



**Project Number 017841**

**NitroEurope IP**

**The nitrogen cycle and its influence on the European greenhouse gas balance.**

**Sixth Framework Programme**

**Priority 6.3**

**Global Change and Ecosystems**

**D.1.5.3**

**Initial analysis of GHG fluxes in relation to N inputs**

Due date of deliverable: **01/07/2008**

Actual submission date: **01/07/2008**

Start Date of Project: **01/02/2006**

Duration: **60 months**

Organisation name of lead contractor for this deliverable :  
**NERC**

Revision: **Final**

<b>Project co-funded by the European Commission within the Sixth Framework Programme (2002-2006)</b>		
<b>Dissemination Level</b>		
<b>PU</b>	Public	X
<b>PP</b>	Restricted to other programme participants (including the Commission Services)	<input type="checkbox"/>
<b>RE</b>	Restricted to a group specified by the consortium (including the Commission Services)	<input type="checkbox"/>
<b>CO</b>	Confidential, only for members of the consortium (including the Commission Services)	<input type="checkbox"/>

## **NEU Deliverable: 1.5.3**

### **Initial analysis of greenhouse gas fluxes in relation to nitrogen inputs**

Sutton MA, Tang YS, Flechard C., van Dijk N, Fauvel Y, Dämmgen U, Djuricic V, Vidic S, Gliha Z, Borovecki D, Mitosinkova M, Hanssen JE, Uggerud TH, Sanz MJ, Sanz P, Chorda JV, Ferm M, Perrino C, de Vries W, van Oijen M, Smith, RI, Helfter C, Janssens I, Bleeker A, Schaufler G, Kitzler B, Skiba U, Butterbach-Bahl K and Zechmeister-Boltenstern S.

## **1. Background**

A key issue for NitroEurope is to estimate the extent to which nitrogen inputs alter net greenhouse gas fluxes. This question is being addressed at several different scales and using different approaches across NitroEurope. Here we summarize the potential for Europe-wide multi-site analysis from the NitroEurope Level 1 network, and the interaction with the independent CarboEurope IP.

## **2. Approaches**

### **2.1. Relationship of nitrogen deposition to carbon sequestration at CarboEurope sites.**

Under the CarboEurope project measurements of net ecosystem exchange (NEE) for CO<sub>2</sub> have been made across a network of c 50 'main sites', including forests and other ecosystems. An analysis of a forest subset of these sites was reported by Magnani et al. (2007), who identified a clear relationship between stand lifetime net ecosystem productivity (NEP) and atmospheric nitrogen deposition.

A remarkable feature of this analysis, which was published in Nature, was that at most of the sites reported by Magnani et al., there were in fact no site based measurements from which to estimate atmospheric nitrogen deposition. The analysis was therefore based on an interpolation of nitrogen wet deposition measurements from a European network operating c. 1990.

In recognition of this limitation, the NEU Level 1 network was established to provide measurement based estimates of N deposition to all the CarboEurope sites, including the NitroEurope Level 3 and Level 2 sites. For this purpose this included:

- Measurements of gaseous and aerosol N air concentrations at 58 sites using an established low cost denuder (DELTA) method.
- Use of the DELTA data combined with micrometeorological data from all the Level 1 sites, and 3 independent dry deposition models, to infer total N dry deposition fluxes.
- Measurements of wet deposition at 15 of the Level 1 sites (number restricted by resource limitations) combined with mapping of wet deposition (which varies regionally, using a European scale atmospheric transport and deposition model (EMEP).

## **2.2. Extending the relationships for other N inputs and GHG exchange**

It was further noted that there was no central database in CarboEurope on site management history, while information on greenhouse gas fluxes was also not available from these sites. In consequence, effort has been placed in:

- Collecting site management history data for all of the CarboEurope sites, including where available, information on mineral fertilization, organic manure application, cutting and harvesting patterns.
- Developing a standard soil trace gas protocol for all of the Level 1 sites, where by soils are collected and subjected to a standard treatment of several temperature and moisture regimes to identify the relationships for potential soil N<sub>2</sub>O, CH<sub>4</sub>, NO and CO<sub>2</sub> exchange.

## **2.3. Re-interpretation of published data**

In addition to the measurement and data collection for the Level 1 sites, the publication of Magnani et al. (2007) provided a stimulus to evaluate the robustness of their conclusions as regards the response of NEP to atmospheric nitrogen deposition.

## **3. Results to date**

### **3.1. Establishment and first results of the NEU Level 1 network**

The first stage to establishing the Level 1 network was sharing of the DELTA technique with several other laboratories across Europe. This technique was originally developed by NERC-CEH for application in the UK National Ammonia and Nitric Acid Monitoring Networks (Sutton et al., 2001). Traditional manual sampling for these components was conducted on an hourly-daily level, involving high analytical costs. In the DELTA approach, monthly sampling is typically used allowing low cost determination of the main spatial patterns and long term trends.

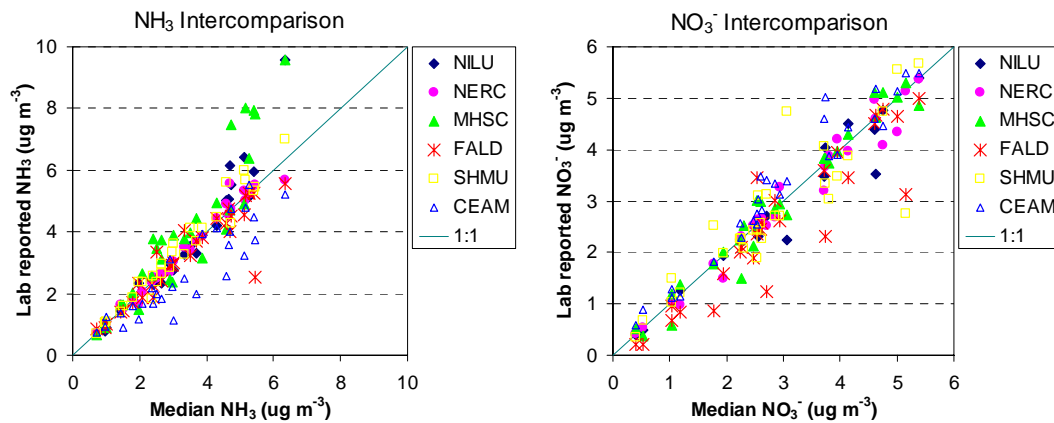
The DELTA approach of NERC-CEH was shared with NILU, MHSC, SHMU, INRA, FALD (VTI) and CEAM, with a first laboratory intercomparison made at 4 sites (Braunschweig, DE; Auchencorth, UK; Montelibretti, IT; Valencia, ES), over 8 sampling periods each of two weeks. These results demonstrated encouraging performance of the different labs in this intercomparison (Figure 1), which also provided a training to the laboratories in operating these systems (Tang et al., 2009).

Actual DELTA sampling in the Level 1 network (Figure 2) commenced in November 2006, with most sites operational from January 2007. Tang et al. (2009) have calculated the concentrations of NH<sub>3</sub>, HNO<sub>3</sub>, aerosol NH<sub>4</sub> and NO<sub>3</sub> for 2007, and these are illustrated in Figures 3 and 4.

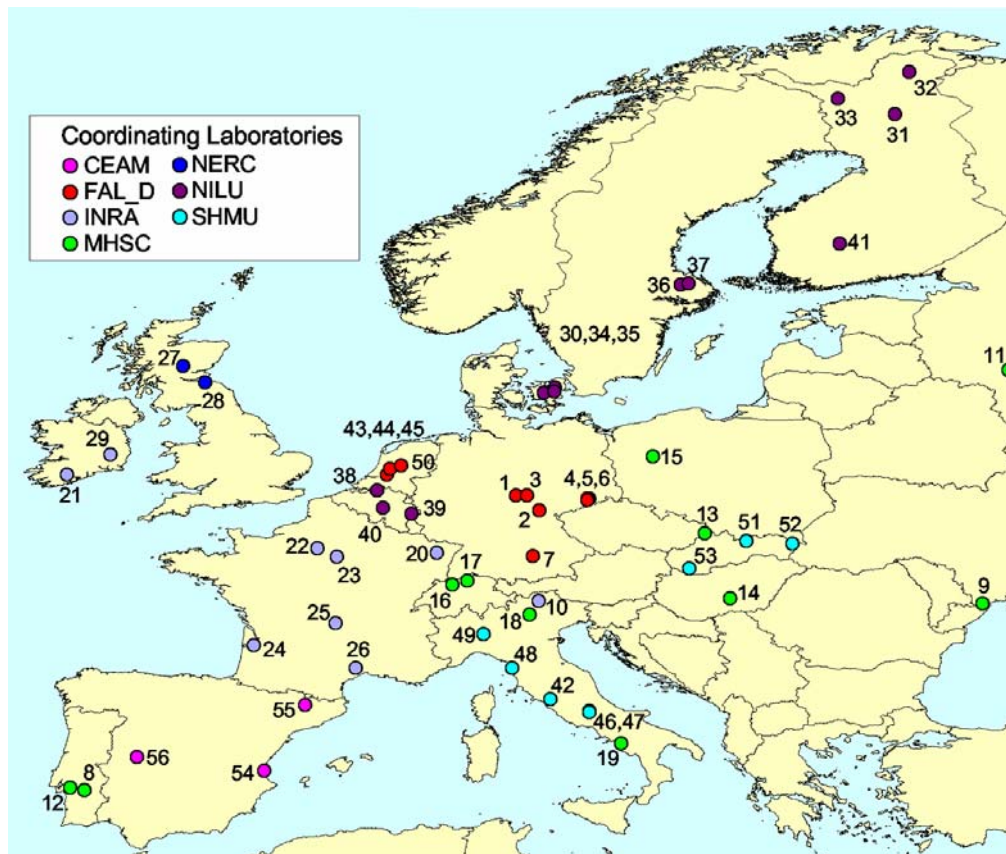
The analysis of Tang et al. (2009) has identified that the sampling for NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup> is rather robust, while the sampling for NO<sub>3</sub><sup>-</sup> corresponds to an upper particle size cut-off of 4-5 µm. For several further uncertainties have been highlighted, with the possibility that the current sampling methodology also records atmospheric HONO. Further tests are being made to quantify and investigate this possible interference.

Wet deposition measurements also commenced at the end of 2007, under the lead of SHMU. These are still under analysis. However, during the data review in Gothenburg (January 2009), it was concluded that more effort could be placed to

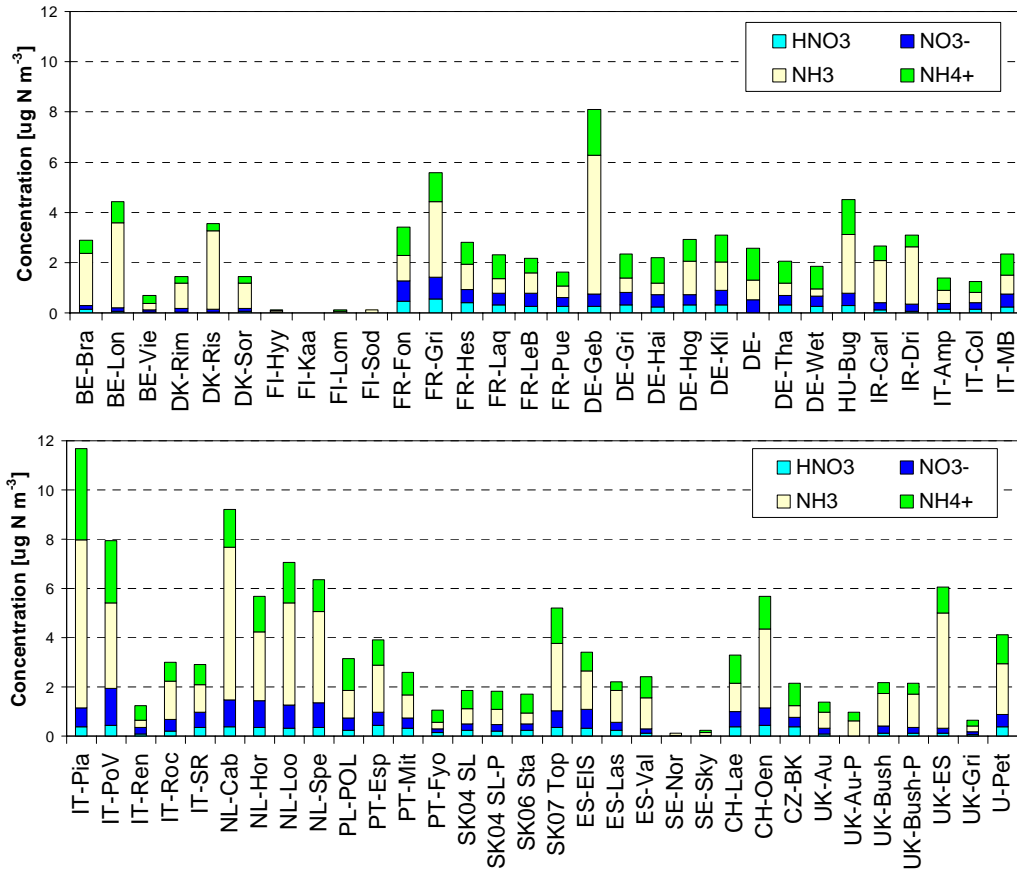
interpreting existing European wet deposition networks, and pending agreement by the NEU Scientific Steering Committee, this will be adopted under Component 6.1.



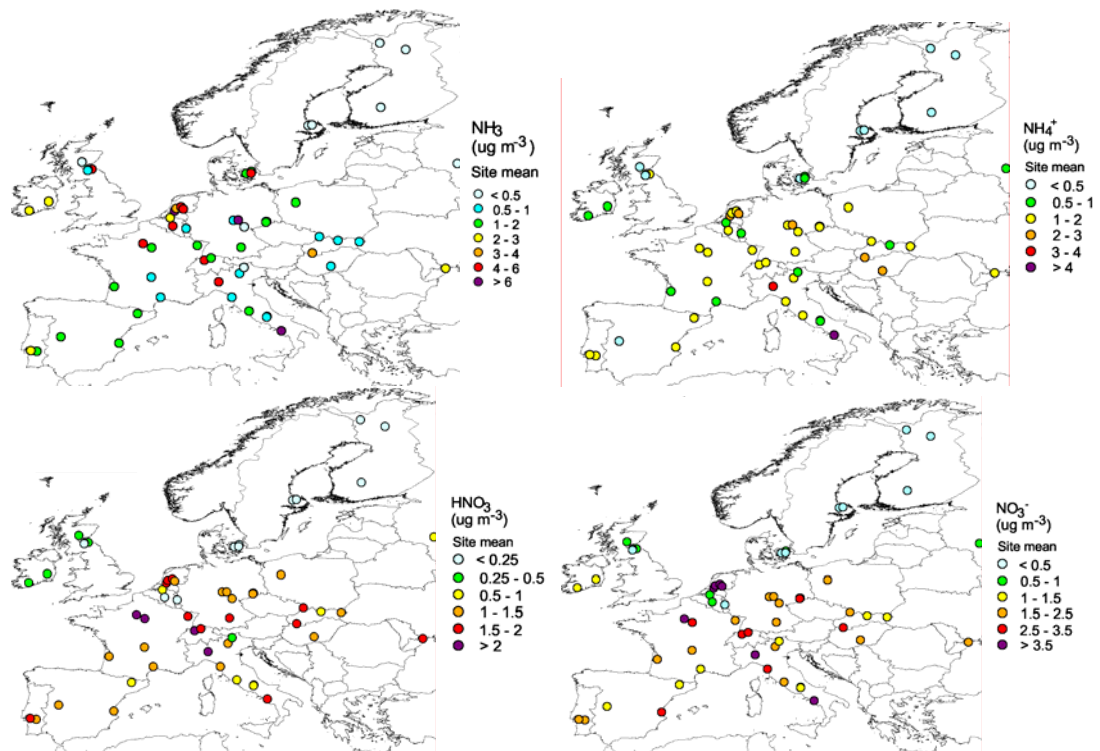
**Figure 1:** Performance of the different coordinating chemical laboratories for ammonia and aerosol nitrate in the first intercomparison (Other results for  $\text{HNO}_3$  and  $\text{NH}_4^+$  are reported by Tang et al., 2009). The under-reading for  $\text{NH}_3$  by CEAM was due to a fault in the initial analysis, and has since been rectified. The points show the results for individual 2-weekly determinations by the different laboratories.



**Figure 2:** Sites of the NEU Level 1 network operating in full from January 2007. The colour of the dots indicates the site allocations of the coordinating chemical laboratories sharing the work. Until August 2007, the French sites were managed by NERC-CEH, and were transferred to INRA due to CEH restructuring requirements.



**Figure 3:** Monitored annual mean concentrations of gaseous  $\text{HNO}_3$  and  $\text{NH}_3$  and particulate  $\text{NO}_3^-$  and  $\text{NH}_4^+$  at the Level 1 sites (Jan07-Dec07).



**Figure 4:** Monitored gaseous  $\text{NH}_3$ ,  $\text{HNO}_3$  and aerosol  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  concentrations in the NitroEurope Level 1 network. Each point is the mean of available for the period January - December 2007.

### **3.2. Collation of land management information**

As far as possible land management information has been now obtained for the Level 1 sites. In many cases it proved difficult to obtain this information for CarboEurope flux sites, and specific questionnaires were sent to all CarboEurope ecosystem site managers. In some cases, it appears that the site management history, including nitrogen fertilization inputs are not known, and uncertainty ranges will need to be set for these sites.

### **3.3. Estimation of N dry deposition fluxes**

Three models for calculating dry deposition are being applied as a means to indicate uncertainties, with the intention to calculate ensemble average estimates. Under the lead of INRA, Flechard has obtained micrometeorological data for each of the Level 1 sites, and applied these in the CBED, EMEP and EDACS models.

Preliminary estimates (Figure 5) show that dry deposited N from ammonia represents the single highest input of atmospheric nitrogen to unfertilized ecosystems, accounting for up to 95 % of the total dry N deposited at sites. While the application of three established and published models helps define the uncertainty range for N deposition estimates for all sites, the comparison of the three models with actual flux measurements at Level 2 and Level 3 sites will, in due course, help validate or improve specific parametrizations (e.g., for  $R_w$  and  $\text{NH}_3$  compensation point) for a wide range of ecosystems and pollution climates. Combining the dry deposition and wet deposition estimates will also, in due course, allow the examination of measured net GHG exchange in relation to atmospheric and agricultural N inputs across the Level 1 network.

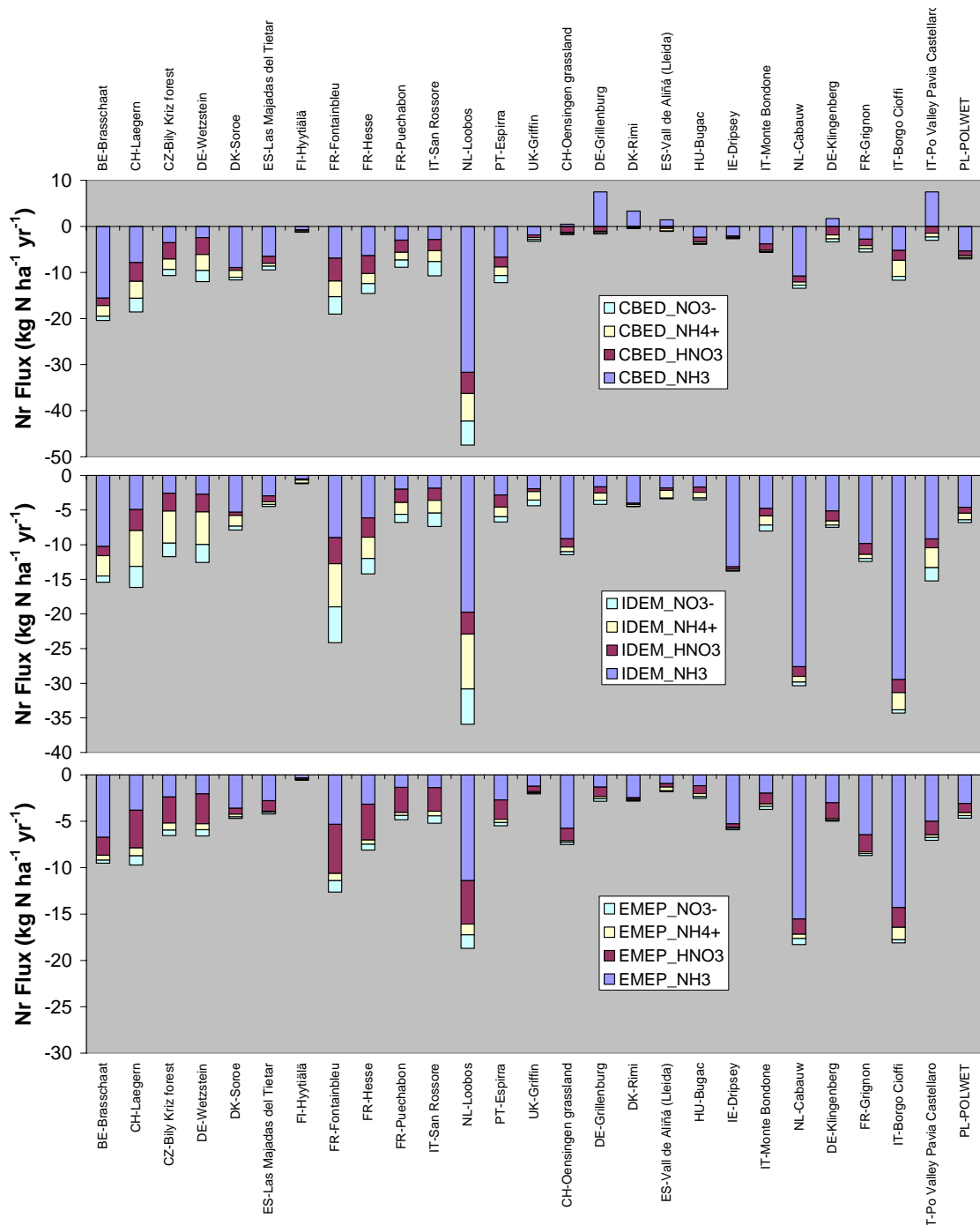
### **3.4. Application of a standardized soil trace-gas bioassay for all Level 1 sites.**

Under the lead of BFW, Zechmeister and colleagues have developed a standard protocol for the treatment of soil cores collected from the Level 1 sites, as reported by Schaufler et al. (2009). In a major analysis, they have collected soil cores from the Level 1 sites, in three tranches, first considering the 13 Level 3 sites of NitroEurope. Entire soil cores (not broken or sieved) were stored frozen and then incubated at a range of different soil temperatures and moisture contents (different water filled pore space, WFPS). After stabilization for each condition, trace gas fluxes were measured including  $\text{N}_2\text{O}$ ,  $\text{NO}$ ,  $\text{CH}_4$  and  $\text{CO}_2$ .

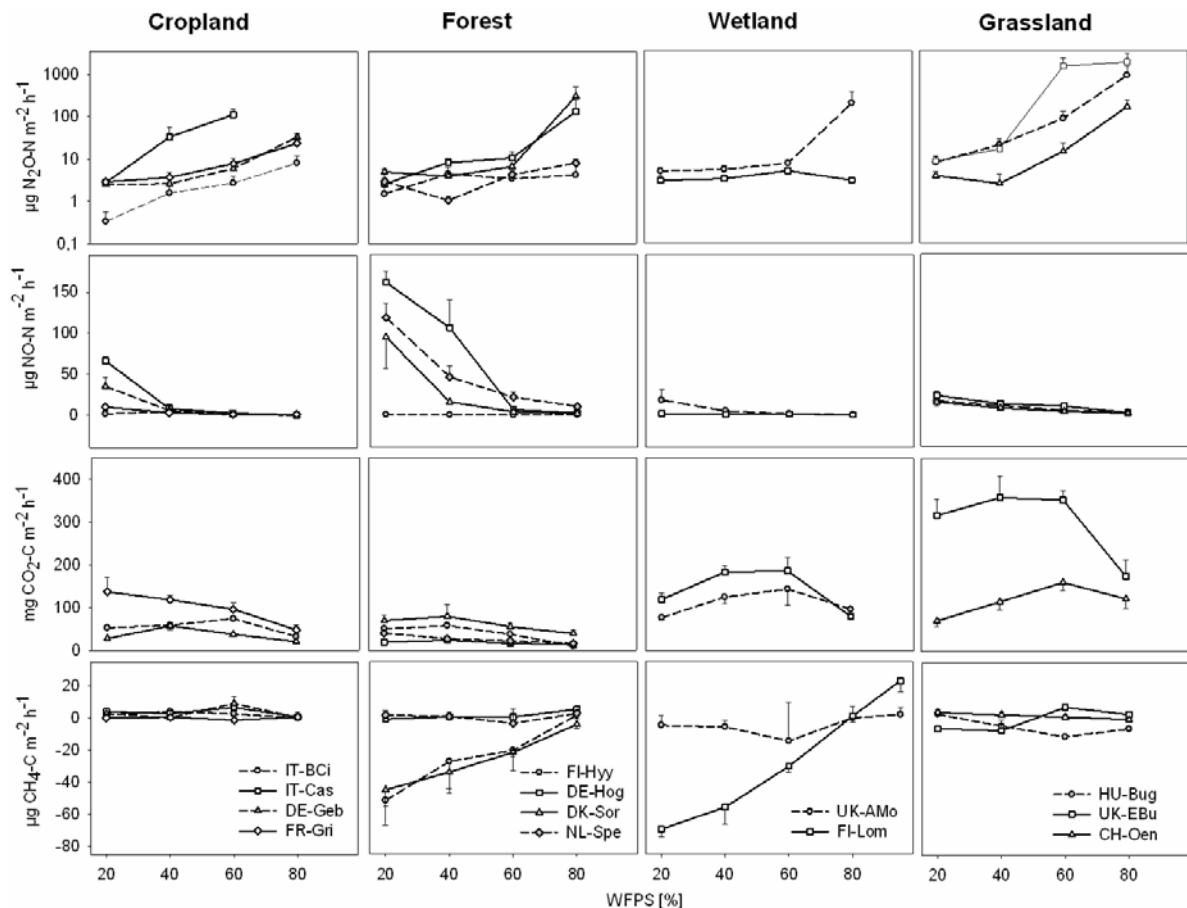
Examples from the first 13 sites studied are shown in Figure 6, demonstrating the clear temperature and moisture dependence for each of the gases. These measurements provide the basis for an inferential approach to estimate soil gas fluxes at the Level 1 sites, which is under development.

### **3.5. Evaluation of published datasets**

A key observation of the dataset of Magnani et al. (2007) was a very high response of NEP to atmospheric N inputs. This generated significant interest, though a nature commentary (Hogberg, 2007) and in the press (Brahic, 2007).



**Figure 5:** Preliminary modelled estimates of annual dry deposition fluxes of reactive nitrogen (Nr) at 27 sites of the NEU inferential network. Negative values denote deposition from the atmosphere.



**Figure 6:** Trace gas fluxes for soil cores collected from a subset of the Level 1 sites. In this figure, the dependence on Water Filled Pore Space (WFPS %) is shown, at 15°C, with sites separated by land use.

Both these commentators highlighted that the C-N response apparently reported by Magnani et al. (2007) was very high, with a figure of 400 kg C being drawn down “for every 1 kg N rained out of the atmosphere” being quoted from the author’s press release. Hogberg (2007) suggested that the response was probably an order of magnitude lower at 40 kg C per 1 kg N deposition.

Two issues emerge from the analysis of Magnani et al. (2007). Firstly, what was the true value of the atmospheric deposition to their sites, and secondly, were there other interactions which would mean such a high C:N response was not realistic?

As regards the first point, the ambiguity of Magnani et al., press release would have mislead many generalist commentators. They had intended “rained out of the atmosphere” to imply specifically wet deposition, excluding dry deposition. In fact, their paper, did not anywhere specify 400:1. However, the slope of the linear portion of their results, at 730 kg C : 1 kg N (wet deposition) was still very high. If 50% of the inputs were as dry deposition, this still amount to a response of around 360:1.

These issues were re-examined in NitroEurope firstly by de Vries et al. (2008), who commented on the uncertainty in the dry deposition estimates. From an independent analysis of 400 forest plots across Europe, these estimated that the C:N response should be of the order of 40:1. Secondly, Sutton et al. (2008) specifically recalculated N deposition to the European sites of Magnani et al. (2007), using the EMEP model,

as well as indicating uncertainties from other estimates. Using the EMEP model inputs, they estimated that the Magnani et al. response (if interpreted as purely a nitrogen result) would have been c. 177:1, much smaller than the original numbers being discussed. Importantly, however, Sutton et al. (2008) also questioned the causality of the Magnani et al. regression, demonstrating significant interaction with growing degree days (>5 degrees C) and moisture availability. If these effects were factored out, Sutton et al. (2008) concluded that the Magnani et al. dataset were consistent with a C:N response of 68:1. They used a modelling exercise at 22 sites, to reproduce the artefact, showing how climatic figures would amplify the apparent C:N response in such a spatial analysis.

This debate has continued, most recently in an open debate at the CarboEurope final conference (Jena, October 2008), and will doubtless run further.

For the present analysis these results highlight the importance and major uncertainty interactions between N deposition and greenhouse gas balance. In this regard, providing real measurement-based site estimates of atmospheric deposition, coupled with associated GHG assay measurements, will provide a major advance to the debate.

#### **4. Conclusions of the initial analysis**

It is clear that the present assessment at the Level 1 sites is an ongoing task. The initial analysis presented here, and based on several published and manuscript contributions highlights:

- 1) the robustness of the DELTA methodology for  $\text{NH}_3$ ,  $\text{NH}_4^+$  and  $\text{NO}_3^-$  and the need for further testing regarding the possible interference of HONO in the  $\text{HNO}_3$  measurements.
- 2) The need to continue the DELTA Level 1 network measurements, especially to quantify the extent of inter-annual variability
- 3) The need to improve datasets on field management practice at carbon flux field sites, and to work further with site managers to obtain data where available.
- 4) The quantitative importance of ammonia in being the largest single contribution to N dry deposition at most sites, and hence the importance for reliable dry deposition models of this compound, particularly considering the bi-directional nature of ammonia fluxes.
- 5) The need to put further effort in estimating wet deposition to the NitroEurope level 1 sites, which is planned to be done by a re-allocation of resources to Activity 6.1, to prioritize analysis of existing European N wet deposition data.
- 6) The need to consider long term management interactions, when finally interpreting the relationships between N deposition and greenhouse gas balance.

#### **5. Ongoing tasks**

The next steps of the work will include:

- 1) Continuation of the DELTA and wet deposition measurements
- 2) Implementation of the three dry deposition models at all the level 1 sites.
- 3) Completion of the Soil trace gas bioassay for Level 1 sites.

- 4) Comparison of the soils trace gas bioassays with detailed measurements at Level 1 sites, and testing of an inferential approach based on modelled soil temperature and WFPS to estimate annual soil trace gas exchange.
- 5) Collation of annual carbon flux data from the CarboEurope project. (It has not yet been possible to obtain these data but they should be available for this study.)
- 6) Further efforts to obtain relevant management and site history data for each of the Level 1 sites.
- 7) Process based modelling of net GHG exchange for the Level 1 sites, and establishing relationships with the measurements.
- 8) Collation of the annual results to provide multi-year estimates to examine the relationships between different site N inputs and net greenhouse gas exchange, including analysis of the associated uncertainties.

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