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**Report on sampling strategy for providing input data to the *NitroScape* model on the different landscapes**

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## Sampling strategy for input and verification data of the NitroScape model

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This report constitutes project deliverables D4.3.2 and D4.3.3:

D4.3.2: Report on sampling strategy for providing input data to the NitroScape model on the different landscapes;

D4.3.3: Report on sampling strategy for providing verification data for the NitroScape model on the different landscapes.

### Introduction

Under the ‘Landscape Analysis’ component (C4) of the EU IP NitroEurope, an analysis of landscape-scale nitrogen fluxes will be carried out through the use of a new multi-component model ‘NitroScape’. NitroScape will be applied to six European landscape study sites (Figure 1). The model requires measurement data obtained at each of the study sites for input to the model as well as measurement data that can be used to verify the model outputs. This report details the strategies for both sets of measurements (model input and verification).

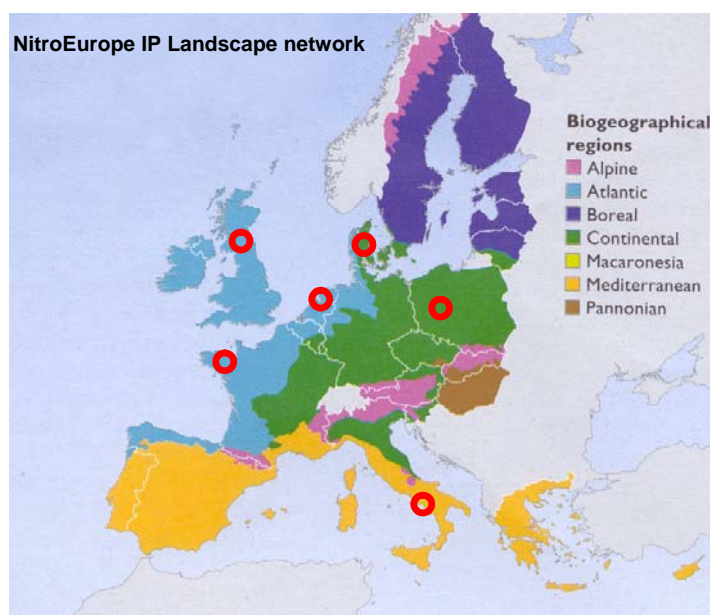


Figure 1: Map showing the approximate locations of the six European landscape study sites

### Measurements for NitroScape inputs

The NitroScape model will consist of four component sub-models representing the following systems: Farm, Ecosystem, Hydrology and Atmosphere. Within the work of C4, a list of component model inputs has been produced. The input data that are being measured in the study areas are summarised in Table 1 and are used as the basis of the measurement strategy. For completeness, all model input variables (including those that are already available or can be derived from standard or assumed values) are listed in Appendix 1.

Table 1: Summary of measurement data needed for NitroScape inputs (units in parentheses).

<b>Soil data</b>		
Typical profiles for each soil type in the landscape (see Appendix 2 for selection protocol) providing the following data:		
<b>Physical properties</b>	<b>Hydrological properties</b>	<b>Chemical properties</b>
Bulk density (g cm <sup>-3</sup> dry soil)	Saturated conductivity (m h <sup>-1</sup> MPa <sup>-1</sup> )	pH (-)
Soil depth (cm)	Field capacity (% water by volume)	C <sub>org</sub> (mg g <sup>-1</sup> dry soil)
Texture (sand, silt, clay %)	Wilting point (% water by volume)	N <sub>org</sub> (mg g <sup>-1</sup> dry soil)
	Infiltration rates (mm h <sup>-1</sup> )	C:N ratio (%)
	pF (soil water retention) curves. This is derived from measurements of volumetric water content (%) at different values of suction applied (- kPa).	
<b>Meteorological data</b>		
The following variables will be measured at a meteorological station within the study area or nearby (hourly if possible):		
Wind speed (m s <sup>-1</sup> )		
Wind direction (degrees from true north)		
Air temperature (degrees Centigrade)		
Precipitation (mm/measurement period))		
Global radiation (W m <sup>-2</sup> )		
Evapotranspiration over grass (mm day <sup>-1</sup> )		
Relative humidity (%)		
Monin-Obukhov length (m)		
N in wet/dry deposition (g N m <sup>-2</sup> y <sup>-1</sup> )		
Atmospheric CO <sub>2</sub> concentration (ppmv)		

Soil data only need to be recorded once during the NitroScape simulation period, whereas the meteorological data are to be measured continuously.

### Measurements for NitroScape verification

The NitroScape model makes many assumptions and relies on running detailed component models with non-detailed input data. In addition to this, the model will simulate a complex three-dimensional system with a large number of elements (e.g. farms, arable fields, grasslands, forests, rivers etc.). It is therefore necessary to verify the model outputs to assess if the simulations are realistic. To achieve this, a series of verification measurements is being carried out at each of the six study areas for the entire NitroScape simulation period (1-2 years, depending on the study area). These measurements are divided into four categories:

- Atmosphere
- Soil solution
- Hydrology
- Ecosystem

A measurement protocol (based on those of Component 1) has been devised for each of these measurement categories. These protocols can be found in Appendices 3 to 7.

## **Measurement Strategies**

### Atmospheric measurements

The atmospheric sub-model of NitroScape will predict spatially and temporally varying atmospheric concentrations throughout the study area. A measurement strategy is therefore needed to capture this spatial and temporal variation. This is being done through sampling networks for each study area to measure mean monthly atmospheric concentrations of ammonia (NH<sub>3</sub>) throughout the NitroScape simulation period. The usefulness of diffusion tube measurements of N<sub>2</sub>O was assessed. The conclusion made was that the reported accuracy of the diffusion tubes (Gradko: ±15%) would not be sufficient to detect local fluctuations above background values (~300 ppbv) and, therefore, these measurements will not be made. The measurement networks will consist of at least ten measurement locations for NH<sub>3</sub>. Ammonia will be measured using one of two methods: CEH ALPHA samplers [1] or Gradko diffusion tubes [2]. Presently there are some doubts over the detection limit of the Gradko tubes, which may be a problem in study sites with low concentrations. An intercomparison of the two methods is currently underway to assess the accuracy and detection limit of the Gradko tubes.

The atmospheric sub-model will also predict emission and deposition fluxes. Since these fluxes are more difficult to measure, measurements will only be carried out where the expertise exists or where they are already being measured in the study area for another project component. Where these measurements are done, NH<sub>3</sub> will be measured using one of three techniques (aerodynamic gradient, eddy covariance or relaxed eddy accumulation) and N<sub>2</sub>O (and CH<sub>4</sub>) fluxes will be measured using eddy covariance or static chambers. For the full measurement protocol see Appendix 3.

### Ecosystem measurements

The spatial variation of the leaf area index (LAI) and the leaf nitrogen content (leaf-N) predicted by the ecosystem sub-model(s) will be verified by comparison with spatial distributions produced from satellite data. To verify the assumptions used in the production of these data, the data must be compared with one-off field measurements. At 3-8 field plots within each study area, measurements of LAI and leaf-N (and possibly leaf chlorophyll) will be made, following the protocol reproduced in Appendix 4.

### Soil solution measurements

The ecosystem sub-model(s) will also predict the spatial and temporal evolution of the soil nitrogen pools. To verify these predictions, measurements of inorganic nitrogen pools (nitrate and ammonium) will be made every two months at a specified number of locations. The detailed protocol can be found in Appendix 5.

### Groundwater measurements

Groundwater measurements provide methods for verifying the predictions of leaching by the ecosystem sub-model(s) and water transfer of the hydrological sub-model of NitroScape. Two types of measurement are required: (i) the depth of groundwater below soil surface (water table depth) and (ii) groundwater concentrations of nitrate, ammonium and total nitrogen. In some landscapes, a network of piezometers will be placed along suitable transects and the measurements made monthly. Appendix 6 provides the full measurement protocol.

### Hydrological measurements

Stream flow data are crucial for the verification of the hydrological sub-model of NitroScape. Data on dissolved stream components can also be used to test the credibility of the coupled hydrological-biogeochemical component as well as the capability of the NitroScape model to simulate in-stream processes. It is proposed that measurements of the following parameters are made across the majority of the 6 study landscapes: water level (which can be translated into discharge through the use of a ratings curve), nitrate ( $\text{NO}_3^-$ ), ammonium ( $\text{NH}_4^+$ ), total nitrogen (TN) and dissolved organic carbon (DOC). Ratings curves provide the relationship between the stream depth and the flow rate at a particular location. They can be constructed by measuring the flow rate for different stream depths using either a current meter or the salt dilution technique. Continuous or periodic stream depth measurements can then be translated into stream flow data. The chemical analyses of the stream water will be done bi-weekly by grab sampling (for streams where continuous analysis is not done). Full details of the measurement protocol are in Appendix 7.

## **References**

- [1] Tang, Y.S., J.N. Cape, and M.A. Sutton (2001) Development and types of passive samplers for monitoring atmospheric  $\text{NO}_2$  and  $\text{NH}_3$  concentrations. In Proceedings of the International Symposium on Passive Sampling of Gaseous Air Pollutants in Ecological Effects Research. The Scientific World **1**, 513-529.
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## Appendix 1

### Complete list of input data required by NitroScape sub-models

#### Domain data

Digital elevation model  
Digital land use classification  
Latitude

#### Atmosphere

Source dimensions  
Emission fluxes  
Roughness length ( $z_0$ )  
Canopy resistance ( $r_c$ )  
Deposition velocity

#### Vegetation

LAI (if available, seasonal development of LAI)  
Maximum canopy height  
Maximum root depth  
Fraction of C in biomass  
Fraction N and P in biomass  
Maximum stomatal conductance  
Grassland functional types (fraction of legumes)  
Shoot biomass  
Root biomass  
Leaf biomass  
Peak biomass  
Shoot biomass C/N  
Root biomass C/N  
Leaf biomass C/N

#### Farm management

Farm system  
Grazing start/end date  
Dry weight biomass consumed daily  
Number of grazing days  
Dry weight manure deposited daily  
Manure composition  
Hay making date  
Animal density  
Fertilizer application  
Crop rotation  
Thinning, cutting  
Description of the herd  
Periods of full time housing  
Batch of animal managed on the same plot  
Imported animals to the farm  
Exported animals from the farm  
Calving distribution  
Herd performance (live, mature, gain or loss weight)

Type of housing per category of animal  
Type of mineral fertilisation  
Type of organic fertilisation  
Amount of mineral fertilisation  
Amount of organic fertilisation  
Date of mineral fertilisation  
Date of organic fertilisation  
Type of roughage/concentrates  
Amount of roughage/concentrates distributed  
Date of roughage/concentrates distribution  
Type of storage for manure  
Fossil fuel consumed on the farm  
FYM/slurry imported onto farm  
FYM/slurry exported from farm

**Meteorology**

Precipitation (daily)  
Min temperature (daily)  
Max temperature (daily)  
Radiation (daily)  
Wind speed (daily)  
Relative humidity (daily)  
ET over grass (daily)  
Et<sub>actual</sub> (daily)  
N in wet/dry deposition  
Atmospheric CO<sub>2</sub> concentration  
Wind direction  
Monin-Obukhov length (L)

## **Appendix 2**

### **Identifying locations for soil surveys**

*(By Paolo Magliulo)*

The understanding of C and N balance in soils is essential for the understanding of their dynamics in the soil-plant-atmosphere system, given that two or three times more C is stored in soils (Dixon et al., 1994) than occurs in the atmosphere as CO<sub>2</sub> and that different soils can have very different C and N storage abilities (Torn, 1997). The aim of this proposal is to provide a basic understanding of the spatial distribution of soil types in the studied sites in order to provide a useful tool for expert to be used for C and N balance calculation at the landscape scale. The main purpose of the proposed soil survey is to subdivide the landscape into units with low variability of soil properties.

This idea, rooted in basic soil science, considers that soil properties (Jenny, 1941) are function of soil forming factors such as climate, lithology, geomorphology, vegetation and age of the land surface on which soil develops. Thus, soils developing on land surfaces on which the above listed soil forming factors are relatively homogeneous are likely to be characterized by similar chemical and physical properties.

The first step of a soil survey is to subdivide the landscape into areas having the same geological substratum. To do this, pre-existing geological maps should be collected, geo-referenced and imported into a GIS. On geological maps, boundaries between areas having different substratum are reported. The boundaries of interest should be digitized using GIS software, e.g. ArcView GIS. The next step is a further subdivision of the landscape into physiographic units by means of aerial photos analysis and geomorphological field survey; analysis of 1:5000 or 1:10000 scale topographic maps would also be very useful. For mainly flat landscapes, a 1:10000 nominal scale of aerial photos is recommended; for hilly landscapes, a 1:25000 or 1:30000 nominal scale is sufficient. For aerial photos analysis, a stereoscope is needed. The boundaries of the detected landforms should be reported on a transparent template, which must be directly overlapped on aerial photos. During the aerial photos analysis, the detected landforms must be still further subdivided, if necessary, on the basis of land-use. The boundaries of the detected physiographic units, previously traced on the transparent template, must then be reported on the lithological map of the study area by using GIS software with the aim to produce a guide-map to use during the following field survey.

The aim of the field survey is both to verify the accuracy of the aerial photos analysis and to determine the features of the soils occurring in the detected physiographic units. In this phase, a soil auger is needed. A density of 15 observation points for a surface of 100 hectares is sufficient; each physiographic unit should have at least one observation point within it. For each observation point, coordinates should be determined using a GPS; observation points can be randomly located (“free-survey”), but a core located approximately in the middle of the physiographic unit is suggested. During the coring, the depth of the boundaries between the soil horizons and the main soil-morphological features (colour, texture, concentrations...) of each horizon should be reported and described, according to soil survey manuals (e.g. USDA, 2002). Once the dominant soil type for each physiographic unit has been recognised, a soil profile should be dug at the same point.. The field description of a soil profile allows, for example, measurement of the effective depth of the root zone, determination of soil structure within each horizon (affecting soil hydraulic properties) and so on. Furthermore, soil sampling within each

horizon allows the identification of changes both in the soil texture, in the bulk density and in pH values.

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## Appendix 3

### NitroEurope – Component 4: Verification measurement protocol:

#### Atmospheric concentration and flux measurements

#### 1. Purpose of the Measurements

The measurement of atmospheric gas concentrations provides a method of verifying the predictions of the atmospheric dispersion sub-model of NitroScape. In an indirect way, they can also be used to verify modelled emission fluxes since the atmospheric dispersion model uses these fluxes as inputs. The measurement of fluxes (land-atmosphere exchange) on the other hand can be used to verify the emission or deposition fluxes predicted by the ecosystem sub-models (arable, pasture, semi-natural etc.). Within Component 4 of NitroEurope it is proposed that measurement of the following gases will be made across the 6 study landscapes: ammonia (NH<sub>3</sub>), nitrous oxide (N<sub>2</sub>O), methane (CH<sub>4</sub>) and nitrogen dioxide (NO<sub>2</sub>). NB. not all of these gases will be measured at all sites.

#### 2. Measurements of Concentrations

Atmospheric concentrations can be highly variable, both spatially and temporally. Measurement methods range from the very simple (e.g. passive samplers) to the complex (e.g. laser spectroscopy). The type of method used will depend on the species to be measured, spatial and temporal resolution required and the resources available. Three measurement approaches will be used: spatial variability, continuous point and mobile measurements.

##### 2.1. Spatial variability measurements

###### 2.1.1. Measurement techniques

#### Ammonia

Due to the high spatial variability of concentrations, it is necessary to measure at a relatively large number of locations. For this reason, it is only possible to use a low-cost method sampling at a relatively long time resolution. Passive samplers such as diffusion tubes are the most suitable for this task. There are two types that are planned for use in Component 4: CEH ALPHA samplers [3] and Gradko diffusion tubes [4]. Due to different techniques being used for different study areas, an intercomparison exercise is necessary.

#### Nitrous oxide and methane

These two gases have been grouped together because the measurement technique that is currently being developed is used for both species. Due to the multiple sites required for this measurement, low-cost methods need to be used. The most suitable method is bag sampling. Aluminium foil bags are slowly filled with atmospheric air using a small pump during the sampling period. The concentrations of N<sub>2</sub>O and CH<sub>4</sub> in the balloon are then measured in the lab and correspond to the mean atmospheric concentrations at measurement location during the sampling period.

### 2.1.2. Measurement strategies

All measured concentrations need to be referenced to the coordinates of the measurement location, preferably with a Geographical Information System (GIS)

#### **Ammonia**

Samples will be placed at a height of 1.5 m above the ground (a standard air quality monitoring height) at a number of locations. The exact number of location required will depend on the size of the study area and the strength and distribution of NH<sub>3</sub> sources. For example, few locations are needed far from sources where concentrations are close to background whereas more locations are needed close to strong sources (e.g. livestock houses) where large horizontal concentration gradients are expected. Near strong sources it is useful to have linear transects away from the sources. A minimum of 10 locations are recommended for each study area although some areas will have many more. Ideally samples should be exposed in triplicate (i.e. three samplers at each location) because this allows the identification of a contaminated sample. Samples should be changed monthly, stored in a cold room (e.g. 2-4 °C) after exposure and sent for analysis as soon as possible.

#### **Nitrous oxide and methane**

Concentrations of N<sub>2</sub>O and CH<sub>4</sub> are less spatially variable than NH<sub>3</sub> and, therefore, fewer measurement locations are required – a minimum of 5 locations per study area are recommended. The inlet should be at a height of 1.5 m and it is beneficial to co-locate the measurements with NH<sub>3</sub> concentration measurements.

## **2.2. Continuous point measurements**

### 2.2.1. Measurement techniques

For some of the study areas, continuous measurement systems will be used to give accurate, high time resolution measurements of NH<sub>3</sub> (and possibly other gas) concentrations.

#### **Ammonia**

The type of system used will depend on the resources and expertise of the researchers in that country. Example systems include, wet-denuder systems (e.g. AMANDA [5]), laser absorption spectroscopy (e.g. tunable diode laser (TDL) [6]) and photo-acoustic instruments. Ideally these measurements should be made at the same height and location as one of the spatial variability measurements to allow an intercomparison.

### 2.2.2. Measurement strategies

#### **Ammonia**

Continuous measurements should be made during the NitroScape modelling period for the respective study area. Ideally measurements should be made continuously throughout the entire period but resources or equipment failure may make this impossible. Periods of nitrogen management activities (e.g. manure spreading) should be the priority periods in which to measure.

### 2.3. Mobile measurements

Where resources allow, mobile measurements (i.e. from a moving vehicle) of gas concentrations will be made at several study areas. This will allow the analysis of the spatial variability of concentrations at short time scales.

#### 2.3.1. Measurement techniques and strategies

##### All gases

Accurate, high temporal resolution instruments will be driven along a pre-determined route within the study area and the trajectory coordinates and the corresponding concentrations are recorded to a computer. The actual routes used will depend on the features of the study area. For example, a typical route may be a circuit around a source region within the study area. The timing of the measurements should correspond with nitrogen management events in the study area and the frequency of the trajectories will depend on the resources available.

### 3. Measurements of Fluxes

Measurements of land-atmosphere exchange fluxes can be done using a variety of techniques, all of which require significant resources (equipment, expertise and time). Due to these constraints, fluxes cannot be measured at all study areas and where they are possible, they are normally measured at a single location. These measurements have the benefit of allowing the verification of fluxes predicted by a single ecosystem model.

#### 3.1. Continuous point measurements

##### 3.1.1. Measurement techniques

##### Ammonia

The most suitable method to use will depend on resources available at each study area. Three main approaches can be used:

1. *Aerodynamic gradient methods* use concentration measurements at multiple heights above the surface combined with vertical profiles of wind speed, temperature and water vapour pressure to determine the average vertical flux within the profile height range. Examples of this method are the AMANDA and COTAG systems [7].
2. *Eddy covariance (EC)* methods require a fast accurate concentration measurement (e.g. by laser spectroscopy) and correlate this with the vertical component of the wind to obtain the vertical  $\text{NH}_3$  flux at the height of measurement.
3. *Relaxed eddy accumulation (REA)* methods measure the concentration of  $\text{NH}_3$  within both the up- and down-drafts of the passing air. Combining these concentrations with the standard deviation of the vertical wind component gives the vertical  $\text{NH}_3$  flux at the height of measurement.

##### Nitrous oxide and methane

Two types of methods can be used to measure fluxes of  $\text{N}_2\text{O}$  and  $\text{CH}_4$ ; chamber measurements [8] and eddy covariance [9]. In chamber measurements, the build-up of  $\text{N}_2\text{O}$  and  $\text{CH}_4$  within a sealed chamber placed on the ground is measured by taking a sample of the

chamber air and analysing the concentrations using a suitable method (e.g. gas chromatography or TDL).

### 3.1.2. Measurement strategies

#### **All gases**

Continuous measurements should be made during the NitroScape modelling period for the respective study area. Measurements can be made continuously throughout the entire period but resources may make this impossible. Periods of nitrogen management activities (e.g. manure spreading) should be the priority periods in which to measure.

#### **References**

- [1] Tang, Y.S., J.N. Cape, and M.A. Sutton (2001) Development and types of passive samplers for monitoring atmospheric NO<sub>2</sub> and NH<sub>3</sub> concentrations. In Proceedings of the International Symposium on Passive Sampling of Gaseous Air Pollutants in Ecological Effects Research. The Scientific World **1**, 513-529.
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## Appendix 4

### NitroEurope – Component 4: Verification measurement protocol:

#### Ecosystem measurements

#### 4. Purpose of the Measurements

Satellite remote sensing based maps of leaf area index (LAI) and leaf nitrogen contents (leaf N) will be prepared. The maps will be used for spatial inter-comparison and validation of the ecosystem component of the NitroScape model. Spatial representation of crop growth and nitrogen contents is important to increase accuracy in nitrogen balance modelling, water balance modelling and CO<sub>2</sub> budget modelling because 1) most of the nitrogen applied to crops is taken up by the plants, 2) LAI is an important control factor of evapotranspiration and 3) leaf nitrogen is an important determinant of the maximum photosynthetic (Rubisco) capacity of leaves. Within component 4 of NitroEurope, one LAI map and one leaf N map will be prepared for each of the 6 landscape sites. The remote sensing based maps will be validated to the extent that field data are available for this purpose.

#### 5. Remote sensing measurements

Spatial continuous remote sensing based maps of LAI and leaf N will be prepared for each of the 6 NitroEurope landscape sites using high spatial resolution (10-20 m) SPOT satellite data.

##### 5.1. Spatial variability measurements

###### 5.1.1. Measurement techniques

Reflectance data in the green, red and near-infrared wavelength region will be acquired by the SPOT high resolution visible and geometric imaging instruments for the purpose of estimating leaf chlorophyll content ( $C_{ab}$ ), leaf nitrogen (leaf N) and green leaf area index (LAI). SPOT reflectance observations will be atmospherically corrected using aerosol data from EOS/MODIS and profiles of air temperature, humidity and ozone from the Atmospheric Infrared Sounder (AIRS). The processed surface reflectance estimates will be used as input for the inversion of a canopy reflectance model (ACRM-PROSPECT). The biophysical parameter retrieval scheme requires a soil map delimiting major soil types and two remote sensing input images for calculating the spectral reflectance of soils (background reflectance) and vegetation, respectively. Assuming a linear relationship between  $C_{ab}$  and leaf N [2], the methodology will be applied for LAI and leaf N mapping in the 6 NEU landscape sites.

###### 5.1.2. Measurement strategies

SPOT images should optimally be acquired during the final stage of the vegetative growth phase but, in practice, the availability of satellite data is dependent on cloud coverage at the time of satellite passage.

The remote sensing-based maps will be validated to the extent that field data of LAI, leaf N (g per m<sup>2</sup> leaf area) and chlorophyll (g per m<sup>2</sup> leaf area) contents are available for this purpose.

Measurements of LAI, leaf N and chlorophyll contents are collected at C1 and C2 plot sites which are located within the landscape sites in Italy, France and UK. These field ecosystem plot measurements will be to some extent supplemented by additional data collected within the landscape sites. All measurements must be referenced to the geographical coordinates of the measurement location.

## 6. Biophysical measurements

In order to verify the remote sensing based leaf N and LAI maps, it is necessary to collect validation field data of leaf N and LAI for the dominant land cover type(s) of each C4 landscape (if possible also leaf chlorophyll). Measurements should only be made for agricultural fields and grasses, not forest and bushes. The extent of validation field data collection is optional, but it is proposed to collect data in 3-8 field plots in each landscape site. Depending on the character of the landscape site, the field plots may all be located to represent the dominant land surface type (i.e. grassland), or they may be representative of different land surface classes.

### 6.1. Point measurements

#### 6.1.1. Measurement techniques and procedures

All measurements should be conducted within representative homogenous fields, or the field plots should be located where the field heterogeneity is minimal. It is important that the locations for all field measurements and field samples are registered using geographical coordinates. Please specify the geographical locations using the European standard GPS coordinates (ETRS89). Alternatively, include information on the coordinate system and datum applied.

#### Leaf area index (LAI) and biomass.

Measurements of LAI are based on destructive sampling and area-measuring of leaves (ie. Licor 3100 Planometer, LI-COR, Lincoln, NE, USA), or an optical sensor (LAI-2000, LI-COR, Lincoln, NE, USA) can be used.

Destructive samples (0.25 m<sup>2</sup>) should be taken in two areas within each field plot. Field plots should have a size of 10 m x 10 m. The samples should be divided into fractions of green leaves and other components. The fresh weight and dry weight (use 18 hours in oven at 80 °C) are measured, and the one-sided projected area of green leaves is estimated from sub-samples using a planometer. The relationship between sub-sample fresh weight and green leaf area is then applied to the total samples for the estimation of LAI, as indicated in the Table below. The samples should be kept at 2 °C until drying. After drying the samples are kept in an airtight bag for later estimation of leaf nitrogen content.

In case of LAI-2000 non-destructive LAI measurements, recordings should be made along a 10 m transect within each plot (100 m<sup>2</sup>). Each LAI estimate should be based on one measurement above the canopy and 10 measurements below the canopy. Measurements must be made in non-rainy weather and diffuse light conditions. Light conditions should not change while doing a measurement sequence. A view cap covering 25 % of the sensor should be used to hide the operator.

#### Vegetation N and leaf chlorophyll measurements

Vegetation N measurements should be made separately for sampled green leaves and for the total plant using the Kjeldahl method or the Dumas method [3]. Estimation of leaf nitrogen content is made for the same sub-samples which were used for leaf area estimation (see Table below).

A portable SPAD-502 chlorophyll meter (Minolta, Spain) can be used for fast non-destructive measurements of leaf chlorophyll. For the purpose of SPAD calibration, the chlorophyll (a + b) content can be extracted from sampled leaves using the common N,N-dimethylformamide solvent method [e.g. 4]. Extinction coefficients published by Porra et al. (1989) for chlorophyll pigments diluted in N,N-dimethyl-formamide can be used for calculating the concentrations. Assuming a species-specific linear relationship between leaf nitrogen and chlorophyll, non-destructive estimates of leaf N can also be made using the SPAD-meter. All SPAD-meter estimates are based on minimum 60 measurements which are evenly distributed from bottom to top of the canopy within the field plots. All measurements are means of duplicate determinations of individual leaves.

	Sample Area, SA (m <sup>2</sup> )	Sample Fresh Weight, SFW (g)	Sample Dry Weight, SDW (g)	Sub-Sample Fresh Weight, SFWs (g)	Sub-sample Leaf Area, LA (m <sup>2</sup> )	Leaf Area Index, LAI (-)	Dry Biomass, DB (g m <sup>-2</sup> )
Green leaves	0.25	<b>SFW</b>	<b>SDW</b>	<b>SFWs</b>	<b>LA</b>	$(LA * SFW) / (0.25 * SFWs)$	-
Total plant	0.25	-	<b>SDW</b>	-			SDW/0.25

	Sub-sample Nitrogen, SN <sub>sw</sub> (g per 100 g dry weight)	Sub-sample Nitrogen, SN <sub>sa</sub> ; (g per m <sup>2</sup> leaf area)	Sample Nitrogen, SN (g per m <sup>2</sup> ground area)
Green leaves	<b>SN<sub>s</sub></b>	SN <sub>sw</sub> /LA	SN <sub>sa</sub> *LAI
Total plant	<b>SN<sub>s</sub></b>	-	SN <sub>s</sub> *SDW

The above tables illustrate the data analysis of destructive measurements (measurements are indicated in bold) to estimate leaf area index, biomass and nitrogen contents separately for leaves and the total canopy.

## References

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## Appendix 5

### NitroEurope – Component 4: Verification measurement protocol:

#### Soil sampling for N dynamics in the root zone

##### 7. Purpose of the Measurements

Measurements of the soil content of mineral nitrogen (nitrate + ammonium = N-min) in the root zone quantify the amount of plant available nitrogen at the time of sampling. The data can be used to verify the capability of the NitroScape model in simulating root zone N dynamics that eventually result in model estimates of N leaching to groundwater (Riley et al. 2001, Ducheyne et al. 2001, Wegehenkel and Mirschel 2006).

Measurements of the following parameters are required: Nitrate ( $\text{NO}_3^-$ ) and ammonium ( $\text{NH}_4^+$ ). Also estimates of soil dry bulk density at the measurement locations must be available.

##### 2. Measurements of Concentrations

Measurements of soil N-min are made by taking soil samples at specific locations and depth intervals, using a soil auger. Well-mixed bulk soil samples are analysed for the content of nitrate and ammonium.

###### 2.1. Soil sampling procedures

At each measurement location and depth, 4-8 soil samples should be collected within an area of approx.  $4 \text{ m}^2$ , representing the local land use. The soil cores should be mixed thoroughly before taking a representative sample of 100-200 g for analysis.

At each measurement location, sampling must be done at least at two depth intervals. The intervals chosen will be landscape dependent and are based on the rooting depth. The top sample should be 25% of the total rooting depth, and the lower sample is taken down to the bottom of the rooting zone.

A soil auger (22-mm diameter) is used for sampling. Bring a hammer and a clean and dry container. Make sure that the soil surface is compressed to prevent loose surface soil from falling into the hole during coring. If coring is disrupted by a stone, try again at a slightly shifted location. Use a screwdriver or similar for emptying the soil into the container. Only soil held in the hollow space of the soil auger should be allowed into the container.

The mixed sub soil sample of 100-200 g can be filled into a labelled air-tight plastic bag and must be kept in a cool box under field conditions. After returning from the field, the samples must be handed over immediately to a local analysis lab or frozen in a cold store. Soil samples must remain frozen while being shipped to an analysis lab.

For the calculation of N-min at an area basis, the dry bulk density of the soil must be known. If not available, a set of undisturbed soil samples representing each sampling site and depths must be dedicated for analysing dry bulk density (NEU\_cookbook 2007).

All sampling results need to be referenced to the coordinates of the measurement locations within a Geographical Information System (GIS).

## 2.2. Sampling intervals and analysis

Sampling should be done at the same time and location as the N<sub>2</sub>O flux chamber measurements. Additional measurements may also be taken.

Analysis: NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> content of the soil samples should be determined colorimetrically in the supernatant of a 1 M KCL soil suspension (NEU\_cookbook 2007).

The mineral N content will be given on a weight basis per unit dry bulk soil. To calculate N-min on an area basis, use

$$\text{N-min} = [\text{nitrate} + \text{ammonium}] \times \text{dry bulk density} \times \text{depth interval}$$

## 3. References

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## Appendix 6

### NitroEurope – Component 4: Verification measurement protocol

#### Groundwater measurements

##### ***Purpose of the Measurements***

The groundwater measurement provides methods for verifying the predictions of the leaching in ecosystem sub-model and water transfer of the hydrological sub-model of NitroScape.

Two types of information are required: (i) the depth of groundwater below soil surface (water table depth) and (ii) its concentrations in nitrate, ammonium and total nitrogen.

##### ***Measurement techniques***

Groundwater will be surveyed with piezometers. Piezometer is the device used to measure water table depth and to collect groundwater samples. Piezometers will be installed at different locations in the landscape.

#### **Groundwater depth**

##### 7.1.1. Piezometer

A piezometer consists of small diameter PVC pipe inserted in soil at depth depending on the location along transect (from less than 2m in riparian zone up to 6m near the divide). Pipe is screened over 50 cm to 100 cm at the bottom. Once the PVC pipe is installed, the borehole is backfilled with quartz gravel along the screen and with bentonite up to the ground surface to prevent any preferential infiltration along the pipe.

##### 7.1.2. Water depth measurement

Water table depth can be measured by two types of system:

- a pressure sensor connected to a datalogger (e.g. STS pressure transmitter with datalogger or Diver pressure sensor). The measurements are performed and registered automatically.
- a sounding device with light and acoustic signals (e.g. piezometric tape Dipper T, SDEC-France). The device is provided with a probe which is connected to a measuring tape with centimetre graduation. The measurements are performed and read out manually.

#### **Groundwater sampling**

Groundwater should be sampled in the piezometer using manual 500 mL sampler. The groundwater is pumped in the piezometer prior to sampling. Pumping is performed until the equivalent of three piezometer volumes are pumped or until the piezometer gets completely empty. Samples are filtered in the field (0.45 µm) and stored in the dark at less than 4°C before analysis.

#### **Groundwater analysis**

The groundwater should be analyzed for nitrate, ammonium and total nitrogen. For details on analytical methods, see the *hydrology* protocol

### ***Measurement Strategy***

The spatial sampling strategy depends on the hydrological functioning of the landscape.

- in shallow groundwater catchments with superficial flow (e.g. DK, FR, PL, SC landscapes), we propose to install 2-3 transects with 4-5 piezometers per transect. The different transect should be chosen to investigate the variation in either land use or vegetation, or the expected hydrological functioning of the slope/sub-catchment.
- In the systems where the water table is not driven by topography or natural hydraulic gradient but closely controlled by man (e.g. IT, NL), piezometers should be installed to investigate (i) the main ecosystems and (ii) the main expected source of change in groundwater depth (e.g. distance to canals).

Sampling and measurements in every piezometer should be made once a month or based on specific events.

## Appendix 7

### NitroEurope – Component 4: Verification measurement protocol:

#### Streamflow (Discharge, Nitrate, Ammonium, Total-N, DOC)

#### 8. Purpose of the Measurements

Streamflow data are a crucial information for the verification of the hydrological and water quality component of the NitroScape model. Together with data from soil solution and groundwater measurements, data on dissolved stream components are used to test the credibility of the coupled hydrological-biogeochemical model components as well as the capability of the NitroScape model to simulate instream processes. Within Component 4 of NitroEurope it is proposed that measurements of the following parameters will be made across the 6 study landscapes: water level (by the use of to be obtained rating curves this information is translated to discharge), nitrate ( $\text{NO}_3^-$ ), ammonium ( $\text{NH}_4^+$ ), total nitrogen (TN) and dissolved organic carbon (DOC).

#### 9. Measurements

The intended measurements and recommended techniques are summarized in the following.

#### Discharge

Discharge is the volume of water flowing past a fixed point in a fixed unit of time. It is the product of flow velocity times the flow through area. The rating curve is the relationship between stage and discharge at a cross section of a river. Data from stream gages will be collected as stage data. In order to model the streams, the data need to be expressed as stream flow using rating curves. Conversely, the output from the hydrologic models will be flow, which can then be expressed as stage.

The stage has to be recorded continuously using a automatic stage recorder connected to a datalogger. Different techniques exist, including float-and-weight systems, bubbler, pressure sensor. Ultrasonic devices are not recommended due to their sensitivity to environmental conditions. The installation of a staff gage for a regular control of the recorder is required. The stage recording device must be set in an adequate location: the stream section must be regular and stable, and backwater conditions must be avoided. The installation of a weir or a flume provides more accurate data, but it is not necessary for the sites not dedicated to hydrological studies.

To develop a rating curve, one has to make a series of streamflow measurements. We suggest to use either a current meter or as an alternative, the salt dilution technique. These sampling points are plotted versus the accompanying stage, and a curve is drawn through the points. There can be significant scatter around this curve. Because of this, when using a rating curve, it is good to keep in mind that the discharge read from the curve is the most likely value, but it could be a little different from the measured value. Also, since rating curves are developed with few stage/discharge measurements, and measurements of high flows are rare, there can be significant errors in rating curves at high levels, especially around record level flows. At times, one has to go out and take measurements during floods and provide these readings. These values can then be used to adjust the upper end of the rating curve.

One has to keep in mind that two (Italy, Netherlands) out of the six selected NitroScape sites are not characterized by typical surface waters and discharge will therefore be not monitored in the classical sense. However, it is assumed that these sites may have some open channels (drainage in the Dutch site and irrigation channels in the Italian site) that can be analysed to capture some lateral export of C and N constituents.

## Water quality parameters

It is assumed that automatic samplers are not available for all sites. Therefore, it is suggested to conduct fortnightly grab sampling for all water quality parameters. Water samples will be manually taken from the centre of the stream and stored in PE containers. Samples should be stored under cool conditions during transport to the lab and then immediately analysed or stored frozen for later analysis. Prior to analysis, samples should be filtered to remove particulates using a 0.45 micron filter. A pre-filter to remove large particles may also be necessary (using a paper filter). For the sake of analytical compatibility we suggest to apply the same analytical technique across all sites. However, due to the availability in the different labs it might be necessary to use some alternative technique, for which a suggestion is also given in the following table.

### Suggested analytical technique

Component	Suggested analytical technique	Alternative technique
Velocity (Discharge)	Current meter	Salt dilution
Nitrate (NO <sub>3</sub> <sup>-</sup> )	Ion chromatography	Photometer
Ammonium (NH <sub>4</sub> <sup>+</sup> )	Ion chromatography	Photometer
Total nitrogen (TN)	TOC/TN <sub>b</sub> analyzer High temperature oxidation (NO) and Chemoluminescence (CLD) or electrochemical detectors (CHD)	Kjeldahl
Dissolved organic carbon (DOC)	TOC/TN <sub>b</sub> Analyzer High temperature oxidation (CO <sub>2</sub> ) and NDIR photometer detection	-