

Challenges in quantifying biosphere-atmosphere exchange of nitrogen species

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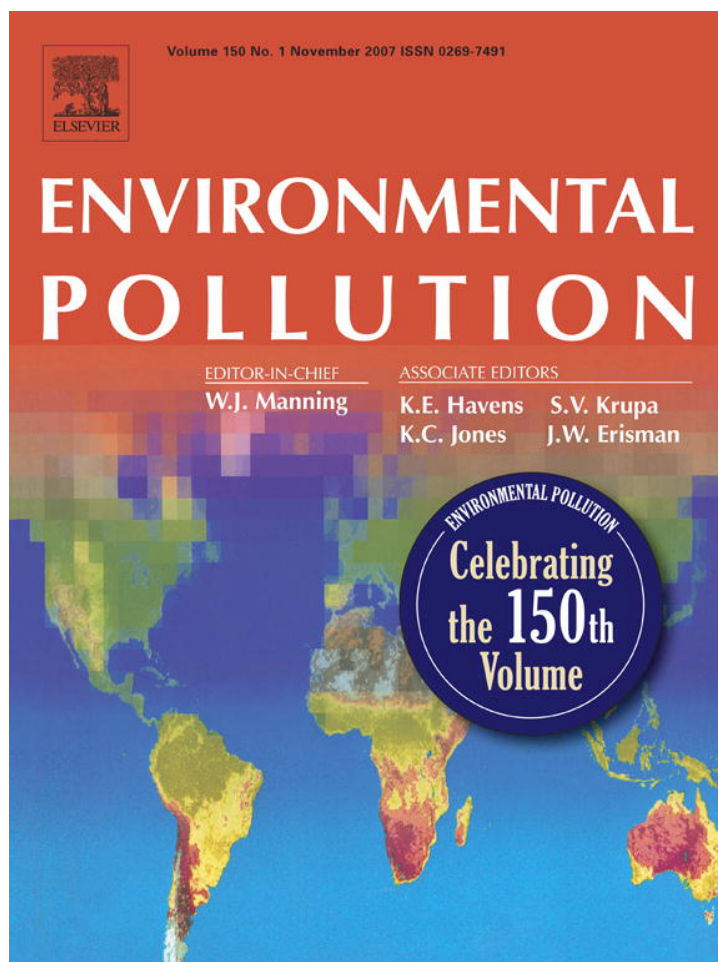
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Review

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Current N research is separated by form; the challenge is to link N components, scales and issues.

Abstract

Recent research in nitrogen exchange with the atmosphere has separated research communities according to N form. The integrated perspective needed to quantify the net effect of N on greenhouse-gas balance is being addressed by the NitroEurope Integrated Project (NEU). Recent

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advances have depended on improved methodologies, while ongoing challenges include gas–aerosol interactions, organic nitrogen and N₂ fluxes. The NEU strategy applies a 3-tier Flux Network together with a Manipulation Network of global-change experiments, linked by common protocols to facilitate model application. Substantial progress has been made in modelling N fluxes, especially for N₂O, NO and bi-directional NH₃ exchange. Landscape analysis represents an emerging challenge to address the spatial interactions between farms, fields, ecosystems, catchments and air dispersion/deposition. European up-scaling of N fluxes is highly uncertain and a key priority is for better data on agricultural practices. Finally, attention is needed to develop N flux verification procedures to assess compliance with international protocols.

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1. Introduction

In the last decade the European research community on biosphere–atmosphere exchange has made excellent progress in the measurement and understanding of individual component processes controlling N fluxes. This has included a number of highly detailed studies on micrometeorological, plot and laboratory scales. However, the emphasis has been on a few selected chemical species, like NO_x, N₂O and NH₃ only. Example collaborations include research projects, such as GRAMINAE, on ammonia fluxes (Sutton et al., 2002), NOFRETETE on the assessment of N₂O and NO emissions from forest soils (e.g. Kesik et al., 2005), GREENGRASS addressing the quantification of net greenhouse exchange (NGE), including N₂O, CO₂ and CH₄ exchange with grasslands (Soussana, 2005) and CLIMOOR investigating the effects of climate change on biogeochemical cycling and trace gas exchange of heathlands (Beier et al., 2004). It can be seen from the selection of projects above how the specific focus has also separated the science communities.

There is thus a current need to bring the different aspects of the N cycle together to address net N biosphere–atmosphere exchange. This represents a key challenge for European science networking (e.g., Cox et al., 2006). Bringing the different communities together is essential for several reasons:

- to develop sufficiently robust understanding of mechanisms to incorporate them in models,
- to bring the different species/phases of the nitrogen cycle together, in measurements and models,
- to quantify the synergies and trade-offs between different N and C forms following perturbation,
- to be able to answer the “big questions”.

Examples of the key questions that the wider science community needs to address are:

- What are the magnitude and components of the European nitrogen budget?
- Is the European N sink strength changing in response to climate, atmospheric chemistry and land-use change?
- What are the consequences of Common Agricultural Policy (CAP) reform and EU enlargement for European N emissions and impacts?
- Will there still be a “nitrogen problem” in 2010, 2020, 2050 ...?

Progress is needed to help deal with key societal problems of N and to support the development of robust environmental policies. A further question to ourselves is: How do we as scientists move to address these big questions, without diluting our efforts on the underpinning scientific mechanisms? This can only be answered through making better links between our different scientific communities. Of course, the challenge to make meaningful links is huge. This is especially the case as large integrated research efforts develop, such as under the framework of EU integrated projects (IPs).

The NitroEurope IP (or NEU for short) represents a major collaborative effort for the period 2006–2010 (<http://www.nitroeuropa.eu>), and is central to develop the needed integrated analysis of the nitrogen cycle and atmospheric composition change. A focal point for NEU is provided by a key question of interest to the European Commission: What is the effect of reactive nitrogen (N_r) supply on the direction and magnitude of net greenhouse gas budgets for Europe? This question is far from trivial as N tends both to increase and decrease the different contributors to net greenhouse gas exchange (NGE, see Table 1). A second key question of NEU focuses on future optimization of abatement strategies: To what extent would a more-integrated management of the N-cycle and its interactions with the C-cycle have potential to reduce greenhouse gas and N_r emissions simultaneously?

NitroEurope itself is structured into six main science components, the activities of which and inter-linkages are

Table 1
Effects of increased reactive nitrogen (N_r) supply on net greenhouse gas exchange (NGE)

| N _r increases equivalent GHG emission | Effect of N _r unclear or variable | N _r decreases equivalent GHG emission |
|--|---|--|
| N ₂ O (inc. secondary N ₂ O from NH ₃ emissions and NO ₃ leaching) | Cattle and other ruminant CH ₄ by affecting animal diet | Increased CO ₂ uptake by plants |
| Increased net CH ₄ emission from wetlands by reducing CH ₄ oxidation | Decomposition of Soil Organic Matter (SOM) to release CO ₂ | N aerosol scatter light and increase potential cloud formation |
| O ₃ (from NO _x) reducing growth and CO ₂ uptake by plants | | |

The overall response of NGE to N will depend on the balance of these competing effects and will differ regionally according to soil, climate and ecosystem type.

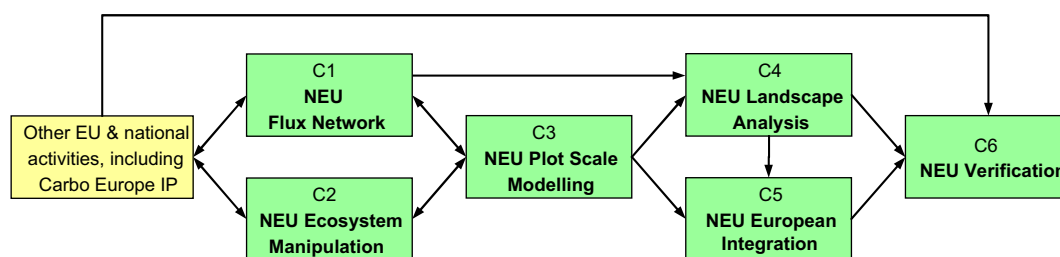


Fig. 1. Summary of the structure of the NitroEurope Integrated Project into six main science components.

summarized in Fig. 1. Here we briefly summarize some of the recent achievements of EU biosphere atmosphere exchange research for N_r interactions, and show how these are providing a foundation to develop the future research priorities.

2. Status and advances in N flux measurements

The scientific progress in quantifying N_r exchange has fundamentally depended on advances in chemical measurement techniques (Fowler et al., 2001; Erisman et al., 2001). The type of flux measurement method that can be applied depends on chemical detection limits and accuracy, sampling response time and degree of automation that is possible. The three most common flux measurement methods: eddy covariance (EC), aerodynamic gradient method (AGM) and cuvette methods (CM) can effectively be seen as the gold, silver and bronze standards. The micrometeorological methods (EC and AGM) are preferred due to their ability to integrate net fluxes over wider areas without disturbing the surface, but require greater sampling precision than CM. Similarly, EC is preferred to the AGM because it requires sampling at only one height and has fewer empirical corrections (e.g., due to atmospheric stability). The ability to sample at one height is a key interest for N_r compounds, which may be subject to chemical production/loss or advection from nearby sources (Nemitz et al., 2004; Loubet et al., 2001). The “holy grail” of N_r flux measurement might be considered as the ability to make multiple EC measurements at different heights, thereby allowing direct quantification of any flux divergences, i.e. change in the flux with height above the surface. In ideal micrometeorological conditions, the flux is constant with height, allowing measurements in the air above to infer fluxes at the surface. By contrast, Fig. 2 shows that there are several reasons for fluxes of N compounds not being constant with height. These include: (a) the effects of advection from nearby sources, (b) the effects within-canopy sources and sinks, changing the flux with height in a plant canopy, (c) the effects of air chemical reactions above the surface, and (d) chemical reactions within plant canopies, which can be important due to the long residence time of air within the canopy. Where EC measurements are not possible (e.g. due to lack of a suitable fast response sensor), relaxed eddy accumulation (REA) also provides the ability to measure at one height (e.g. Nemitz et al., 2001a), although experimental precision has so far limited direct measurement of flux divergence. Similarly, inverse dispersion methods can provide an alternative method to quantify N_r emission sources (Loubet et al., 2001). It should

be noted that a number of conditions exist (e.g. complex terrains and experimental manipulations at field scale) where the standard requirements needed for the EC measurements are not met. In such situations CM measurements provide a valuable alternative to EC, REA or gradient methods like AGM.

Three examples serve to illustrate the advances in flux measurement. In the last decade, substantial progress has been made in the use of tunable diode laser absorption spectroscopy (TDLAS). The precision and fast response of this approach has allowed the first EC measurements of field scale N_2O fluxes (e.g., Laville et al., 1999; Scanlon and Kiely, 2003; Di Marco et al., 2005). N_2O is, however, highly spatially variable and TDLAS has also permitted a “fast box” approach to quantify spatial variability in emissions, as illustrated by Fig. 3 for grazed grassland. Such measurements of spatial variability in N_2O emission would be extremely difficult to conduct using traditional chromatography systems.

Until now the AGM using continuous wet chemical denuders (AMANDA, Wyers et al., 1993) has provided the state-of-the-art for ammonia flux measurement, but this is extremely labour intensive and limits the analysis of vertical flux divergence. The current capability is illustrated by Fig. 4, which shows a comparison of three AMANDA (CEH, FRI, FAL-D) and a MINI-WEDD system (FAL-CH, Neftel et al., 1998) from the GRAMINAE/ BIATEX-2 experiment,

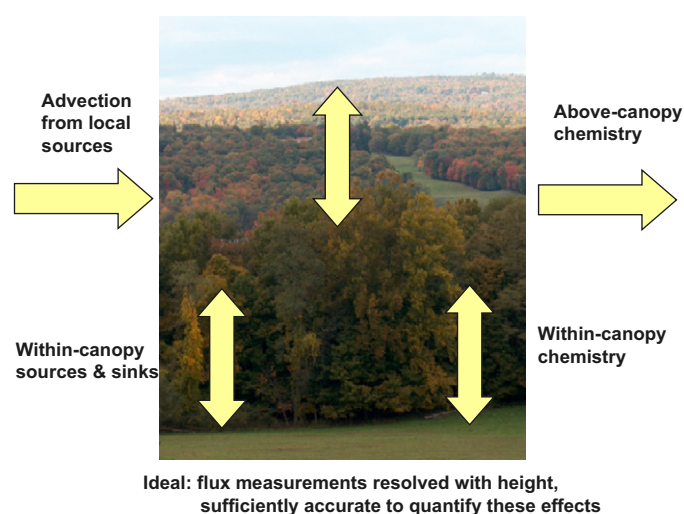


Fig. 2. Reasons why fluxes of nitrogen species between the land and atmosphere may not be constant with height. Quantifying these effects represents a major challenge for the research community.

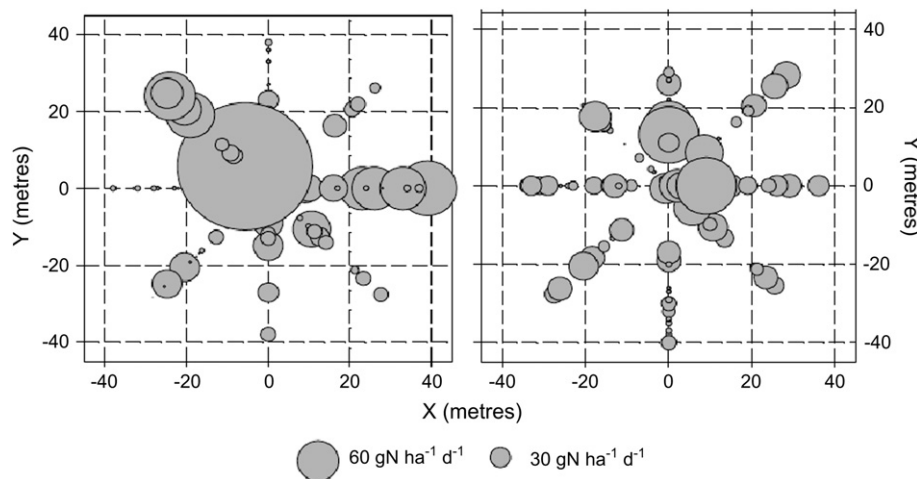


Fig. 3. “Fast box” measurements of N_2O emission using TDLAS from grazed grassland (Laqueuille, France). The left hand side is for an extensively grazed sward, while the right hand side for an intensively grazed sward. The axes indicate the spatial location in the two adjacent fields, while the size of the filled circles indicates the intensity of the N_2O emission flux. These results demonstrate the high degree of spatial variability in N_2O emissions from grazed pasture and the consequent difficulty to detect significant differences between treatments.

demonstrating that substantial uncertainties remain, even when such an intensive effort is made.

Until now measurements of NH_3 fluxes by eddy covariance have been extremely limited (Famulari et al., 2005), and subject to substantial uncertainty (e.g., Shaw et al., 1998). Recent advances with TDL technology have improved this: Fig. 5 demonstrates the first robust inter-comparison of EC flux measurements for ammonia. A lead-salt TDL system (operated by CEH) was compared with a Quantum Cascade Laser (operated by University of Manchester), with overall performance similar to that obtainable by the AMANDA systems (Twigg et al., 2005).

With regard to the issues of flux divergence, recent progress has been made to assess the effects surface perturbation on the interaction between biosphere atmosphere exchange and gas-particle inter-conversion in the HNO_3 , NH_3 , NH_4NO_3 system (Fig. 6). Apparently small particles were emitted (EC measurements showing negative deposition velocity, V_d , in Fig. 6A), while HNO_3 and HCl deposition velocities, measured by AGM, were less than possible by turbulence (Fig. 6C), indicating a reduced N input to the site. However, at the same time, deposition velocities of NH_4^+ aerosol, measured by AGM, were larger than expected (Nemitz et al., 2004) (Fig. 6B). By detailed modelling, however, Nemitz and Sutton (2004) were able to show that these effects were actually the opposite of what they initially seemed. High surface temperature led to aerosol evaporation within and above the canopy. This provided more HNO_3 and HCl near the surface (giving the appearance of lower than maximum deposition velocities), while explaining the very large apparent NH_4^+ deposition velocities, which, being derived from gradient measurements, were partly due to evaporative depletion of NH_4^+ near the surface. The apparent emissions of small particles by the EC measurement (Fig. 6A) were actually a reflection of particle evaporation: as particles evaporated, they moved from larger to smaller size classes, thereby explaining the appearance of more aerosols in smaller size classes in updrafts of air from the surface. The overall effect of this

process in this instance could actually have been to increase net N deposition, as slowly depositing aerosol was transformed into more quickly depositing acid gases.

An example of the importance of advection fluxes is shown in Fig. 7 from the GRAMINAE/BIATEX Braunschweig Experiment. This issue is typically avoided by site selection for biosphere–atmosphere exchange measurements of reactive N species. By contrast, this experiment deliberately selected a site downwind of a farm NH_3 source (200–800 m west of the study field), the investigation and quantification of the effects of advection errors on vertical fluxes. Fig. 7 shows both positive and negative advection errors to the vertical NH_3 flux. While the experiment set out to quantify the errors due to advection from a nearby source (positive errors), it actually showed that the largest errors (in absolute terms) were due to advection over the field itself. This occurred when the field was a strong NH_3 source, with concentrations therefore increasing with distance into the measurement field, even though there was had a large fetch (400 m for westerly winds) at the main measuring point.

3. Nitrogen flux measurement strategy

The complexity and expense of N flux measurements, especially considering the multiplicity of N_r forms, means that it is not feasible to implement a ~ 50 site flux measurement network for N in the same way has been done for carbon (cf. CarboEurope IP, <http://www.carboeurope.org>). A more structured measurement strategy is therefore needed to meet the range of data needs using measurement methods appropriate to each question. Under NEU, a three-tier flux network structure has therefore been designed, and this complements the three-level approach under the new EMEP monitoring strategy (UNECE, 2004):

Level 3: 13 “Super Sites” provide for intensive flux measurements with a focus on improving process understanding of multiple N_r species and quantification of net N budgets.

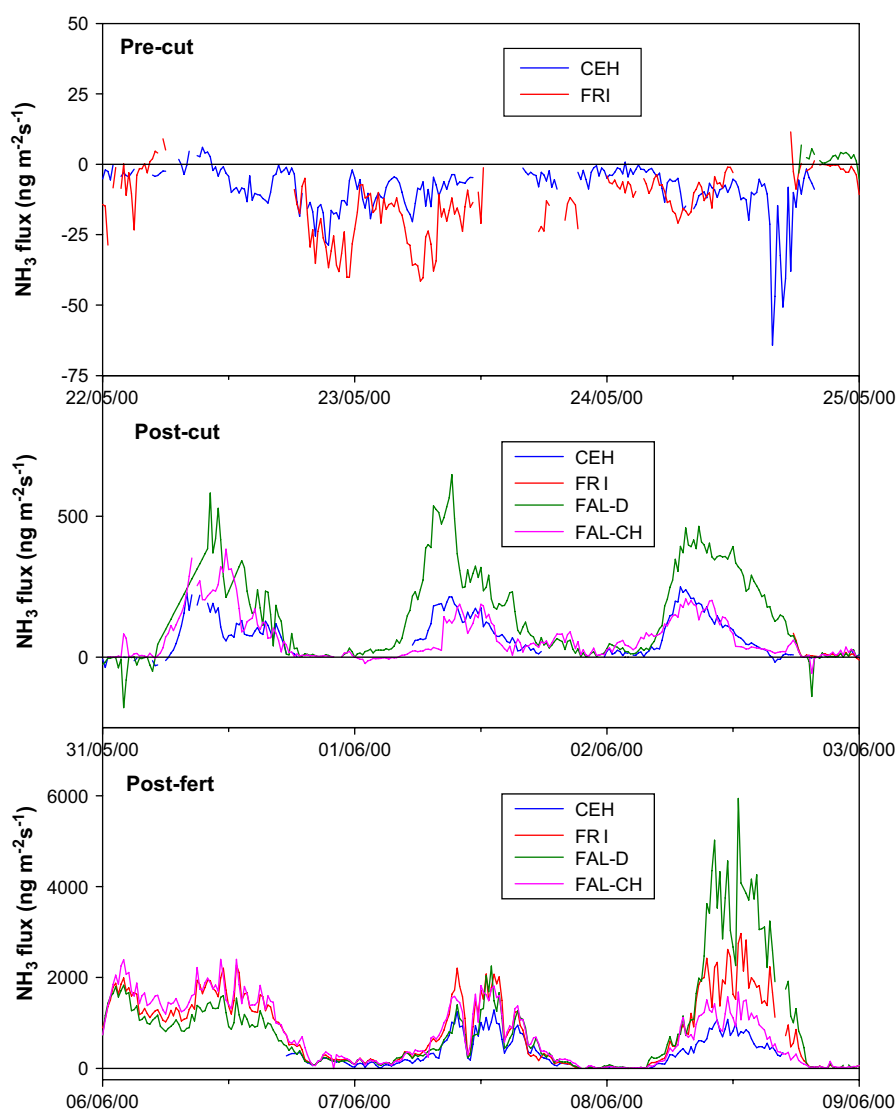


Fig. 4. Intercomparison of continuous profile systems for measuring ammonia fluxes by the aerodynamic gradient method (AGM), from the GRAMINAE Braunschweig Experiment. Although highly scattered, this flux intercomparison is unique and represents the current state-of-the-art in chemical detection systems for ammonia. Increased emissions due to cutting of the underlying grass sward (29 May) and the effect of N fertilization with (100 kg N ha^{-1} , 5 June) are clearly shown (Sutton et al., 2002). Note that the flux scale differs between the three periods.

These sites also provide the focus for developing new flux methods and for detailed plant and soil process studies.

Level 2: 8 “Regional Sites” focus on the application of low-cost methods to measure key N_r fluxes (e.g., dry deposition of NH_3 , HNO_3 and aerosol) and N_2O emissions, with low temporal frequency to allow cost-effective estimation of long-term trends in N_r fluxes. Based upon successful testing, the number of such sites could be increased in future.

Level 1: 50 “Inferential Sites” provide long-term N_r concentration and indicator measurements across Europe at the CO_2 flux sites of the CarboEurope IP, allowing C fluxes to be interpreted in relation to inferential model estimates of N deposition and N_r responses.

In parallel to the three-level flux observation network, NEU has established a major network of “Manipulations Sites”, to address ecosystem responses to the main global change drivers

(climate change, atmospheric composition change, land-use change and land-management change). The rationale is that the manipulation network is needed to help interpret results of the regional observing system, since there are always multiple differences between such sites (i.e., climate, atmospheric deposition, soils, ecosystem type and management). The NEU Manipulation network therefore draws together a critical mass of ecosystem manipulation experiments, each of which addresses relevant drivers of change according to ecosystem and regional sensitivity. Overall, NEU has brought together 36 manipulation studies, with a focus on establishing standard protocols for measuring trace gas fluxes of N and GHGs and for supporting biogeochemical and site data necessary for subsequent model application. The network includes:

- (a) 22 “Core Manipulation Sites” that represent key experiments for the ecosystem types, which are aimed at

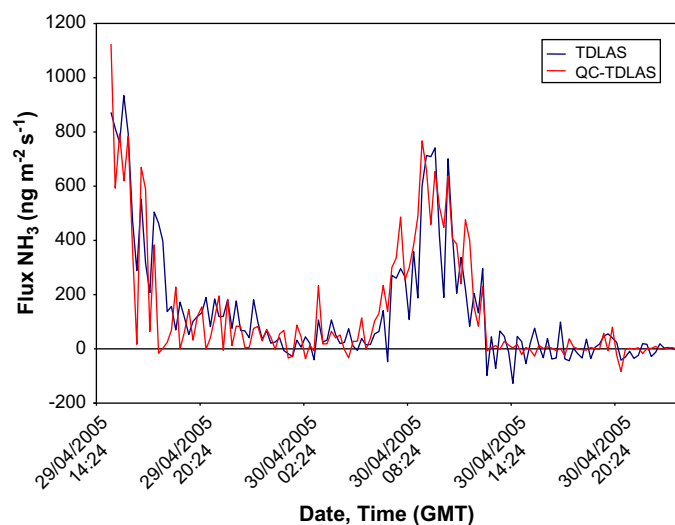


Fig. 5. Fluxes of NH_3 measured by eddy covariance over intensively managed grassland (Easter Bush, Scotland) several days after the application of liquid manure to the grassland.

providing detailed measurement and retrospective data to apply plot scaled models and test the relative effect of manipulations, and

- (b) 14 “Associated Manipulation Sites” that represent experiments for the key ecosystem types (including chronosequences) aimed at widening the statistical comparison and to provide information on specific processes.

The Level 1 Flux Network sites coincide with the CarboEurope C flux sites and cover most major ecosystem types across European climatic conditions. The Level 2, Level 3 and Manipulation sites are distributed widely across Europe, with a wide coverage of different major ecosystem types (forest, grassland, arable and shrubland/wetland, as shown in Fig. 8).

A simple geographical view of the situation of the different sites involved in NEU (Fig. 8) may, however, be misleading in regard of the types of climatic condition covered. For example, more southerly experimental forest sites may be located at higher altitudes (Sutton et al., 2000). The Level 3 and Level 2 sites are therefore re-plotted in Fig. 9 in relation to European “climate space”: the average temperature axis provides a surrogate for N-S (plus altitude effects), while the temperature-range axis represents a surrogate for E-W, together giving a climatic view of the NEU flux sites in Europe. For comparison, the grey dots show the conditions at each half degree location across the continent, demonstrating the comprehensive European coverage of the NEU network.

While the focus of the Level 3 and Level 2 sites is on flux measurements, the Level 1 sites need to deliver a low-cost approach for measuring atmospheric N compounds. One of the key techniques to be deployed at Level 1 are “DELTA” denuders (Sutton et al., 2001b; Tang et al., 2003), which provide such a low cost approach for gas and aerosol concentrations (NH_3 , NH_4^+ , HNO_3 , NO_3^-) by monthly time-integrated sampling.

The focus of the manipulation network is to investigate the effects of changes in external drivers, including combinations

of drivers, on the exchange of N_r and GHGs between the ecosystem and the atmosphere. The network utilizes existing manipulation studies, and given the plot areas of manipulation treatments, flux measurements at these sites are made by cuvette methods.

Fig. 10 shows results from the CLIMOOR project (Beier et al., 2004), demonstrating the importance of the manipulation approach. This experiment utilized four sites across Europe, which are now included in the NEU Manipulation Network, where the effects of soil warming and drought treatments were compared with the effects of natural variation in ambient variations (Emmett et al., 2004). The response of soil respiration to temperature between sites was found to differ between the ambient observations (Fig. 10A) and the controlled warming treatment (Fig. 10B): in the ambient measurements, the UK and Spanish sites indicated the largest temperature response (Q_{10}); conversely, the UK and Spanish sites showed the smallest response to experimental warming by 1 °C. A possible explanation is that other factors are temporally correlated with ambient temperatures, so that the simple observational approach (Fig. 10A) does not adequately distinguish the specific effects of soil temperature and water shortage on soil respiration, as shown in Fig. 10B.

4. Modelling N fluxes between the biosphere and atmosphere

The NEU flux and manipulation networks both provide key data for the development and testing of models. Specifically, the combination of two networks at the European scale, and the inclusion of the different N_r and GHG components, provides a unique approach to advance the modelling capability. Substantial progress has already been made in modelling N_r and GHG exchange utilizing emerging datasets from the earlier European projects. The relevant models and recent progress can be considered in three groups:

- (a) *Inferential models*, which use measured air concentrations together with estimated transfer resistances and deposition velocities (e.g., Fowler et al., 1989), but have also been advanced to include treatment of bi-directional fluxes (e.g., Sutton et al., 1995; Nemitz et al., 2001b).
- (b) *Dynamic leaf surface chemistry models*, which treat the interaction between acid and basic species with leaf surface wetness and exchange processes, allowing both adsorption and desorption to the atmosphere (Sutton et al., 1998; Flechard et al., 1999).
- (c) *Dynamic ecosystem models*, which describe the plant-soil interactions with carbon and nitrogen cycling (e.g., Li et al., 1992; Riedo et al., 1998, 2002).

Soil Vegetation Atmosphere Transfer (SVAT) models using the resistance approach now include NH_3 compensation points as standard (Sutton et al., 1998; Nemitz et al., 2001b; Fig. 11). While being largely process based, these models incorporate steady-state approximations to both cuticular uptake of trace gases (usually parameterized by cuticular resistance as a function

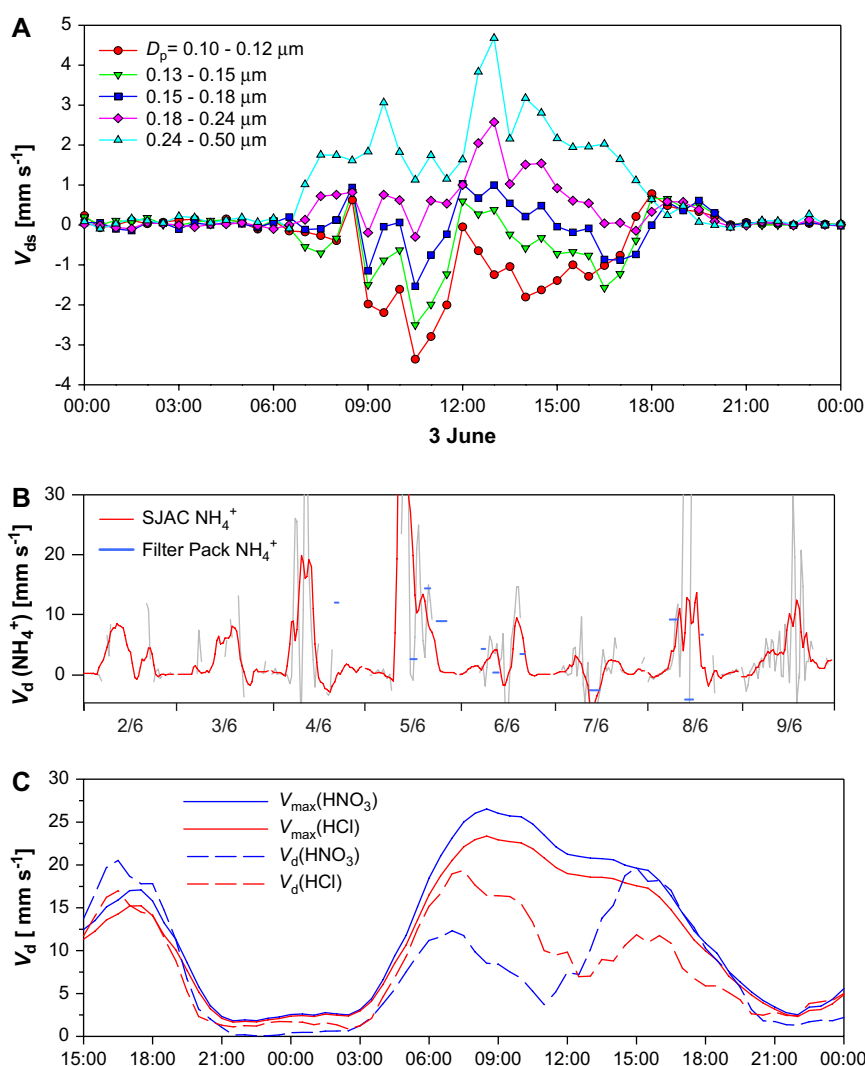


Fig. 6. Example results trace gas and aerosol exchange over a Dutch Heathland (Espeetche Veld) (Nemitz et al., 2004). The results from optical particle flux measurements (ASASP-X) showed bi-directional fluxes (A) with apparent emission for small size categories. Conversely, mass fluxes of NH_4^+ aerosol (B) estimated by a SJAC system (Oms et al., 1996) indicated very rapid deposition. In parallel, measurements using wet rotating batch denuders (Keuken et al., 1988), showed dry deposition velocities (V_d) of HNO_3 and HCl dry deposition (C) that were less than the normally expected rates at V_{\max} . The explanation for these observations is that particles were evaporating at the surface and actually delivering more dry deposition in gaseous form than would have otherwise occurred (see text).

of wetness/humidity) and of the compensation point (using fixed values of the apoplastic or intercellular concentration ratio $\Gamma_s = [\text{NH}_4^+]/[\text{H}^+]$). These Γ_s values can vary substantially between different management practices, plant growth stage and species. Measurement of apoplastic concentrations is, however, difficult, so it is of interest that there is a significant correlation between Γ_s and the more easily measurable total foliar $[\text{NH}_4^+]$ (Loubet et al., 2002; Mattsson and Schjoerring, 2002).

Dynamic models have been developed to treat the cuticular interaction as an adsorption–desorption process (Sutton et al., 1998; Flechard et al., 1999). In the initial model of Sutton et al. (1998), which has also been applied by Mosquera et al. (2001), the ammonia adsorption was treated as a capacitance charge in relation to modelled changes in leaf surface water content (the capacitance), as defined by standard solubility equilibria. However, the leaf surface pH remained a key unknown, and needed to be provided based on measured or estimated values. This

limited the approach, since it was already well established that different pollutant mixtures may affect adsorption processes, such as co-deposition of NH_3 and SO_2 , which would affect leaf surface pH (e.g. Adema et al., 1986; Erisman and Wyers, 1993; Sutton et al., 1994). The dynamic leaf surface model approach was therefore extended substantially by Flechard et al. (1999) to consider the full ion balance of the leaf surface allowing the calculation of leaf surface pH, as well as consideration of how this is affected by air chemistry, wet and dry deposition. At the same time, the feed back influence of leaf chemistry on dry deposition/bi-directional exchange is calculated. Such a model is not easy to run and requires substantial effort in parameterization and application. However, it provides a key tool to understand the interactions between N_r species (such as NH_3 , HNO_3 , HONO etc.) and other pollutants. The major challenges to refine this modelling approach are to improve the description of the chemistry of

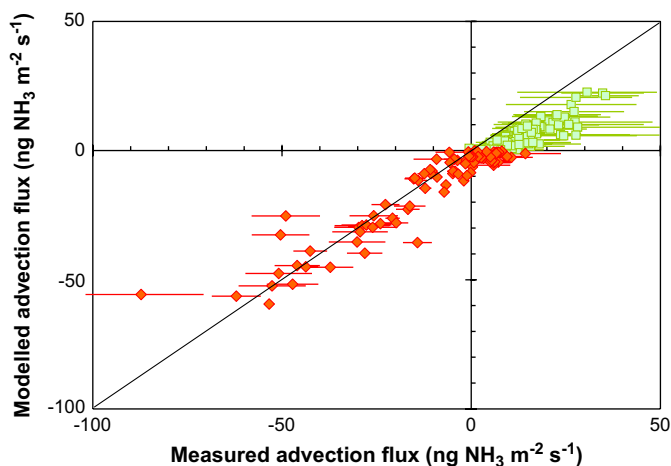


Fig. 7. Advection error at 1 m height ($F_{adv}\{1m\}$) at a site 550 m east of a farm in the GRAMINAE/Biatex Braunschweig Experiment (see Fig. 4). The advection error is estimated with the FIDES model (Loubet et al., 2001) as a function of $F_{adv}\{1m\}$ from the horizontal concentration gradients during the GRAMINAE Integrated Experiment. Advection errors due to dispersion from the farm are shown as positive fluxes, while advection due to the field itself are shown as negative fluxes. Error bars are standard deviation of the concentration estimates at the measurement sites. Data have been filtered for wind direction $\pm 15^\circ$ within the wind sector of the farm.

concentrated solutions attached to leaf surfaces and to quantify better the role of base-cation leaching in affect in canopy surface chemistry.

Dynamic models for N_2O emission in relation to soil processes have been available for some time (e.g., Li et al., 1992) and these have been developed for different ecosystems in recent years and other N species (e.g. Butterbach-Bahl et al., 2004). Models such as DNDC simulate the biosphere–atmosphere exchange of $N_2O/NO/N_2$ based on individual production, consumption and emission processes, and their interactions. Thus, they explicitly describe microbial N processes (e.g., ammonification, nitrification, denitrification, immobilization), physico-chemical processes such as diffusion or leaching as well as plant growth, associated N uptake and litter production in dependence from environmental conditions (e.g. temperature, soil moisture, soil and stand properties), as well as human management (e.g. fertilization, harvest).

Extensive testing of dynamic models versus field measurements has demonstrated the capability of the DNDC model to simulate N_2O and NO exchange at the soil/ecosystem–atmosphere interface on time-scales from days to years (Fig. 12; Li et al., 2005; Kesik et al., 2005). However, there is still some significant uncertainty in the simulation results, which

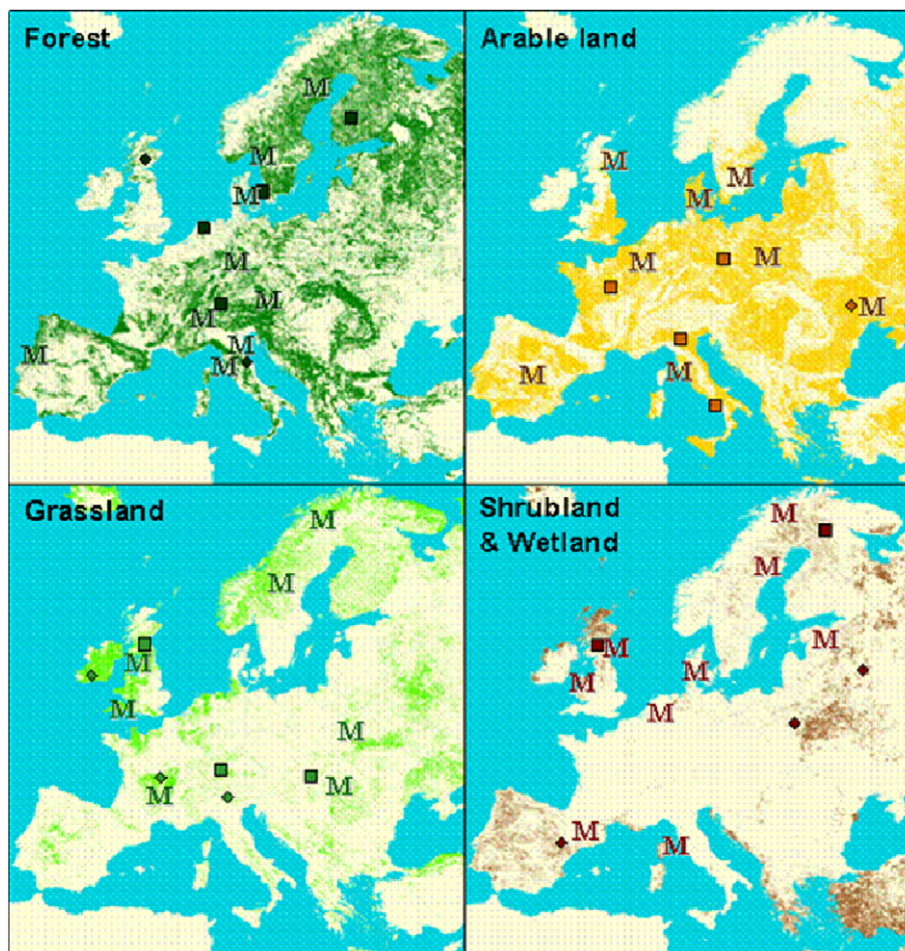


Fig. 8. Location of the main observation and experimental sites of the NitroEurope IP Flux Network and Manipulation Network. Flux Network: large squares show the locations of 13 Level-3 “Super Sites”, while diamonds show the locations of 9 Level-2 “Regional Sites”; the locations of 50 Level-1 “Inferential Sites” are the main sites of the CarboEurope IP (not shown). Manipulation Network: the locations of the ecosystem experiments (M) include 22 Core Sites and 14 Associated Sites.

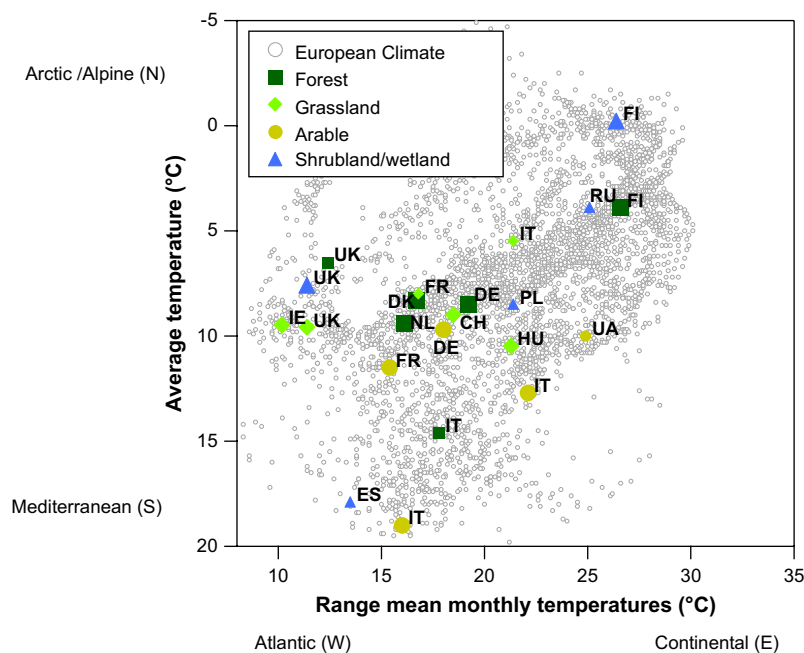


Fig. 9. View of the NEU Level 3 “Super sites” (large symbols) and Level 2 “Regional Sites” (smaller symbols) of the NitroEurope Integrated Project shown in European “climate space”. The average temperature axis provides climate scalar related to latitude (N, S), while the annual range of mean monthly temperature provides a scalar related to continentality (W,E). The grey dots indicate the climate of each $0.5^\circ \times 0.5^\circ$ pixel in Europe (Sutton et al., 2000). The international two-letter country codes are given adjacent to each of the Level 3 and Level-2 points.

is at least partly due to the still limited knowledge about ecosystem processes involved C and N cycling. Dynamic models have been used to explore different agricultural management options for reducing GHG emissions (Li et al., 2005), to evaluate the importance of N deposition for N_2O and NO emissions from forest soils, and also to calculate regional emission inventories by linking models to GIS databases (Kesik et al., 2005).

Another example of a dynamic model is the PaSim model for grasslands. This model provides the first approach to couple the NH_3 compensation point to C–N turnover processes and ecosystem functioning (Riedo et al., 2002). PaSim was originally developed as a model of CO_2 and H_2O exchange (Riedo et al., 1998), incorporating N dynamics as these have a large effect on CO_2 exchange processes. A key point of this model was that it included a distinction between total nitrogen in the plants and the “substrate nitrogen” available for plant growth. It was postulated (Sutton et al., 2001a) that this substrate N of PaSim should be most closely linked to trace gas N fluxes, since the structural N is unavailable for emission, being built into plants as proteins etc. Riedo et al. (2002) subsequently modified PaSim to consider the substrate N as two sub-pools: the symplastic nitrogen (available N in the cells) and the apoplastic nitrogen, being most closely linked to exchange in the sub-stomatal cavity. The apoplastic N concentration was linked to an estimate of Γ_s , which, along with the canopy temperature, provided the NH_3 compensation point. This enabled a functional analysis of the links between NH_3 fluxes and ecosystem functioning to be made for the first time, showing for example how cutting and fertilization increased the value of Γ_s , thereby providing an explanation of the observed values (cf. Fig. 4).

While flux measurements and models at field scale can provide a robust process assessment, limitations become apparent if the attempt is made to compare complete systems and address N_r abatement options. In particular, net fluxes depend on the scale on which an analysis is made. Fig. 13 illustrates this point by reference to the net greenhouse gas exchange (NGE) of nine European grasslands from the GREENGRASS project. Net Ecosystem Exchange (NEE) accounts for just the CO_2 exchange as measured by EC, showing that grasslands are a strong C sink. However, if N_2O emissions and cattle CH_4 emissions are included to provide the actual field GHG balance, the sink strength is considerably less. Net biome productivity (NBP) accounts for the net CO_2 uptake, minus off-site losses, in particular from hay cutting, and so is less again. The attributed field GHG balance includes CH_4 and N_2O emissions associated with the fate of the cut grass for that field, and is therefore even smaller. Finally, the “farm gate” GHG balance considers overall effect of the entire farm enterprise, showing that it acts as a net GHG source.

5. Modelling N fluxes at the landscape scale

These scale effects highlight the importance of looking at complete systems. One way to do this is to consider fluxes explicitly in their local spatial context at the landscape scale. Landscapes provide the scale at which the different spatial interactions overlap: N management between the farm buildings and fields, the role of semi-natural areas as buffers and wildlife habitats, hydrological dispersion in catchments, and local scale atmospheric dispersion between sources and sinks for nitrogen (Dragosits et al., 2002; Berntsen et al., 2003; Sutton et al., 2004;

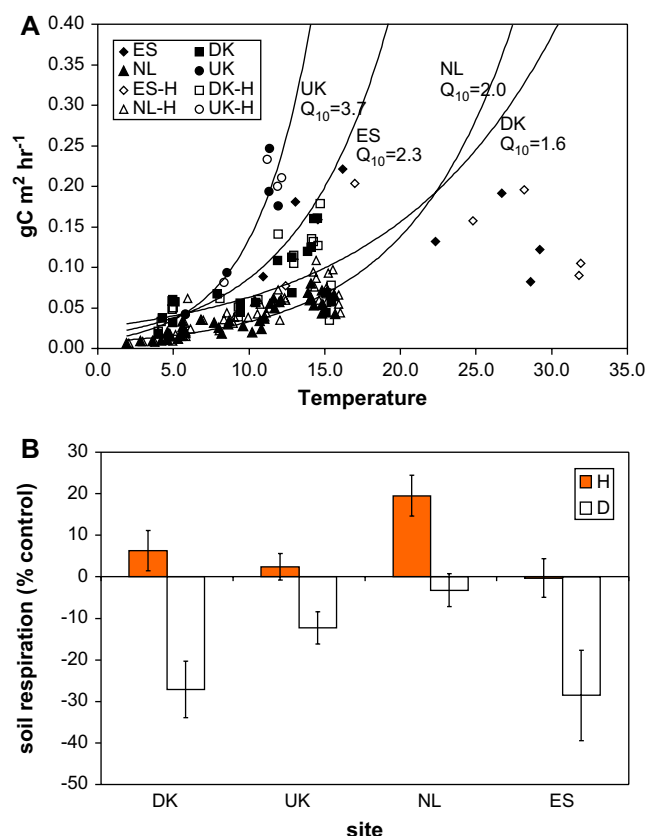


Fig. 10. Comparison of the observed effect of temperature on soil respiration and drought from four shrubland ecosystems across Europe (VULCAN sites in Spain (ES), Wales (UK), The Netherlands (NL) and Denmark (DK)). (A) Measured soil respiration in relation to ambient temperatures for control plots and plots experimentally warmed by 1 °C (H), together with the estimated Q_{10} (B) Percentage change in soil respiration caused by the field scale experimental warming (H) and a 6-week summer drought period (D) (Emmett et al., 2004).

Theobald et al., 2004). Thus landscapes represent both the scale at which land management decisions are taken and the scale at which environmental impacts occur.

Analysing N fluxes at the landscape level represents a major emerging challenge requiring the involvement of both measurement and modelling research communities. Issues such as local advection as investigated at Braunschweig (Fig. 7), become key topics in relation to their role in net fluxes and spatial variability. An example of recent progress in modelling landscape level N fluxes is shown in Fig. 14. The UK LANAS model used a framework approach to link farm, grassland and crop models (FYNE, N-GAUGE, SUNDIAL) to a local atmospheric dispersion and deposition model (LADD) via a central database and GIS (Theobald et al., 2004). Under NitroEurope, the target is to extend such approaches to include distributed hydrological modelling (Hutchings et al., 2004) and to apply the coupled model framework to contrasting N landscapes across Europe, with implications for abatement strategy evaluation and methods for regional up-scaling. A conceptualization of the framework (“Nitroscape”) that is required is shown in Fig. 15, which illustrates the coupling that is necessary between the component models. Under NitroEurope, the expectation is to develop the coupled model framework, with application using detailed inventory data in areas c. 25–40 km² of France, Scotland, Denmark, Italy, Netherlands and Poland. The relevant inventories will include land cover, hydrology, farm and field management as well as meteorological input data, and provide the basis for driving the models, allowing comparison with observed N_r concentrations and fluxes.

Such work at the landscape scale emphasizes the need for integration between the different scientific communities, linking expertise between different nitrogen forms, between

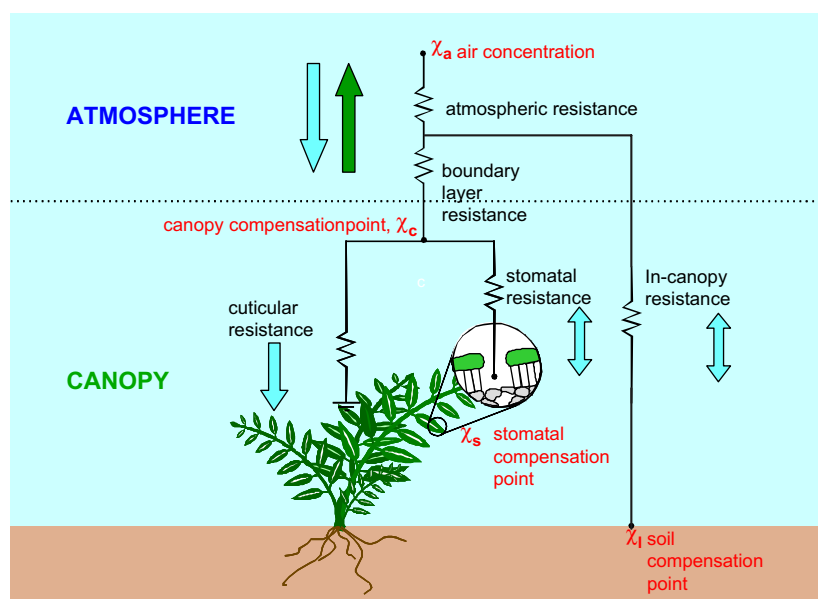


Fig. 11. Soil vegetation atmosphere transfer (SVAT) model scheme now being used as standard for ammonia and other trace gas transfer (Sutton et al., 1995; Nemitz et al., 2001b). The model applies a canopy compensation point (χ_c) approach, which resolves the competition between leaf surface deposition and bi-directional stomatal and soil fluxes. Given the possibility of bi-directional fluxes, deposition velocities (V_d) are not concentration independent, so the method focuses on linking directly between the component resistances and net fluxes. Where compensation points are zero (e.g. for O_3), the model simplifies to the original canopy resistance and deposition velocity model (Fowler et al., 1989; Wyers and Erisman, 1998; Erisman et al., 2001).

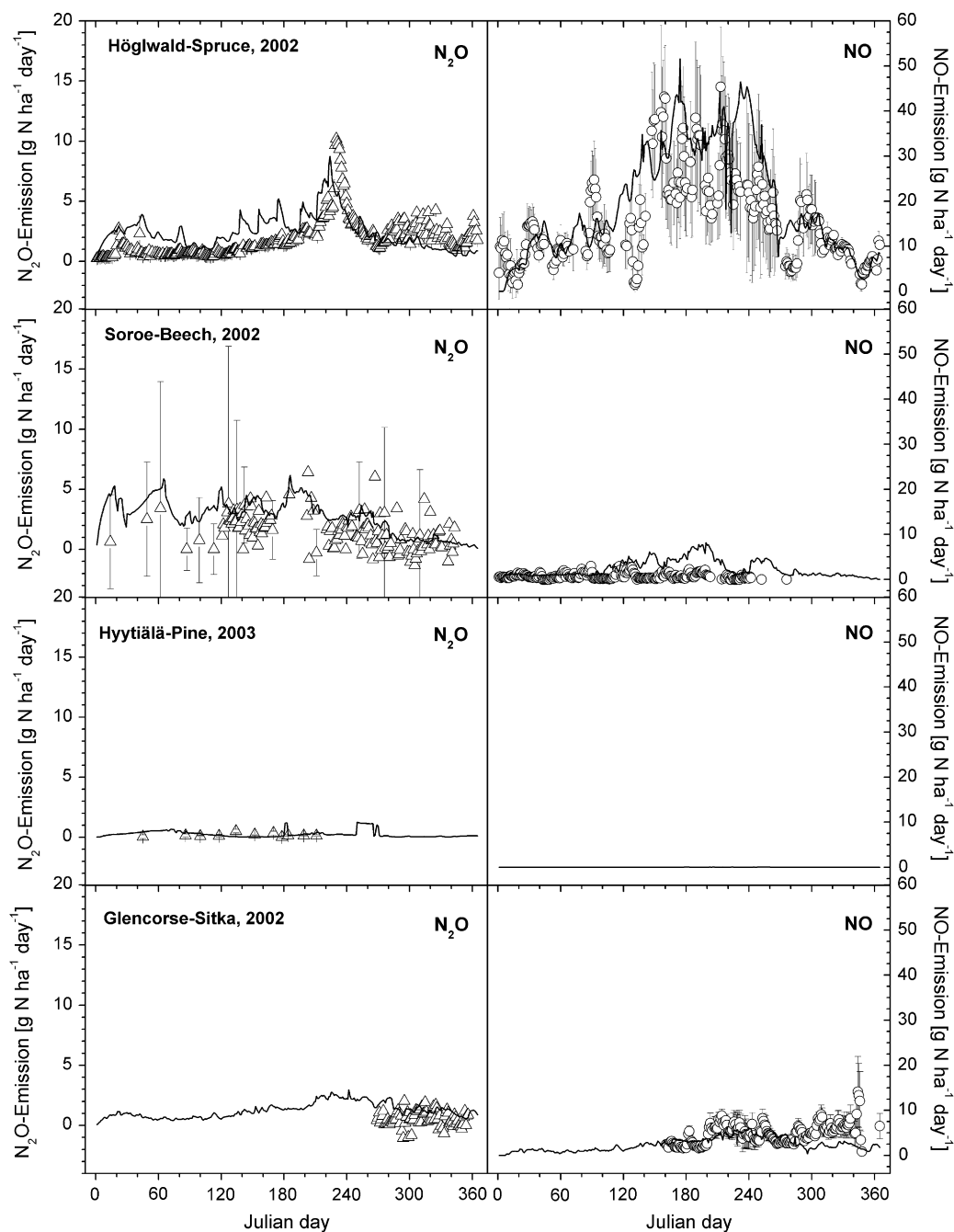


Fig. 12. Comparison of measured average daily N_2O (circles) and NO (triangles) emissions with and simulations (solid lines) using the DNDC model for different forest sites across Europe (from Kesik et al., 2005).

experimentalists and modellers and between atmospheric, agricultural and hydrological and soil scientists. These interactions are clearly highlighted by the model framework shown in Fig. 15. Equally, the community faces significant technological challenges as it evaluates different software options for coupling component models.

6. European up-scaling and verification of N fluxes

At present there are major uncertainties in up-scaling N fluxes for Europe and in estimating net European N_r budgets.

Inventories of NO_x and NH_3 emissions as used in EMEP are well established, but contain major uncertainties, especially linked to differences in agricultural practices. Up-scaling of N_2O emissions is even more uncertain, and perhaps hardest for grasslands due to the wide range of grassland types and management practices. Fig. 16 illustrates the N_2O inventories of two recent modelling approaches from GREENGRASS. Two models were applied: PASIM and DNDC (Sutton and Soussana, 2005). Due to the lack of hard information on regional grassland management practices (e.g. fertilization, manure, cutting, types, rates, timing), an approach was developed in PASIM to simulate

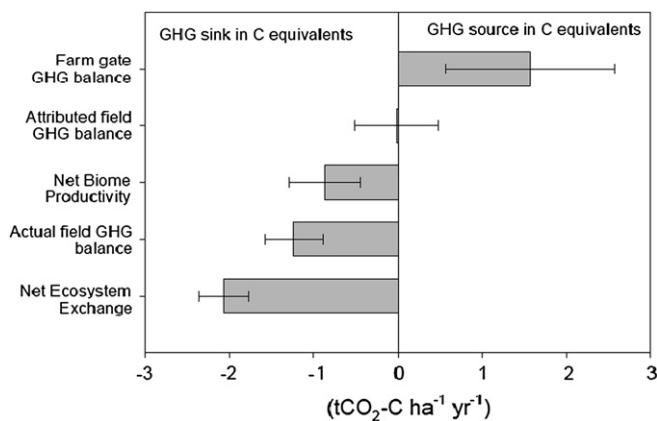


Fig. 13. Results of C and Net Greenhouse gas exchange (CO₂, N₂O, CH₄) for the average of nine European grasslands, showing how the estimation of grasslands as net sinks or sources depends on the scale of the assessment.

the N needs that would be optimal given the climatic limitation to C sequestration, by light, temperature and water availability etc. (the “intelligent farmer” approach) (Vuichard et al., 2005). By contrast, for the DNDC application, a survey of “grassland management typologies” was conducted and used to input management timelines for different regions in Europe (Levy et al., 2005). The differences between the resulting estimates (which are large) highlight the current uncertainties and point to the need for obtaining more comprehensive input data on the detailed land management practices.

Work under NEU will substantially improve such European upscaling of N_r pools and fluxes. In addition to addressing estimates of land management practices, past land-use reconstructions will be developed, putting the current N_r fluxes into

their historical perspective, in detail from 1970 and in outline from 1900. Similarly, future scenarios will be addressed, especially in relation to reform of EU Agri-Environment financing mechanisms, incorporating results from the CAPRI model (Britz, 2005). A multi-sector model (“Integrator”), focusing primarily on land use and agricultural fluxes, will integrate N fluxes with agricultural, forest and semi-natural ecosystems, incorporating industrial sources, and linking with atmospheric N_r inputs. Such a system will necessarily be rather simplified, and will be complemented by the application of classical ecosystems models, such as DNDC, for different land surface types (e.g. forest, grassland etc.).

Finally, attention is needed in the verification of regional N_r fluxes using independent datasets. Two aspects can be distinguished: the first is the verification of the scientific models, like DNDC, PASIM and others at plot and regional scales; the second is the verification of the official national inventories used for international protocols. In both cases independent datasets are needed, while improved techniques are essential to address statistical uncertainty as part of the verification procedures. For non-reactive components, such as N₂O and CH₄, inverse regional modelling from tall-tower measurements (Bergamaschi et al., 2004) represents a developing approach to the estimation of regional emissions. For reactive components, where such inversions become increasingly uncertain, ground-based and satellite observations are available to support the verification process.

7. Conclusions

It is apparent that quantifying the biosphere–atmosphere exchange of nitrogen is extremely complex, both due to the

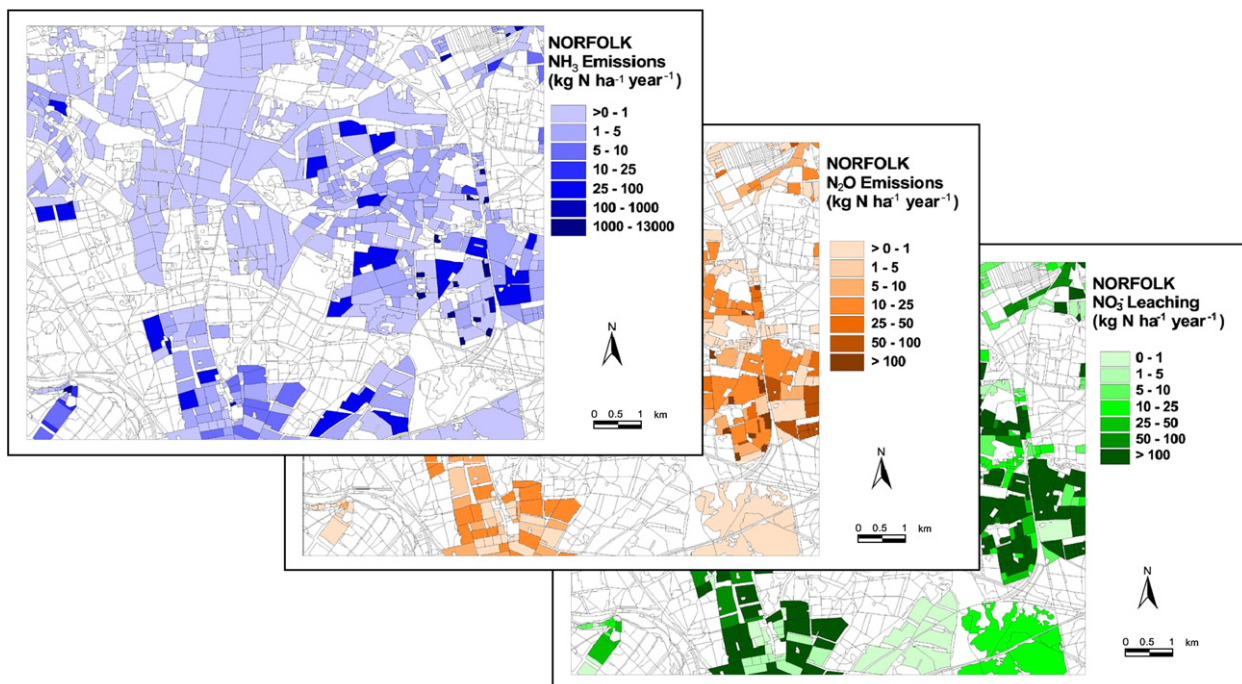


Fig. 14. Example results of landscape-level modelling of N fluxes from the LANAS model (Landscape Analysis of Nitrogen and Abatement Strategies) of Theobald et al., 2004).

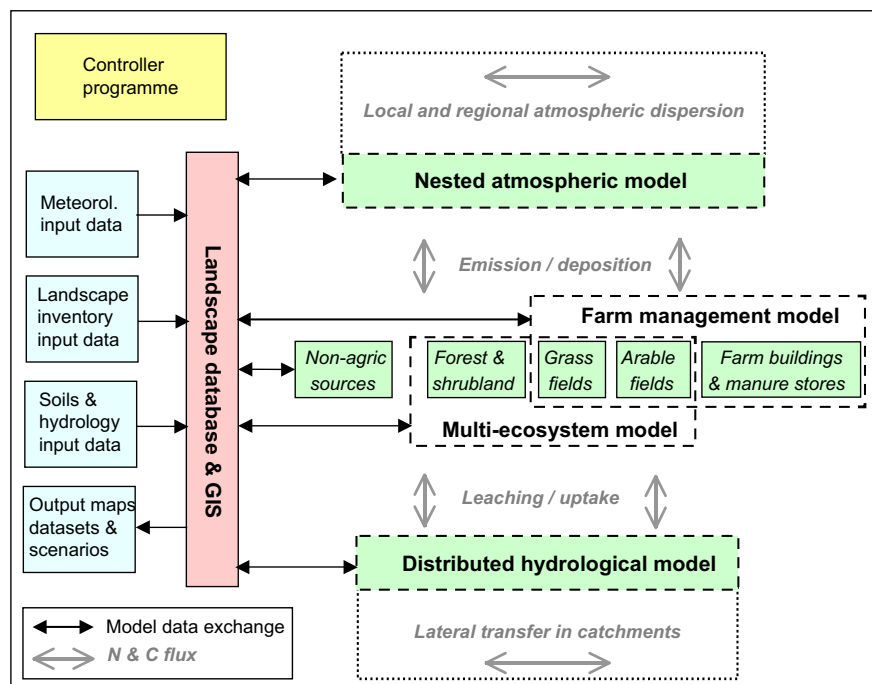


Fig. 15. Conceptualization of the modelling approach needed to provide a fully integrated treatment of N exchange fluxes at the landscape scale. The landscape (modelled at e.g. 20–50 m pixel level) is envisaged as integrating farms, fields, semi-natural land, non-agricultural sources, with lateral dispersion fluxes through the atmosphere and hydrosphere.

wide variety of nitrogen forms that need to be considered and due to the difficulty in measuring many of the components. While the different research communities have until now been rather separate, these communities have provided the foundation for both measurement methods and process understanding. With a more joined-up approach to European nitrogen research over the next years, there is now a means to integrate this understanding across research communities. This will deliver more comprehensive datasets and models addressing the interactions between nitrogen forms, thereby allowing the synergies and trade-offs between different nitrogen and carbon forms to be quantified.

The link between spatial and temporal scales is equally important. While the past focus has been on the plot or field scale, with regional upscaling applying ecosystem models,

the complex interactions of the nitrogen cycle mean that we must go beyond this. The landscape scale is critical to making these advances, as it links the local spatial interactions inherent in the nitrogen cascade and human nitrogen management. Understanding the links between atmospheric and water dispersion of nitrogen at farm and landscape scales will also inform how we upscale nitrogen fluxes to Europe. Here an iterative approach is needed, and the first step will be to compare the estimates derived from the new Nitroscape (landscape) and Initiator (European) models which are currently being developed in order to quantify the limitations of the simpler approach.

Together, the measurement datasets and the new models will provide the basis to address major concerns in the nitrogen cycle, as illustrated at the start of this paper. The nitrogen

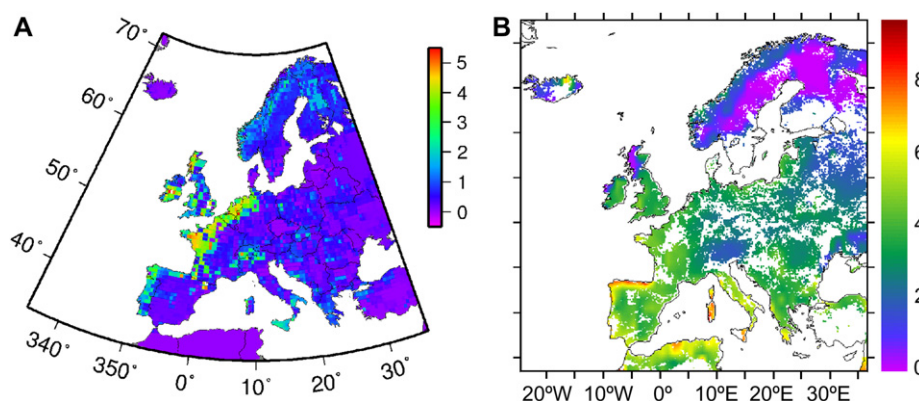


Fig. 16. Estimated distribution of N₂O emissions (kg N₂O-N ha⁻¹ year⁻¹) from European grasslands. (A) DNDC model using regional grassland management typologies, (B) PASIM using the “intelligent farmer” model approach, where the model estimates the nitrogen requirements and inputs.

flux observation system being developed provides a baseline to understand current and future conditions, while the manipulation network represents a resource to understand the effects of changing climate, atmospheric chemistry and land-use. Using the developed models, it will then be possible to address scenarios, such as the effects of CAP reform on future European nitrogen fluxes. With these tools, it will become possible to begin to quantify many of the synergies and trade-offs (as listed in Table 1) that define the net effect of nitrogen on the greenhouse gas balance. Particular progress can be expected as regards integrating the different greenhouse gases, where the global warming potentials are well known. Conversely, even wider collaboration will be needed if we are to integrate fully other radiative effects of N_r , such as through atmospheric aerosol loading.

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