

Interactive comment on “Significant non-linearity in nitrous oxide chamber data and its effect on calculated annual emissions” by P. C. Stolck et al.

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Nitrous oxide (N_2O) fluxes from concentration data from chamber measurements are usually calculated with linear regression. Non-linearity in this N_2O concentration data can give large underestimations in the resulting flux. This non-linearity is more common for large fluxes than for small fluxes and can seriously affect cumulative fluxes. To take this non-linearity into account, non-linear regression methods can be used to calculate the fluxes. In this study we used quadratic regression.

Both linear and quadratic regressions have their strengths. A reason to use linear regression could be the small number of concentration data (in this study $n=4$). Linear regression has only two regression parameters ($k=2$), which reduces the chance of overfitting the regression compared to quadratic regression with three regression parameters ($k=3$). Reasons to use quadratic regression could be the negative feedback

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of the increasing concentration in the chamber on the flux or simply the fact that non-linearity in concentration data in chambers is often observed.

Usually one regression method is chosen for all measurements. In this study we pleaded not to choose a priori for linear or non-linear regression, but to decide for each individual measurement which regression method to use. As a decision criterion we used adjusted r-square, r^2_a , because it takes into account the difference in degrees of freedom between the methods. We decided to use quadratic regression if $r^2_{a,qua} > r^2_{a,lin}$. With this decision criterion quadratic regression was used for 32% of the data, increasing the annual flux with 21% tot 53% compared to the flux determined from linear regression alone.

The author of the comment suggests using residual variances σ^2 in stead of r^2_a as decision criterion on which regression model to use for each individual measurement, by using an F-test with the following hypotheses:

$$H_{0,lin}: \sigma^2_{lin} \leq \sigma^2_{qua}$$

$$H_{1,lin}: \sigma^2_{lin} > \sigma^2_{qua}$$

and

$$F = \sigma^2_{lin} / \sigma^2_{qua}$$

with

$$\sigma^2 = \Sigma(\hat{C}_t - C_t)^2 / (n-k)$$

These hypotheses can be interpreted as "linear regression is better than quadratic regression, unless ...", i.e. an a priori choice for linear regression. In our opinion also the opposite could be true, namely "non-linear regression is better than linear regression, unless ...", which is expressed in the following hypotheses:

$$H_{0,qua}: \sigma^2_{qua} \leq \sigma^2_{lin}$$

$$H_{1,qua}: \sigma^2_{qua} > \sigma^2_{lin}$$

and

$$F = \sigma_{qua}^2 / \sigma_{lin}^2$$

Performing the F-test for both pairs of hypotheses ($\alpha = 0.10$), $H_{0,lin}$ is rejected for 56 measurements out of 3549, whereas $H_{0,qua}$ is rejected for 7 measurements. These results show that only for 63 out of 3549 measurements any of the regression methods is significantly better; for most measurements it cannot be stated with statistical significance which one of the regressions is better. This implies that the outcome of this test is highly dependent on the a priori choice of the regression model. Therefore the F-test is not suited for our purpose.

Still, we could use the residual variance σ^2 as a decision criterion on which regression method to use and use quadratic regression if $\sigma_{qua}^2 < \sigma_{lin}^2$. This is comparable to an F-test, but without the a priori choice for one of the two regression models. With this decision criterion quadratic regression is used for 773 measurements (22%), increasing the annual flux with 9% tot 45% compared to the flux determined from linear regression alone.

It is clear that, irrespective of the decision criterion, the choice between linear or non-linear regression per individual measurement has large implications for the cumulative flux. The actual decision criterion seems to be a matter of taste, but could be better statistically underpinned with a larger sample size, i.e. by taking more concentration measurements per chamber closing period.

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