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

D1.3.1

The first operational state-of-the art continuous European measurement network for Nr and GHG fluxes and N-C pools

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RE	Restricted to a group specified by the consortium (including the Commission Services)	☐
CO	Confidential, only for members of the consortium (including the Commission Services)	☐

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1. Ongoing Activities

Progress of the Activities 1.1 to 1.5 was reported and discussed at the NEU AGM (Feb 07) in Paestum, Italy; later in the year Activity 1.2 met in June 07 in Edinburgh, UK, Activities 1.1 – 1.4 in September 07 in Copenhagen , DK and Activity 1.5 in October 07 in Edinburgh, UK.

Activity 1.1

Task 1.1.1: Standard protocols for the calculation and QC/QA of eddy-covariance fluxes of CH_4 and N_2O.

A workshop has been arranged at the Hyytiala (Finland) field centre for April 2008, in collaboration of NitroEurope with ICOS and iLEAPS, to review eddy-covariance measurement approaches, discuss problems and to develop unified strategies for eddy-covariance analysis and gap filling. Background documents are being drafted.

Task 1.1.2: Development/improvement of TDL-AS systems.

Inlet characterization has continued on the UoM QCL-AS to test inlet materials for ammonia flux measurements. The instrument was compared against an AMANDA NH_3 gradient system at Easter Bush (Scotland, UK) after a fertilization period. The TDL-AS system for $^{13}CO_2$ of IMK has been deployed for initial gradient and cuvette measurements. Analysis is ongoing, but, due to very wet conditions, fluxes were close to the detection limit. In addition, through national funding, a commercial proton transfer reaction mass spectrometer (PTRMS) has been adapted for eddy-covariance measurements of NH3 and is being compared with an NH_3 gradient system.

Task 1.1.3: Development of Aerosol / Acid Gas Flux Instrumentation.

An intercomparison study for measurement systems for concentrations and fluxes of NH_3 and HNO_3 has been organized for three weeks commencing 18 August 2008. The GRAEGOR instruments are now fully operational and a paper describing the measurement system has been submitted to Environmental Science and Technology, in collaboration between NERC, MPI-Mainz and ECN. A 2nd generation prototype of the NH_3 photo-acoustic analyser has been developed and is being tested against an AMANDA NH_3 analyser at Bugac (Hungary). First results are looking very promising. A 2nd generation Aerosol Mass Spectrometer, based on a time-of-flight mass spectrometer has been purchased by NERC with national resources, providing a much improved basis for eddy-covariance flux measurements of NO_3^- and NH_4^+. The eddy-covariance software for data acquisition and analysis is being developed in collaboration with national UK funding and a US collaboration. A joint experiment has been

scheduled in June/July 2009 at Speulder Bos (The Netherlands) to use this state-of-the-art instrumentation to study aerosol fluxes and gas / aerosol interactions at this site.

Tasks 1.1.4 & 1.1.5: Chemistry Models & Inverse-Lagrangian Approaches.
Less progress has been made with these two tasks. A field campaign is currently being designed to study the NO-NO_2-O_3 triad, taking into account the limitations imposed by existing instrumentation. The revision of the inverse Lagrangian code and distribution throughout the community has still to happen.

Activity 1.2

1.2.1: Theory development

Existing flux data of NH_3 and CO_2 have been used to simulate time-averaged protocols and to quantify errors induced by averaging information on turbulence and concentration differences separately, ignoring the co-variance between these two. In addition, micrometeorological data from the Level-2 and Level-3 sites were used to investigate the frequency of atmospheric stability distribution at the various measurement sites to assess the suitability of the different measurement approaches across the network. These investigations informed the decision on which low-cost instrumentation to develop for the flux measurement of NH_3 / HNO_3. A paper is in preparation.

Task 1.2.2: Development and testing of low-cost instrumentation
Much effort has gone into continuing the development and testing of low-cost micrometeorological measurement approaches for reactive nitrogen compounds. Three systems were tested: a time-averaged gradient (TAG) system and two long-term relaxed eddy accumulation (REA) systems, using either filter packs or denuder / filter combinations. A major challenge was found to be a reliable yet cost effective flow control for fast switching REA systems. The TAG system was identified to be the most reliable and validated system at present, suitable for measurement of NH_3 and HNO_3 fluxes above low vegetation. The test indicated, however, that gradients of the aerosol components (NH_4^+, NO_3^-) are too small to be resolved with the analytical techniques available. Deposition of these components will need to be derived by inferential modelling; using the models developed under A1.5 and the Special Topic aerosol flux measurements of A1.1/A1.3. A validated approach suitable for forests has not yet been identified, and thus testing of REA and TAG approaches over forest will continue before a decision is made.
In addition, an integrating bag sampler has been developed and tested in conjunction with a commercial UIT autochamber. This system was then successfully inter-compared with hourly measurements.

Task 1.2.3: Development and implementation of Level-2 sampling strategy
The TAG approach has been refined and a system has been identified, which will be deployed at 18 Level-2 and Level-3 sites across Europe, covering the low vegetation semi-natural sites and selected agricultural sites. This system is limited to NH_3 and, at selected sites, HNO_3. Testing of REA and TAG approaches continues at the forest

sites to finalise the strategy for aerodynamically rough surfaces. Meanwhile, the TAG system will be placed at four forest sites implemented as "conditional concentration" monitoring system.
The low cost chamber sampling system for N_2O and CH_4 was developed and tested using the UIT autochambers. To cut costs further and to increase the number of replicate samples, for the final product we have decided to use a modified version of the chamber built by MPI, Jena.
Tender specifications for both systems have been drawn up and are currently openly advertised throughout and beyond the NitroEurope community.

Task 1.2.4: Start of Level-2 flux measurements.
The start of the Level-2 measurements has been postponed further from 1 April 2008 (Month 27) to 1 May 2008 (Month 28).

Task 1.2.5: Measurement of N_2 fixation.
N_2 fixation was identified to be important at only one single Level-2 site. At this site a more detailed (isotopic labelling) approach will be deployed to quantify the magnitude of the fixation. However, development of low-cost approaches for the estimation of N_2 fixation will continue throughout the project to develop techniques that could form the basis for the future extension of the network.

Activity 1.3

NEU Flux network

The 13 Level 3 sites (4 forests, 3 grasslands, 4 arable and 2 moorland sites) are set up and the bulk of the mandatory measurements are made at the appropriate frequency. The data are compiled in standardised Excel spreadsheets, which was developed in C7 with feedback from the C1 and C2 community. Data are submitted every 6 months and will eventually coincide with the Carboeurope submission dates. To date, activity 1.3 has submitted data for following periods: 01/08/2006 to 31/12/2006, 1/1/2007 – 30/6/2007. Interesting data and Special Topics measurements (Task 1.3.2) beyond the mandatory list include: at Hyytiälä, FIN, pine forest, N_2O and CH_4 fluxes measured by static chambers and soil profiles show good agreement. The N_2O flux is temperature dependent and small 2-8 µg N m^{-2} h^{-1}. Also at Sorø, DK, beech forest, N_2O and NO fluxes (measured by gradient) are small, but a laboratory study has shown significant losses of N_2. This group is optimizing the mass balance equation for calculation of NO fluxes. At Speulder Bos, NL, a Douglas fir/oak mixed forest, in addition to the mandatory measurements, NH_3 concentrations are initiated above the canopy using the GRAHAM NH_3 gradient analyzer, and the fourth forest site, a spruce forest in Hőgelwald, GER, has a record of highest coverage of mandatory measurements since at least 2005. The arable site Gebesee, GER, makes monthly measurements of microbial biomass and has developed a very economic static autochamber for soil GHG flux measurements. The group at Grignon, FR, has found that GHG flux measurements made by enclosing a mature maize plant with a transparent chamber does not provide very consistent data. The rice crop at Castellaro, Italy, showed the typical behaviour of high N_2O fluxes after N fertilisation before flooding. Flooding reduced the N_2O peak but increased the CH_4 emission. At Borgo Cioffi, Italy, good agreement between eddy covariance and chamber measurements of CH_4 fluxes was observed over a crop of Lolium perenne. N fertilisation did not affect the CH_4 flux. Also, at the intensively managed grazed grassland at

Easter Bush, UK, good agreement between eddy covariance and static manual chamber measurements, here for N_2O, were observed. At the grassland site at Oensingen, CH, NO fluxes were almost always below the detection limit, but denitrification to N_2 appears to be a significant loss mechanism which has been identified to be the largest uncertainty in the N budget. At the much drier grassland site at Bugac, HU, a steady increase in the NO/N_2O emission ratio coinciding with a reduction in soil water content was observed. Here an intercomparison between the Bugac and Hogelwald flux chambers showed a good agreement for N_2O, but a not so good agreement for CH_4 fluxes. At the two semi-natural sites on organic soil (Auchencorth Moss, UK and Lompolojänkkä, FIN) N fluxes were very small. Interestingly at both sites N_2O concentrations in the peat were the same as in the air, but CH_4 and CO_2 concentrations in soil were much larger than in air.
The mandatory measurements will continue, with the ongoing debate of the importance of reduction of N to N_2.

Acitivty 1.4

The activity 1.4 is subdivided in several tasks, all of which made substantial progress in this 6 months reporting period. In particular, with regards to Task 1.4.1, key laboratory studies were performed to investigate foliar exchange of NH_3 and N_2O with the atmosphere, in interactions with N dissolved in soil solution (inorganic N, amino acids), as well as with amino acids (1 μg N/g 10-25%) and soil NO_3. Additionally specific protocols were prepared to distribute to Level 3 and Level 1 sites for sampling of plant material for N analyses. With regards to Task 1.4.2, a major field campaign was conducted to sample soil cores at the Level 3 sites. Cores were sampled and divided into depth interval for the measurement of bulk density and of C and N pools in the bulk soil and in soil organic matter fractions. The analyses are in progress.
With regards to Task 1.4.3, progress was made towards the completion of PLFA analyses of soil sampled at Level 3 sites. For Task 1.4.4, a protocol for litter collection was distributed to level 3 sites, which are currently collecting the litter and sending it to the partner UT for the determination of litter production and the preparation of litter bag studies. For the Mediterranean study (Task 1.4.5), the study site was identified and a field campaign took place in early September to layout the plots, characterise the soil profile and collect soil samples. A meeting will take place in December to finalise the experimental work-plan and define the specific contributions by the different partners joining in the Mediterranean study.
About the investigation of the control of plant-soil N cycle (Task 1.4.6), a laboratory study under controlled condition was performed on fresh grassland soil from Massif Central (Clermont Ferrand). Soil was manipulated with sand addition to change the soil organic carbon concentration and incubated with differing amounts of cellulose. Microbial analysis (C, PLFA, B-ARISA, F-ARISA, 18S rDNA) were performed on the soil samples. To assess the sources of N_2O (Task 1.4.7) key laboratory experiment were conducted that demonstrated interference of ^{18}O exchange with H_2O during N_2O formation. Thus, the need was identified to modify the current methodology, possibly including the use of $N^{18}O_3$. A literature review was completed and it is now published (Kool et al., 2007, Rapid Communication in Mass Spectrometry, 21: 3569-3578).

Activity 1.5

Inferential N fluxes and C interactions

Task 1.5.2: Level 1 DELTA network

- Following a major DELTA inter-comparison exercise conducted at 4 sites with 6 laboratories (CEAM, FALD, MHSC, NERC, NILU, SHMU) between Jul and Oct-06, measurements in the Level 1 network formally started in November 2006.

- There are 58 sites (this includes 2 existing UK DELTA sites that are already operating under separate UK funding: Auchencorth and Bush) in the network. Some measurements started in Nov-06, whilst all site measurements were under way by Jan-07. The first annual estimates of atmospheric N inputs from the network should therefore be available by April 2008. The network will provide monthly measurements of NH_3/NH_4^+, HNO_3/NO_3^-, as well as SO_2/SO_4^{2-}, $HCl/Cl^-$and the base cations Ca^{2+}, Mg^{2+} and Na^+.
- As part of the QAQC of the network, a second smaller scale DELTA intercomparison was conducted from July to August 2007 at two contrasting sites: Auchencorth (UK) and MonteLibretti (Italy). Such intercomparisons are important to establish that good agreement can be obtained between laboratories in different climatic conditions. A 3rd DELTA intercomparison exercise is planned for spring 2008 at Auchencorth, UK and Braunschweig (Germany).
- Site questionnaires were sent to all sites at the beginning of November to update and to gather information for the NEU website metadatabase.

Task 1.5.3: Establishment of an inferential SVAT modelling framework

This task is to estimate monthly net exchange from measured monthly air concentration from the L1 network and (micro-)met data. The inferential modelling framework has been established, utilizing input from three existing models, and progress are made in establishing the availability of input meteorology. The work was moved from FAL-CH to INRA in Jul-07, associated with transfer of key staff between the institutes

Task 1.5.4: An annual simple soil/plant bioassay

This work is conducted by BFW. Work on the soils bioassay commenced in Spring 2006, starting with the Level 1 sites which are also “super sites” (level 3 sites). Work at all L3 sites was completed in autumn 2006 with good results, and the soil bioassay work is being extended to all L1 sites. Work began this spring, starting with 15 sites in Southern Europe. Each site was provided with sampling device for soil core sampling and a soil sampling protocol by the BFW team.
Sites covered:
Portugal: Mitra II, Espirra
Spain: El Saler, Vall de Aliná, Las Majades del Tietar
Italy: Po Valley Pavia, Piana del Sele, Roccarespampani, Amplero, Collelongo, San Rossore, Monte Bondone
France: Le Bray, Laqueuille, Puechabon

Task 1.5.5: Monthly bulk (wet) deposition measurements

Measurements of bulk wet N deposition were rescheduled to be started once the L1 DELTA network was fully operational, and are now being established. A short-list of 15 sites has been made (official commitment is to do 12-15, for monthly sampling), and a suitable bulk sampling method selected (Rotenkamp sampler). A draft bulk sampling protocol was also written and disseminated to the sites, and agreement was obtained from 14 of the sites to run the equipment at their sites. Rotenkamp samplers were ordered from the manufacturer in Germany in late August 2007, and were shipped directly to the 14 sites during October and early November 2007 following confirmation from sites. Chemical analysis of the monthly bulk samples is expected to be undertaken by SHMU, and possibly one or two other labs (to be confirmed). Bulk (wet) deposition measurement is expected to commence in Jan 08.

Task 1.5.6: Analysis of the CarboEurope CO_2 fluxes and NEU GHG emission potentials in relation to initial estimates of atmos. and agricultural N inputs.

Preliminary analysis will provide the basis to refine the later assessment of relationships and implications for the role of N on European GHG budgets.

Task 1.5.7. Analysis of intercomparison of low cost denuder sampling.

The 2006 (4 sites, 6 labs), and 2007 (2 sites, 6 labs) DELTA inter-comparison between labs intercomparison will be synthesised and written up. Adoption of the conclusions from DELTA intercomparison will be used to provide potential improvement of measurements in the Level 1 network.

Products and Dissemination (incl. papers submitted)

1.1. List of milestones/deliverables, including due date and actual/foreseen achievement date

Deliverable	Description	Due date (month)	Status or foreseen due date
D1.1.2	Inverse modelling tool for canopy sources & sinks for distribution within the NEU community sensor.	18	22
D 1.1.3	Prototype open photo-acoustic NH_3	18	Achieved
D 1.2.4	Design specifications for the low-cost instrumentation	16	Achieved
D 1.2.5	Protocol for low-cost N_2 fixation essay	18	24
D 1.3.2	A first year of data on detailed high time-resolution fluxes of Nr and GHG, for analysis and model verification within A3.3	18	Achieved
D 1.3.3	Initial analysis of Nr budgets and NGE in relation to detailed measurements of soil and plant N-C pools and processes	18	24
D 1.4.2	Dataset on plant nitrogen pools at Level 3 sites	18	30
D 1.4.3	Dataset on N source preferences in relation to root N acquisition at different environmental conditions	18	24
D 1.4.4	Dataset on soil C and N pools by depth intervals	18	24
D 1.4.5	A tested methodology for distinguishing between the various microbial sources of N_2O and N_2 using $^{15}N/^{18}O$ tracing	18	Achieved
D 1.5.2	1styr database on atmos. and agric. N deposition at CE main sites	18	Achieved
D 1.5.3	Initial analysis of GHG fluxes in relation to N inputs	18	24

1.2. List of publications submitted, including name of the journal reference

D. M. Kool, N. Wrage, O. Oenema, J. Dolfing and J. W. Van Groenigen 2007. Oxygen exchange between (de)nitrification intermediates and H_2O and its implications for source determination

of NO_3 and N_2O: a review. Rapid Commun. Mass Spectrom. 21, 3569–3578.

Gu, J., X. Zheng, Y. Wang, W. Ding, B. Zhu, X. Chen, Y. Wang, Z. Zhao, Y. Shi, J. Zhu, 2007. Regulatory effects of soil properties on background N_2O emissions from agricultural soils in China. Plant and Soil 295, 53-65.

Zheng, X.,B. Xie, C. Liu, Z. Zhou, Z. Yao, Y. Wang, Y. Wang, L. Yang, J. Zhu, Y. Huang, K. Butterbach-Bahl, 2007. Quantifying Net Ecosystem Carbon Dioxide Exchange (NEE) of a Short-Plant Cropland with Intermittent Chamber Measurements. Global Biogeochemical Cycles (submitted).
Zheng, X., B. Mei, Y. Wang, Y. Wang, H. Dong, H. Xu, G. Chen, Z. Cai, J. Yue, J. Gu, F. Su, J. Zou, 2007. Nitrous oxide emissions from plants sometimes might have been improperly quantified. Plant and Soil (submitted).

Zheng, X., B. Xie, B. Mei, Y. Wang, Y. Wang, H. Dong, J. Zhu, 2007. N_2O emission from soils or soil-plant systems might have sometimes been improperly quantified? Plant and Soil (submitted).

Bordás, Á., Weidinger, T., Horváth, L., Pintér, K., Machon, A. and *Gyöngyösi, A. Z.*, 2007: Uncertainties in gradient and profile methods for trace gas flux calculations. *Geophysical Research Abstracts*, Vol. **9**, EGU2007-A-08917, AS2.01-1WE4P-0094.

Grosz, B., Machon, A., Horváth, L. and *Weidinger, T.*, 2007: Measurement and modelling of N_2O and CH_4 fluxes at a grassland ecosystem in Hungary. *Marie Curie ILEAPS workshop Helsingborg*, Sweden, October 2007. (Poster.)

Machon, A., Grosz, B., Horváth, L. and *Weidinger, T.*, 2007: Measurement and modelling of fluxes of nitrogen compounds above a semi-natural grassland ecosystem in Hungary. *Marie Curie ILEAPS workshop Helsingborg*, Sweden, October, 2007. (Poster.)

Machon A., *Horváth L.*, *Grosz B.*, *Weidinger T.*, *Pintér K.*, *Nagy Z.* and *Tuba Z.*, 2007: Simulation of Nitrogen budget components from landscape scale using the DNDC model. *33rd Scientific Days of Meteorology, 2007. State of atmospheric environment: ecological interactions and health risks.* (Editors: *Bozó, L.*, *Gelencsér, A.* and *Horváth, L.*), *Hungarian Meteorological Service*, Budapest, p22. (In Hungarian.)

Pintér, K., Nagy, Z., Balogh, J., Barcza, Z., Kristóf, D., Weidinger, T., Grosz, B., Machon, A., Horváth, L. and *Tuba, Z.*, 2007: Components and micrometeorological measurement of carbon and nitrogen budget on landscape scale. *32nd Scientific Days of Meteorology, 2006. Cloud physics and micrometeorology.* (Editors: *Weidinger, T.* and *Geresdi, I.*), *Hungarian Meteorological Service*, Budapest, 161–168. (In Hungarian.)

Weidinger T. and *Bordás Á.*, 2007: Basic questions of surface and boundary layer meteorology. *32nd Scientific Days of Meteorology, 2006. Cloud physics and micrometeorology.* (Editors: *Weidinger, T.* and *Geresdi, I.*), *Hungarian Meteorological Service*, Budapest, 105–124. (In Hungarian.)

Weidinger, T., Bordás, Á., Mihailovic, D. T., Gyöngyösi, A. Z., Machon, A., Pintér, K. and *Horváth, L.*, 2007: Uncertainties in surface layer flux calculations using gradient and profile methods. *First Serbian Congress on Theoretical and Applied Mechanics, Kopaonik, Serbia*, 10-13 April, 2007. Proceedings, Editors: *Sumarac, D* and *Kuzmanovic, D.*, 267–274.

Weidinger, T., Gyuró, Gy., Orgoványi, A., Döri, I., Kalapos, T., Victor, A., Juhász, I., Tóth, P. and *Machon, A.*, 2007: The GLOBE program in the Hungarian environmental education. *Geophysical Research Abstracts*, Vol. **9**, EGU2007-A-09451, ES3-1TH5P-0005.

M. Pihlatie, J. Pumpanen, J. Rinne, H. Ilvesniemi, A. Simojoki, P. Hari and T. Vesala: Gas concentration driven fluxes of nitrous oxide and carbon dioxide in boreal forest soil Tellus 59B, 458-469, 2007.

Mäkiranta, P., Hytönen, J., Aro, L., Maljanen, M., Pihlatie, M., Potila, H., Shurpali, N., Laine, J., Lohila, A., Martikainen, P.J., and Minkkinen, K. 2007. Soil greenhouse gas emissions from afforested

organic soil croplands and cutaway peatlands. Boreal Environment Research, 12:159-175.

Ute Skiba, Eiko Nemitz, Chris Flechard, Timo Vesala, Per Ambus, Nicolas Brüggemann, Arjan Hensen, Jan Duyzer, Pierre Cellier, Annette Freibauer , Endzo Magliulo, Günther Seufert, Albrecht Neftel, Laslo Horvath, Julia Drewer, Sim Tang, Daniela Famulari , Tuomas Laurila (14), Sophie Zechmeister-Boltenstern, Francesca Cotrufo , David Fowler, and Mark Sutton (2007) Land atmosphere exchange of reactive nitrogen, extended abstract extended abstract of oral contribution to the 2nd ACCENT symposium, Urbino, July 2007, submitted to ACCENT Project Office

2. Other issues (problems, delays, …)

Activity 1.2: the manufacture and testing of the low-cost flux measurement systems (TAG and autochambers) is somewhat delayed, but a clear time-table is agreed. The development and testing of the low-cost micrometeorological techniques has been more difficult than anticipated and has consumed more resources than originally allocated. A clear strategy has been developed for rolling out the TAG approach to low vegetation. Testing for application above forest is still continuing as a robust approach has not yet been identified. In addition, there was a change of autochamber we decided to use. This change was based on the high costs of the UIT chamber we originally we wanted to use. The new chamber, developed by MPI Jena, is very low cost, and will allow us to stock more sites with more chambers.