Nitrous oxide flux measurement with a closed chamber system: data treatment

Introduction
The present study is part of the AgriGES project, which aims at quantifying methane and nitrous oxide emission from pastures and crop fields, respectively. Experimental measurement campaigns of N₂O fluxes have been performed in the area of Gembloux, using a system of dynamic closed chambers. In this poster, we discuss how to estimate fluxes from the N₂O concentration data, using different curves to fit these data points. The goodness-of-fit of these curves is used to sort between relevant and irrelevant fluxes. A comparison of the fluxes estimated by these different fits is also performed. These points will be illustrated with the data collected during an experimental campaign on a bare soil with control of water and nitrogen inputs, from the 25th of August to the 28th of September 2014.

Experimental setup
Experimental setup is shown in fig 1. It is composed of eight chambers which are closed each one in turn for 30 minutes, forming a cycle of 4 hours + 30 minutes during which all chambers are left wide open for the system to purge. During the enclosure period, N₂O accumulates in the chamber and its concentration within the chamber is measured every 30 seconds. These data are then used to estimate the flux emitted from the soil to the atmosphere. Two moisture probes are placed at the center of the two squares delimited by the chambers.

Flux estimation method
A software has been coded in C++ in order to visualize the chamber concentration data. Several fits (polynomial and Non-steady Diffusive Flux Estimator (NDFE, Livengston et al. 2005 and 2006) ) can be performed on these data, using the least square method, and the flux is supposed proportional to the slope of the fit at time t=0, i.e. at the time where the flux is the least influenced by the chamber enclosure.

Linear vs. NDFE fit
Linear fits are still widely used in the literature to estimate N₂O fluxes, despite several well-referenced drawbacks compared to more elaborate fits. Its main drawbacks are: 1) there is no theoretical basis to explain why the linear fit should be used, 2) a poor performance compared to other fits (see fig 3b), and 3) a strong tendency to underestimate fluxes compared to other fits. See fig 2 and 3a for an illustration. During the measurement period from the 25th of August to the 28th of September 2014, cumulative flux estimated by the linear interpolation was 40% lower than the cumulative flux estimated by the NDFE fit.

Sorting data - Goodness-of-fit
Due to the precision of the measurement device, temporary failures (e.g. a chamber incorrectly closed) and/or exceptional conditions perturbing the system (e.g. heavy winds influencing pressure in the chambers), a large part of the estimated fluxes cannot be considered as relevant and should therefore be dismissed.

Discriminate between relevant and irrelevant can be partially automated using the goodness-of-fit of the concentration fit. The most widely used statistical parameter is the correlation coefficient (R²). However, the R² coefficient always tends to be lower for lower fluxes. Thus, using R² alone, one tends to preferentially eliminate lower fluxes, leading to an artificial increase of the background flux (see fig 3c). On the examined data set, the root mean square error (RMSE) of the fit seems the best parameter in order to sort the fluxes, since we observe a very low correlation between the flux value and the corresponding RMSE (see fig 3d).

Results - Flux dynamics vs Soil moisture
Fig. 4 represents the emitted nitrous oxide flux (red), evaluated with the NDFE model, over the measurement period. On the same graph, the soil moisture is also represented in black. One can clearly see the moisture peaks resulting from the weekly watering (plus soluble nitrogen input) and the emission peaks appearing 24 to 48 hours after the watering events. These peaks are due to the denitrification process occurring in anoxic conditions, i.e. when the soil is wet and there is not enough oxygen anymore for the denitrifying bacteria to respire.

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