and subsequent conductivity measurement (Wyers et al., 1993).

3.2.4 Atmospheric dispersion modelling

There are several models available for modelling NH_3 dispersion, which were recently reviewed by Loubet et al. (2009). For this study, the LADD (Local Area Dispersion and Deposition) model was used to simulate atmospheric dispersion and deposition of NH_3 within the study landscape (Hill, 1998). The advantages of LADD are that it operates at 3D (with 44 vertical layers), is computationally fast and accounts for land cover-specific dispersion and deposition characteristics (Loubet et al., 2009). Model input data include land cover and emission data for each grid square (see section 3.2.2), wind statistics for the period to be modelled as well as NH_3 concentrations at the domain boundaries. Suitable roughness length (z_0) and canopy resistance (R_c) for each given land cover type were selected and assigned in LADD. The roughness length is used to calculate vertical dispersion and dry deposition rates whilst the canopy resistance is used in the calculation of dry deposition velocities within each grid square. Wind statistics were calculated from data collected at a continuous measurement site within the study area (M. Coyle, pers. comm. 2010). Ammonia concentrations for 44 model layers at the domain boundaries were calculated using the FRAME (Fine Resolution Atmospheric Multi-pollutant Exchange) model, run at national scale at 5 km x 5 km resolution (Dore et al., 2007). Boundary concentrations were highest at ground level, ranging from 1.34 μg NH_3 m^{-3} at the eastern boundary to 1.85 μg NH_3 m^{-3} in the south.

LADD was applied for the year 2008 at 25 m x 25 m grid resolution over an area of 7 km x 7 km, for which the detailed emission inventory had been prepared, with the model domain extended by 500 m on all sides to limit possible edge effects. Annual average NH_3 concentrations at 1.5 m height above ground level and dry deposition were simulated and analysed with ArcGIS (ESRI).

3.2.5 Assessment of model performance

Model performance was assessed by comparing modelled annual concentrations with measured annual concentrations at the 31 sampling sites. The following statistical metrics were used for model evaluation: the fraction of modelled concentrations within a factor of two of observed concentrations (FAC2), the correlation coefficient (R), the geometric mean bias (MG) and the geometric variance (VG) (Chang and Hanna, 2004; Theobald et al., 2009).

$$\text{FAC2} = \text{fraction of data that satisfy } 0.5 \leq M_i/O_i \leq 2.0 \quad (1)$$

$$R = \frac{\overline{(O_i - \overline{O}_i)(M_i - \overline{M}_i)}}{\sigma_{O_i}\sigma_{M_i}} \quad (2)$$

$$MG = \exp(\overline{\ln O_i} - \overline{\ln M_i}) \quad (3)$$

$$VG = \exp[\overline{(\ln O_i - \ln M_i)^2}] \quad (4)$$

Where O_i are the observed (measured) concentrations, M_i are modelled concentrations, σ is the standard deviation and overlined variables stand for the mean of those variables. FAC2 is the most robust measure as it is not affected by outlyers. Model performance is considered “acceptable” if FAC2 is 50% or greater, i.e. if FAC2 $\geq$ 0.5 (Chang and Hanna, 2004). The correlation coefficient R measures the linear relationship between modelled and observed concentrations. The closer R is to 1, the stronger the linear relationship. MG and VG are recommended for atmospheric dispersion modelling where concentrations vary over several orders of magnitude and distribution is not normal but rather log-normal (Chang and Hanna, 2004). MG measures the mean relative bias and only indicates systematic errors. It represents the ratio of the geometric mean of O_i to the geometric mean of M_i, thus the optimum value is MG = 1. An “acceptable” model performance is expected to result in a mean relative bias within ± 30%, i.e. $0.7 < MG < 1.3$. VG is a measure of mean relative scatter of a log-normal distribution and reflects both systematic and random error. The optimum value is VG = 1. An “acceptable” model would be expected to have a relative scatter of less than a factor of two (i.e. $VG < 1.6$) or three (i.e. $VG < 3.3$). Overall model performance is evaluated as acceptable when more than 50% of the criteria are met (Hanna and Chang, 2010).

3.2.6 Assessment of potential environmental impacts

Areas within the landscape which exceeded Critical Levels (CLEs) and Critical Loads (CLOs) were identified to assess the environmental impact of local NH_3 sources on surrounding ecosystems. For the analysis of CLE exceedance, modelled NH_3 concentrations at a height of 1.5 m above ground were used. CLO exceedance is based on total N deposition: the dry deposition of NH_3 simulated by LADD plus the wet deposition of reduced N and the dry and wet deposition of oxidised N. The contribution of particulate ammonium (NH_4^+) to the dry deposition of reduced N is considered minor compared to NH_3 (e.g. Asman et al., 1998; Duyzer, 1994). The additional N deposition components were calculated using the FRAME model run for 2008 at 1 km x 1 km resolution. FRAME gives three different deposition rates for each grid square: a) the average deposition, taking into account the mix of land cover in the grid square; b) the deposition to all woodland in the square; c) the deposition to all low-height semi-natural vegetation in the square. These were applied depending on the land cover in each 25 m grid square. The CLO exceedance was calculated for woodland, hedgerows, shrubs, moorland and rough grass. To those land cover categories, a CLO of 10 kg N ha^{-1} yr^{-1} was applied. This is the lower limit of the range shown in Table 3.1 to protect the most sensitive species of the respective ecosystems. The CLO exceedance was calculated by subtracting the CLO from the total N deposition.

Table 3.1: Land cover categories of the study landscape, the associated ecosystem types* with the corresponding critical loads for N deposition from the UNECE (2010).

Land cover category	Ecosystem type	Critical Load [kg N ha^{-1} yr^{-1}]
Woodland, hedgerows	Broadleaved deciduous woodland	10-20
Shrubs	Calluna dominated wet heath (upland moorland)	10-20
Moorland, rough grass	Heath (Juncus) meadows and humid (Nardus stricta) swards	10-20

* Ecosystem types were allocated to land cover categories by expert judgement of the local vegetation (Sheppard, pers. com. 2011)

3.3 Results and discussion

3.3.1 Spatial variability of measured NH_3 concentrations

The spatial variability of NH_3 concentrations in the landscape is large with monthly NH_3 concentrations varying from 0.2 to 57.5 µg m^{-3} between the measurement sites (Figure 3.2). Monthly coefficients of variation of replicate samplers varied between 0 to 24%, with values over 15% occurring at sites with monthly mean concentrations below 1 µg m^{-3}. The variability of the measured NH_3 concentrations is attributed to the diverse land use, which can be shown by putting sites into three categories: a) “Background sites” located far from agricultural NH_3 sources, b) “Field sites” that are influenced by agricultural NH_3 sources such as grazing or fertiliser applications, but are not in close proximity to large point NH_3 sources, c) “Poultry sites” within 300 m of large point sources, i.e. the poultry houses. Annual mean NH_3 concentrations in 2008 ranged between 0.4 and 22.9 µg NH_3 m^{-3} and generally increased from Background to Field to Poultry sites (Figure 3.3). Two Field sites were high exceptions: Site 24 was close to an open cattle shed and an intensively used field and site 25 was relatively close (320 m) to a poultry house.

The largest NH_3 concentrations were measured downwind and close to a poultry house with an NH_3 emission strength of 5,900 kg N yr^{-1} (site 31). A measurement transect of three sites downwind of this house illustrate the gradient with distance from large sources. Measured annual concentrations were 22.9 µg m^{-3}, 14.7 µg m^{-3} and 4.8 µg m^{-3} at distances of 70 m, 160 m and 900 m from the house. Figure 3.4

compares these results to concentration decreases with distances found in Fowler et al. (1998) and Pitcairn et al. (1998) for poultry houses emitting 4,800 kg N yr^{-1} and 14,000 kg N yr^{-1}, respectively. All three studies were conducted in agricultural areas, however the concentration decrease with distance in this study is much more gradual, possibly due to high background concentrations in the area caused by the large number of emission hotspots.

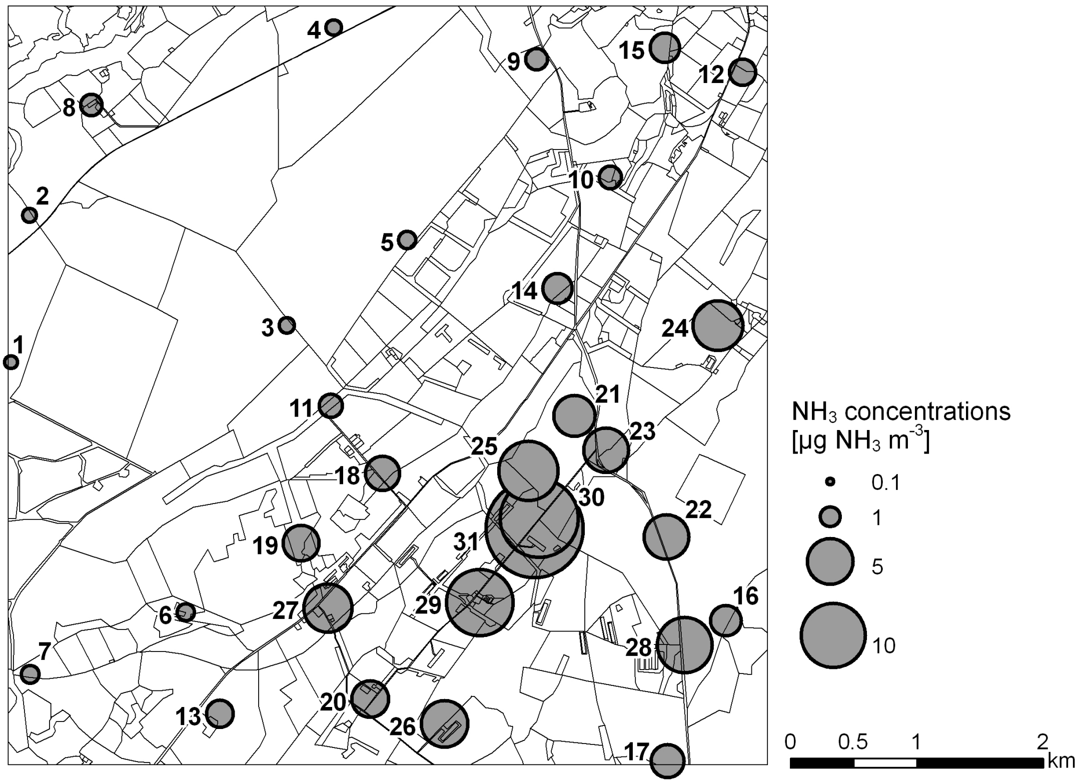

Figure 3.2: Map of numbered site locations showing annual mean NH_3 concentrations by proportionally sized circles.

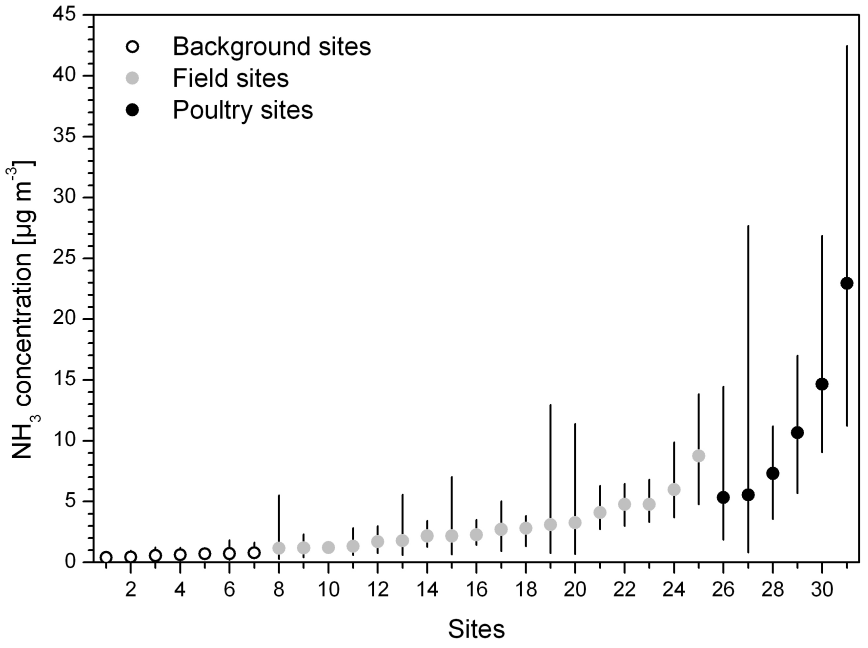

Figure 3.3: Annual mean concentrations and monthly minima and maxima in 2008 for the Background sites (open circles), Field sites (grey circles) and Poultry sites (black circles).

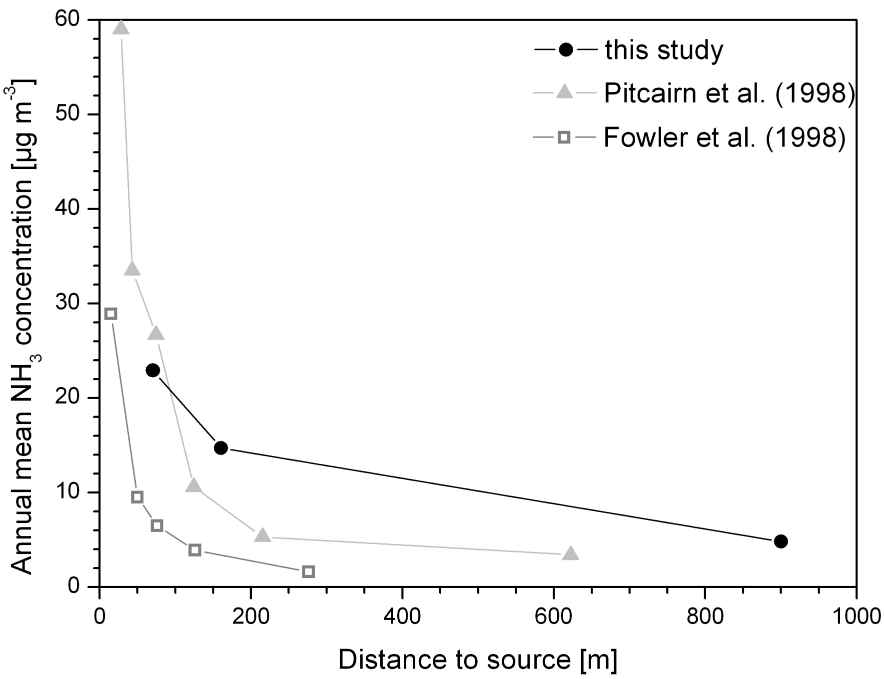

Figure 3.4: Concentration decrease with distance to the source of this study (sites 31, 30, 23) compared to results of Pitcairn et al. (1998) and Fowler et al. (1998).

3.3.2 Temporal variability in measured NH_3 concentrations

A strong correlation was found between mean NH_3 concentrations of all sites in 2007 and 2008. In 2007, data were only collected from April to December, thus only the equivalent data in 2008 were used for comparison. This strong correlation (R^2 = 0.98) indicates that the site location, i.e. the surrounding land use, is the main driver of concentration variation. The ratio of monthly concentration maxima to annual mean concentrations can be used as an indicator of temporal variability on an intra-annual basis (Figure 3.5) with Tang et al. (2009) conducting a similar assessment at national scale. Most sites show a ratio below 3:1 which seems to represent typical temporal variation about a mean of a relatively constant NH_3 concentration (e.g. Figure 3.6a). Monthly maximum concentrations of those sites with larger ratios (up to 5:1) occur in spring or summer 2008. For example, site 27 (Figure 3.6b) is located around 200 m south of four poultry houses, but it is also located close to a field which was spread with manure in May 2008. This manure application also affected concentrations of site 19 and site 13, the latter affected as May 2008 had frequent northeasterly winds. Manure heaps and applications also accounted for monthly maxima at sites 8 (Figure 3.6c), 15 and 20 (Figure 3.6d). Site 8 was located 150 m northwest of a manure heap which received fresh manure in May 2008. Site 15 was located next to a field which received manure in May 2008 and site 20 was located adjacent to a field onto which manure was applied in August 2008. These sites, which are affected occasionally by a large NH_3 source, show a higher temporal variability than other sites.

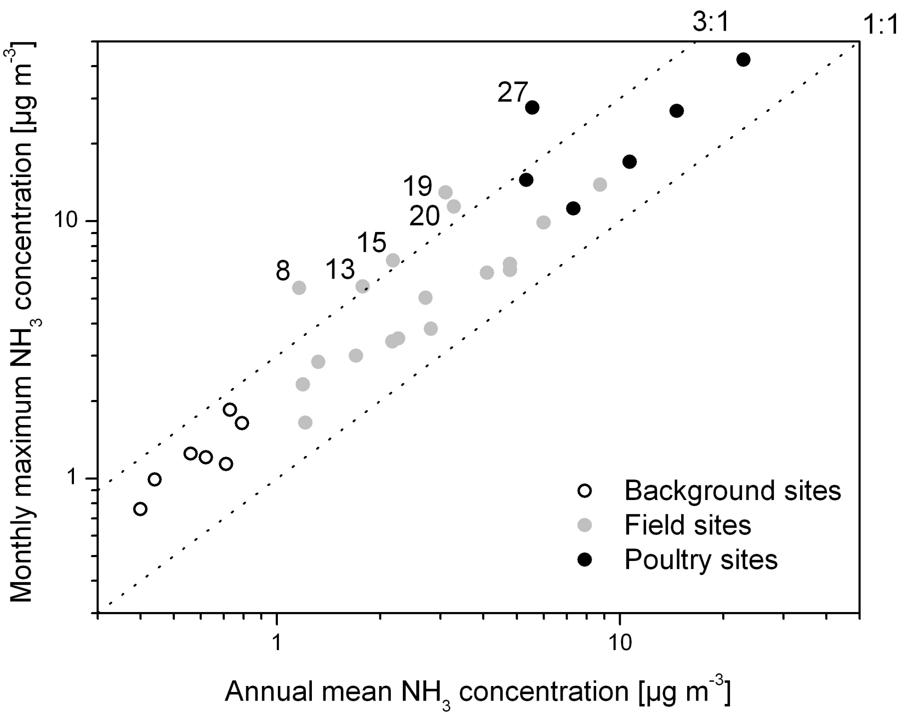

Figure 3.5: Relationship between monthly maximum and annual mean concentrations in 2008 of Background sites (open circles), Field sites (grey circles) and Poultry sites (black circles). Site numbers are shown for sites with monthly maximum to annual mean ratios higher than 3:1.

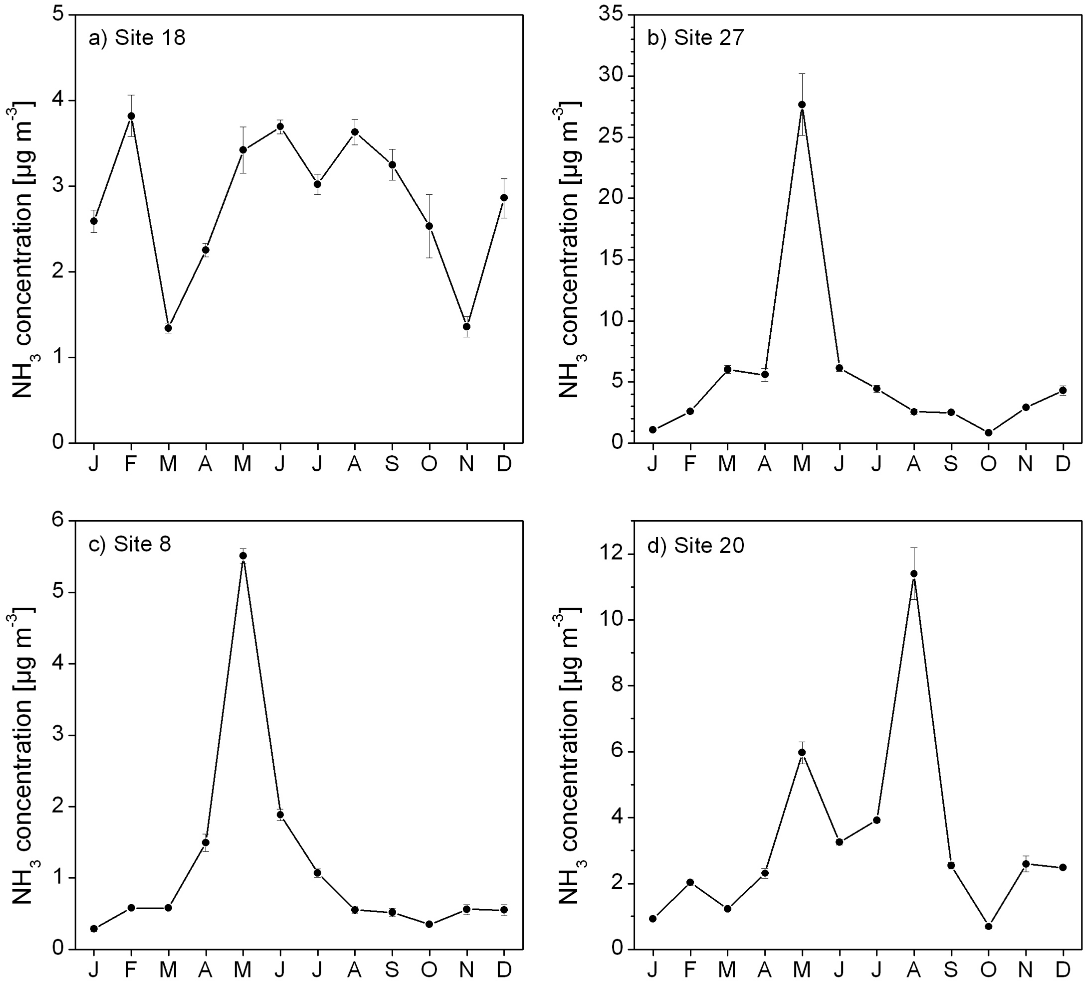

Figure 3.6: Temporal variation of monthly NH_3 concentrations (± 2x standard deviation) during 2008 at four sites: a) Site 18 with a ratio of max/mean below 3:1 and b), c) and d) showing sites with higher ratios than 3:1.

3.3.3 LADD modelling

The LADD model was initially run using UK inventory EFs. This model run resulted in the general pattern of NH_3 concentrations being reproduced, however there was a significant concentration overestimation in the landscape (Figure 3.7, left). This overestimation was attributable to the emissions from six of the poultry houses (see circled houses in Figure 3.1) which contained ~ ¾ million caged layers. Those houses were the only houses in the landscape which had frequently cleaned belt-systems ($\geq$ 2 week^{-1}). The EF for a UK average caged layer is calculated assuming 40% of the caged layers being housed in deep-pit houses and 60% in belt-system houses with less frequently cleaned belts (≤1 week^{-1}) (Misselbrook et al., 2009). Belt-systems with less frequent cleaning (EF = 0.092 kg NH_3-N bird^{-1} yr^{-1}) are considered to reduce emissions by 56% compared to the deep-pit poultry houses (EF = 0.164 kg NH_3-N bird^{-1} yr^{-1}), resulting in an average UK caged layer EF of 0.121 kg NH_3-N bird^{-1} yr^{-1} (Misselbrook et al., 2009). The IPPC (2003) reports an EF of 0.029 kg NH_3-N bird^{-1} yr^{-1} for frequently cleaned belt-systems, more than four times lower than that for the UK average caged layer. LADD runs were repeated using the IPPC EF for the six poultry houses concerned and modelled concentrations decreased considerably (Figure 3.7, right).

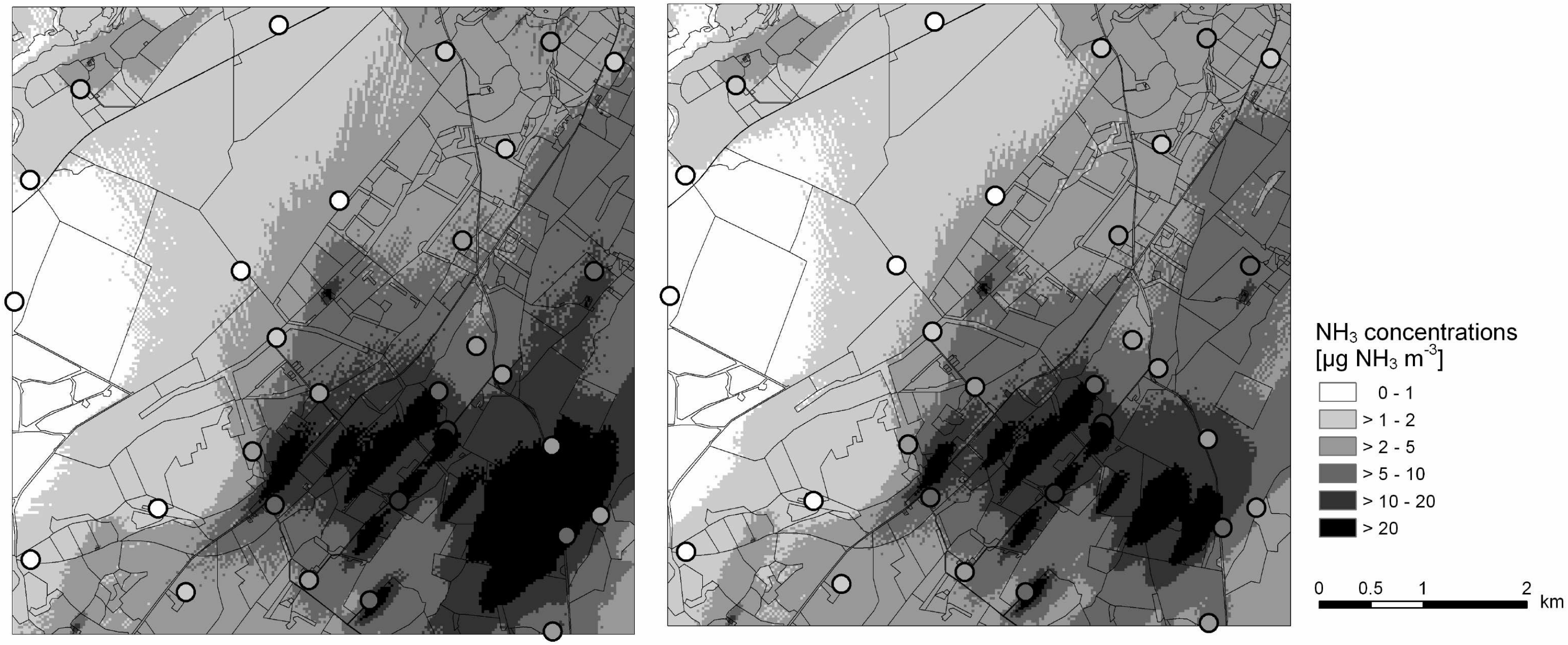

Figure 3.7: Measured (circles) and modelled (background colours) NH_3 concentrations within the landscape. Left map: UK inventory emission factors were applied to all NH_3 sources; Right map: the IPPC (2003) EF was applied to six poultry houses that had frequently cleaned manure-belt systems

Figure 3.8 shows a scatter plot between modelled and measured concentrations and Table 3.2 summarises the statistical metrics. Overall model performance is evaluated as acceptable as the FAC2, R and VG metrics all indicate acceptable model performance when compared against measurements at all sites. However, the MG is lower than recommended for acceptable model performance, indicating a systematic overestimation by the model. This systematic overestimation of concentrations is apparent at all distances from sources.

Recent work by Theobald et al. (2011) suggests that LADD overestimates concentrations around very elevated sources (> 5 m) with high exit velocities. LADD failed to meet any performance measures when compared with measurements around a source of this type. Concentration overestimation in these cases may be due to LADD not including plume rise equations which describe the rise of the plume after leaving the source. However, poultry houses in this study area predominantly have emission heights of 4 to 5 m and most vents are located at the house walls, i.e. most plumes are not expected to exit vertically. For other situations with ground and building emission sources Theobald et al. (2011) reported acceptable agreement between LADD and measured concentrations.

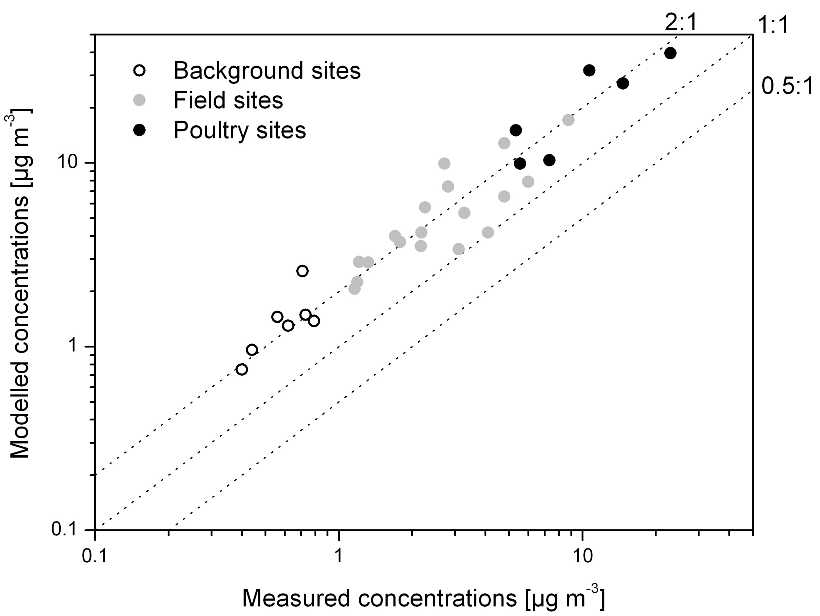

Figure 3.8: Relationship between modelled and measured concentrations of Background sites (open circles), Field sites (grey circles) and Poultry sites (black circles) on logarithmic axes.

Table 3.2: Statistical metrics of model performance comparing results: All sites and separate site categories (see section 3.3.1 for category definition).

	Target performance	All sites	Background sites	Field sites	Poultry sites
FAC2 (%)	≥ 50.0	51.6	28.6	55.6	66.7
R	-	0.95	0.64	0.84	0.89
MG	0.7 – 1.3	0.50	0.45	0.52	0.50
VG	< 3.3	1.77	2.03	1.68	1.76

3.3.4 Model calibration

In order to use modelled concentrations and deposition fluxes for risk assessment of environmental impacts, the systematic overestimation was addressed by calibrating the modelled against measured concentrations. Modelled concentrations were corrected by the slope of the regression between measured and modelled results ($[NH_3]_{meas} = 0.49*[NH_3]_{model} + 0.15$, $R^2 = 0.90$), i.e. all modelled concentrations were multiplied by a constant factor. The intercept was not statistically significant. A map of measured and calibrated modelled concentrations is shown in Figure 3.9. Modelled concentrations range from 0.3 to 77.9 µg m^{-3} within the study landscape. Statistics comparing measured and calibrated modelled concentrations show good agreement for all site categories. Results of the calibrated model are considered suitable for assessing environmental impacts in the study landscape.

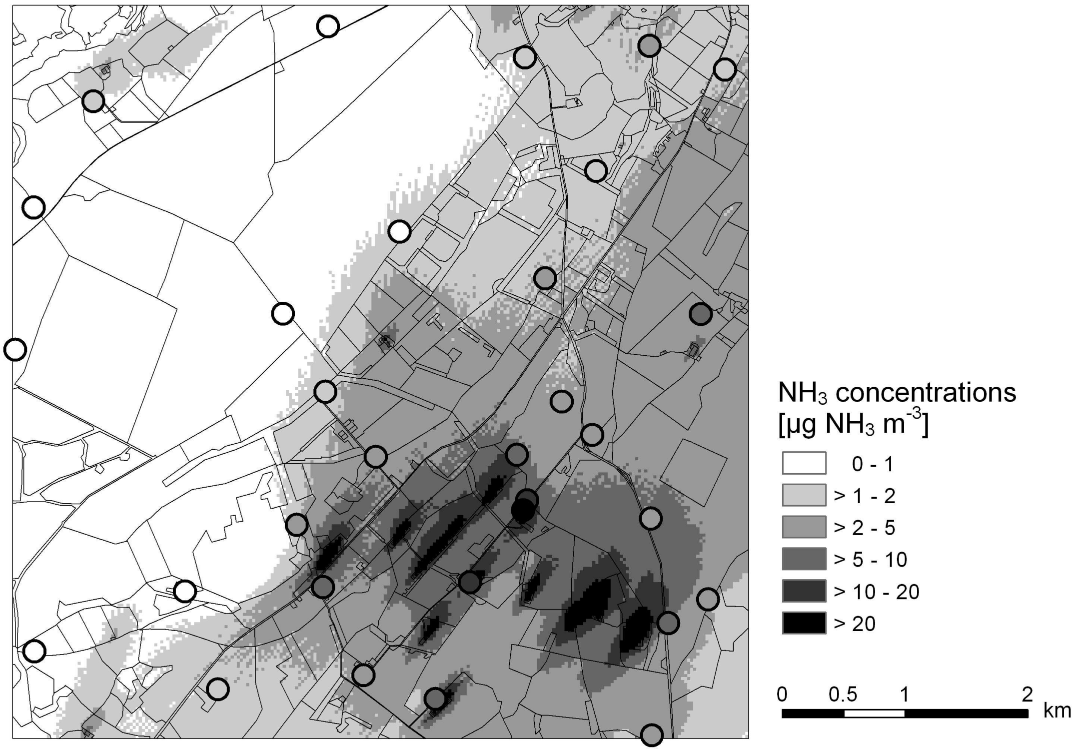

Figure 3.9: Measured (circles) and calibrated modelled (background colours) NH_3 concentrations within the landscape. For all NH_3 sources, except for six frequently cleaned poultry houses, UK inventory emission factors were used as model input.

3.3.5 Risk assessment of environmental impacts

To assess the environmental impact of local NH_3 sources to ecosystems within the study landscape, critical level (CLE) exceedances and critical load (CLO) exceedances were calculated using the calibrated model outputs. Results were compared to the output of the UK national model FRAME with a resolution of 1 km x 1 km.

3.3.5.1 Concentrations and critical level (CLE) exceedance

For sensitive vegetation, i.e. lichens and bryophytes, the long term CLE for NH_3 of 1 $\mu g\ m^{-3}$ is exceeded in 60% of the landscape (Figure 3.10). Moorland ecosystems naturally contain vegetation sensitive to NH_3 and, within the study area, the CLE is exceeded for 8% of the moorland areas. Those ecosystems could thus be expected to show long term effects of local NH_3 sources. Although this affects a considerable moorland area (39 ha), it is still relatively modest considering the extremely high emission fluxes close by. This is due to most of the moorland in the study area being located northwest of the poultry houses in a region with frequent southwesterly winds. The CLE of 3 μg m^{-3} for higher plants is exceeded in 25% of the landscape. Most of this area is agricultural land: 81% is grass or arable land. Of all semi-natural areas in the landscape, 7% show an exceedance of the CLE of 3 μg m^{-3} and thus may be impacted adversely. However, all semi-natural areas exceeding the CLE of 3 μg m^{-3} consist of relatively small patches within the agricultural area, i.e. the large area of moorland and rough grass in the northwest of the study landscape is not exposed to NH_3 concentrations exceeding 3 μg m^{-3}.

These results at 25 m resolution were averaged over 1 km x 1 km and compared to concentrations modelled by FRAME at 1 km resolution (Table 3.3). For this comparison, it has to be noted that FRAME is, in contrast to LADD, run at national scale with UK inventory EFs. FRAME predicts CLE exceedances for 1 μg m^{-3} for the whole landscape and no exceedances for the 3 μg m^{-3} CLE, i.e. it overestimates the impact to the sensitive moorland area northwest of the emission hotspots, but substantially underestimates the impact downwind of the hotspots. Thus, FRAME does not capture the spatial variability of NH_3 concentrations and therefore seems to be unsuitable for the assessment of environmental impacts at 1 km resolution. In contrast, LADD concentrations averaged out at the same resolution as those of FRAME capture enough of the spatial variability to assess the area of CLE exceedances (Table 3.3). This suggests that the smoothing out of NH_3 concentrations over landscapes is largely introduced by coarse scale model input data, i.e. by averaging emission input data over large areas, emission hotspots “disappear” and thus the spatial variability cannot be reproduced.

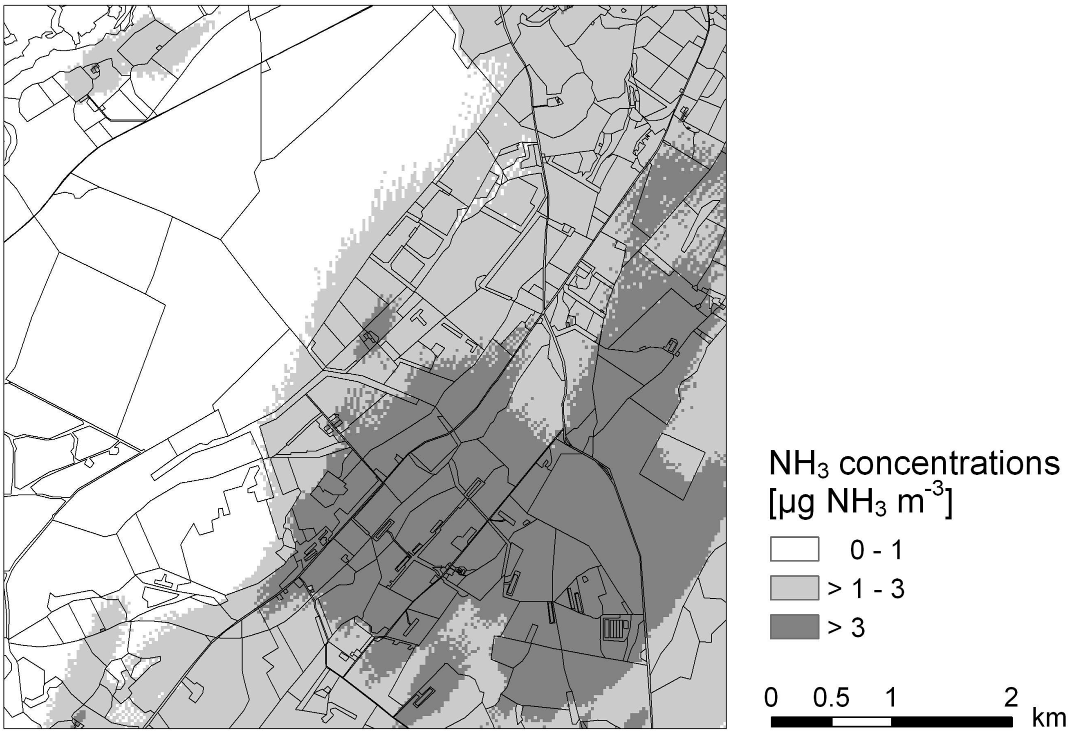

Figure 3.10: Map of modelled NH_3 concentrations (calibrated) within the study landscape with CLE exceedances indicated for sensitive vegetation (light and dark grey) and less sensitive vegetation (dark grey).

Table 3.3: Comparison of the modelled NH_3 concentration range within the study landscape and the percentage of CLE exceedance modelled by LADD (25 m and 1 km resolution) and FRAME (1 km resolution).

	LADD – 25 m	LADD – 1 km	FRAME – 1 km
Min (µg m^{-3})	0.3	0.4	1.1
Max (µg m^{-3})	77.9	10.7	2.9
% CLE exceedance 1 µg m^{-3}	60	64	100
% CLE exceedance 3 µg m^{-3}	25	31	0

To study the magnitude of the effect of poultry house emissions on CLE exceedance in the landscape, LADD was run without poultry emissions. The 1 µg m^{-3} CLE for sensitive vegetation was then exceeded in 12% of the landscape, compared to 60% when poultry house emissions were included, and the 3 µg m^{-3} CLE for higher plants was exceeded in 0.2%, compared to 25% when poultry house emissions were included. This highlights the large contribution of emission hotspots to atmospheric NH_3 concentrations in the study landscape.

3.3.5.2 Deposition and critical load (CLO) exceedance

Modelled dry deposition of NH_3 within the landscape has a high spatial variability ranging from 0.1 to 1200 kg NH_3-N ha^{-1} yr^{-1}. The extremely high deposition fluxes at the upper end of this range can be considered theoretical as the deposition rate is expected to be reduced close to large sources as the plants become saturated. To illustrate the importance of capturing the spatial variability, the deposition flux to a coniferous woodland downwind of a poultry house was analysed and compared to estimates by FRAME (circled area in Figure 3.11). The woodland of 6.5 ha is situated between 150 m and 500 m from to the house. The NH_3 dry deposition flux to the woodland modelled by LADD varies spatially between 31 and 172 kg N ha^{-1} yr^{-1} and amounts to a total of 394 kg N yr^{-1} which represents 6.7% of the poultry house emission. FRAME simulates a woodland specific dry deposition flux to this area between 10.8 and 11.9 kg N ha^{-1} yr^{-1} which results in a total NH_x dry deposition of 74 kg N yr^{-1}. Thus, FRAME underestimates the impact of NH_x dry deposition to this particular ecosystem compared with LADD.

Total N deposition (LADD NH_3 dry deposition + FRAME NH_x wet & NO_y deposition) ranges from 5.6 to 1206 kg N ha^{-1} yr^{-1} (Figure 3.11). A map with areas showing CLO exceedance is shown in Figure 3.12. The CLO applies to the land cover categories woodland, hedgerows, shrubs, moorland and rough grass in the landscape, i.e. CLOs were calculated only for these areas, equivalent to 38% of the study area. In 34% of this area the CLO is exceeded which represents 13% of the overall landscape area. The CLO is, on average, exceeded by 17.6 kg N ha^{-1} yr^{-1}, the median CLO exceedance is 6.5 kg N ha^{-1} yr^{-1}. Table 3.4 shows statistics of CLO exceedance for the different land cover categories.

Table 3.4: Land cover specific statistics* for critical load exceedance in kg N ha^{-1} yr^{-1}.

	Woodland	Shrubs	Rough grass	Moorland
Mean	20.1	21.6	11.6	1.9
Median	7.4	17.6	2.7	0.7
Maximum	1195.6	401.9	406.5	10.5
% exceeding CLO	74.2	97.0	28.0	1.7

*Land cover category hedgerows covered only one 25 m x 25 m grid and was therefore not considered for these statistics

When combining FRAME results with 25 m x 25 m land cover data (see section 3.2.6), FRAME predicts a CLO exceedance in 51% of the area to which a CLO applies, compared to 34% simulated by LADD (Table 3.5). FRAME simulates a CLO exceedance over a larger area than LADD, but the extent of CLO exceedance is smaller compared to LADD. Due to FRAME not capturing the spatial variability of NH_3 dry deposition, areas exceeding CLO in the whole study landscape are overestimated whereas the extent of CLO exceedance in areas close to sources is underestimated.

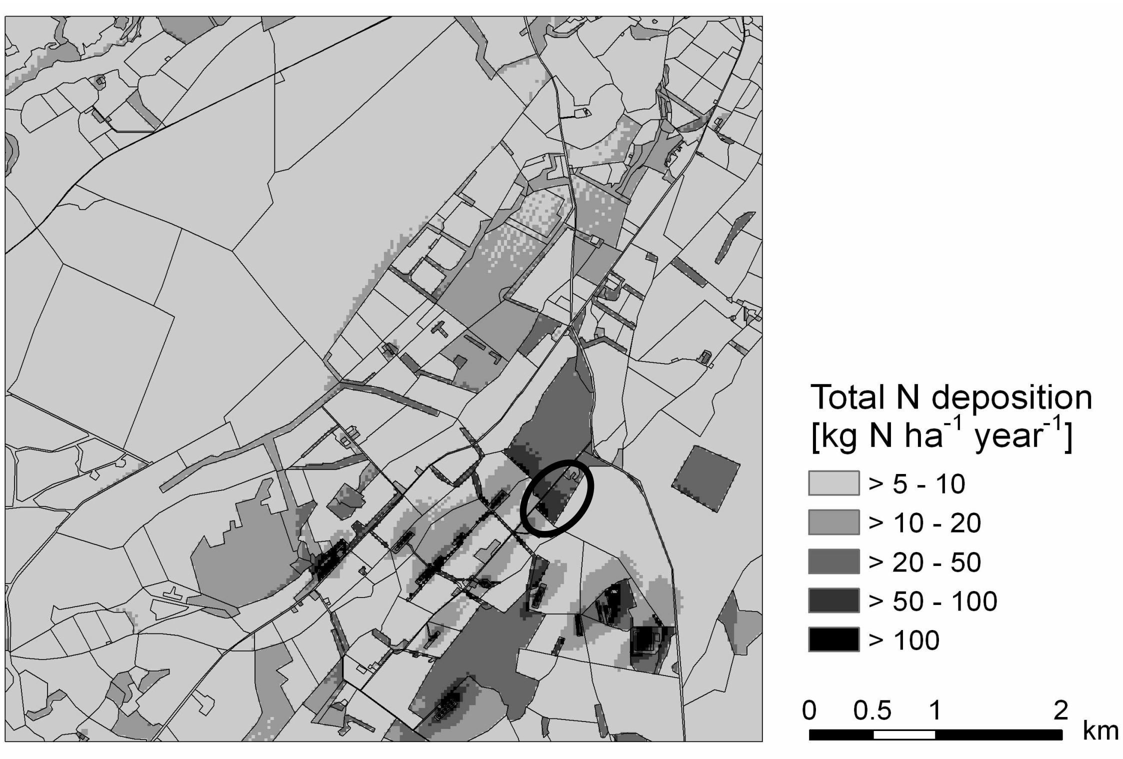

Figure 3.11: Map of total N deposition calculated by combining dry deposition of NH_3 simulated by LADD (calibrated) with the remaining components of N deposition from FRAME. The circled area shows the woodland analysed in more detail.

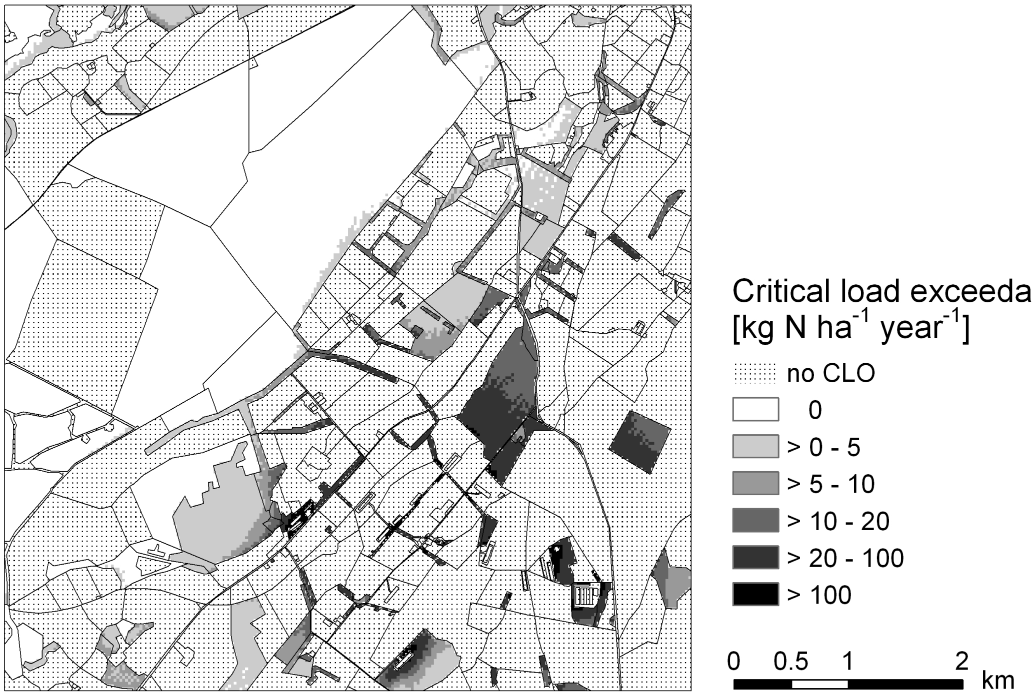

Figure 3.12: Map of critical load exceedance calculated combining dry deposition of NH_3 simulated by LADD (calibrated) with the remaining components of N deposition from FRAME.

Table 3.5: Comparison of CLO exceedances (kg N ha^{-1} yr^{-1}) within the study landscape between LADD and FRAME

	LADD	FRAME
Mean	17.6	3.2
Median	6.5	2.4
Maximum	1195.6	10.8
% exceeding CLO	34	51

3.4 Conclusions

The detailed landscape inventory of all farm activities in the study year 2008 provided data to estimate NH_3 emissions at 25 m resolution. This is essential for studying the actual spatial variability of NH_3 in a landscape. The combination of a large number of long term NH_3 concentration measurements across the landscape and the high resolution LADD model output allowed spatially precise assessment of NH_3 concentrations and dry deposition. Measured and modelled NH_3 were highly correlated (R^2 = 0.90), but model estimates needed to be calibrated for environmental risk assessment. It is recommended to always include verification measurements in such an assessment in order to calibrate model estimates. This is important since the particular situations in which models, such as LADD, perform well are not always predictable.

However, for this modelling work the NH_3 emission factors of six of the 24 poultry houses had to be adjusted to account for the specific manure management practices as the emission factor of the UK national inventory resulted in a considerable overestimation of concentrations in the surroundings of those houses. Thus, for the environmental impact assessment of large livestock houses, rather than national average emission factors, more specific factors are needed which take into account the specific husbandry system and manure management.

In this study area, frequent southwesterly winds cause most of the poultry house emissions to disperse to the northeast. As most sensitive ecosystems are located northwest of the poultry houses, only a relatively small part is affected by the nearby poultry houses with NH_3 emissions exceeding 100 t N yr^{-1} in total. Most semi-natural land at risk of potential impacts from NH_3 concentrations are patches of woodland, shrubs and rough grass situated within the agricultural area. Impact assessment by the CLE approach suggested that 8% of the semi-natural moorland may be adversely affected by NH_3 concentrations above 1 μg m^{-3} (= long term CLE for lichens and bryophytes). However, the impact assessment of total N deposition suggests that only 2% of the moorland area is under threat (i.e. area of CLO exceedance). The national model FRAME at 1 km resolution could not capture the spatial variability of NH_3 within the study landscape, largely due to coarse scale emission input data. This emphasises the need for high resolution emission data obtained at the farm level for assessing environmental impacts of NH_3.

This study illustrates the importance of the spatial arrangement of NH_3 sources and sinks within a landscape to the environmental impact of NH_3. In the study landscape, most sensitive ecosystems are located upwind of the large NH_3 sources nearby and thus are considered to be at relatively small environmental risk. This shows how landscape planning can be used to reduce the impact of intensive agriculture on sensitive ecosystems. Future landscape scale NH_3 studies should focus on improving atmospheric dispersion models so that they can be applied in a range of situations without verification measurements. The detailed farm inventory and the measurement data set collected for this landscape with large emission variability may also be useful for testing other NH_3 dispersion models.

Acknowledgements

This work was funded by the NitroEurope Integrated Project, supported by the European Commission, 6th Framework Programme, the Centre for Ecology and Hydrology, the Scottish Agricultural College, together with complementary inputs from the UK Department of Food and Rural Affairs, COST 729 and the NinE network of the European Science Foundation. The authors are grateful for the cooperation of all farmers in the study landscape.

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4 Paper III: Effect of land use on fluxes and concentrations of organic and inorganic nitrogen in streams

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Abstract

We present annual downstream fluxes and spatial variation in concentrations of dissolved inorganic nitrogen (NH_4^+ and NO_3^-) and dissolved organic nitrogen (DON) in two adjacent Scottish catchments with contrasting land use (agricultural grassland vs. semi-natural moorland). Inter- and intra-catchment variation in N species and the relation to spatial differences in agricultural land use were studied by determining catchment N input through agricultural activities at the field scale and atmospheric inputs at 25 m resolution. The overall average agricultural N input of 52 kg N ha^{-1} yr^{-1} to the grassland catchment exceeded by more than four times the input of 12 kg N ha^{-1} yr^{-1} to the moorland catchment, supplemented by 12.3 and 8.2 kg N ha^{-1} yr^{-1} through atmospheric deposition, respectively. The grassland catchment was associated with an annual downstream total dissolved nitrogen (TDN) flux of 14.4 kg N ha^{-1} yr^{-1}, which was 66% higher than the flux of 8.7 kg ha^{-1} yr^{-1} from the moorland

catchment. This difference was largely due to the NO_3^- flux being one order of magnitude higher in the grassland catchment. Dissolved organic N fluxes were similar for the two catchments (7.0 kg ha^{-1} yr^{-1}) with DON contributing 49% to the TDN flux in the grassland compared with 81% in the moorland catchment. The results highlight the importance of diffuse agricultural N inputs to stream NO_3^- concentrations and the complexity of DON sources in extensively grazed areas.

Keywords: nitrogen, organic nitrogen, stream export, catchment flux, land use

4.1 Introduction

Human actions at the landscape scale impact the ecological state of stream ecosystems, particularly through land use change (Allan, 2004; Likens and Bormann, 1974). In the past centuries, land use change has taken place on a global scale increasing the area of different types of agricultural land (Goldewijk, 2001). One of the most significant changes in agricultural systems is the elevation in nitrogen (N) inputs caused by applications of mineral and organic fertiliser as well as organic wastes associated with grazing livestock (Nieder and Benbi, 2010; Wade et al., 2005). However, there remain significant uncertainties about the influence of land use on N export to the aquatic system at the catchment scale, due to the complexity of N dynamics (Alvarez-Cobelas et al., 2008).

In aquatic ecosystems, N enrichment at the catchment scale can have significant impact on water quality and is well known to be linked to eutrophication (e.g. Grizzetti et al., 2011). The main forms of reactive, i.e. biologically available, N dissolved in streamwater are ammonium (NH_4^+), nitrate (NO_3^-) and dissolved organic nitrogen (DON). However, most studies on catchment N export have focused on single N compounds, particularly on NO_3^- as this was understood to be the dominant form of N leaching from agricultural systems (Alvarez-Cobelas et al., 2008; Van Kessel et al., 2009). Generally, high soil organic matter content is considered to result in high streamwater dissolved organic carbon and nitrogen compounds (Neff et al., 2003). A number of studies on the organic nitrogen fraction in streamwater have been conducted in forested systems associated with organic soils (e.g. Campbell et al., 2000; Perakis and Hedin, 2002). In recent years the importance of organic N as a significant form of streamwater N not only in semi-natural but also in agricultural areas has become apparent (e.g. Murphy et al., 2000; Scott et al., 2007), although the behaviour and origin of DON in streamwater is not fully understood (Durand et al., 2011). Catchment studies therefore need to take into account all forms of streamwater N, including organic forms, to gain better understanding of N export.

In this study, we investigated two Scottish catchments with contrasting land use, one dominated by grazed grassland, the other dominated by semi-natural moorland. Annual downstream fluxes of NH_4^+, NO_3^- and DON were established by sampling at the gauged catchment outlets at both fortnightly and hourly intervals during selected high flow events during 2008. A detailed landscape inventory provided data on spatial N input to the catchments through agricultural land use. The relationship between agricultural land use N input and spatial concentration variability within the catchments was studied by conducting synoptic intensive samplings throughout different seasons of the year. This study aims to quantify the interrelationship between land use and streamwater N concentrations with particular emphasis on understanding the speciation of the aqueous N forms.

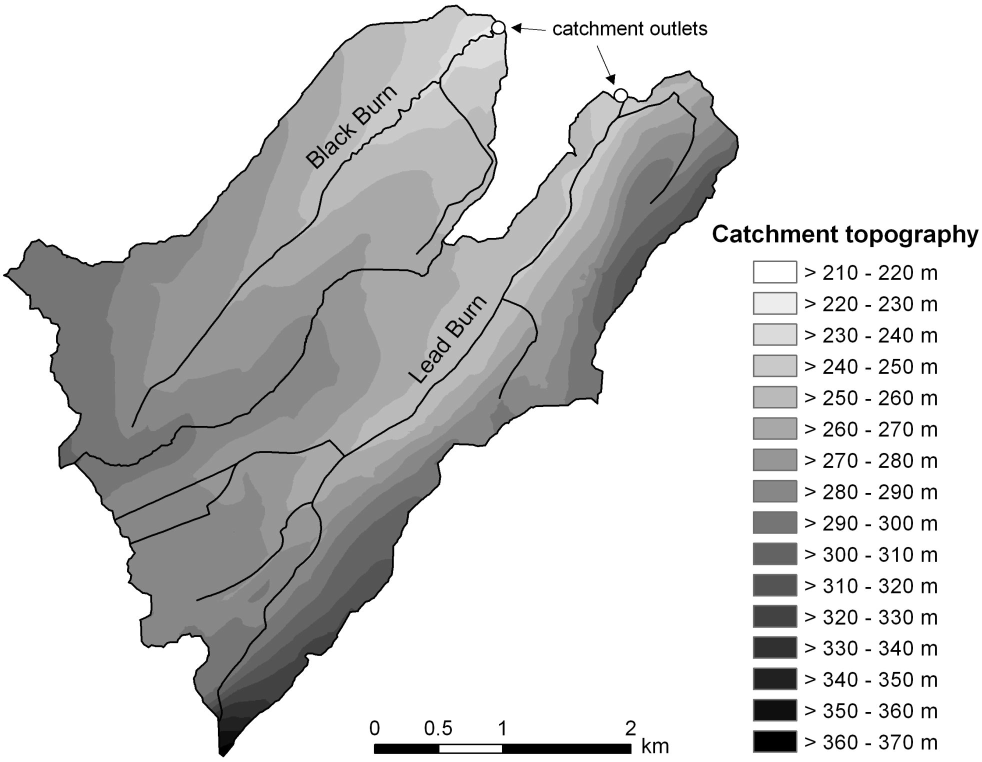
4.2 Site and methods

4.2.1 Study area

Black Burn and Lead Burn are located approximately 20 km south of Edinburgh in southern Scotland. They flow in a northeast direction and are subcatchments of the North Esk River. The Black Burn catchment covers an area of 6.2 km^2, has an average slope of 1.7° and an average altitude of 270 m (range of 218 to 303 m) (Figure 4.1). The upper part of this catchment has been studied previously in terms of its hydrochemistry (Billett et al., 2004; Dinsmore and Billett, 2008; Dinsmore et al., 2010). The main soil type of the Black Burn catchment is peat (67%), with lesser amounts of brown forest soils (16%) and peaty gleys (10%). Semi-natural moorland accounts for 63% of the land cover, a further 12% is used for peat extraction in the southwest of the catchment, 10% is rough grass and 2% woodland. Only 11% of the Black Burn catchment is improved grassland, with no arable land. Two thirds of this semi-natural moorland are grazed by sheep at a very low stocking density (<1 sheep ha^{-1}) and the remaining third is a protected Site of Special Scientific Interest (SSSI) with no grazing.

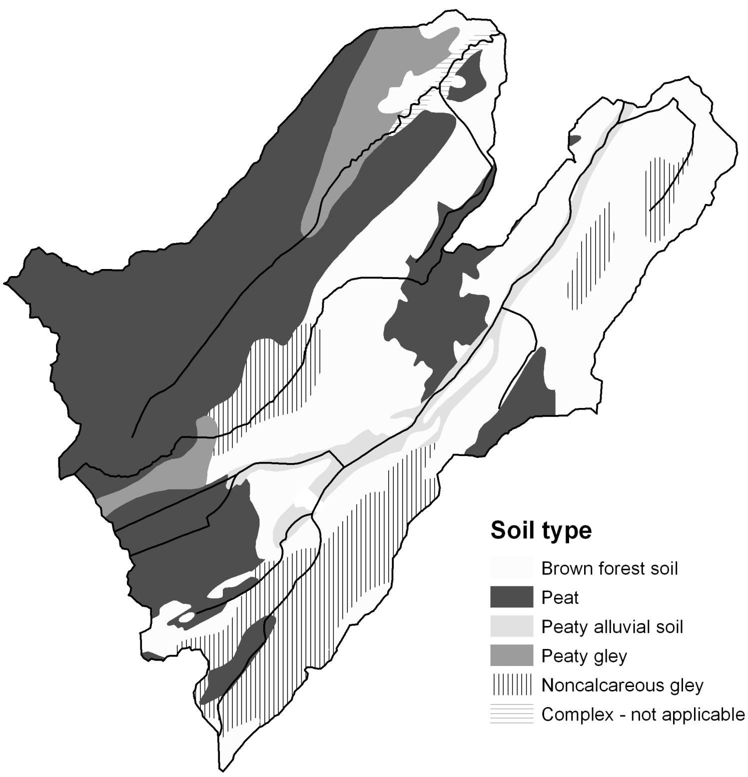
The Lead Burn catchment covers an area of 8.9 km^2 and has an average slope of 3.1° and average altitude of 280 m (range of 241 to 368 m) (Figure 4.1). Approximately half of the catchment consits of brown forest soils (48%), associated with noncalcareous gleys (21%) and peat (21%). The main land cover types are improved grassland (59%), rough grassland (10%), woodland (14%), moorland (5%), shrubs (3%), peat extraction (2%) and arable land (2%). The agricultural land is grazed by beef cattle and sheep (stocking density: <1 beef cattle ha^{-1} and 10 sheep ha^{-1}); it also contains six poultry houses with over ¼ million laying hens. The poultry farming operations are largely disconnected from the catchment hydrology, as feeds are imported and manure exported by road. However, ammonia emissions from the poultry houses contribute to atmospheric N inputs to both catchments as has been estimated by Vogt et al. (2011, Chapter 3, this volume).

The catchments lie to the south of the Southern Upland Boundary Fault in an area dominated by sandstone, containing thin bands of limestone, mudstone, coal and clay (Billett et al., 2004). Southern Scotland has a temperate and oceanic climate. In 2008, the catchments received an annual rainfall of 1208 mm (Coyle, pers. com. 2009), measured at Auchencorth Moss field site within the Black Burn catchment. The air temperature varied from -8.3 °C to 25.4 °C with and annual average of 7.6 °C.



catchment outlets
Black Burn
Lead Burn
Catchment topography
> 210 - 220 m
> 220 - 230 m
> 230 - 240 m
> 240 - 250 m
> 250 - 260 m
> 260 - 270 m
> 270 - 280 m
> 280 - 290 m
> 290 - 300 m
> 300 - 310 m
> 310 - 320 m
> 320 - 330 m
> 330 - 340 m
> 340 - 350 m
> 350 - 360 m
> 360 - 370 m
0 0.5 1 2
km

(a)



Soil type
Brown forest soil
Peat
Peaty alluvial soil
Peaty gley
Noncalcareous gley
Complex - not applicable

(b)

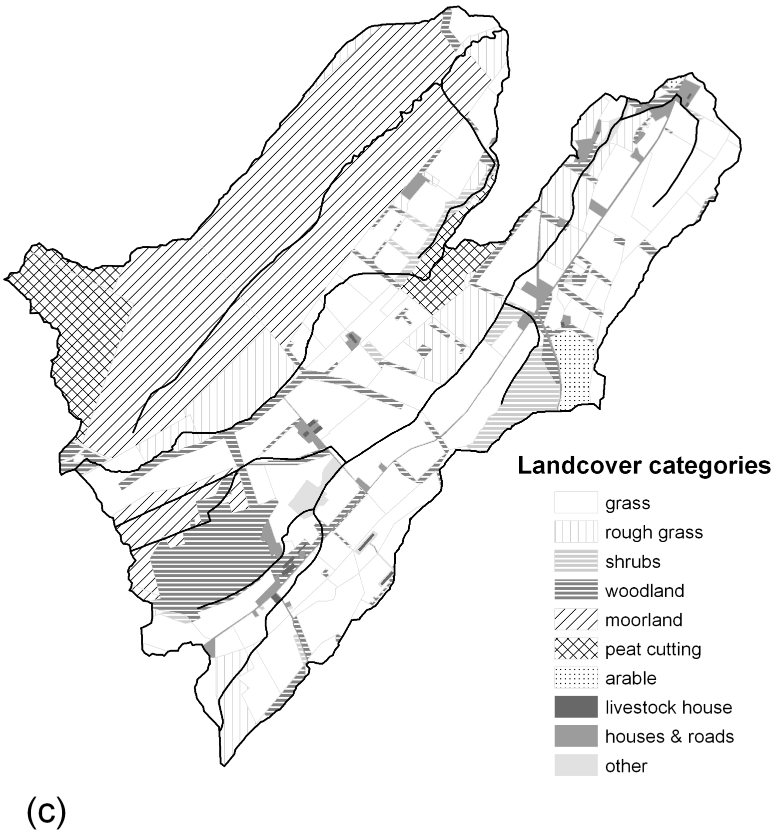


Figure 4.1: Maps of (a) topography[a], (b) soil[b] and (c) land cover of the Black Burn and the Lead Burn catchment. Streamwater samplings and discharge measurements were carried out at the catchment outlets. Not all tributaries of the main streams are shown.

[a] © Intermap Technologies Inc. 2010

[b] © The Macaulay Land Use Research Institute 2008 (license MI/2008/296). Soil types are based on the Scottish Soil Survey, the equivalent FAO names are: brown forest soil = cambisol, peat = histosol, peaty alluvial soil = humic fluvisol, peaty gley = humic gleysol, noncalcareous gley = gleysol (FAO/UNESCO, 1974)

4.2.2 Discharge measurements

Discharge was measured continuously in both streams using Level Troll® (In-Situ Inc.) pressure transducers, located at the catchment outlets. Measurements were made at 1 Hz with 15 minute averaging. In-stream pressure was corrected for atmospheric pressure and stage height data were established by a linear regression between pressure data and gauge height readings (for both streams: $r^2 = 0.99$, $n = 17$). Continuous discharge was then calculated using a curvilinear regression between stage height data and a series of dilution gauging measurements (Black Burn: $r^2 = 0.98$, $n = 14$; Lead Burn: $r^2 = 0.92$, $n = 15$).

4.2.3 Streamwater sampling

During 2008, streams were sampled using three approaches. (a) Fortnightly samples were collected at the outlet of each of the two study catchments to establish annual downstream fluxes. (b) Automatic water samplers (Teledyne Isco) were installed at the catchment outlets to collect hourly streamwater samples during several high flow events (4 Oct, 7 Oct, 9-11 Oct, 12/13 Dec 2008) for improving annual flux calculations. (c) Streamwater chemistry was sampled spatially during synoptic intensive samplings at stable low flow on consecutive days for both streams on 22/23 July, 25/26 September and 9/10 December 2008. The aim of the latter approach was to capture changes in the concentration of N species across the two catchments by sampling the main streams and their tributaries (36 samples from Black Burn and 46 from Lead Burn).

All water samples were collected in prewashed and dried bottles (either 1 L PP or 125 ml PE (Nalgene)), filtered on the same day in the laboratory and frozen prior to analysis.

4.2.4 Chemical determination of NH_4^+, NO_3^-, TDN and DOC

All water samples were filtered through 0.45 µm syringe filters (Minisart® NML, Sartorius Stedim Biotech). The syringe filters were preflushed with sample water. Each sample was stored in two 24 ml PE bottles (Kartell) and two 2 ml glass vials (Chromacol) and frozen at -18°C until analysis. Ammonium (NH_4^+) and nitrate (NO_3^-) were determined using a dual channel continuous-flow colourimetric analyser

(ChemLab Instruments Ltd). Total dissolved nitrogen (TDN) was determined using an 8060-M HPLC-CLND (Antek Instruments Inc.), which catalytically oxidises nitrogen and detects the resulting nitric oxide (NO) with chemiluminescence (Gonzalez Benitez et al., 2010). The detection limit for TDN is 0.01 mg L^{-1}. As dissolved organic nitrogen (DON) in water samples cannot be quantified directly (Gonzalez Benitez et al., 2009), it was calculated as the difference between TDN and dissolved inorganic nitrogen (NH_4^+-N + NO_3^--N). Dissolved organic carbon (DOC) was determined by ultra-violet oxidation and subsequent infra-red detection with a LABTOC® analyser (Pollution Process Monitoring Ltd) (Billett et al., 2006). The detection limit for DOC is 0.5 mg L^{-1} and the repeatability ± 2%.

4.2.5 Flux calculation

Nutrient export fluxes for NH_4^+-N, NO_3^--N, DON and DOC in kg ha^{-1} yr^{-1} were calculated according to 'Method 5' of Walling and Webb (1985). This method is recommended when continuous discharge and non-continuous concentration data are available (e.g. Dawson et al., 2002; Hope et al., 1997). 'Method 5' is described by equation (1), where K is the conversion factor for scaling up to annual fluxes (i.e. number of seconds in one year), Q_r is the mean annual discharge [L s^{-1}] and C_F is the flow-weighted mean concentration [mg L^{-1}].

$$Flux = K \cdot Q_r \cdot C_F \tag{1}$$

C_F is calculated according to equation (2), where C_i are concentration values [mg L^{-1}] associated with Q_i [L s^{-1}], the discharge values at the time.

$$C_F = \sum_{i=1}^{n} \left(C_i \cdot Q_i \right) / \sum_{i=1}^{n} Q_i \tag{2}$$

The subsequent downstream flux in mg yr^{-1} was converted into kg ha^{-1} yr^{-1}. The percentage contribution of the inorganic and organic fraction to the overall nitrogen flux was determined.

Standard errors of the flux estimates were calculated using equation (3) (Hope et al., 1997), where F is the total annual discharge [L yr^{-1}] and $var(C_F)$ [mg L^{-1}] the variance of C_F. The standard error (SE) in mg yr^{-1} has to be converted into the same unit as the downstream flux.

$$SE = F \cdot var\left(C_F \right) \tag{3}$$

The variance of C_F is calculated according to equation (4), where Q_n [L s^{-1}] is the sum of all individual Q_i values.

$$var(C_F) = \left[\sum_{i=1}^{n} (C_i - C_F)^2 \cdot Q_i / Q_n \right] \cdot \sum_{i=1}^{n} (Q_i^2 / Q_n^2) \tag{4}$$

4.2.6 Soil, land use and topography data

All spatial data were processed with the geographical information system ArcGIS (ESRI). The digital soil map was acquired from the Macaulay Land Use Research Institute under license (MI/2008/296). Land use data for 2008 were obtained through a local farm and field inventory carried out by CEH and SAC staff (Dragosits et al., 2011). Inventory data include information on each livestock house (e.g. type of livestock, animal numbers, manure management) and management for each field (e.g. grazing intensity, fertiliser and manure applications). From these data, nitrogen inputs were calculated for every field within the catchments (see section 4.2.7). Surface topography data at a resolution of 5 m were derived from a Digital Terrain Model (DTM) (Intermap Technologies Inc., 2010). From these data, subcatchments were derived in ArcGIS for sample locations of the intensive spatial samplings along the main streams. This resulted in 8 and 10 main subcatchments for the Black Burn (ranging in size from 2.6 to 6.2 km²) and the Lead Burn (ranging in size from 4.1 to 8.9 km²), respectively.

4.2.7 Land use and atmospheric nitrogen input

For each field within the catchments, the nitrogen input was calculated from grazing livestock, manure and fertiliser applications during 2008 from the detailed farm and field inventory. Nitrogen input from grazing livestock was estimated using grazing records and daily nitrogen excretion data from the UK ammonia inventory (Table 4.1). A typical nitrogen content was assigned to different manure types according to DEFRA guidelines (2010) (Table 4.2). Nitrogen inputs estimated from grazing livestock (estimated uncertainty: ±50%), manure (±30%) and fertiliser applications (±10%) were added up for each field and the total input per (sub) catchment was calculated.

Table 4.1: Values of total N excreted per grazing animal used for calculating land use nitrogen input to catchments (Misselbrook et al., 2009).

Livestock category	**Total N excreted [kg N animal^{-1} yr^{-1}]**
Adult sheep (upland)	9.9
Lambs (< 1 year, upland)	0.7
Beef cows & heifers	79.0
Beef cattle 1-2 years	56.0
Calves (< 1 year)	38.0
Horses	50.0
Young horses & ponies (est. as ½ horse)	25.0

Table 4.2: Typical N content of different manure types used for calculating land use nitrogen input to catchments (DEFRA, 2010).

Manure type	**N content [kg N t^{-1}]**
Cattle/sheep/goat farm yard manure (FYM)	6.0
Cattle slurry	2.6
Solid poultry manure	19.0

Atmospheric N deposition was estimated by Vogt et al. (2011, Chapter 3, this volume), on the basis of a) dry deposition of ammonia (NH_3) resulting from poultry and other farming activities within the surrounding 6 km x 6 km landscape using the LADD model at 25 m resolution (Dragosits et al., 2002), and b) imported contributions of wet deposition of reduced nitrogen (NH_x) as well as wet and dry deposition of oxidised N compounds (NO_y) from UK and European sources using the FRAME model at 1 km resolution (Dore et al., 2007).

4.3 Results

4.3.1 Stream discharge

Mean discharge, measured continuously in 2008 and averaged over 15 minute intervals, was 140 L s^{-1} for Black Burn and 225 L s^{-1} for Lead Burn (Table 4.3). The difference is largely due to the difference in catchment size as the mean specific discharges were 23 L s^{-1} km^{-2} for Black Burn and 25 L s^{-1} km^{-2} for Lead Burn. Discharge is highly variable in both streams (Figure 4.2) with the percentage of the standard deviation to mean discharge being 204% for Black Burn and 132% for Lead

Burn. High discharge events make an important contribution to the overall discharge. In 2008, the highest 10% of the data (90th percentile) contribute 53% to the total discharge in Black Burn and 40% in Lead Burn. This indicates that for calculating annual catchment fluxes, it is important to incorporate high discharge events in the estimation of nutrient fluxes (e.g. Bowes et al., 2009; Vidon et al., 2009). In summary, Black Burn is a hydrologically more "flashy" stream compared to Lead Burn with consistently lower base flow levels in Black Burn throughout the year.

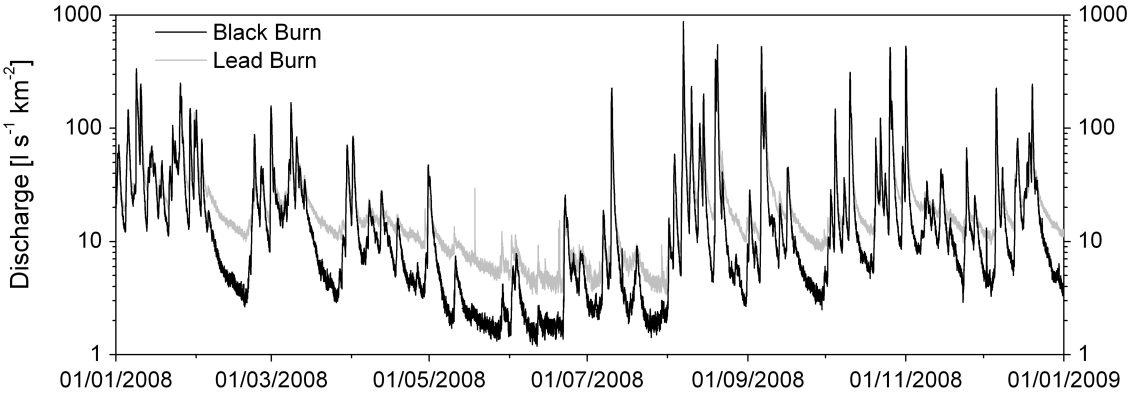


Figure 4.2: Specific discharges (log axis) in 2008 in Black Burn (black) and Lead Burn (grey).

Table 4.3: Discharge characteristics during 2008 for Black Burn and Lead Burn. Discharge values are presented in L s^{-1} and L s^{-1} km^{-2}.

	Black Burn		Lead Burn	
	[L s^{-1}]	[L s^{-1} km^{-2}]	[L s^{-1}]	[L s^{-1} km^{-2}]
Mean	140	23	225	25
Median	56	9	141	16
Standard deviation	285	46	296	33
Range	7 - 5469	1 - 881	30 - 3012	3 - 337

4.3.2 Fortnightly streamwater concentrations

Time series of fortnightly NH_4^+-N, NO_3^--N, DON and DOC concentrations during 2008 are shown in Figure 4.3 and basic statistical analysis in

Table 4.4. Annual median NH_4^+-N concentrations were not significantly different between the two streams. However, the streams differed in their NH_4^+-N contribution to TDN, which amounts to 16% in Black Burn and 6% in Lead Burn. Figure 4.3 also shows that concentrations of NH_4^+-N during winter months were greater in Black Burn than those in Lead Burn.

Median streamwater NO_3^--N concentrations were significantly lower in Black Burn (0.12 mg L^{-1}) compared to Lead Burn (1.46 mg L^{-1}). Hence, in Lead Burn NO_3^--N accounts for most of the TDN (64%), and makes a much larger contribution to the total N concentration than in Black Burn (13%).

Dissolved organic N concentrations were not significantly different between the two streams. However, Figure 4.3 shows clear differences in DON behaviour between the streams with large changes in concentration in Lead Burn, particularly during the first half of the year. The contribution of DON to TDN in Lead Burn was much lower (31%) compared to Black Burn (72%). Dissolved organic C concentrations were not significantly different between the two streams and followed a similar temporal pattern throughout the year (Figure 4.3). Ratios of DOC:DON differed significantly between the streams. From fortnightly samples, the median DOC:DON ratio was 37 at Black Burn and 26 at Lead Burn, while the variation of DOC:DON ratios was also much larger in Lead Burn compared to Black Burn.

Significant correlations between chemical species are shown in Table 4.5. For Black Burn, a significant positive correlation between DOC and DON concentrations was observed (Figure 4.4). However, no such relationship existed for Lead Burn. In both streams, NO_3^--N and DOC concentrations were negatively correlated.

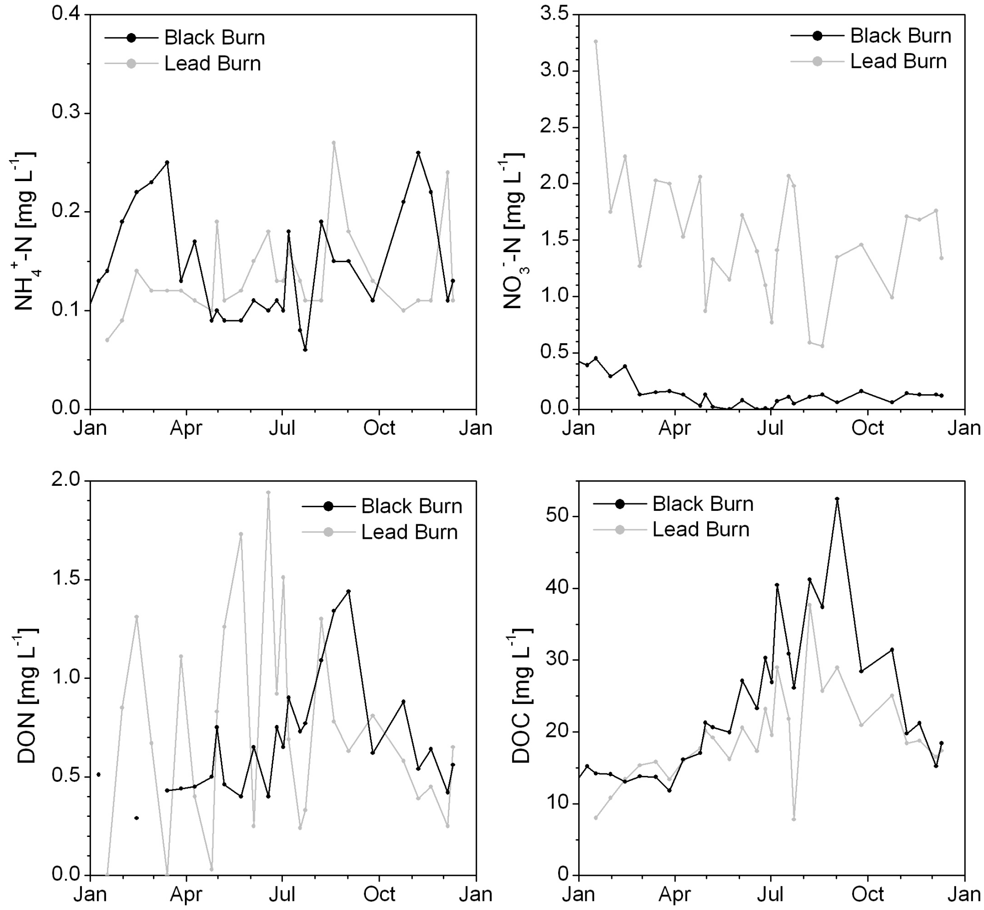


Figure 4.3: Concentration time series of NH_4^+-N (top left), NO_3^--N (top right), DON (bottom left), DOC (bottom right) in Black Burn (black) and Lead Burn (grey) from fortnightly samples in 2008.

Table 4.4: Statistics of annual streamwater concentrations for Black Burn and Lead Burn from fortnightly samplings in 2008. Median concentrations were tested to see if significant differences existed between the streams by Whitney-Mann *U* test at a two-tailed 95% significance level (p = 0.05).

	NH_4^+-N [mg L^{-1}]	NO_3^--N [mg L^{-1}]	DON [mg L^{-1}]	DOC [mg L^{-1}]	DOC:DON
Black Burn					
Mean	0.15	0.12	0.67	23.9	39
Median	0.13	0.12	0.63	21.2	37
Standard deviation	0.06	0.11	0.29	10.2	7
Range	0.06-0.26	0.00-0.45	0.29-1.44	11.8-52.5	27-58
% of TDN	15.7	12.8	71.5	-	-
Lead Burn					
Mean	0.13	1.53	0.74	19.1	33
Median	0.12	1.46	0.67	18.4	26
Standard deviation	0.04	0.58	0.52	6.5	22
Range	0.07-0.27	0.56-3.26	0.00-1.94	7.8-37.7	9-91
% of TDN	5.6	63.7	30.7	-	-

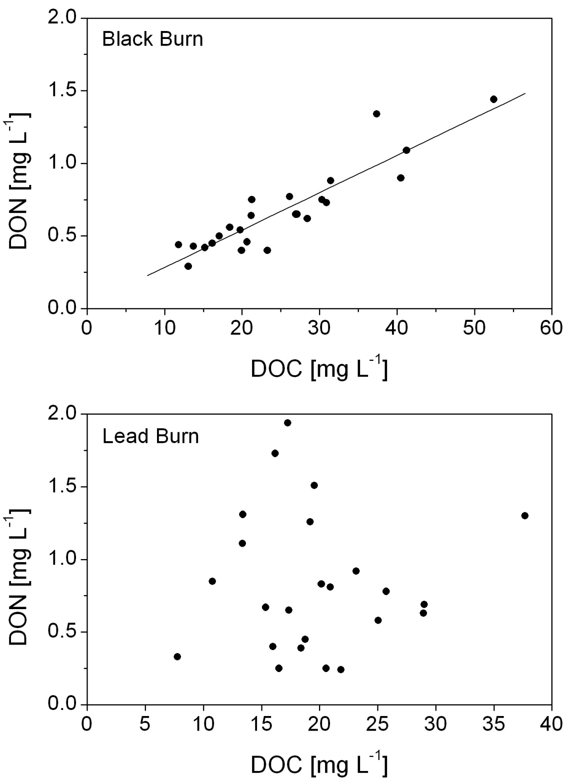


Figure 4.4: Relationship between DOC and DON concentrations from fortnightly samples from Black Burn (top) and Lead Burn (bottom) in 2008.

Table 4.5: Spearman rank correlation coefficient ρ of significant correlations (p = 0.05, two-tailed) between concentrations of different chemical species.

	Black Burn	Lead Burn
NO_3^--N - NH_4^+-N	0.86	ns
NO_3^--N - DOC	-0.51	-0.58
NO_3^--N - DON	ns	-0.56
DON - DOC	0.85	ns

ns = not significant

4.3.3 Measurements at high flows

As fluxes associated with high flow events can make a significant contribution to annual fluxes, one aim of this study was to conduct high frequency measurements during several (four) high flow events (Figure 4.5). Those measurements, whilst rarely capturing the complete storm event, were used to establish concentration-discharge relationships and improve our annual downstream flux estimates (see section 4.3.4). A regression analysis was carried out to test relationships between discharge and streamwater concentrations of samples collected fortnightly and during high flow events (Table 4.6). Scatter plots between streamwater concentrations and log discharge are shown in Figure 4.6. In both streams, discharge was negatively related with NO_3^--N and positively to DOC concentrations. However, while Black Burn discharge was also positively related with DON concentration, no such relationship was observed for Lead Burn.

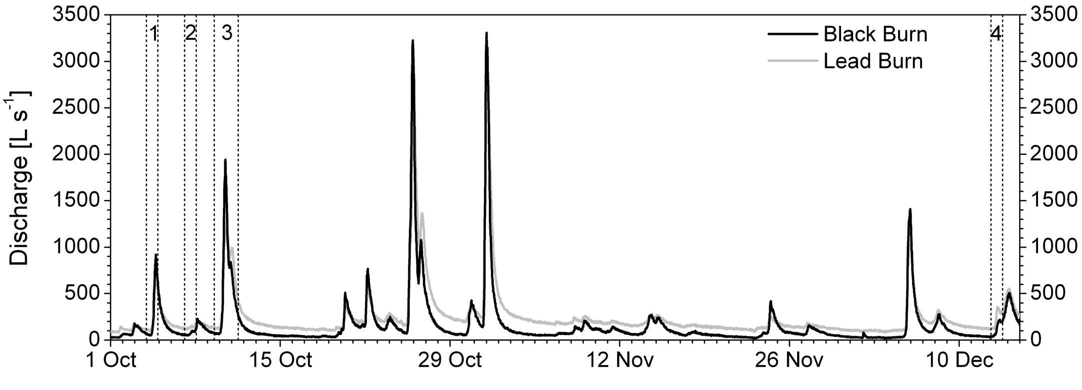


Figure 4.5: Continuous discharge data from October to December 2008. Periods of high frequency samplings 1, 2, 3 and 4 are indicated by dotted lines.

Table 4.6: Coefficients of determination r^2 calculated between log discharge and streamwater concentrations of both streams.

	Black Burn	Lead Burn
NH_4^+-N	0.02	0.00
NO_3^--N	0.04* (-)	0.25* (-)
DON	0.15* (+)	0.01
DOC	0.13* (+)	0.25* (+)

* regression slope significant (p = 0.05, two-tailed), (-) = negative slope, (+) = positive slope

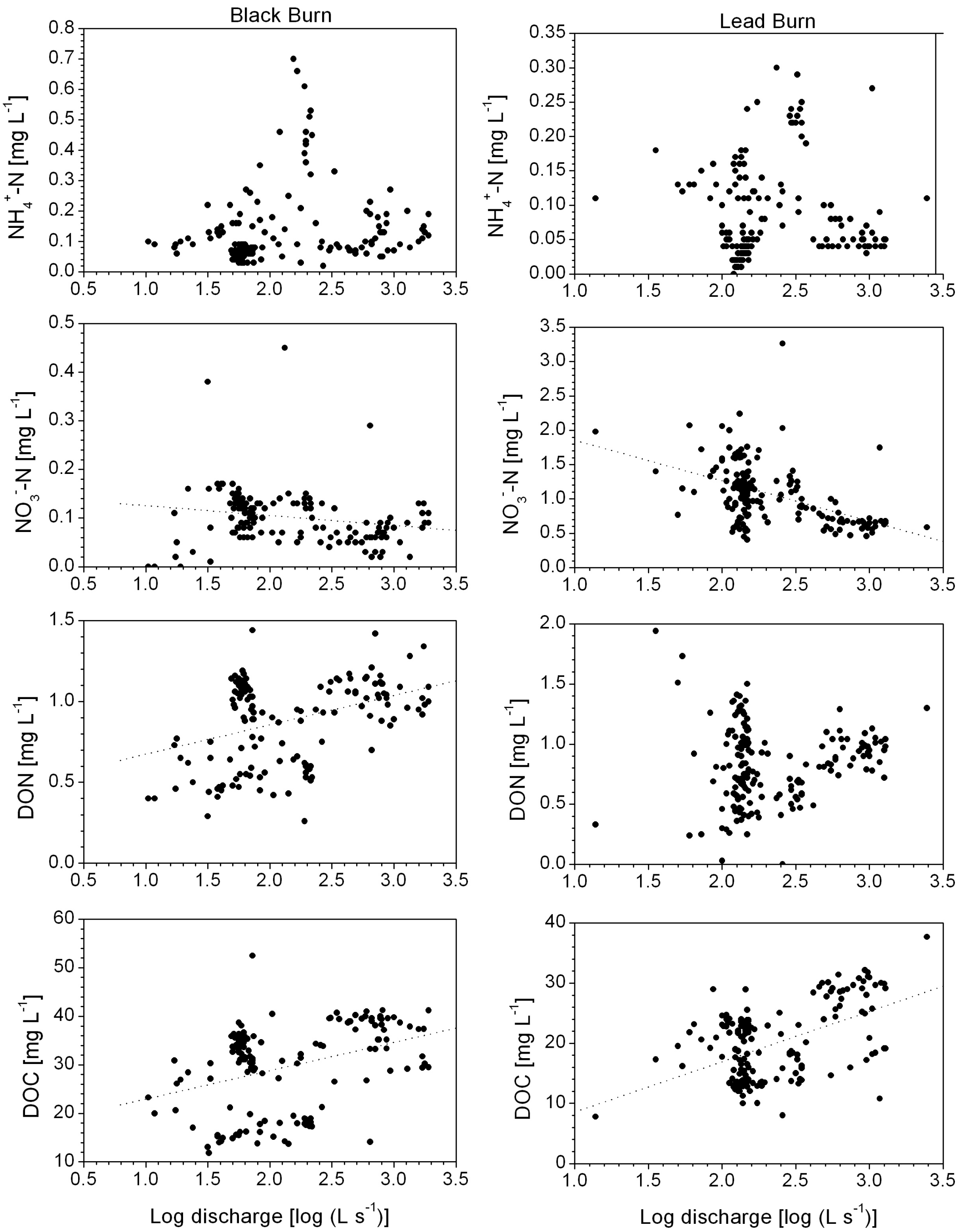


Figure 4.6: Scatter plots of streamwater concentrations and log discharge of Black Burn (left) and Lead Burn (right). Regression analysis and significance are summarised in Table 4.6.

4.3.4 Catchment fluxes

Annual downstream fluxes of NH_4^+-N, NO_3^--N, DON and DOC for 2008 were calculated using both data from fortnightly sampling and from high frequency sampling during high flow events (Table 4.7). The contribution of NH_4^+-N, NO_3^--N, DON to the catchment TDN flux of both streams is illustrated in Figure 4.7.

Table 4.7: Annual downstream fluxes of Black Burn and Lead Burn for 2008 (± SE)

	Black Burn [kg ha^{-1} yr^{-1}]	Lead Burn [kg ha^{-1} yr^{-1}]
NH_4^+-N	1.01 (± 0.001)	0.63 (± 0.000)
NO_3^--N	0.66 (± 0.001)	6.76 (± 0.015)
DON	7.02 (± 0.006)	7.02 (± 0.006)
DOC	235.3* (± 7.57)	184.5* (± 5.07)

* 10 kg C ha^{-1} yr^{-1} is equivalent to 1 g C m^{-2} yr^{-1}

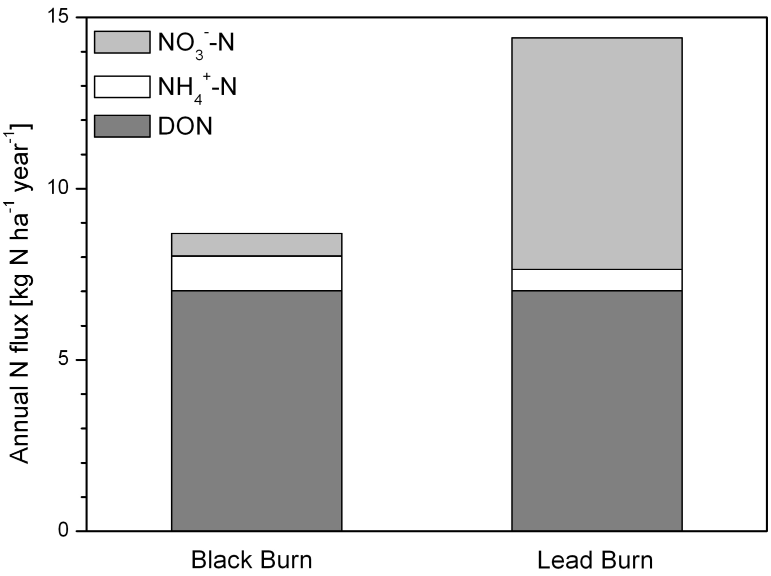


Figure 4.7: Composition of the annual catchment TDN flux in Black Burn (left) and Lead Burn (right).

The Lead Burn TDN flux (14.4 kg ha^{-1} yr^{-1}) is 66% higher than the TDN flux for Black Burn (8.7 kg ha^{-1} yr^{-1}). This difference is mainly due to the NO_3^--N flux in Lead Burn being about 10 times higher than in Black Burn. The relative contributions of the different N components to the total flux therefore vary considerably. In Black Burn, DON makes up the largest proportion (81%), followed by NH_4^+-N (12%) and NO_3^--N (8%). In contrast, DON (49%) and NO_3^--N (47%) make a similar contribution to the total flux in Lead Burn. The NH_4^+-N flux, although relatively small, is 60% higher in Black Burn compared to Lead Burn. Annual DOC fluxes were also higher in Black Burn.

4.3.5 Spatial concentration variability

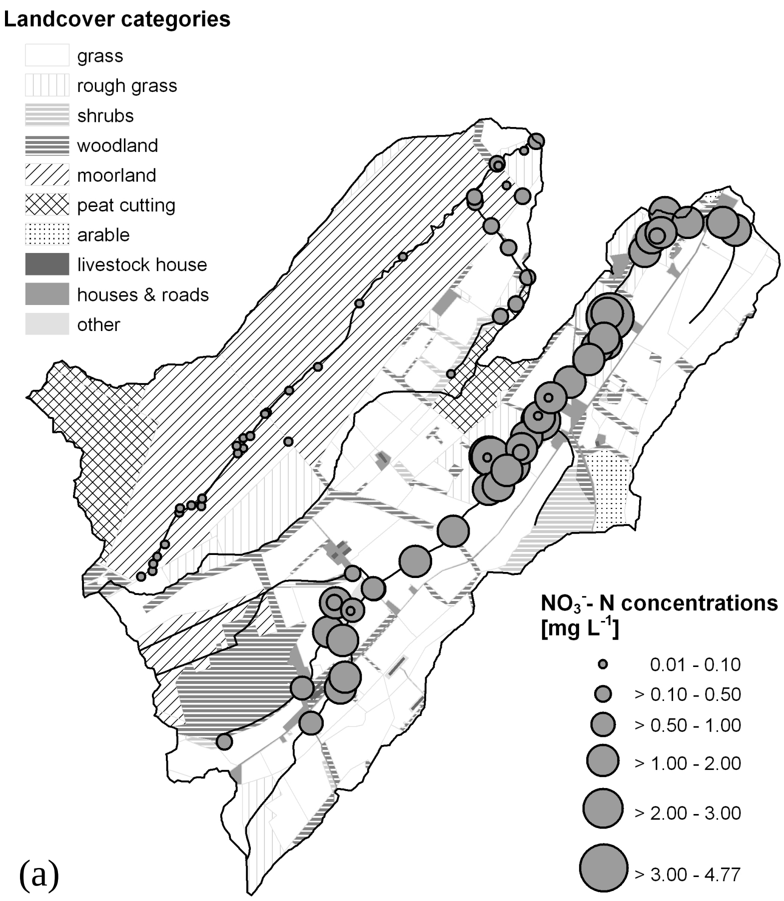
Thirty-six sampling locations within the Black Burn catchment and 46 sampling locations within the Lead Burn catchment were sampled at stable low flow conditions on three separate occasions (summer, autumn, winter 2008). From these three values, an annual mean concentration for each sample location was calculated (Figure 4.8). Table 4.8 shows the mean, median and range of those annual mean concentrations for both catchments.

Table 4.8: Variability of spatial annual mean concentrations* [mg L^{-1}] within the catchments (SD = standard deviation).

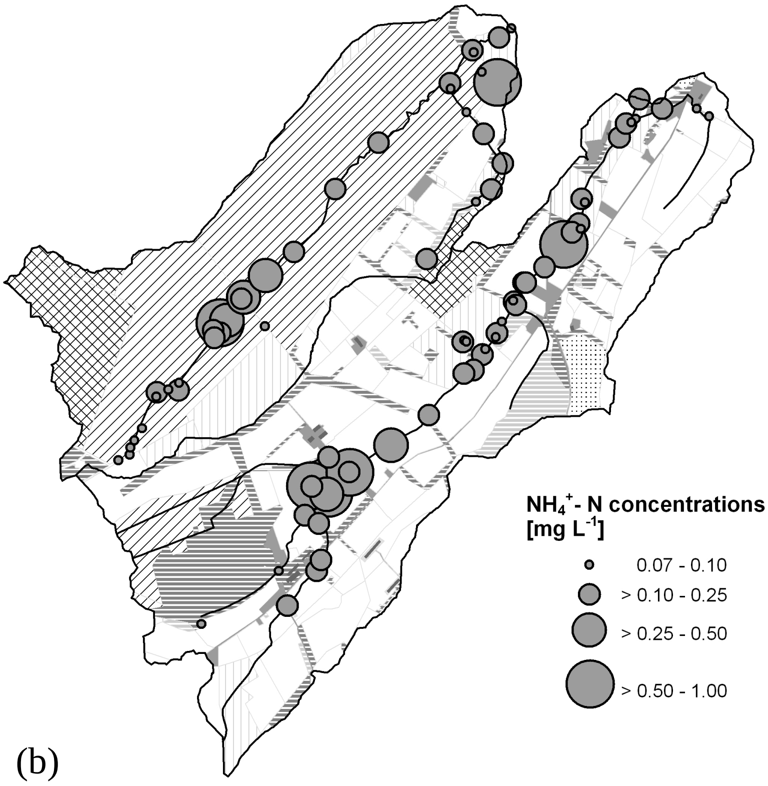
		Black Burn	Lead Burn
NH_4^+-N			
	Mean	0.17	0.20
	Median	0.11	0.14
	SD	0.18	0.19
	Range	0.07-0.97	0.07-0.84
NO_3^--N			
	Mean	0.08	1.32
	Median	0.05	1.30
	SD	0.09	0.87
	Range	0.01-0.39	0.02-4.77
DON			
	Mean	0.92	0.73
	Median	0.84	0.66
	SD	0.26	0.30
	Range	0.59-1.71	0.13-1.93
DOC			
	Mean	31.1	18.7
	Median	28.0	15.7
	SD	7.9	7.7
	Range	17.3-53.9	7.9-51.2

* For each sampling location, annual means were calculated from sampling in July, September and December 2008 (n = 3).

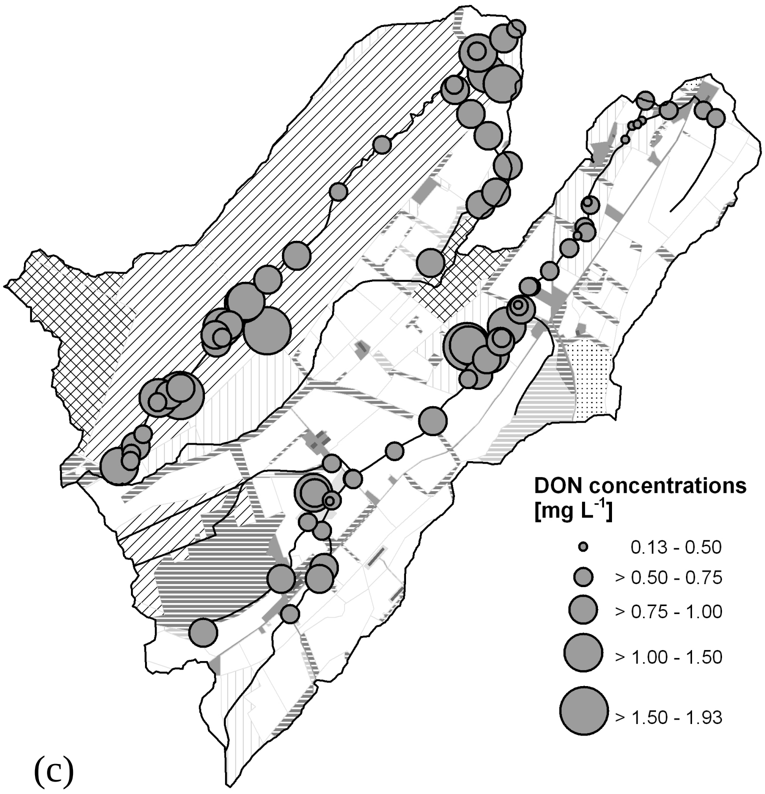
In relative terms, the greatest spatial variability within each catchment was shown by the inorganic N fraction. In the Black Burn, the standard deviation relative to the mean was 108% for NH_4^+-N and 112% for NO_3^--N; for Lead Burn, it was 95% and 66%, respectively. The dissolved organic fraction was more variable in Lead Burn with standard deviations of 41% for both DON and DOC, compared to 28% and 26% in Black Burn. Spatial differences in streamwater concentrations between the streams were tested using the Whitney-Mann *U* test (p = 0.05). Ammonium concentrations were not significantly different between the two catchments, although NO_3^--N, DON and DOC varied significantly. The clearest differences were for NO_3^--N concentrations with Lead Burn characterised by >16 times higher mean concentration than Black Burn. Means of spatial DON and DOC concentrations are greater in Black Burn than in Lead Burn.



(a)



(b)



(c)

Figure 4.8: Maps of annual mean concentrations derived from spatial samplings in July, September and December 2008: (a) NO_3^-, (b) NH_4^+, and (c) DON.

4.3.6 *Relationships between spatial concentrations and nitrogen input*

Nitrogen input to land through agricultural activities, such as grazing livestock and fertiliser applications, were calculated for both catchments and their individual subcatchments. The N input from agricultural activities per catchment varied substantially between Black Burn (12.1 kg N ha^{-1} yr^{-1}) and Lead Burn (51.9 kg N ha^{-1} yr^{-1}). Grazing livestock contributed the majority of those inputs in both catchments. In the Black Burn catchment, 73% of the agricultural N input was derived from grazing livestock, whereas organic fertiliser contributed 17% and mineral fertiliser 10%. In the Lead Burn catchment, grazing livestock contributed 51%, organic fertiliser 31% and mineral fertiliser 18%. Compared to the agricultural N input, the input from atmospheric deposition was estimated to be smaller at 8.2 kg N ha^{-1} yr^{-1} to the Black Burn catchment and 12.3 kg N ha^{-1} yr^{-1} to the Lead Burn catchment.

Based on the pattern of drainage the Black Burn catchment (6.2 km^2) was divided into 8 subcatchments and the Lead Burn catchment (8.9 km^2) into 10 subcatchments. A regression analysis was carried out between subcatchment N input (land use and deposition) and streamwater concentrations at the outlet of each subcatchment (Table 4.9, Figure 4.9). As the residence time for N in the catchment is not known, the underlying assumption of the regression analysis is that N inputs remain similar from year to year. Both streams showed significant negative relationships between NH_4^+-N concentrations and N input and significant positive relationships between NO_3^--N concentrations and N input. Thus, the higher the N input from land use and atmospheric deposition, the lower the streamwater NH_4^+-N concentrations and the higher NO_3^--N concentrations. For DON concentrations, no strong relationship was observed in either catchment.

Table 4.9: Coefficients of determination r² calculated for N input through land use and atmospheric deposition and concentrations of subcatchments in Black Burn and Lead Burn.**

	Black Burn	Lead Burn
NH_4^+-N	0.92*(-)	0.77*(-)
NO_3^--N	0.67*(+)	0.61*(+)
DON	0.38	0.14
DOC	0.78*(-)	0.16

* regression slope significant (p = 0.05, two-tailed), (-) = negative slope, (+) = positive slope
** one sample from one Lead Burn subcatchment taken in July was left out as with a very high NH_4^+ concentration (2.2 mg L^{-1}) and a very low NO_3^- concentration (0.03 mg L^{-1}) it is likely to represent a local anomaly rather than the subcatchment characteristics.

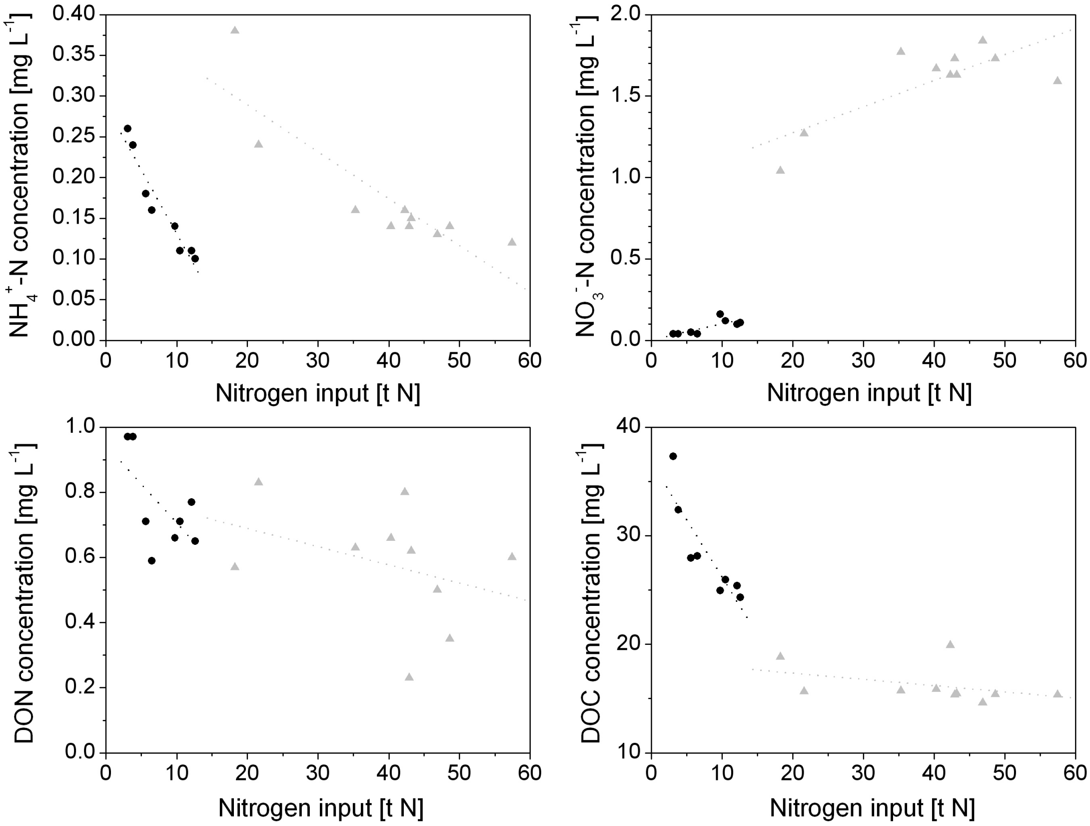


Figure 4.9: Scatter plots of N input and concentrations of subcatchments in Black Burn (black) and Lead Burn (grey). Linear fitted regressions are indicated as dotted lines.

4.4 Discussion

4.4.1 Concentrations and sources of NH_4^+

Ammonium concentrations in both the Black Burn and Lead Burn were relatively low compared with concentrations of other forms of N. However, NH_4^+ concentrations were higher than in 28 Scottish streams studied by Chapman et al. (2001), who reported an annual mean concentration of 0.03 mg NH_4^+-N L^{-1} compared to 0.15 and 0.13 mg L^{-1} for the Black Burn and Lead Burn, respectively. Chapman et al. (2001) also found that NH_4^+ concentrations were constant through the seasons and accounted for 5% of TDN. A similar pattern was observed in Lead Burn, although in Black Burn NH_4^+ concentrations showed a tendency to be higher during winter. The annual contribution of NH_4^+-N to TDN was also much higher (16%) in Black Burn. The dominance of peat soils in the Black Burn catchment is likely to have a significant effect on streamwater NH_4^+ concentrations. Previous studies have found that waterlogged peat catchments associated with anaerobic conditions inhibit the oxidation of NH_4^+ to NO_3^- allowing deposited NH_4^+ to transfer into ground and surface waters (Cresser et al., 2004; Evans et al., 2000). The atmospheric N deposition to the Black Burn catchment has been estimated by Vogt et al. (2011, Chapter 3, this volume) to be 8.2 kg ha^{-1} yr^{-1}, 60% consisting of NH_x deposition.

The influence of wet peaty soils on streamwater NH_4^+ concentrations is a likely explanation as to the seasonal differences in Black Burn and the differences between Black Burn and Lead Burn. These findings are consistent with a negative relationship between streamwater NH_4^+ concentrations and N input (Figure 4.9), suggesting that the main source of NH_4^+ in streamwater are the wetter peaty soils which receive less agricultural N inputs. Furthermore, short lived concentration increases at the beginning of the sampled high flow events (not shown) suggest that the source of NH_4^+ in streamwater could be very shallow and close to the stream. Our results may thus indicate that catchments with wet peaty soils in areas subject to atmospheric N pollution are especially vulnerable to NH_4^+ leaching into streamwaters.

4.4.2 Concentration and sources of NO_3^-

The streamwater NO_3^- concentrations observed in this study with annual means of 0.12 mg L^{-1} in Black Burn and 1.53 mg L^{-1} in Lead Burn were similar to those observed in other comparable studies. For example, Betton et al. (1991) collected information from >700 sites in Britain and found that mean annual NO_3^--N concentrations in Scotland were <1 mg L^{-1}, whereas Chapman et al. (2001) found that a group of 28 Scottish catchments had a mean annual NO_3^--N concentration of 0.39 mg L^{-1}, accounting for 50% of the TDN. Streamwater NO_3^- concentrations were significantly positively related to more N input, which was primarily driven by agricultural land use (Table 4.9, Figure 4.9). Furthermore, Lead Burn NO_3^- concentrations were negatively correlated with discharge. This dilution of streamwater NO_3^- during storm events has been observed in other agricultural systems (Durand et al., 2011), although increasing concentrations with increasing discharge have also been observed (e.g. Van Herpe and Troch, 2000). Hence, it is generally considered that NO_3^- reacts inconsistently to changes in discharge which leads to complex hysteresis patterns (e.g. Oeurng et al., 2010). This is probably due to contrasting NO_3^- concentrations in different water sources contributing to the streamwater and to variation in their contribution during the storm events (Durand and Torres, 1996). Well drained soil porewater and shallow groundwater exhibit usually high NO_3^- concentrations, while rainwater, wet soil porewater and deep groundwater are usually less concentrated (Durand et al., 2011). Depending on the water pathways in the catchment, one or another of these stores may be predominant during storm events, causing either dilution or concentration. In the Lead Burn catchment, less concentrated water types predominate during high flows, which is probably wet soil porewater, since it is associated with high DOC (see below).

4.4.3 Concentrations and sources of dissolved organic N and C

Dissolved organic nitrogen concentrations of both streams in this study were relatively high with annual means of 0.67 mg L^{-1} in Black Burn and 0.74 mg L^{-1} in Lead Burn, compared to those reported in the literature. Chapman et al. (2001) report a range of annual DON concentrations in 28 Scottish catchments of 0 to 0.87 mg L^{-1}. On average, DON concentrations reported by Chapman et al. (2001) were 0.18 mg L^{-1} and accounted for 40% of TDN. Lower DON concentrations were reported by Willett et al. (2004). They analysed 102 streams in Wales and found DON concentrations ranging from 0.03 to 0.22 mg L^{-1} with a mean of 0.09 mg L^{-1}. The contribution of DON to TDN varied from 4 to 85% with a mean of 39%. Adamson et al. (1998) found slightly higher DON concentrations of 0.37 mg L^{-1} (79% of TDN) in a peat dominated catchment in England. Although the concentrations found in the current study were much higher than the reported means, they lie within the range that Chapman et al. (2001) found for Scottish sites. Contributions of DON to TDN vary greatly in the literature with peat dominated catchments usually showing a larger contribution of organic N compared to NO_3^-.

Positive relationships between DON/DOC and discharge were found in the Black Burn (as found for Black Burn DOC in Dinsmore et al., 2010), indicating storm events lead to an increase in streamwater DOC concentrations through flushing of riparian soil water DOC into the stream (e.g. Boyer et al., 1997; Morel et al., 2009; Scott et al., 1998). Furthermore, DON and DOC concentrations in Black Burn were positively correlated which indicates that they originate from the same sources (Bernal et al., 2005). The overall DOC:DON ratio of the Black Burn streamwater of 34:1 (derived from the ratio of annual downstream fluxes) was close to the C:N ratio of peat.

Lead Burn DON and DOC concentrations appeared to follow different temporal patterns (Figure 4.3), with large changes in DOC:DON indicating changes in the dominant source (e.g. Hagedorn et al., 2000). High DOC:DON ratios are usually connected to terrestrial sources (e.g. Mattsson et al., 2009) and lower ratios to in-stream sources (Chapman et al., 2001). In addition, organic fertiliser or sewage catchment inputs may reduce the C:N ratio (Helliwell et al., 2001). Thus, Lead Burn streamwater DON may have multiple significant sources with contributions of organic-rich soil porewater causing high streamwater C:N ratios and agricultural activities causing leaching of organic matter with low C:N ratios, probably linked to animal excretion.

4.4.4 Catchment fluxes

Annual TDN fluxes of 8.7 kg N ha^{-1} yr^{-1} and 14.4 kg N ha^{-1} yr^{-1} for Black Burn and Lead Burn, were in the range of total N flux values (< 2 to > 40 kg N ha^{-1} yr^{-1}) quoted for European catchments (Billen et al., 2011). The present study sites were characterised by a relatively large fraction of DON, with NO_3^- not significantly exceeding the threshold of 1.5 mg N L^{-1} for high potential threat on ecosystems, as estimated by Grizzetti et al. (2011). Nevertheless, the larger catchment N fluxes at

Lead Burn compared with Black Burn were associated with a predominantly agricultural catchment. The 66% higher annual TDN flux of the agricultural Lead Burn catchment compared to the peat dominated Black Burn catchment was entirely due to the higher NO_3^- flux, which was positively related to the magnitude of N inputs (Figure 4.9). In both catchments, the DON accounted for the largest contribution to the TDN flux with 81% in Black Burn and 49% in Lead Burn. In European streams, DON has been observed to contribute between 11% and 100% to TDN (Durand et al., 2011). Dissolved organic nitrogen fluxes of 7.0 kg N ha^{-1} yr^{-1} in both studied streams were relatively high compared to fluxes reported in the UK of 3.1 kg N ha^{-1} yr^{-1} in a Welsh moorland catchment (Reynolds and Edwards, 1995) and fluxes of 5.7, 6.0 and 6.5 kg N ha^{-1} yr^{-1} in three English peat catchments (Adamson et al., 1998).

Annual DOC fluxes of the Black Burn catchment of 235 kg ha^{-1} yr^{-1} are in line with fluxes of 186 kg ha^{-1} yr^{-1} in 2007 and 322 kg ha^{-1} yr^{-1} in 2008, measured by Dinsmore et al. (2010) at a site further upstream, representing thus the peat rich part of the catchment.

In both study catchments, a high proportion of the total annual discharge was delivered during high flow events. Hence, it is important to include event sampling to accurately quantify annual nutrient exports from the catchments. In this study, high frequency concentration data were collected during four high flow events. Thus, a large number of high flow events during 2008 were not sampled which may have an effect on the calculated flux.

4.5 Conclusions

The effect of agricultural land use on streamwater concentrations and fluxes of NH_4^+, NO_3^- and DON was evident from both the inter- and intra-catchment variability. The use of detailed farm inventory data to establish high resolution, i.e. field specific, N input was a key component of this analysis and to our knowledge this is the first time that it has been done at this level of detail. The overall agricultural N input to the Lead Burn (grassland dominated) catchment of 51.9 kg N ha^{-1} yr^{-1} was about four times higher than the input to Black Burn (moorland dominated) catchment of 12.1 kg N ha^{-1} yr^{-1}. These inputs were larger than the corresponding inputs from atmospheric deposition at 12.3 kg N ha^{-1} yr^{-1} and 8.2 kg N ha^{-1} yr^{-1}, respectively.

The annual downstream TDN flux of the Lead Burn catchment of 14.4 kg ha^{-1} yr^{-1} was 66% higher than the Black Burn flux of 8.7 kg ha^{-1} yr^{-1}. This difference between the catchments was due to the differing NO_3^- flux of 6.8 kg ha^{-1} yr^{-1} and 0.7 kg ha^{-1} yr^{-1}, respectively. Thus, despite the relatively high DON flux of 7.0 kg ha^{-1} yr^{-1} in both catchments, the contribution of DON to the TDN flux differed from 49% in Lead Burn to 81% in Black Burn.

Intensive spatial sampling of streamwater chemistry gave further insight into land use effect on streamwater concentrations. In particular, streamwater NO_3^- was the only species significantly positively related to N input from agricultural land use and atmospheric deposition within each catchment. By contrast, NH_4^+ was significantly negatively related to N input and therefore linked to the wet peaty rich areas of the catchments soils which receive less agricultural N input and inhibit (due to anaerobic conditions), the oxidation of NH_4^+ to NO_3^-. Sources of DON and DOC differ between the catchments. In Black Burn, DON and DOC mainly originated from peat runoff, indicated by positive relationships with discharge and the similarity between the streamwater DOC:DON ratio and the peat C:N ratio. The sources of Lead Burn DON and DOC change frequently as streamwater DOC:DON ratios were highly variable. Potential sources of Lead Burn DON and DOC may be high C:N soil porewater and low C:N organic matter leached from agricultural sources, in particular from manure applications and grazing livestock excreta. The additional agricultural sources of DON in the Lead Burn catchment are likely to be the cause of the similarly high DON flux as in the Black Burn catchment, while at the same time the Lead Burn DOC flux remains much lower. Our data therefore show that streamwater chemistry is sensitive to landscape scale changes in N input and that the organic N fraction is a significant component of fluvial N export which should receive much more attention in future studies that focus on the determination of specific sources and processes within agricultural areas, particularly in grazed areas.

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5 Paper IV: Estimation of nitrogen budgets for contrasting catchments at the landscape scale

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Abstract

Complete nitrogen (N) budgets were estimated for two contrasting catchments (agricultural grassland vs. semi-natural moorland) at the landscape scale in southeast Scotland. A soil budget approach was used as catchment soil input and output fluxes can be related to the downstream export flux. Local scale atmospheric dispersion modelling and detailed farm and field inventories provided high resolution estimations of input fluxes. Agricultural land surface input (i.e. grazing excreta, organic and synthetic fertiliser) accounted for most of the catchment N inputs, however, atmospheric deposition also accounted for a significant contribution, particularly in the moorland catchment. The estimated catchment N budgets highlight the key uncertainties, particularly N_2 emissions from total denitrification and stream N export. Nitrogen budgets suggest that the grazed grassland catchment stored 5.9 +7.4/-12.3 (error) kg N ha^{-1} yr^{-1} in soil, vegetation and groundwater. In contrast, the moorland catchment was estimated to release 1.6 +3.8/-3.4 (error) kg N ha^{-1} yr^{-1} from the catchment storage. The catchment N retention, i.e. the amount of N which is either stored within the catchment or lost through atmospheric emissions, was

estimated to be 3% of the net anthropogenic input in the moorland and 55% in the grassland catchment. These values are different from the larger catchment retentions of net anthropogenic input estimated within Europe at the regional scale ranging between 50% and 90% with an average of 82% (Billen et al., 2011). This study emphasises the need for detailed budget analyses to identify the N status of catchments at the landscape scale.

Keywords: nitrogen budget, landscape scale, catchment budget

5.1 Introduction

Human activities dominate the global nitrogen (N) budget by adding reactive forms of nitrogen (N_r) to the environment (Galloway et al., 2004). The main forms of anthropogenic N_r are reduced (e.g. NH_3, NH_4^+), oxidised (e.g. NO_2, N_2O, NO_3^-) and organic forms of N (e.g. urea). Between 1995 and 2005 alone, the anthropogenic production of N_r increased by 20% which is largely due to agricultural activities (Galloway et al., 2008). The environmental consequences of N_r input can be significant, such as the loss of biodiversity in terrestrial and aquatic ecosystems through eutrophication and acidification (Vitousek et al., 1997). Nitrogen balances as indicators of the environmental pressure have been developed at various scales (de Vries et al., 2011), ranging from the farm and field level (e.g. Ammann et al., 2009; Schröder et al., 2003) to the regional catchment (e.g. Billen et al., 2009; Howarth et al., 1996) and global scale (e.g. Bouwman et al., 2005; Seitzinger et al., 2005). However, studying catchment budgets at the landscape scale is a critical part of quantifying the impact of disturbance on nutrient cycling (McDowell and Asbury, 1994). A landscape is defined as a spatially heterogeneous area that includes interacting ecosystems and extends from hectares to many square kilometres (Turner and Gardner, 1994). Nitrogen is transported between those ecosystems by atmospheric, hydrological and human transfers (Cellier et al., 2011). Fluxes of N_r at the landscape scale are particularly relevant as both management decisions (e.g. through farm activities) and the environmental impact occur at this scale, particularly in European rural landscapes (Cellier et al., 2011; Sutton et al., 2007). However, the accurate estimation of N fluxes at high spatial resolution poses a significant challenge (de Vries et al., 2011), e.g. the estimation of the spatially variable N dry deposition represents one of the key uncertainties in quantifying nitrogen inputs to terrestrial ecosystems (Tang et al., 2009).

In this study, we estimate N budgets for two adjacent catchments at the landscape scale. The catchments contrast in their land use: one is dominated by semi-natural moorland, the other by grazed grassland. To the authors' knowledge, this is the first study of catchment N budgets at the landscape scale which includes high resolution atmospheric modelling combined with a detailed spatial landscape inventory of field specific agricultural activities. The study shows how an analysis of nitrogen budgets at the landscape scale can provide insight into the main N fluxes, the key uncertainties and overall implications for the environmental status of the landscape.

5.2 Methods

5.2.1 Study landscape

As part of the NitroEurope Integrated Project (Sutton et al., 2007), a landscape study area of 6 km x 6 km was established in southern Scotland, an area with a temperate oceanic climate, for detailed inventory of agricultural activities, N_r concentration and flux measurements (for further details see Vogt et al. 2011, Chapter 3 & 4, this volume). For the present assessment of N budgets, two contrasting catchments within the landscape were compared: a moorland dominated catchment (621 ha) and a grassland dominated catchment (895 ha). Together these two catchments represent 42% of the study landscape.

A detailed local survey of all farms and fields in the study landscape was conducted throughout 2008. This provided land cover and farm activity data, which were collated into a relational database and spatially represented in a geographical information system (ArcGIS, ESRI). Land cover and soil types within the landscape together with the boundaries of the two studied catchments are shown in Figure 5.1. Moorland and rough grass, including peat cutting and areas of both deciduous and coniferous afforestation dominate the northwestern part of the landscape and the Black Burn catchment (the moorland catchment), whereas the southeast and the Lead Burn catchment (the grassland catchment) is dominated by agricultural land (see Table 5.1 for catchment details). Agricultural activities in the landscape range from extensive beef cattle and sheep farming to intensive poultry farming, with 24 poultry houses in the study area containing nearly 1.5 million laying hens.

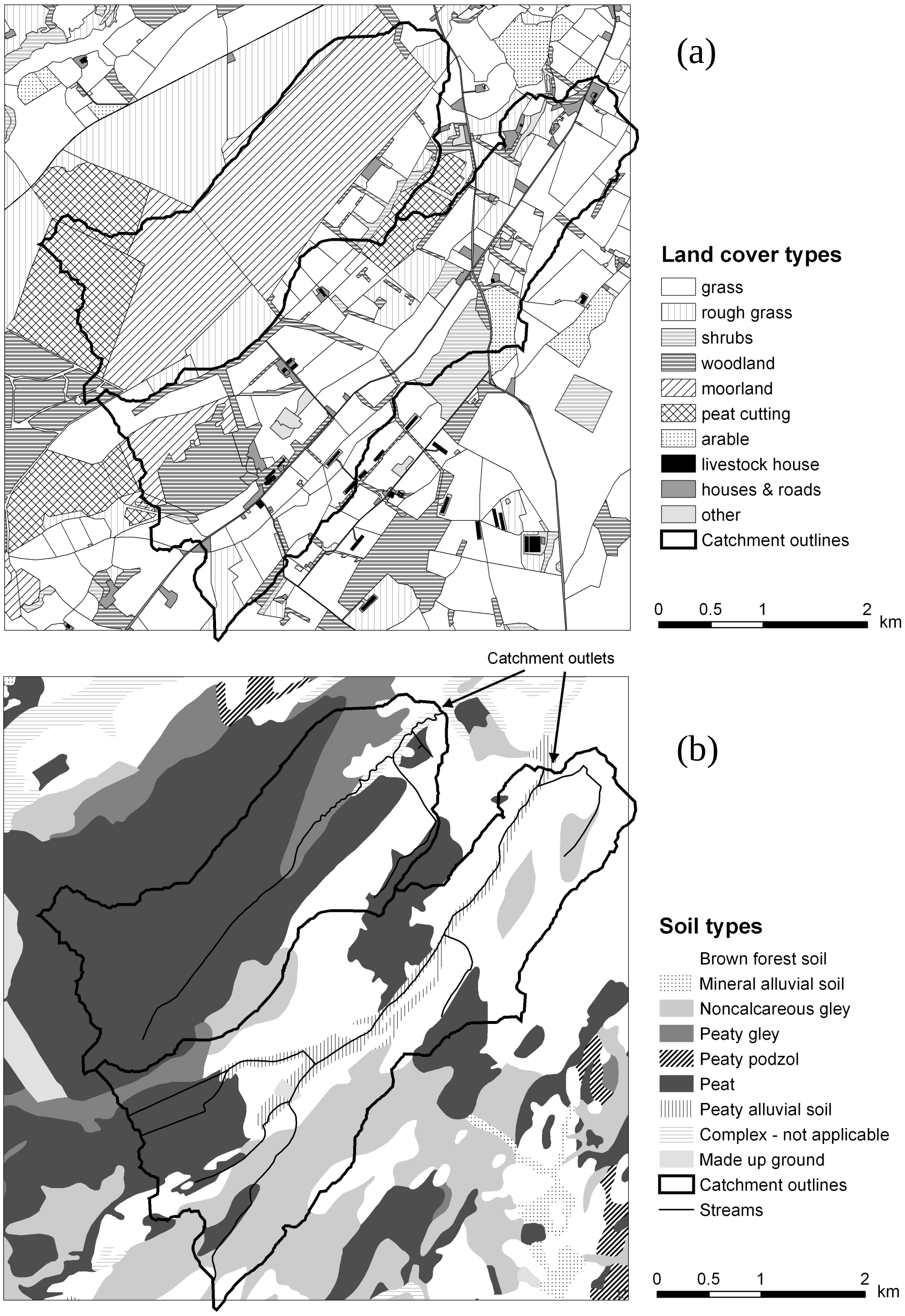


Figure 5.1: Maps of land cover (a) and soil types[a] (b) within the study landscape with outlines of the two studied catchments[b].

[a] © The Macaulay Land Use Research Institute 2008 (license MI/2008/296). Soil types are based on the Scottish Soil Survey, the equivalent FAO names are: brown forest soil = cambisol, mineral alluvial soil = fluvisol, noncalcareous gley = gleysol, peaty gley = humic gleysol, peaty podzol = humic podzol, peat = histosol, peaty alluvial soil = humic fluvisol

[b] Some features of this map are based on data licensed from Intermap Technologies Inc. © 2010 Intermap Technologies Inc. All Rights Reserved.

Table 5.1: Characteristics of the moorland and the grassland catchment

	Moorland catchment	Grassland catchment
Area (km²)	6.2	8.9
Average altitude	270	280
% main land cover types:		
Grassland	11	59
Rough grass	10	10
Moorland	63	5
Peat cutting	12	2
Woodland	2	14
% main soil types:		
Brown forest soils	16	48
Peat	67	21
Peaty gleys	10	2
Noncalcareous gleys	5	22

5.2.2 Catchment N budgets

Annual N budgets of the moorland and the grassland catchment were assessed for 2008 using a soil budgeting approach (de Vries et al., 2011; Oenema et al., 2003), i.e. all N that enters and leaves the soil was accounted for. This type of budget was chosen as the inputs and outputs are directly associated with the catchment soils and linked to the downstream flux. The balance of the N input and output terms indicates the change within the catchment of N storage over time. It was noted that there were significant N fluxes occurring in connection with the poultry housing, i.e. housing emissions and farming operations such as feed import, manure export or livestock export. The N budget accounting for these fluxes will be detailed in a future study, but for the purpose of a soil budget approach, housing emissions and farming operations not affecting the catchment land surface were considered decoupled from the soil and are thus excluded from this approach, except via the deposition fluxes resulting from the housing emissions.

The catchment soil N budgets were calculated as

$$\begin{aligned}\Delta N / \Delta t = {} & N_{NH3\,dry\,dep} + N_{NHx\,wet\,dep} + N_{NOy\,dep} + N_{syn\,fert} + N_{org\,fert} + N_{excreta} + N_{bio\,fix} \\ & - N_{NH3} - N_{N2O} - N_{NO} - N_{N2} - N_{harvest} - N_{grass} - N_{stream}\end{aligned} \tag{1}$$

where $\Delta N/\Delta t$ is the change in N balance (ΔN) over time (Δt); $N_{NH3\ dry\ dep}$ is the atmospheric dry deposition of NH_3; $N_{NHx\ wet\ dep}$ is the atmospheric wet deposition of NH_x; $N_{NOy\ dep}$ is the atmospheric dry and wet deposition of NO_y; $N_{syn\ fert}$ is the N content in applied synthetic fertiliser; $N_{org\ fert}$ is the N content in applied organic fertiliser; $N_{excreta}$ is the amount of N excreted by grazing livestock; $N_{bio\ fix}$ is the biological N_2 fixation; N_{NH3}, N_{N2O}, N_{NO} *and* N_{N2} are emissions of NH_3, N_2O, NO and N_2 to the atmosphere; $N_{harvest}$ is the N offtake through harvested vegetation for silage and hay production; N_{grass} is the N offtake through harvested grass by grazing livestock; N_{stream} is the downstream export flux of total dissolved nitrogen.

The uncertainties of individual budget terms are given by estimated positive and negative errors (section 5.3.7). The overall uncertainty of the N balance ($E_{\Delta N / \Delta t}$) was calculated as the square root of the sum of the error (E) squares, hereby accounting for the depending variables N_{grass} and $N_{excreta}$:

$$E_{\Delta N / \Delta t} = \mathrm{sqrt}[(E_{NH3 dry\ dep})^2 + (E_{NHx\ wet\ dep})^2 + (E_{NOy\ dep})^2 + (E_{syn\ fert})^2 + (E_{org\ fert})^2 + (E_{grass} - E_{excreta})^2 + (E_{bio\ fix})^2 + (E_{NH3})^2 + (E_{N2O})^2 + (E_{NO})^2 + (E_{N2})^2 + (E_{harvest})^2 + (E_{stream})^2] \quad (2)$$

In the following sections the method of quantifying individual budget terms and their uncertainties is described.

5.2.3 Catchment N inputs

5.2.3.1 Atmospheric deposition

The spatial and temporal variability of atmospheric NH_3 across the landscape, in which the two catchments are contained, was described in detail by Vogt et al. (2011, Chapter 3, this volume). Monthly mean NH_3 concentrations at 31 sites were measured through 2008 with ALPHA passive diffusion samplers (Tang et al., 2001). Sites were distributed across the study landscape with an emphasis on capturing high and low emission areas as well as the variability around the sources. Ammonia emissions were calculated for each individual field, manure store and livestock house, based on the field and farm activities on monthly basis combined with emission rates for each activity (manure housing, storage and spreading, grazing and fertiliser application, Vogt et al. 2011, Chapter 3, this volume). The emission estimates were used in the Local Area Dispersion and Deposition model (LADD) (Hill, 1998; Loubet et al., 2009) at a resolution of 25 m x 25 m to model spatial concentrations and dry deposition of NH_3 within the study landscape. Measured annual mean concentrations of the 31 sampling sites were used for verification of the LADD model. As NH_3 has a high dry deposition rate (Cellier et al., 2011) and is thus expected to be driven by local sources, NH_3 dry deposition inputs to the studied catchments ($N_{NH3\ dry\ dep}$) were calculated from fluxes modelled by LADD within the study landscape only. This N budget term is considered to carry a relatively low uncertainty of ±20% due to the detailed local study, involving an intensive measurement programme and local atmospheric dispersion modelling.

Catchment atmospheric inputs due to NH_x wet deposition ($N_{NHx\ wet\ dep}$) and dry and wet deposition of NO_y ($N_{NOy\ dep}$) which are expected to be largely driven by non-local sources (e.g. Hertel et al., 2011; Sutton et al., 1998) were simulated by the UK national model FRAME (Fine Resolution Atmospheric Multi-pollutant Exchange) (Dore et al., 2007; Hallsworth et al., 2010) at a resolution of 1 km x 1 km. The contribution of particulate ammonium (NH_4^+) to NH_x dry deposition is considered minor compared to NH_3 (e.g. Asman et al., 1998; Duyzer, 1994). FRAME simulations were combined with land cover data of 25 m x 25 m resolution in order to apply land cover specific deposition rates to different land cover types, as described in detail by Vogt et al. (2011, Chapter 3, this volume). For the atmospheric inputs of NH_x wet deposition and dry and wet deposition of NO_y, national modelling at a relatively fine scale resolution, applied to local land cover data, is considered to deliver adequate deposition estimates for this purpose with a relatively low uncertainty in the range of ±20%.

5.2.3.2 Agricultural land surface input

Agricultural inputs to the land surface through applications of synthetic fertiliser ($N_{syn\ fert}$), organic fertiliser ($N_{org\ fert}$) and excreta of grazing livestock ($N_{excreta}$) were derived from farm activity data in Vogt et al. (2011, Chapter 4, this volume). A typical N content was used for the different manure types (DEFRA, 2010). The N input from grazing livestock was estimated using grazing records and daily N excretion data as used in the UK NH_3 inventory (Misselbrook et al., 2009). The N input through applications of synthetic fertiliser are considered accurate with an estimated uncertainty of ±10% as this value is known by individual farmers. A higher uncertainty of ±30% is associated with the N input through applications of organic fertiliser, as a typical N content was applied to different manure types as specified by the farmer. The uncertainty associated with the N input through grazing livestock excreta is estimated to be ±50% as the N content of the grazed grass is not known.

5.2.3.3 Biological N_2 fixation

Experimentally derived data on biological N_2 fixation are rare in the literature. DeLuca et al. (2008) measured fixation rates to mainly range between 1 and 2 kg ha^{-1} yr^{-1} in a Swedish boreal forest; Limmer and Drake (1996) cite a mean fixation rate of 1 kg ha^{-1} yr^{-1} from studies conducted in European and Northamerican forests and Waughman and Bellamy (1980) measured a fixation rate of 0.7 kg N ha^{-1} yr^{-1} in German bogs. The catchment N input through biological N_2 fixation ($N_{bio\ fix}$) was thus estimated to be 1 kg N ha^{-1} yr^{-1} for both catchments as there was little or no clover in most of the grassland. The N input through biological N_2 fixation is highly uncertain (-70/+300%) as this term is estimated from a few experimentally derived literature values.

5.2.4 Catchment N outputs

5.2.4.1 Gaseous emissions from land surfaces

Ammonia emissions were calculated by applying UK average emission factors (EF) of the UK emission inventory to the land surface inputs from synthetic and organic fertiliser and grazing excreta (Misselbrook et al., 2009). The housing emissions and manure storage emissions were excluded from the calculation of catchment budgets as discussed in section 5.2.2. As calculations of NH_3 emissions are based on the local farm inventory and national emission factors, there uncertainty is estimated relatively low, at ±20%.

Direct N_2O emissions are associated with soil N input ($N_{NH3\ dry\ dep}$ + $N_{NHx\ wet\ dep}$ + $N_{NOy\ dep}$ + $N_{syn\ fert}$ + $N_{org\ fert}$ + $N_{excreta}$) and were calculated using the method of Lesschen et al. (2011), which uses specific EFs depending on the source of N input, soil type and annual precipitation. The clay soil EF parameterisation in Lesschen et al. (2011) was selected linked to the modification of the catchment surface soils by agricultural activity. The local 2008 annual precipitation of 1208 mm was used to derive a precipitation adjustment factor (f_p) in the method of Lesschen et al. (2011) of 2.16. Peat cutting areas and other peat bog areas without agricultural activities are assumed to have insignificant N_2O emissions due to soil C/N ratios exceeding 25 (Klemedtsson et al., 2005). Also, measurements within the moorland catchment showed negligible N_2O emissions (Drewer et al., 2010). Indirect N_2O emissions, i.e. degassing of N_2O from waters resulting from soil leaching, were estimated using the 2009 IPCC Guidelines (De Klein et al., 2009).

Emissions of NO were derived by applying a Tier 1 EF of 2.6% to synthetic fertiliser N applied as recommended in the EEA/EMEP guidelines (McGlade and Vidic, 2009). As there is no specific EF recommended for applications of organic fertiliser and grazing livestock excreta a literature value of 0.5% was applied (Bouwman et al., 2002).

The uncertainty of N_2O and NO emissions is estimated at ±50% as they are based on data from the farm inventory and also literature emission factors. Emissions are known to vary substantially depending on the soil conditions.

Emission factors of N_2 are highly uncertain. Recently, Ammann et al. (2009) applied a literature-derived EF of 12.5% to N inputs from fertilisation and biological N_2 fixation for a Swiss grassland with an error of ±100%. Jones et al. (*in prep.*) modelled N_2 emissions for a grazed grassland in southern Scotland (< 10 km from this study landscape) and calculated an EF of 10% of applied N through grazing excreta and synthetic and organic fertilisation (Skiba, pers. com. 2011). This N_2 EF from Jones et al. (*in prep.*) was applied to all fields with agricultural activities in our study catchments. It is noted that there is a large uncertainty (-50/+200%) associated with this budget term (section 5.3.7).

5.2.4.2 Harvested vegetation

Nitrogen output also occurs via removal of vegetation by harvesting ($N_{harvest}$) and by grazing livestock (N_{grass}). The amount of harvested crop and grass removed by farmers for silage and hay production was derived from the farm survey activity data with a specific N content applied to each main crop type (Møller et al., 2005). The uncertainty of $N_{harvest}$ is thus estimated at ±20%. The amount of N removed through grass consumption by grazing livestock (N_{grass}) was estimated as follows:

$$N_{grass} = N_{excreta} + N_{animal} - N_{feed}$$

where $N_{excreta}$ is the amount of N excreted by grazing livestock (section 5.2.3.2), N_{animal} is the N content in the exported wool and meat, calculated according to Jones et al. (*in prep.*) using N content values in Roche (1995) and Flindt (2003) and N_{feed} is the N content of the supplementary animal feed, derived by farm activity data and a specific N content of different feed types (Møller et al., 2005). Both N_{animal} and N_{feed} are estimated to have an uncertainty of ±20%, however combined with the ±50% uncertainty associated with $N_{excreta}$, the uncertainty of N_{grass} is estimated at ±50%.

5.2.4.3 Fluvial export

Annual downstream fluxes (N_{stream}) of total dissolved nitrogen (TDN), which is the sum of NH_4^+-N, NO_3^--N and DON, were established by Vogt et al. (2011, Chapter 4, this volume) by sampling at gauged outlets of the two catchments at both fortnightly and hourly intervals during selected high flow events through 2008. As N_{stream} is based on local measurements conducted throughout the study year, it is considered to carry a relatively low uncertainty, conservatively estimated at ±20%. Additional information on sources of streamwater N concentrations within the catchments was derived by spatial sampling at stable low flow conditions, conducted in July, September and December 2008.

5.3 Results and discussion

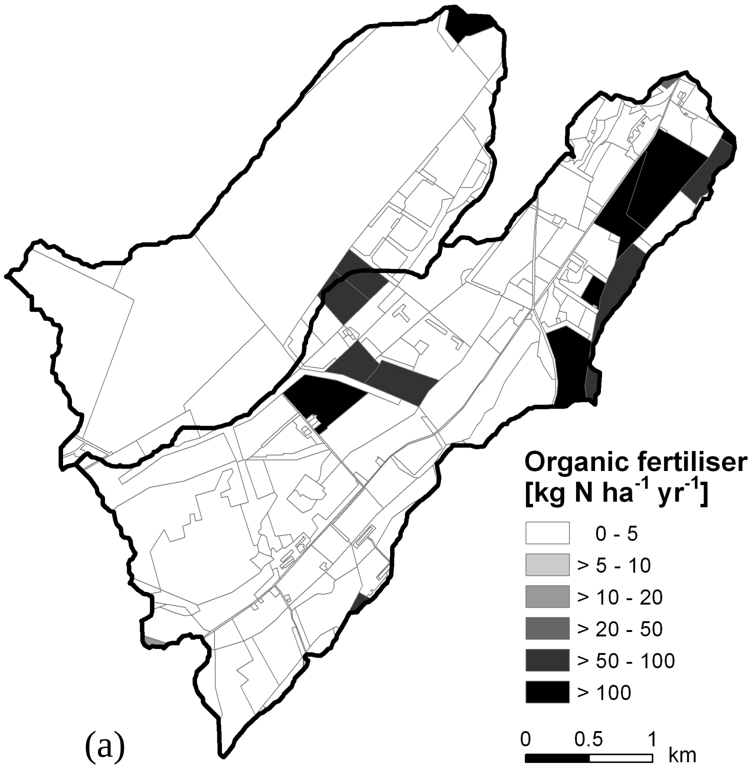
The following sections introduce spatially differentiated results of the agricultural land surface N input, the associated land surface N emissions and atmospheric N deposition and discuss fluvial N export. In addition, the catchment N inputs and output terms are summarised and the overall catchment N budgets are given with a discussion of uncertainty.

5.3.1 Agricultural land surface N input

Agricultural N inputs to the land surface were dominated by grazing excreta in both catchments (Figure 5.2). In the moorland catchment, grazing excreta contributed 73%, organic fertiliser 17% and synthetic fertiliser 10% to the land surface input. In the grassland catchment, grazing excreta contributed 51%, organic fertiliser 31% and synthetic fertiliser 18%. Most of the N in grazing excreta originated from sheep with contributions of 89% in the moorland and 69% in the grassland catchment. Fields within the grassland catchment received more than four times the land surface N input (51.9 kg N ha^{-1} yr^{-1}) than fields in the moorland catchment (12.1 kg N ha^{-1} yr^{-1}).

The range of land surface inputs between fields was large, varying from 0 to 261 kg N ha^{-1} yr^{-1} in the moorland and up to 346 kg N ha^{-1} yr^{-1} in the grassland catchment.

No fields of the study landscape are located within a Nitrate Vulnerable Zone (NVZ), thus agricultural practice is not restricted by the Nitrate Directive (DEFRA, 2012). However, 1% of the moorland and 4.5% of grassland catchment received manure, through organic fertiliser applications or grazing excreta, exceeding the recommended 170 kg N yr^{-1}, although it is noted that there are significant uncertainties associated with the calculation of agricultural land surface N input.



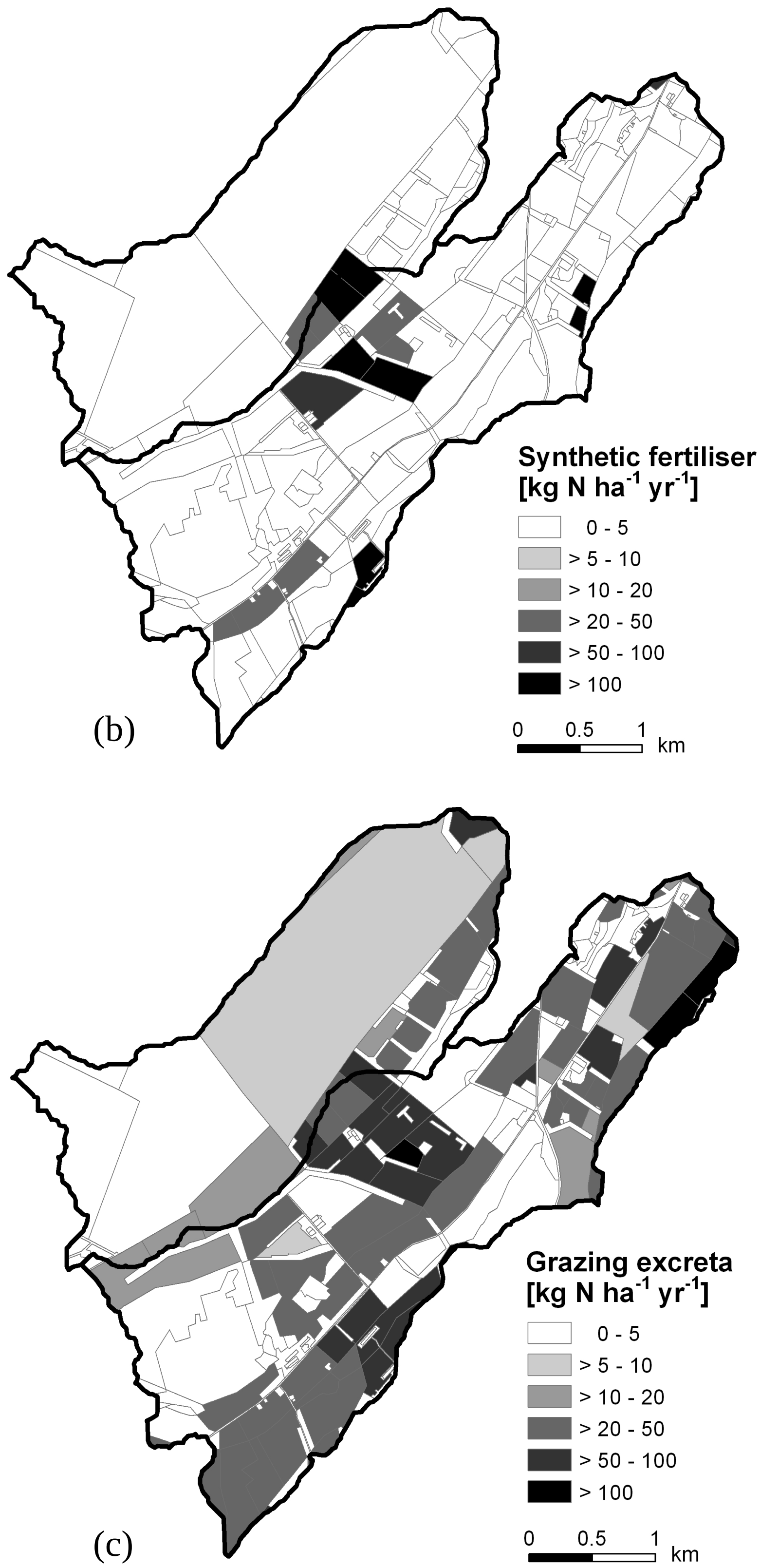


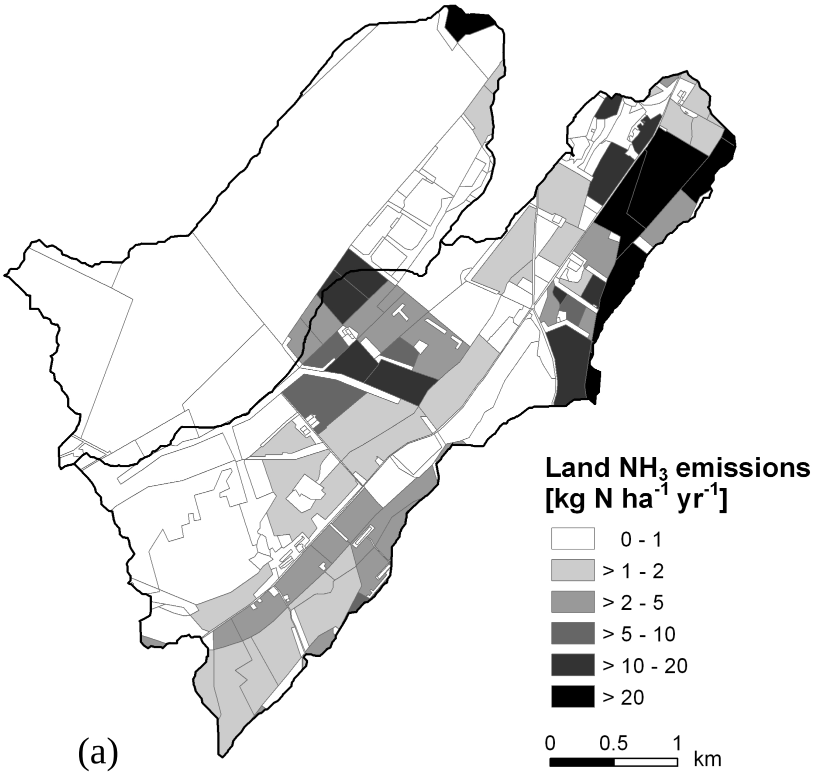
Figure 5.2: Catchment maps of field specific land surface N input through (a) organic fertiliser, (b) synthetic fertiliser, and (c) grazing livestock excreta

5.3.2 Atmospheric N emissions

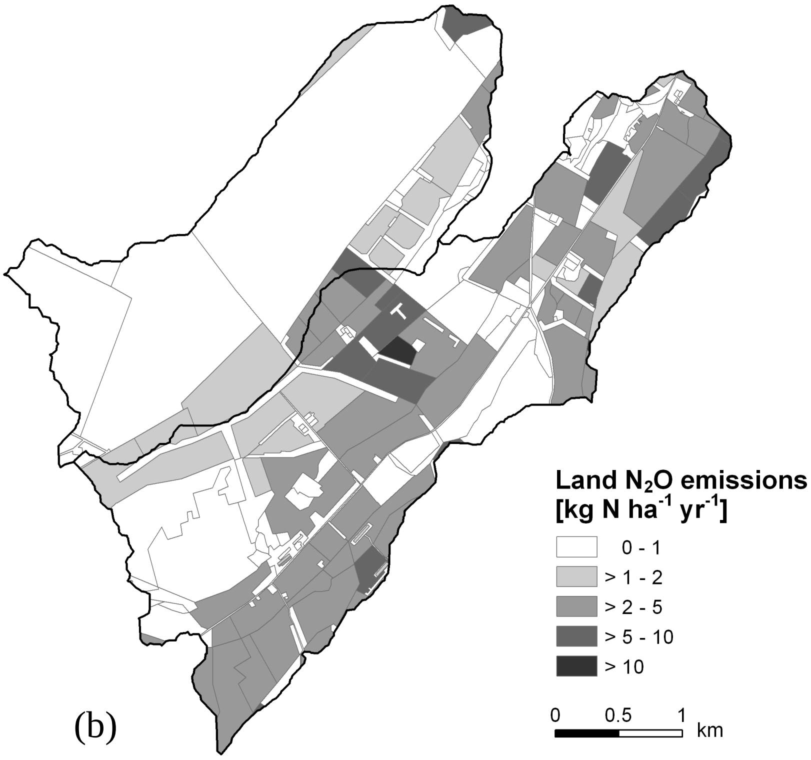
Gaseous NH_3 emissions from the catchment land surface (excluding housing and manure store emissions) are shown in Figure 5.3a. In the moorland catchment, field based emissions ranged from 0 to 48 kg N ha^{-1} yr^{-1} (mean: 0.9 kg N ha^{-1} yr^{-1}) with 58% originating from applications of organic fertiliser, 40% from grazing excreta and 2% from synthetic fertiliser. In the grassland catchment, NH_3 emissions ranged from 0 to 53 kg N ha^{-1} yr^{-1} between individual fields (mean: 4.5 kg N ha^{-1} yr^{-1}) with 66% arising from organic fertiliser, 30% from grazing excreta and 4% from synthetic fertiliser. Despite most of the agricultural land surface input originating from grazing excreta (section 5.3.1), the dominant source of NH_3 emissions were applications of organic fertiliser in both catchments due to high NH_3 volatilisation losses. In contrast, almost all N in grazing excreta (~ 95%) can be expected to enter the catchment soils and thus contribute to soil emissions of N_2O and N_2 or can be leached. Overall, 7% of the agricultural land surface input of N to the moorland catchment was estimated to be emitted as NH_3 compared with 9% in the grassland catchment.

Direct N_2O emissions from the moorland catchment averaged to 0.8 kg N ha^{-1} yr^{-1} with field emissions ranging from 0 to 7.0 kg N ha^{-1} yr^{-1} (Figure 5.3b). The grassland catchment emitted 2.4 kg N ha^{-1} yr^{-1} as N_2O with emissions ranging from 0.4 to 12.5 kg N ha^{-1} yr^{-1} between fields. Most of the direct N_2O emissions were from grazing excreta (79% in the moorland and 75% in the grassland catchment). Around 7% of the grazing excreta were estimated to be lost as N_2O in both catchments. Figure 5.3c shows field emissions of N_2 within the catchments. In the moorland catchment, N_2 emissions (1.2 kg N ha^{-1} yr^{-1}) are estimated to be similar to N_2O emissions, whereas in the grassland catchment, N_2 emissions (5.3 kg N ha^{-1} yr^{-1}) are about 2.5x higher than N_2O emisions. Emissions per field ranged from 0 to 26.3 kg N ha^{-1} yr^{-1} in the moorland and from 0 to 36.2 kg N ha^{-1} yr^{-1} in the grassland catchment. However, the uncertainties within those field based emission estimates were relatively large (see uncertainty estimates in Table 5.4) as there is substantial within field variation of N_2O and N_2 emissions due to the heterogeneity of soil processes (e.g. Hofstra and Bouwman, 2005).

Soil NO emissions were estimated to be insignificant for both catchments with emissions of 0.1 kg N ha^{-1} yr^{-1} in the moorland and of 0.3 kg N ha^{-1} yr^{-1} in the grassland catchment. The field with the highest NO emission was common to both catchments, thus the field specific emission range of 0 to 1.8 kg N ha^{-1} yr^{-1} was the same for both catchments.



(a)



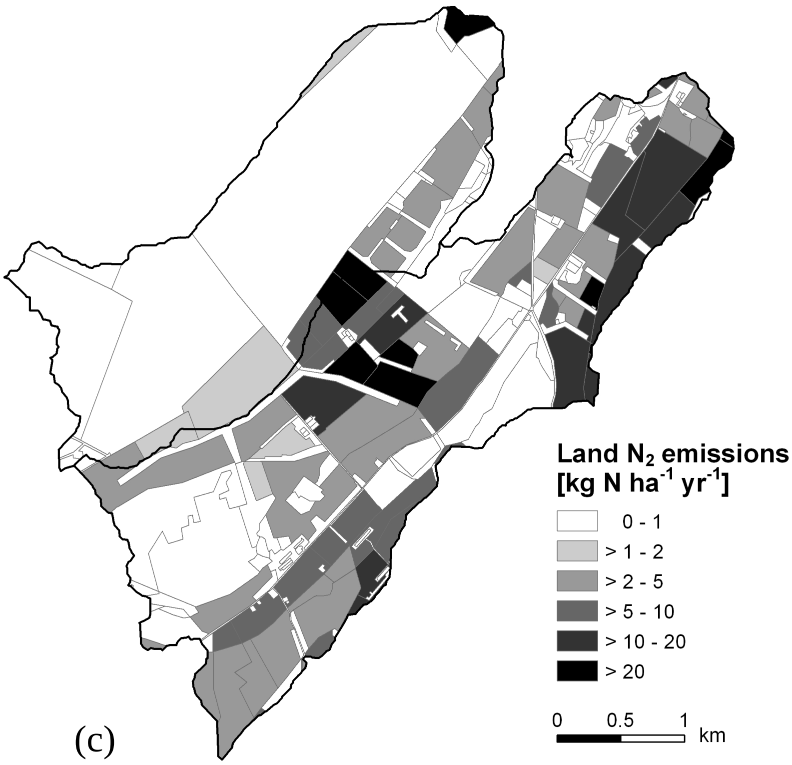


Figure 5.3: Field specific land surface emission maps of (a) NH_3 emissions, (b) direct N_2O emissions, and (c) direct N_2 emissions.

5.3.3 Atmospheric N deposition

Total atmospheric N deposition within the study landscape (including the two catchments) is shown in Figure 5.4. The total atmospheric N deposition to the two studied catchments was estimated to be 8.2 kg N ha^{-1} yr^{-1} in the moorland and 12.3 kg N ha^{-1} yr^{-1} in the grassland catchment. The estimated dry deposition of NH_3 to the study catchments ($N_{NH3\ dry\ dep}$) was estimated by modelling emissions of all agricultural NH_3 sources within the study landscape, including housing and manure storage emissions (section 5.2.3.1). Ammonia dry deposition showed a high spatial variability at 25 m x 25 m grid resolution within the catchments, ranging from 0.1 to 23 kg N ha^{-1} yr^{-1} in the moorland (mean: 2.4 kg N ha^{-1} yr^{-1}) and from 0.2 to >100 kg N ha^{-1} yr^{-1} in the grassland catchment (mean: 6.4 kg N ha^{-1} yr^{-1}). The larger input to the grassland catchment was due to the catchment containing six intensive poultry farming houses with an overall NH_3 emission of 28 t N yr^{-1}.

Catchment inputs from NH_x wet deposition were similar for both catchments (2.5 and 2.6 kg N ha^{-1} yr^{-1}, respectively), as were inputs from NO_y deposition (both 3.3 kg N ha^{-1} yr^{-1}). Atmospheric deposition to the moorland catchment was estimated to be driven by non-local sources with $N_{NHx\ wet\ dep}$ and $N_{NOy\ dep}$ contributing 71% to the total N deposition, while 52% of deposition to the grassland catchment was estimated to originate from local sources ($N_{NH3\ dry\ dep}$) and 48% from non-local sources ($N_{NHx\ wet\ dep}$ + $N_{NOy\ dep}$).

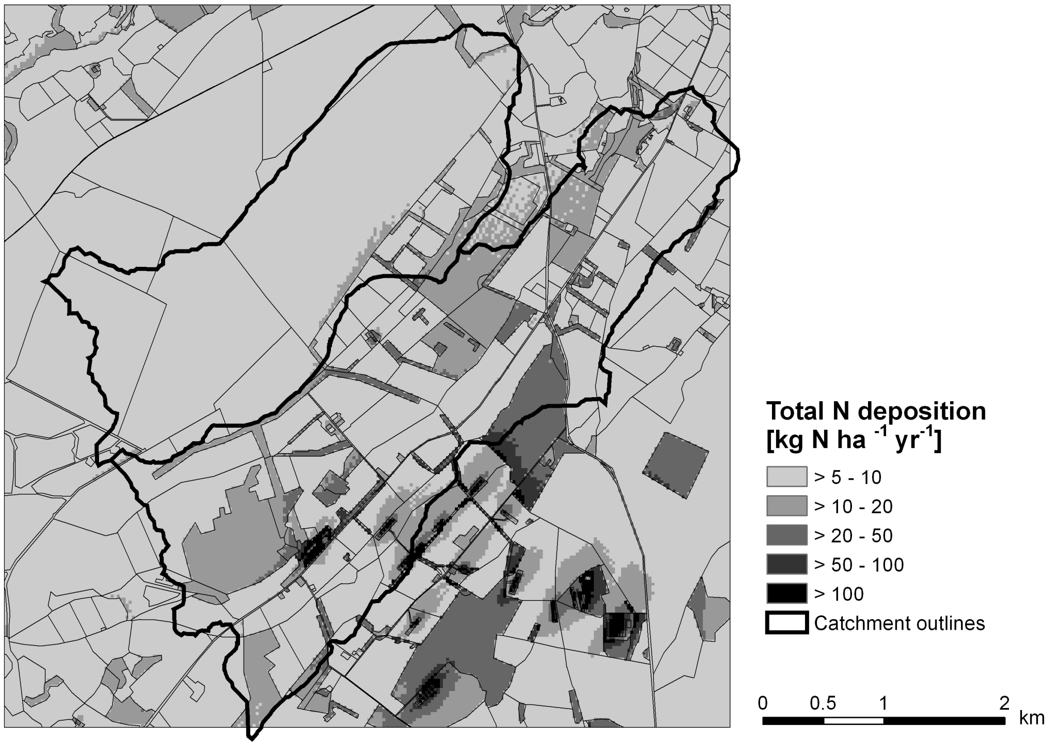


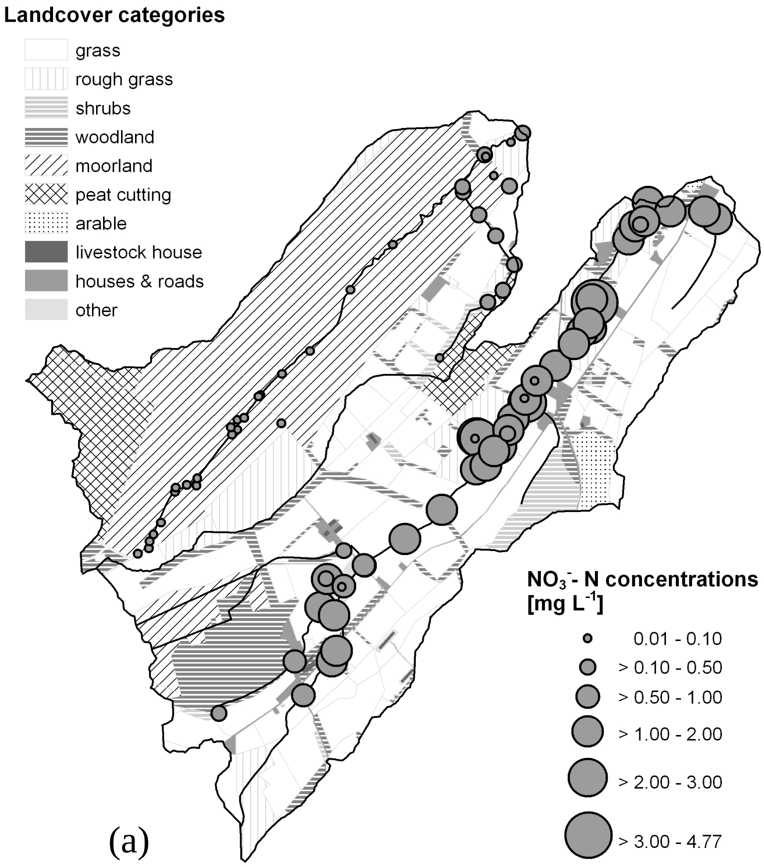
Figure 5.4: Map of total N deposition within the study landscape. Source: Vogt et al. (2011, Chapter 3, this volume)

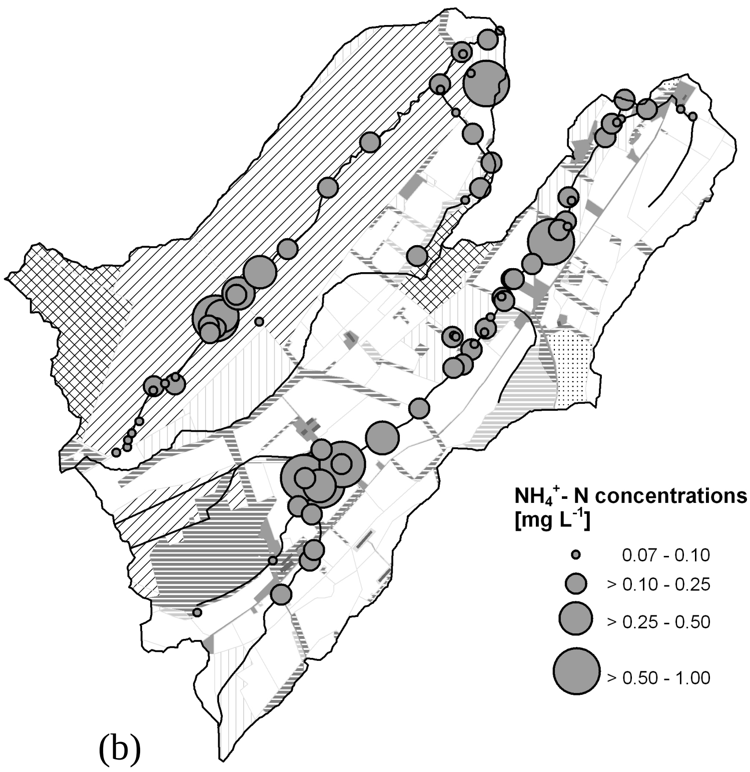
5.3.4 Fluvial N export

Both catchments were characterised by highly variable stream flow with high discharge events making an important contribution to annual downstream fluxes (Vogt et al. 2011, Chapter 4, this volume). For example, in 2008, the highest 10% of the discharge data contributed 53% to the total discharge in the moorland and 40% in the grassland catchment. The annual downstream flux (N_{stream}) of total dissolved nitrogen (TDN) was 8.7 kg ha^{-1} yr^{-1} in the moorland and 14.4 kg N ha^{-1} yr^{-1} in the grassland catchment. The difference in the TDN flux was mainly due to the significantly larger nitrate (NO_3^-) flux in the grassland catchment. Dissolved organic nitrogen (DON) contributed 81% to the TDN flux in the moorland and 49% in the grassland catchment. However, the absolute annual DON flux of 7.0 kg ha^{-1} yr^{-1} was very similar in both catchments.

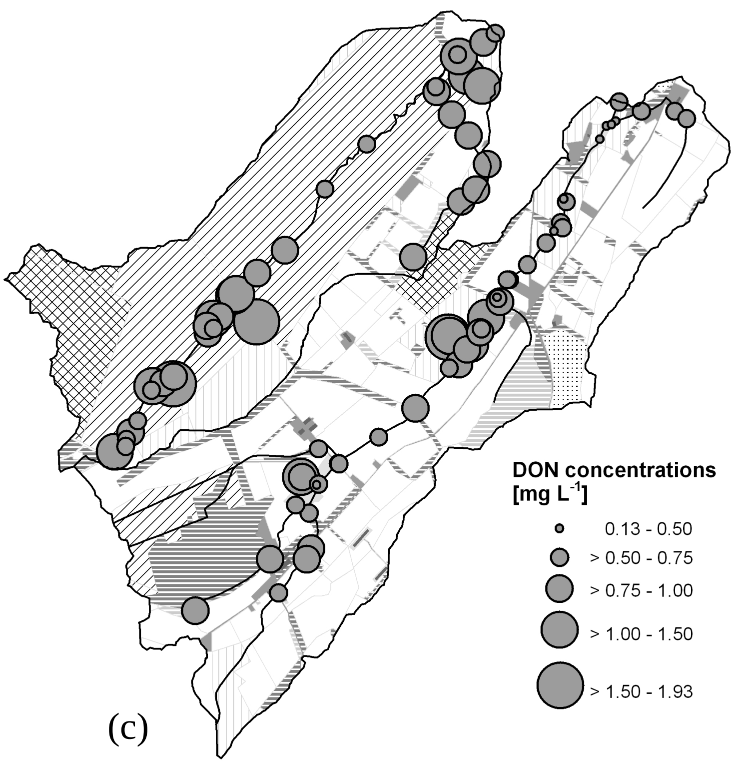
Maps of annual mean concentrations of NO_3^-, NH_4^+ and DON measured during the three spatial sampling campaigns are shown in Figure 5.5, together with the underlying land cover. The streamwater NO_3^- concentrations of both catchments have been shown to be significantly positively related to N input through agricultural land surface and atmospheric deposition (Vogt et al. 2011, Chapter 4, this volume). Ammonium concentrations were significantly negatively related to N input and could be related to the coverage of wet peaty soils (Vogt et al. 2011, Chapter 4, this volume). However, local point source contributions, such as suspected sewage discharge observed while collecting samples, may also contribute to the large spatial variability of NH_4^+ concentrations within the grassland catchment. The sources of DON can vary widely and differed between the catchments (Vogt et al. 2011, Chapter 4, this volume). In both catchments, flushing of organic-rich soil water contributed to streamwater DON concentrations, however in the grassland catchment, there were additional major sources, such as agricultural runoff.

To analyse the potential contribution of the peat cutting area to the DON as well as to the linked dissolved organic carbon (DOC) export flux of the moorland catchment, the catchment was divided into eight subcatchments based on the drainage pattern. A regression analysis between the % area of peat soil in these subcatchments and DON and DOC concentrations at the subcatchmet outlets mostly showed a positive relationship between DOC and DON concentrations and the % area of peat soil (Figure 5.6a and b). This relationship was more pronounced for DOC than DON, however in both cases there is quite a lot of scatter in the data. Other studies (e.g. Aitkenhead et al., 1999) have shown that the area of peat soil in a catchment is directly related to streamwater DOC concentration. Clark et al. (2004) found DON concentrations to be positively related to peat cover in the summer only. In this study, the relationship between DON concentrations and % area of peat soil is also the strongest in July. The same regression analysis with % peat cutting area also showed a similar positive relationship to DOC and DON concentrations (Figure 5.6c and d) with a slightly stronger relationship observed between concentrations and % peat cutting area (compared to % peat). This is likely to be a reflection of peat cutting taking place in the areas of deepest peat in the catchment leading to the enhanced effect shown in Figure 5.6c and d. The areas affected by peat cutting are mostly in the upper parts of the catchment, with the effect decreasing significantly downstream. Also, a previous study in the same moorland catchment noted that DOC concentrations were not significantly different in a large tributary originating from an area of peat cutting compared to concentrations in the main stream (Dinsmore et al., 2010). Thus, peat rich areas (whether cut or not) are considered to be the main source of streamwater DOC and DON concentrations. However, peat cutting will change hydrological flow paths which may enhance the “peat effect” on DOC and DON concentrations and contribute to higher annual fluxes because of greater runoff due to drainage. The longer term effect of peat cutting on the catchment fluvial N flux are beyond the scope of this study.





(b)



(c)

Figure 5.5: Maps of annual mean concentrations derived from spatial samplings in July, September and December 2008: a) NO_3^-, b) NH_4^+, and c) DON. Source: Vogt et al. (2011, Chapter 4, this volume).

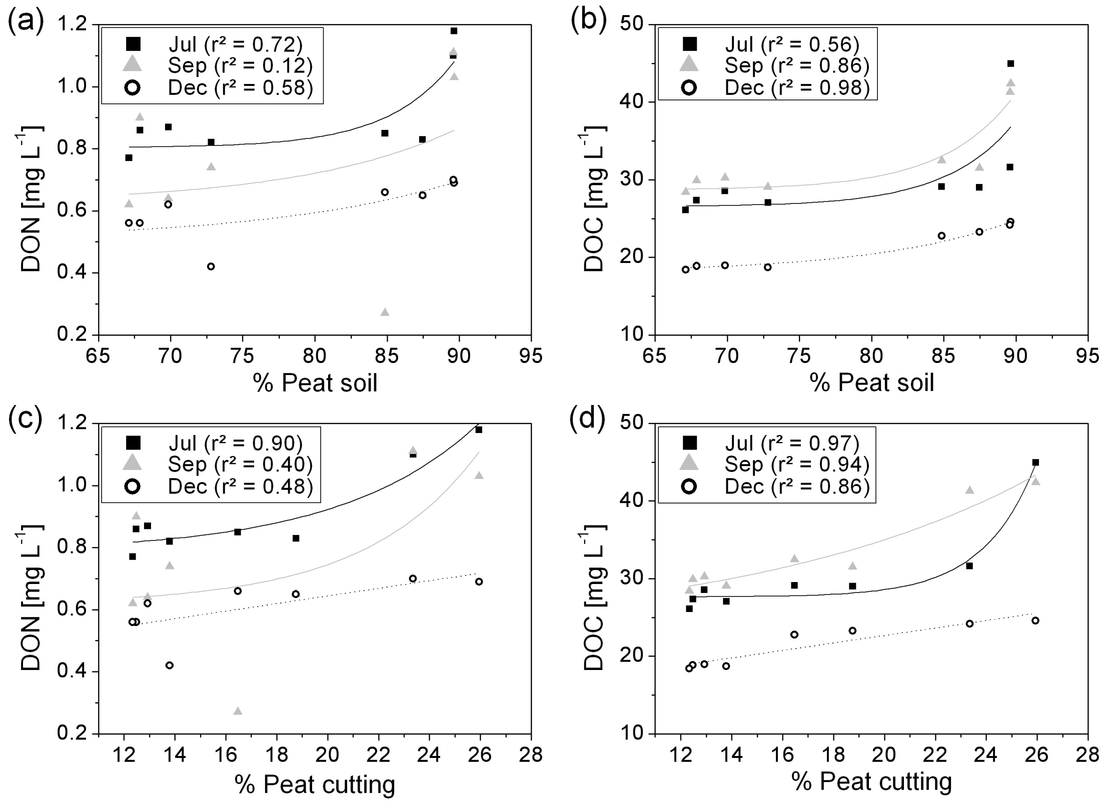


Figure 5.6: Relationships (exponential growth: y = A*exp(x/t) + y0) between % area of peat soil (a, b) and peat cutting (c, d) in eight subcatchments of the moorland catchment and spatial concentrations of DON (a, c) and DOC (b, d) at subcatchment outlets in July (black squares and line), September (grey triangles and line) and December (black circles and dotted line) with coefficients of determinations r^2 given for each campaign.

5.3.5 N inputs for the study catchments

The various components which contribute N inputs to the two study catchments are summarised in Figure 5.7 (input estimates expressed per hectare) and Table 5.2 (total input per catchment area). Overall, the inputs to the grassland catchment (65.2 kg N ha^{-1} yr^{-1}) were about three times higher than those to the moorland catchment (21.3 kg N ha^{-1} yr^{-1}). Inputs were largely driven by agricultural land surface inputs. In the grassland catchment, 80% of all N inputs originated from agricultural land surface inputs, 18% from atmospheric N deposition and 2% from estimated biological N_2 fixation. Atmospheric deposition accounted for a larger contribution in the moorland catchment with 38% of all N inputs, however, the majority (57%) originated from agricultural land surface inputs and 5% from estimated biological N_2 fixation. Grazing livestock excreta represented the largest single input source, contributing 41% to the inputs in the moorland and 40% in the grassland catchment. The fraction of the grazing excreta subject to gaseous emissions (section 5.3.2) was estimated to be around 21%, thus the majority of the catchment input through grazing excreta stayed either within the system, i.e. in soil or vegetation, or is leached into surface or groundwaters.

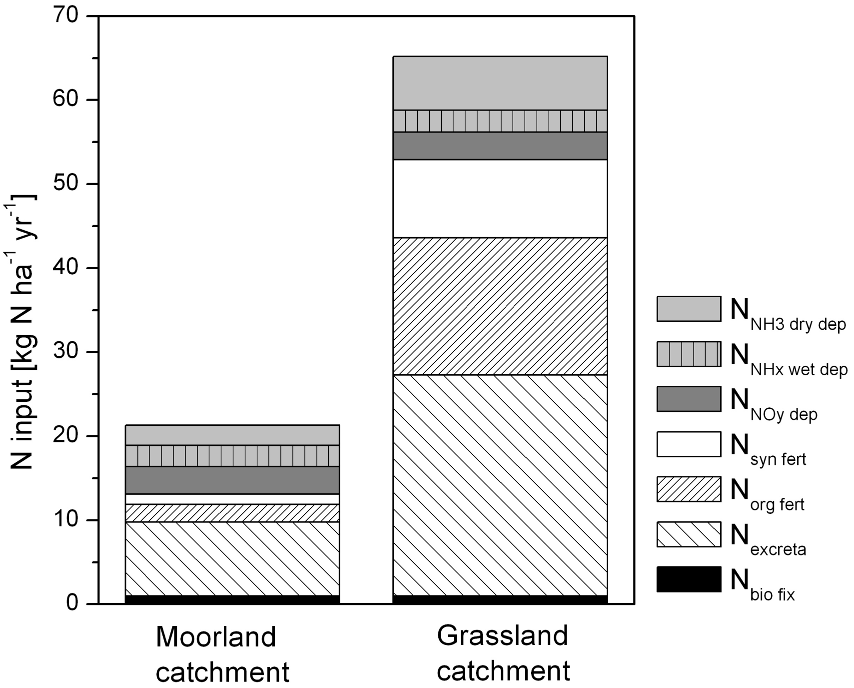


Figure 5.7: N inputs (kg N ha^{-1} yr^{-1}) to the moorland (left) and the grassland catchment (right)

Table 5.2: Catchment totals of N inputs (kg N yr^{-1})

	Moorland catchment	Grassland catchment
$N_{dry\ NH3\ dep}$	1,480	5,700
$N_{wet\ NHx\ dep}$	1,560	2,310
$N_{NOy\ dep}$	2,030	2,980
$N_{syn\ fert}$	760	8,290
$N_{org\ fert}$	1,310	14,590
$N_{excreta}$	5,460	23,570
N_{fix}	620	890
Total input	13,220	58,340

5.3.6 N outputs for the study catchments

Catchment outputs are shown as per hectare values in Figure 5.8 and as per catchment values in Table 5.3. The gaseous land surface emissions of N_r (N_{NH3} + N_{N2O} + N_{NO}) led to losses of 1.7 kg N ha^{-1} yr^{-1} from the moorland and 7.3 kg N ha^{-1} yr^{-1} from the grassland catchment. Whereas emissions of N_2O are similar to those of NH_3 in the moorland catchment, emissions from the grassland catchment were dominated by NH_3 emissions (62%). Emissions of NO were insignificant in both catchments: 0.1 kg N ha^{-1} yr^{-1} in the moorland and 0.3 kg N ha^{-1} yr^{-1} in the grassland. The estimated N_2 emissions were large compared to the N_r fluxes of the catchments, contributing 42% to the overall N emission flux from both catchments. However, the uncertainty within the N_2 emission estimations is large (see Table 5.4 in section 5.3.7).

Grazed grass (N_{grass}) constituted a large output term in both catchments, contributing 45% to the overall catchment output in the moorland and 46% in the grassland catchment. However, these losses were mostly recycled back to the soil by grazing livestock excreta ($N_{excreta}$) with $N_{excreta}$ representing 83% of N_{grass} in the moorland and 96% of N_{grass} in the grassland catchment. Thus, the main importance of this “grazing livestock N cycle” is the increased soil N dynamics associated with the grazing excreta which lead to gaseous and streamwater losses. When considering the grazed grass as a recycling budget term, the largest output fluxes of both catchments were the stream exports.

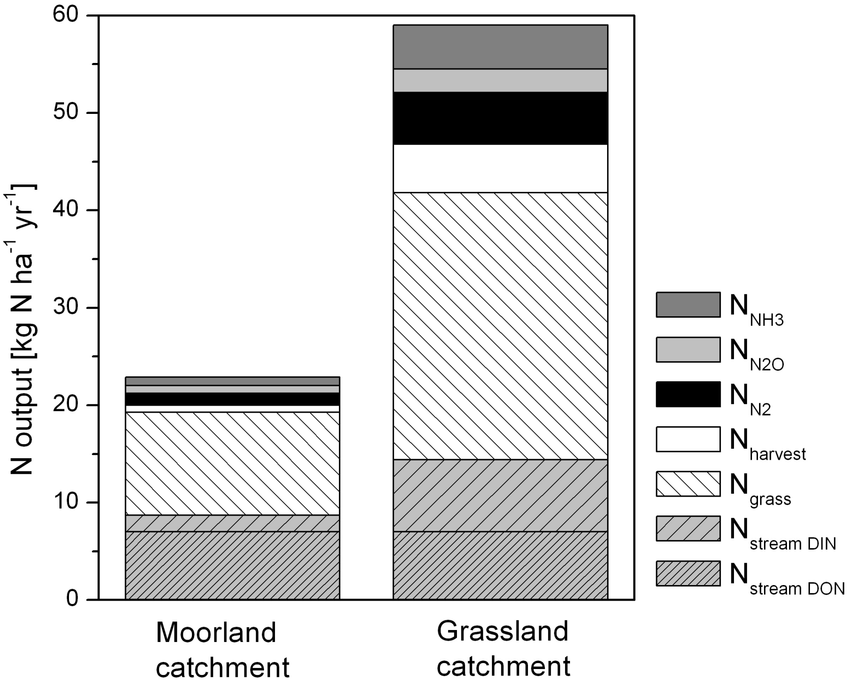


Figure 5.8: N outputs (kg N ha^{-1} yr^{-1}) to the moorland (left) and the grassland catchment (right). Stream TDN export fluxes (N_{stream}) are split into the dissolved inorganic flux ($N_{stream\ DIN}$ = fluxes of NH_4^+ and NO_3^-) and the dissolved organic flux ($N_{stream\ DON}$).

Table 5.3: Catchment totals of N outputs (kg N yr^{-1})

	Moorland catchment	Grassland catchment
N_{NH3}	540	4,050
N_{N2O}	470	2,160
N_{NO}	43	300
N_{N2}	770	4,730
$N_{harvest}$	450	4,460
N_{grass}	6,580	24,520
N_{stream}	5,370	12,860
Total output	14,230	53,080

5.3.7 Total N budgets for the study catchments

The overall nitrogen budgets for two catchments are compared in Table 5.4 and Figure 5.9. The moorland catchment showed a negative N balance of -1.6 +3.8/-3.4 (error) kg N ha^{-1} yr^{-1}, potentially indicating a small release of N from catchment storage to the stream, however within the uncertainties the catchment N budget could also be in balance. This is in contradiction to the conclusion of Reynolds and Edwards (1995) that N accumulation is to be expected in this type of moorland catchment. However, Reynolds and Edwards (1995) did not take stream exports of DON into account due to lack of data. The present study thus shows the importance of DON as a component of stream export: DON accounted for 81% of TDN export. The negative N balance found for the moorland catchment is in agreement with the N budget of a field site within the same moorland as reported by Drewer et al. (2010). Drewer et al. (2010) compiled budget terms from different years, accounting for inputs through inorganic N deposition as well as losses through N_2O emissions and stream export of measured inorganic and estimated organic N, and concluded an overall N loss of -2.4 kg N ha^{-1} yr^{-1}.

Nitrogen saturation has been defined for “an ecosystem where N losses approximate or exceed the inputs of N” (Ågren and Bosatta, 1988; Butterbach-Bahl et al., 2011). Thus, according to our catchment soil budget approach the moorland catchment showed signs of N saturation. If the moorland catchment is losing N, it is of interest to know whether carbon (C) loss is also occuring. Recently, Dinsmore et al. (2010) showed the DOC downstream flux to be a significant loss within the C budget of the moorland catchment, although the moorland was still found to act as a C sink, mainly due to a large C uptake from the atmosphere. However, in the past the same moorland has also been found to be a C source (Billett et al., 2004). Those differing C balances are mainly due to differences in the budget term of C uptake from the atmosphere which were in turn influenced by the annual climatic fluctuations. Thus, the studied moorland catchment may still act as an overall C sink, but at the same time release a significant amount of C from the catchment via downstream DOC export. The effects of future climate change on catchment scale C and N budgets remain highly uncertain.

The grassland catchment had a positive soil N balance, indicating that the catchment stored 5.9 +7.4/-12.3 (error) kg N ha^{-1} yr^{-1} of the inputs in soil, vegetation and groundwater in 2008. However, the stream export of the grassland catchment still represented a relatively large budget term compared to the other terms. By comparison with other European regional catchment budgets (Billen et al., 2011), the retention of N within the grassland catchment was limited (section 5.3.9).

Table 5.4: Soil N budgets for the moorland and the grassland catchment with fluxes and errors shown in kg N ha^{-1} yr^{-1} (see subsections under 5.2.3 and 5.2.4 for details of individual error estimations).

		Moorland catchment		**Grassland catchment**	
		Fluxes	Error	Fluxes	Error
Catchment N inputs:					
NH_3 dry deposition	$N_{NH3\ dry\ dep}$	2.4	± 0.5	6.4	± 1.3
NH_x wet deposition	$N_{NHx\ wet\ dep}$	2.5	± 0.5	2.6	± 0.5
NO_y deposition	N_{NOy}	3.3	± 0.7	3.3	± 0.7
Synthetic fertiliser applications	$N_{syn\ fert}$	1.2	± 0.1	9.3	± 0.9
Organic fertiliser applications	$N_{org\ fert}$	2.1	± 0.6	16.3	± 4.9
Grazing livestock excreta	$N_{excreta}$	8.8	± 4.4	26.3	± 13.2
Biological N_2 fixation	N_{fix}	1.0	+3.0/-0.7	1.0	+3.0/-0.7
Total N input		21.3		65.2	
Catchment N outputs:					
NH_3 emission	N_{NH3}	0.9	± 0.2	4.5	± 0.9
N_2O emission	N_{N2O}	0.8	± 0.4	2.4	± 1.2
NO emission	N_{NO}	0.1	± 0.0	0.3	± 0.2
N_2 emission	N_{N2}	1.2	+2.5/-0.6	5.3	+10.6/-2.6
Harvested silage and hay	$N_{harvest}$	0.7	± 0.1	5.0	± 1.0
Grazed grass by livestock *	N_{grass} *	10.6	± 5.3	27.4	± 13.7
Stream export	N_{stream}	8.7	± 1.7	14.4	± 2.9
Total N output		22.9		59.3	
N balance		-1.6	+3.8/-3.4	+5.9	+7.4/-12.3

* $N_{grass} = N_{excreta} + N_{animal} – N_{feed}$
N_{animal} is N exported via wool and meat production
N_{feed} is N imported via supplementary animal feed
Moorland catchment: N_{animal} = 2.0 kg N ha^{-1} yr^{-1}, N_{feed} = 0.2 kg N ha^{-1} yr^{-1}
Grassland catchment: N_{animal} = 5.4 kg N ha^{-1} yr^{-1}, N_{feed} = 4.3 kg N ha^{-1} yr^{-1}

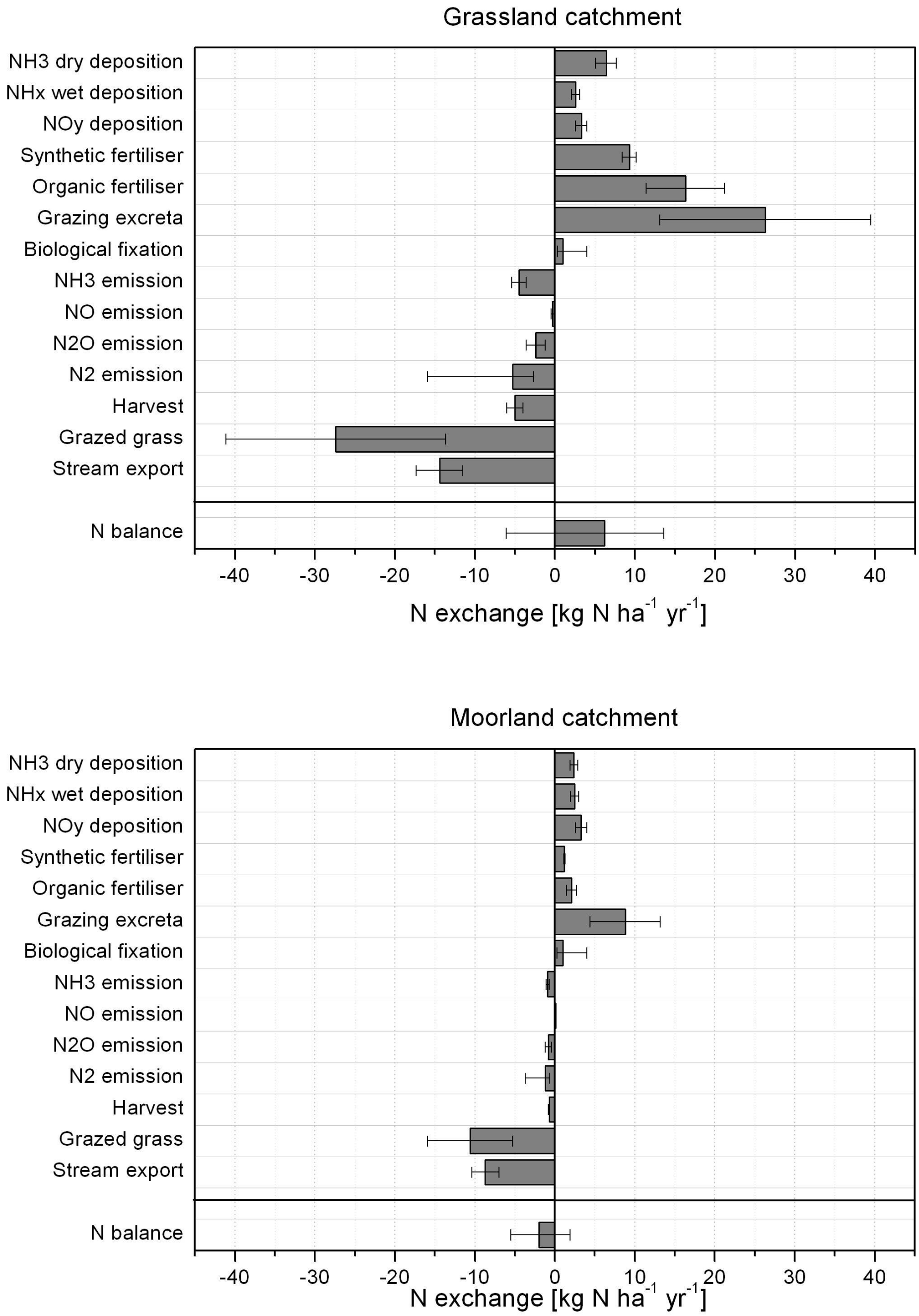


Figure 5.9: Catchment soil N budgets for the grassland catchment (top) and the moorland catchment (bottom). Inputs and outputs are shown as positive and negative N exchanges (kg N ha^{-1} yr^{-1}) with the overall N balance shown at the bottom. Error bars represent the uncertainty for the individual budget terms (see subsections under 5.2.3 and 5.2.4) with the N balance error calculated accordingly (see section 5.2.2).

5.3.8 Uncertainties in the catchment nitrogen budgets

The budget terms with the largest error bars were the outputs through grazed grass (N_{grass}) and the input through grazing excreta ($N_{excreta}$). However, those terms are interdependent and thus the difference between them contributes to the overall uncertainty of the N balance calculation. In the moorland catchment, the budget terms contributing the most to the uncertainty of the N balance were biological N_2 fixation, stream export and N_2 emissions. In the grassland catchment, the terms contributing the most to the N balance uncertainty were the N_2 emissions, followed by applied organic fertiliser and stream export. The overall uncertainty of the N balances were large, the moorland catchment balance being -1.6 kg N ha^{-1} yr^{-1} with estimated upper and lower balance values of +2.2 and -5.0 kg N ha^{-1} yr^{-1}, accounting for uncertainties. Similarly, the upper and lower estimates of the grassland catchment of +5.9 kg N ha^{-1} yr^{-1} range between +13.3 and -6.4 kg N ha^{-1} yr^{-1}. Thus, despite the detailed budget analysis, the uncertainties remain significant such that the N balances are not estimated to be different to zero whithin the range of uncertainties.

There are several terms still missing from the N budget calculation which may add more uncertainty to the current balance estimate. In particular, atmospheric deposition of gaseous and particulate organic N compounds were not quantified nor estimated due to lack of information, although organic deposition may be an important input (Cape et al., 2004; Neff et al., 2002). Moreover, fluvial N export through particulate organic N (PON) was not measured, although the PON flux is likely to be insignificant compared to the DON flux as was the POC flux to the DOC flux measured in the same moorland catchment in Dinsmore et al. (2010). Another source of uncertainty is the assumption that land use and N input remain approximately constant with time allowing the balancing of N exported through the aqueous system with the N exchanges of the surface.

5.3.9 Comparison with a regional catchment N budget approach

Regional scale catchment N budgets have been estimated for many European catchments (Billen et al., 2011). The approach combines a calculation of the net anthropogenic input of reactive nitrogen (NANI, Howarth et al., 1996) to the catchment including atmospheric NO_y deposition, crop N fixation, fertiliser use and import of food and feed. This is a simple approach which can be applied to large regions but does not account for processes like NH_3 volatilisation or soil denitrification. In European regional catchments, NANI ranges between 0 and 84 kg N ha^{-1} yr^{-1} (mean: 37 kg N ha^{-1} yr^{-1}) (Billen et al., 2011). The relative difference of NANI to the stream export of total N (TN = DIN + DON + PON) is then associated with catchment N retention. Catchment retention refers to the amount of N which is either stored in soils and groundwater or lost through emissions to the atmosphere. In regional European catchments, catchment N retention varies between 50% and 90% of NANI (mean: 82%) (Billen et al., 2011). There is some evidence that the fraction of NANI exported by the stream is larger in northern European catchments with high discharges.

Those regional budget calculations differ substantially to the one presented in this study, (e.g. coarser scale data, no NH_x deposition, no land emissions, no organic fertiliser applications); however, the catchment retention calculated as the percentage of the net anthropogenic input which is stored or emitted using our budget terms for the landscape scale may emphasise the differences of regional and landscape scale N budgets. Thus, a *landscape NANI* was calculated (see section 5.2.2 for budget term definitions):

$$landscape\ NANI = N_{NH3\ dry\ dep} + N_{NHx\ wet\ dep} + N_{NOy\ dep} + N_{syn\ fert} + N_{org\ fert} + N_{excreta} - N_{harvest} - N_{grass} \qquad (3)$$

The *landscape NANI* differs to the budget calculation of equation (1) in that biological N_2 fixation, the land emissions and stream export are not taken into account. Atmospheric emissions were not considered to be able to calculate catchment retention. *Landscape NANI* was 9.0 kg N ha^{-1} yr^{-1} for the moorland and 31.8 kg N ha^{-1} yr^{-1} for the grassland catchment. These values are relatively small compared with the NANI calculated for European regional catchments with an average of 37 kg N ha^{-1} yr^{-1} (Billen et al., 2011). The stream N export (not including PON) represented, therefore 97% of *landscape NANI* in the moorland, compared with 45% in the grassland catchment. This implies a catchment retention of 3% of *landscape NANI* in the moorland and 55% in the grassland catchment. These values are low, particularly the retention of the moorland catchment, compared to the catchment retention calculated at regional scale in Europe with an average of 82%

(Billen et al., 2011). Reasons of the discrepancy between these two budget approaches are likely to be the finer scale resolution of our landscape scale study allowing, firstly, for more accurate quantification of the N budget terms and secondly, for the calculation of more budget terms to account for the net anthropogenic input related to catchments soils.

5.4 Conclusions

Nitrogen budgets for two catchments (with contrasting land use) within a single landscape unit were calculated taking into account all agricultural activity and most of the important gaseous and aqueous inputs and outputs. This allowed a detailed analysis of catchment inputs and outputs at a much higher spatial resolution than used in other studies. The negative N balance of the moorland catchment indicates a small net release of N from the catchment. The N balance of the grassland catchment indicates storage of N within the catchment soils, vegetation or groundwater. Nevertheless, the N balances are estimated not to be different to zero accounting for uncertainties. Key uncertainties of our N budget approach were N_2 emissions and stream N export. This emphasises, firstly, the need for more studies addressing the quantification of N_2 emissions and, secondly, the importance of estimating downstream fluxes accurately.

Catchment N retentions, calculated as the percentage of net anthropogenic N input which is stored or emitted, of 3% in the moorland and 55% in the grassland catchment are relatively small compared with estimated catchment retentions in European catchments at the regional scale, ranging from 50% to 90% (Billen et al., 2011). This may either indicate that both catchments of the current study are extreme by European standards or that regional budget approaches do not work well in identifying sensitive areas at the landscape scale. Whereas larger regional scale approaches to estimating catchment input and output may be important for a global overview, these approaches clearly overlook landscape scale N dynamics and thus the local scale environmental impact of human activities.

Although our study was highly detailed, it was carried out over a relatively short time period of one year which may affect some of the conclusions drawn from the data. In particular, there are indications that stream export fluxes are also affected by inter-annual climatic variations (Gascuel-Odoux et al., 2010). Further study on the N budgets of these catchments is needed to clarify the role of annual variation. In conclusion, the present study emphasises the importance of a more holistic approach to ecosystem N dynamics and the significant improvements that can be made in landscape scale N budgeting.

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6 Discussion

The concept of landscape scale analysis has been used in this thesis to study nitrogen (N) flows by connecting different ecosystems and different pathways of hydrological and atmospheric N dispersion. Landscape N fluxes were used to assess the environmental pressures resulting from added N through farming activities. This study highlighted the large spatial variability of farm, atmospheric and hydrological N fluxes at the landscape scale. Capturing this variability is important for assessing the environmental pressures upon ecosystems and developing appropriate mitigation measures. However, the quantification of landscape scale N fluxes remains a challenging, resource intensive task.

6.1 Atmospheric ammonia

Paper I and Paper II focused on atmospheric ammonia (NH_3) fluxes within the study landscape. As described in detail in Paper I and II, there were multiple large point sources of NH_3 from poultry housing in the landscape (e.g**.** Figure 2.1**)**. Measurements were used to quantify both the emission and the deposition of NH_3 to the landscape. In the following sections, the results of Paper I and II are integrated to assess success and implications of the approaches.

6.1.1 Assessment of the inverse plume method

Paper I was a novel study combining high time resolution measurements of atmospheric NH_3 concentrations and micrometeorology downwind of several poultry houses in order to constrain the magnitude of housing NH_3 emissions with a simple inverse Gaussian plume model. Emission fluxes for two deep pit free-range layer houses were estimated from two measurement campaigns in spring 2007 and spring/summer 2008.

The approach was work intensive and due to problems with the measuring instrument less data were obtained than planned. Additionally, the wind direction was not always appropriate for detecting housing plumes at the measurement site and the Gaussian plume model did not perform well at all times, e.g. due to changes in atmospheric conditions, so that more than half of the obtained data were excluded from the emission factor (EF) calculations. A general limitation of the presented method is the difficulty of separating emissions from clustered sources. Also, the distance of the measurement site to the source is considered best between 100 m and 1000 m to avoid building turbulence effects and to minimise the influence of plume depletion. Hence, this method can only be applied to estimate livestock house emissions located in suitable landscapes.

Factors contributing to the uncertainty of the EFs estimated in Paper I include a possible temperature/ventilation rate dependence of emissions, the timing of the measurements in relation to production cycle (which may have led to larger than typical values), and the role of surface exchange processes (emissions and dry deposition) with the grassland located between the farm and the measurement point.

6.1.2 Ammonia emission factors

Emission factors used in national inventories are derived from averaging results with a relatively large variability from a range of studies. Moreover, many studies are based on limited datasets, collected over short periods of time, which are then extrapolated to derive annual emission factors. Daily estimated EFs from Paper I led to an extrapolated annual average emission factor of 0.27 ± 0.07 kg NH_3 bird^{-1} yr^{-1}. Although this EF is 35% higher than the EF for housing emissions from free-range systems currently used in the UK national inventory of 0.20 kg NH_3 bird^{-1} yr^{-1} (Misselbrook et al., 2009), it lies within the range of estimates used to calculate this national average EF. For assessing the local impact of specific poultry houses, the average UK EF is not always appropriate to use. A more specific EF is needed for the specific husbandry system and manure management.

The wide range of layer poultry EFs found in the literature (Table 2.1) for different husbandry and manure managements as well as for different climatic conditions support this finding (e.g. Fabbri et al., 2007; Groot Koerkamp et al., 1998; Nicholson et al., 2004). For example, reported EFs of caged layers range from 0.04 kg NH_3 bird^{-1} yr^{-1} for weekly scraped belt-systems in Ireland (Hayes et al., 2006) to 0.52 kg NH_3 bird^{-1} yr^{-1} for deep pit houses in the midwestern USA (Keener et al., 2001).

A similar conclusion as reached in Paper I was also drawn from Paper II which investigated spatial NH_3 concentrations and deposition fluxes at a 25 m grid resolution. Monthly concentration measurements throughout 2008 were used to verify modelled NH_3 concentrations by the LADD (Local Area Dispersion and Deposition) model (Dragosits et al., 2002; Hill, 1998). However, for this analysis the original NH_3 EFs from the UK inventory had to be adjusted for six of the 24 poultry houses to account for the specific manure management practices, as the UK average EF resulted in a considerable overestimation of concentrations. These were poultry houses with belt-systems from which manure was removed at least twice a week. The IPPC report (2003) cites an EF for this particular manure system that is more than four times lower than the EF used in the UK inventory, which is derived by averaging EFs across different manure management systems. The findings show that using NH_3 poultry EFs derived from averaging emissions across a range of different management practices does not always work well when estimating local emission impacts.

6.1.3 Spatial variability

The combined measurement and modelling work of Paper II illustrated the high spatial variability of mean annual NH_3 concentrations (0.3 to 77.9 µg NH_3 m^{-3}) and dry deposition fluxes (0.1 to > 100 kg NH_3-N ha^{-1} yr^{-1}) within the landscape. Moreover, this study demonstrated the importance of scale in NH_3 dispersion modelling. The UK national model FRAME (Fine Resolution Atmospheric Multi-pollutant Exchange) (Dore et al., 2007) operating at the relatively fine resolution of 1 km x 1 km (Hallsworth et al., 2010) was limited for capturing the spatial variability of NH_3 within the study landscape compared with dispersion modelling at a 25 m x 25 m resolution. This was largely due to relatively coarse scale (1 km x 1 km) emission input data, which smooth out the emission hotspots, and uncertainties in these 1 km x 1 km estimates which are derived from a combination of parish census data and 1 km x 1 km land cover data. Such a model approach is useful at the national scale, but limited when it comes to detailed assessment for a particular location. As atmospheric NH_3 mainly originates from hotspots (Loubet et al., 2009), i.e. mainly livestock houses with a large livestock density in a small area, it is important to model NH_3 dispersion at a scale which recognises the hotspots. In the study landscape, 90% of the NH_3 emissions originated from point sources (i.e. livestock houses and manure stores) and only 10% from field sources (i.e. grazing excreta, applications of manure and fertiliser).

Paper II also indicated the importance of spatial location regarding the impact of NH_3 emissions of large point sources on sensitive ecosystems. In areas with strong prevailing wind directions, it is essential to consider the relative spatial location of sources and sinks, as the impact downwind of the sources differs substantially from the impact upwind. In the study landscape, frequent southwesterly winds caused most of the poultry house emissions to disperse to the northeast. Thus, only small parts of the large moorland area located to the northwest of the poultry houses were estimated to be at environmental risk, despite NH_3 emissions of >100 t N yr^{-1} from poultry houses nearby.

6.1.4 Total landscape fluxes

Agricultural NH_3 emissions add up to 122 t N yr^{-1} for the study landscape and the NH_3 dry deposition modelled by LADD adds up to a total of 19 t N yr^{-1}, indicating that ~ 15% of the locally emitted NH_3 is deposited within the study landscape. This figure is within the range of 8-50% of NH_3 emissions being locally deposited within 5 km grid squares, as reported for the UK by Sutton et al. (1998), who found the local NH_3 emission recapture by the vegetation at the surface to vary regionally depending on agricultural intensity. In this study area, most land downwind of the emission hotspots is used for agricultural activities, i.e. emission recapture is limited. The wet deposition of NH_x, which is less spatially variable than dry deposition and mainly driven by non-local sources (Sutton et al., 1998), is estimated at 9 t N yr^{-1} for the landscape (FRAME, 1 km resolution). Thus, it is estimated that local sources contribute two thirds to the NH_x deposition in the study landscape, whereas long distance sources are estimated to contribute one third which emphasises the importance of local sources to NH_x deposition.

6.2 Stream nitrogen

Paper III explores the influence of landscape structure, i.e. the variation in land use, on streamwater nitrogen. Understanding this influence is important due to the immense changes in landscapes as agricultural land is being extended globally. In this unique study, spatial and temporal changes in streamwater nitrogen as well as agricultural land use were monitored for a year in two catchments contrasting in their land use (agricultual grassland vs. semi-natural moorland).

6.2.1 *Annual export fluxes*

Annual downstream fluxes of ammonium (NH_4^+), nitrate (NO_3^-) and dissolved organic nitrogen (DON) were established by continuous discharge measurements and sampling at the catchment outlets fortnightly throughout 2008 and at hourly intervals during selected high flow events. The highly variable discharge and the important contribution of high discharge events to the overall discharge in both streams show that it is essential to incorporate high discharge events in the calculation of catchment nutrient fluxes. Annual fluxes of total dissolved nitrogen (TDN) of 8.7 kg N ha^{-1} yr^{-1} in the moorland and 14.4 kg N ha^{-1} yr^{-1} in the grazed grassland catchment were in the range of total N flux values (<2 to >40 kg N ha^{-1} yr^{-1}) quoted for European catchments (Billen et al., 2011). The 66% higher annual TDN flux of the grassland compared to the moorland catchment was due to the higher NO_3^- flux, which was positively related to catchment N inputs.

The DON downstream flux made a significant contribution to the TDN flux in both catchments, accounting for 49% in the grassland and 81% in the moorland catchment. This emphasises the importance of budgeting stream export fully, taking both inorganic and organic fractions into account.

6.2.2 *Dissolved organic nitrogen*

The importance of streamwater DON in agricultural systems has received relatively little attention in the past, and thus a significant pathway of N loss from agricultural systems may have been overlooked (Van Kessel et al., 2009). Recently, it has been recognised that the DON flux constitutes not only the dominant component in semi-natural catchments, but also remains a significant component in agricultural catchments (Durand et al., 2011; Scott et al., 2007). Although Paper III could not determine specific processes leading to DON in streamwater, it showed that the origin of streamwater DON in the grazed grassland catchment is complex, with multiple significant sources. The spatial origin of streamwater DON still represents a major uncertainty (Durand et al., 2011). Moreover, the roles and controls of DON within ecosystem N cycling are yet to be fully established (Neff et al., 2003).

6.2.3 Spatial variability

The large spatial variability of land use at the landscape scale leads to a large spatial variability of both catchment N input and of streamwater N. This demonstrates the importance of landscape structure in terms of environmental pressures imposed upon aquatic ecosystems.

The spatial variation in streamwater concentrations was studied by campaign based synoptic intensive sampling at stable low flow conditions in July, September and December 2008. Results showed a large spatial variability of streamwater N at the landscape scale, with spatial variation in land use being a major influencing factor. The grassland catchment received an overall average agricultural N input through grazing excreta and applications of organic and synthetic fertiliser of 52 kg N ha^{-1} yr^{-1}, which is more than four times the input of 12 kg N ha^{-1} yr^{-1} to the moorland catchment. The atmospheric wet and dry deposition of reduced (NH_x) and oxidised N (NO_y) was 50% higher in the grassland catchment with 12 kg N ha^{-1} yr^{-1}, compared to 8 kg N ha^{-1} yr^{-1} in the moorland catchment. Within both catchments, streamwater NO_3^- was significantly positively related to N input through agricultural activities and deposition. Nitrate is relatively mobile in the soil, thus a considerable amount of soil N input can get transported to aquatic ecosystems (e.g. Butterbach-Bahl et al., 2011).

The positive link between anthropogenic N input and streamwater NO_3^- concentrations and export fluxes has been shown at the regional scale (Boyer et al., 2002; Howarth et al., 1996; Vitousek et al., 1997). With the detailed farm and field inventory and the local atmospheric deposition data, this study could also prove N input to account for inter-catchment variation at the landscape scale. This demonstrates the importance of taking local agricultural activities into account if N in streamwater is to be reduced.

However, one source of uncertainty within this analysis is the assumption that land use and N input remain approximately constant over the years. This assumption is not true over the time scale of decades.

6.3 Landscape scale nitrogen budgets

Nitrogen budgets were calculated for the two main catchments in the study landscape (Paper IV). The balances of N budgets are a relatively new concept and are being developed for use as indicators of environmental pressure (de Vries et al., 2011). Complete landscape scale N budgets have rarely been carried out before, hence this work represents an important step forward in an important area of research, as much environmental impact from nitrogen becomes visible at this scale. For the budget analysis, high resolution data were available from the detailed farm and field inventory, local scale atmospheric deposition data (Paper II) and analyses of streamwater fluxes and concentrations (Paper III).

6.3.1 Catchment N balances

Deriving complete N budgets at the landscape scale, as it has been carried out here for two catchments, is a challenging task. A substantial amount of detailed data is needed to establish high quality input and output fluxes. Estimated soil N budgets suggest that the grazed grassland catchment stored 5.9 (+7.4/-12.3) kg N ha^{-1} yr^{-1} in soil, vegetation and groundwater. By contrast, the moorland catchment was estimated to lose 1.6 (+3.8/-3.4) kg N ha^{-1} yr^{-1} from its storage. This negative N balance of the studied moorland catchment indicates N saturation (Butterbach-Bahl et al., 2011).

However, despite there being an extensive amount of detailed data available to draw on, the uncertainty of the estimated overall N balance remained large and does not allow differentiation from zero when accounting for the uncertainties. This indicates the considerable uncertainty that coarser regional scale N budgets are likely to involve (e.g. Boyer et al., 2002; Howarth et al., 1996).

6.3.2 Budget uncertainties

Major uncertainties in the N budgets were associated with fluxes of N_2, particularly with N_2 emissions but also with biological N_2 fixation. This is due to relatively little attention being given to N_2 fluxes within N research, as the environmental impact is caused by N_r fluxes. However, accurately estimated N_2 fluxes become particularly important when deriving N budgets, as a large uncertainty within those budget terms results in a large uncertainty in the overall budget balance, i.e. in the assessment of the environmental pressure imposed on the system.

The role of peat cutting regarding DON and DOC stream export fluxes of the moorland catchment needs further study. A large N output of the moorland catchment is the stream export DON flux. In Paper III it was shown that DON and DOC streamwater concentrations are correlated with each other and that both originate mainly from peat rich areas in the catchment. If the moorland catchment is losing N, it is of interest whether C loss is also occuring. In the past, the moorland catchment was shown to act both as a C sink (Dinsmore et al., 2010) and as a C source (Billett et al., 2004). However, even if the C uptake from the atmosphere is, in some years, so large that the moorland acts as an overall sink, both studies showed that the catchment releases a significant amount of C via downstream DOC export. The areas affected by peat cutting are mostly in the upper reaches of the catchment, with the effect decreasing significantly downstream. Peat cutting will change the hydrological flow paths of the catchment, leading to higher annual downstream fluxes because of greater runoff due to drainage.

6.3.3 Drivers of catchment N input

The importance of agricultural activities to landscape N inputs has been demonstrated by Paper IV. Most catchment inputs originated from land surface inputs through grazing excreta, organic and synthetic fertiliser application, 80% in the grassland and 57% in the moorland catchment. However, atmospheric deposition also made a significant contribution, at 18% in the grassland and 38% in the moorland catchment. This agrees with findings for a number of rural regional catchments where catchment N input is either dominated by agricultural input or atmospheric deposition (Boyer et al., 2002).

6.3.4 Landscape versus regional budget

European regional catchment N budgets suggest a catchment N retention of 50 to 90% of the net anthropogenic N input (NANI, Billen et al., 2011), where “catchment retention” refers to the amount of N which is either stored within the catchment or lost through emissions to the atmosphere. The retention estimated for the landscape scale catchments of this study is 55% in the grassland and 3% in the moorland catchment. These results indicate a limited catchment N retention compared with regional estimates in Europe (Billen et al., 2011).

It is considered that the budget at finer scale resolution, as presented in Paper IV, allows for more accurate estimation of the budget terms and thus more realistically reflects the environmental pressures caused by anthropogenic N input. Thus, larger regional budget approaches are likely to overlook landscape scale N dynamics and thus the local scale environmental impact of human activities.

Though this study was ground-breaking in its level of detail, it was beyond the scope of this study to analyse the differences of different N budget approaches. This area requires further research as it remains largely unclear which specific budget approach at which scale is needed for which purpose. This has wide ranging consequences as the long term trajectory of nutrient balance will be difficult to predict until N budgets can be compiled with higher precision (Neff et al., 2003).

6.4 Recommendations for further study

Using an inverse Gaussian plume model to derive NH_3 EFs of poultry houses proved to be a useful approach in a landscape without complex terrain. However, in order to establish annual average EFs, measurements should ideally be made through all seasons and the entire laying hen production cycle. There is a particular lack of established EFs for free-range poultry.

There are alternative dispersion models which can be used to estimate NH_3 emissions by high-resolution downwind concentration measurements, e.g. the process based models FIDES (Loubet et al., 2001) and MODDAAS (Loubet et al., 2006) and the WindTrax model (Flesch et al., 2005). Where the Gaussian model is a very simple approach aiming to be a rapid analytical tool for assessing emissions, the mentioned alternatives are more sophisticated, with disadvantages such as being computionally slow or requiring a large numbers of parameters. Future studies should compare the different approaches in different farm settings.

In this study, the atmospheric transport model LADD was used to estimate spatially varying NH_3 concentrations and dry deposition fluxes across the study landscape. The advantages of the LADD model include its simplicity and the ability to estimate ecosystem specific NH_3 dry deposition. However, LADD needed to be calibrated against concentration measurements, as it systematically overestimated NH_3 concentration across the landscape by around 50%. Further study is needed to identify the causes of this overestimation.

The spatial NH_3 concentration measurement data and the farm inventory of this study would provide useful datasets for comparing the NH_3 dispersion modelling performance at the landscape scale of different atmospheric transport models, such as OPS (van Jaarsveld, 2004; van Pul et al., 2008) or AERMOD (Cimorelli et al., 2005). AERMOD is a complex dispersion model used by the US EPA, however it is not particularly designed for NH_3 and requires user specified deposition parameters. OPS is a simpler model used in the Netherlands, however, the single dry deposition value applied to the entire model domain does not account for spatially varying land use at the landscape scale (Theobald et al., 2011).

This study has shown that DON contributes significantly to stream nitrogen export in both semi-natural and agricultural catchments. However, the sources and processes contributing to stream DON are not yet well established and need further study, particularly in agricultural areas.

The N budgets calculated for the two catchments at the landscape scale indicate various ways in which further study is needed. Firstly, the estimated catchment retentions of this study are different to European regional estimates of Billen et al. (2011). Different budget approaches should be compared in detail to identify differences and to be able to recommend specific budget approaches for different scales and purposes. Secondly, to reduce the uncertainties of landscape scale N budgetting, further studies are needed to develop suitable N_2 emission factors. Thus, measurements of N_2 emissions should be conducted for different land uses. Thirdly, the role of annual variation within the estimated N budgets of the two catchments would need to be clarified by future studies. Finally, long term investigations would be required to identify the role of peat cutting in the moorland catchment regarding loss of DON and DOC.

This study provides a valuable dataset to the research community and it will be used for further work. For instance, the obtained dataset will be used to verify the NitroScape model (Duretz et al., 2011) being developed as part of the NitroEurope project (Sutton et al., 2007). NitroScape integrates four types of models, a farm (FASSET, Berntsen et al., 2003), ecosystem (CERES-EGC, Gabrielle et al., 2006), atmospheric (OPS, van Jaarsveld, 2004) and a hydrological model (TNT, Beaujouan et al., 2002), simulating N fluxes and transformations at the landscape scale. This modelling work will also involve scenario analysis to identify effective mitigation measures to reduce the environmental impact of nitrogen.

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7 Conclusions

This thesis demonstrates the usefulness of the landscape scale concept in the context of studying nitrogen processes affecting the environment. Nitrogen fluxes between landscape components represent crucial processes of the human impact on the environment. Understanding the spatial variability of nitrogen at the landscape scale is key to be able to reduce this impact.

The combined approach of using detailed measurements, farm and field inventories and atmospheric dispersion models was successfully employed to quantify nitrogen fluxes at the landscape scale. Key uncertainties were identified which currently limit our overall understanding of the anthropogenic pressures upon ecosystems via agricultural activity. The following brief conclusions were drawn, that all illustrate how land use and, particularly, farm management determine landscape nitrogen fluxes:

a) Average national ammonia emission factors are not always adequate for accurately describing annual emissions from large livestock houses. Emissions and hence emission factors can vary considerably between individual houses. This study concluded that more specific emission factors need to be used taking into account the specific husbandry and manure management system when assessing the local environmental impact of large livestock houses.

b) Local atmospheric dispersion modelling at fine scale resolution demonstrated clearly the large spatial variability of ammonia concentrations and dry deposition fluxes occurring at the landscape scale. Such a fine scale approach in a heterogeneous landscape was demonstrated to be essential in order to assess the local environmental impact of ammonia emission hotspots, i.e. large livestock houses, as national modelling does not capture the spatial variability of ammonia due to coarse scale emission input data.

c) The impact of ammonia emissions of large livestock houses to sensitive ecosystems can be significantly reduced by considering local meteorological conditions. In areas with prevailing wind directions, this impact is considerably decreased when sensitive ecosystems are located upwind of the emission sources. This provides a basis for the use of spatial planning to minimise environmental impacts of atmospheric ammonia.

d) In landscapes containing large ammonia emission sources, these sources are the major contributor to the overall reduced nitrogen deposition. For the study area, this contribution of local sources was estimated to be two thirds. This emphasises the importance of assessing atmospheric ammonia at the landscape scale in areas with large emission sources to be able to quantify the environmental impact of nitrogen deposition.

e) Land use was observed to drive the large spatial variability of streamwater nitrogen at the landscape scale. Local agricultural activities significantly determine nitrate in streamwater. It was concluded that nitrogen in streamwater can only be decreased by implementing local agricultural mitigation measures.

f) This work concluded that the organic nitrogen fraction is a significant component of stream nitrogen export fluxes in both semi-natural and agricultural catchments. This emphasises the importance of budgeting stream nitrogen fully taking both inorganic and organic fractions into account. Moreover, the environmental impact of dissolved organic nitrogen is not well understood and it was concluded that this should be an area of emphasis for future studies, particularly in agricultural systems.

g) Catchment nitrogen input is primarily driven by agricultural land use, although atmospheric deposition makes a significant contribution, particularly in semi-natural catchments. The atmospheric deposition of dissolved organic nitrogen remains an outstanding unknown.

h) The concept of a nitrogen budget at the landscape scale has been demonstrated by this work. The results indicate that the studied catchments have limited capacity to store nitrogen within soils, vegetation and groundwater. This important finding contrasts with regional scale estimates. Due to errors associated with some components of the nitrogen budget, it was not possible to determine whether the catchments are in nitrogen balance, are losing or gaining nitrogen. Future research, particularly improving the understanding of emission and fixation rates of N_2, would allow the budgets to be more accurately determined.

i) This work of compiling landscape scale nitrogen budgets represents the beginning of a better understanding of the anthropogenic impact via agricultural activities on European landscapes. Within the NitroEurope project, the outcomes of this study will be analysed in the context of nitrogen fluxes and budgets quantified in landscapes across Europe, differing in their agricultural land use and climate. This will allow a quantitative assessment of the anthropogenic component of the nitrogen cycle within European landscapes.

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Declaration

I hereby certify that the research contained within this thesis is my own work, and that it has not been submitted for any other degrees or professional qualifications.

Esther Vogt