Biogeosciences Discuss., 6, S136–S138, 2009
www.biogeosciences-discuss.net/6/S136/2009/

Biogeosciences Discussions

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

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Received and published: 20 February 2009

Non-linearity in concentration data of chamber flux measurements of trace gases is an important topic. It has recently come into focus that the flux estimate can be severely biased when the linear regression model is applied inappropriately. However, there is yet no consistent method in use for the decision when the usually used linear model or a non-linear model is more suitable for chamber flux calculation.
Here, the authors compare the adjusted coefficient of determination (R_a^2) of the linear and the non-linear model. R_a^2 accounts for the different degrees of freedom of the two models, which is especially necessary, when the sample size is small ($n = 4$). The authors select the non-linear model when its R_a^2 is larger than the one of the linear model and define this as 'significant' non-linearity.

Generally, it is recommended to have a larger sample size ($n \geq 7$) to calculate non-linear models (Kutzbach et al., 2007). Admittedly, this is hardly possible when concentration analysis is done by gas chromatography. Although the use of R_a^2 is recommended among other indicators, it could be critical here: It does not punish the additional parameter of a non-linear regression as strongly as other criteria, e.g. the Akaike Information Criterion with small sample second order bias correction (Kutzbach et al., 2007). In my view, it selects the non-linear model too easily which can cause yet another bias. Principally, a non-linear concentration change in the chamber has to be expected since the chamber method itself inherently changes the gas concentration gradients which drive the diffusive gas fluxes. This bias should be corrected for if possible. However, the non-linear curvature should be reliably separated from the measurement noise and chamber artifacts due to soil disturbances particularly during chamber deployment. This is difficult when the sample size is small (Forbrich et al., in prep.). Thus, I suggest to use a conservative, i.e. stricter, criterion to define non-linearity. Here, it might be more helpful to evaluate the residual variances (Kutzbach et al., 2007; Kroon et al., 2008) by an F-test, which additionally provides the information of the *statistical* significance. This information is usually derived by hypothesis testing where a certain significance level (α) is defined which the p-value (the error probability of rejecting the null hypothesis (H_0)) has to fall below when H_0 is to be discarded (Lehmann, 1986). Here, it is suitable to test whether the residual variance of the linear model (σ_{lin}^2) is significantly larger than the one of the non-linear model ($\sigma_{non-lin}^2$) which could be tested by an F-test of residual variances (Kutzbach et al., 2007):
H_0: $\sigma_{lin}^2 \leq \sigma_{non-lin}^2$
H_1: $\sigma_{lin}^2 > \sigma_{non-lin}^2$

$$F = \frac{\sigma_{lin}^2}{\sigma_{non-lin}^2} \quad (1)$$

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with $\sigma^2_{lin} = \frac{\sum(\hat{c}_{(lin)t} - c_t)^2}{df_{lin}}, \sigma^2_{non-lin} = \frac{\sum(\hat{c}_{(non-lin)t} - c_t)^2}{df_{non-lin}}$
and $df_{lin} = n - k_{lin} = 4 - 2 = 2, df_{non-lin} = n - k_{non-lin} = 4 - 3 = 1$

In this case, H_0 is discarded, when $F > F_{(df_{lin}, df_{non-lin}, \alpha)}$. For $df_{lin} = 2$ and $df_{non-lin} = 1$, the critical F-values are e.g. $F = 199.5$ for $\alpha = 0.05$ or $F = 49.5$ for $\alpha = 0.1$. Consequently, the differences in the residual variances of the two models have to be substantial for a significantly better fit of the nonlinear model compared to the linear model.

Additionally, it would be helpful if the authors could include examples of non-linear measurements in Figure 1 together with the regression function and line to facilitate a visual evaluation of non-linearity.

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Interactive comment on Biogeosciences Discuss., 6, 115, 2009.