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Can soil denitrification models be validated with the N2/Ar-method? Results from a comparison between DENUZ and the N2/Ar-method in Lower Saxony (Germany)

Wolfram Eschenbach (1), Jörg Elbracht (2), Heinrich Höper (2), Ralf Kunkel (3), Reinhard Well (1), and Frank Wendland (3)

(1) Thünen-Institut für Agrarklimaschutz, Bundesallee. 50, D-38116 Braunschweig, Germany (reinhard.well@ti.bund.de), (2) Landesamt für Bergbau, Energie und Geologie, Stilleweg 2, D-30655 Hannover, Germany (Joerg.Elbracht@lbeg.niedersachsen.de), (3) Forschungszentrum Jülich GmbH, 52425 Juelich, Germany (r.kunkel@fz-juelich.de)

Diffuse NO_3^- emissions derived from agricultural N surpluses are the main cause of NO_3^- pollution of aquifers and open water bodies. Denitrification is the key process for the attenuation of these anthropogenic NO_3^- concentrations in soils and groundwater. Since the greenhouse gas N2O is an obligate intermediate of denitrification this process is also a major regulator of N2O emissions from soils and indirect N2O fluxes from aquifers and open water bodies which result from NO_3^--leaching. To predict NO_3- leaching from the agricultural field and asses the maximal permissible agricultural N surplus to guarantee a mean long-term nitrate concentration in percolation water below 50 mg NO_3-/l validated, soil denitrification models are needed.
Validation of models predicting denitrification and NO_3- leaching is difficult due to lack of suitable data sets and the complexity of denitrification. Moreover, existing groundwater well networks can currently not be used to check the modelled NO_3- leaching because NO_3- itself might be already partly or totally reduced in the groundwater below soils. In this study we assessed the possibility of validating the soil denitrification model DENUZ (Wendland et al., 2009) with calculated initial NO_3^- concentrations in the groundwater at the time of groundwater recharge (NO_3^-t0). NO_3-t0 values can be derived from groundwater samples of normal groundwater monitoring wells using the N2/Ar-method (Weymann et al., 2008). Therefore we compare NO_3^- emission concentrations (pot-NO_3^-) obtained by groundwater modelled using DENUZ with NO_3^-t0 values, calculated from measured dissolved gas concentrations (N2, N2O, Ar) and measured NO_3^- in groundwater samples. We analysed groundwater samples from 484 groundwater monitoring wells throughout Lower-Saxony (Germany).
Median NO_3^- and NO_3^-t0 concentrations were 0.3 and 30 mg NO_3^- l^-1 respectively, showing that a considerable proportion of the anthropogenic N-surplus is denitrified within the saturated zone. DENUZ and N2/Ar-method results were compared using the Bland-Altman-Approach (Bland and Altman, 1986). Therefore we analysed the repeatability of the N2/Ar-method at groundwater wells and calculated the bias between DENUZ and N2/Ar-method. Results showed that there is a strong scatter between both methods at individual monitoring wells, which resulted in very wide 95%-limits of agreement between both methods. The 95%-limits of repeatability of the N2/Ar-method were 1.5±47 mg NO_3-t0 L-1. These wide limits show that either time series of NO_3^-t0 values are needed to check denitrification model results in the catchment area of a single monitoring well or that groups of monitoring wells are needed to check denitrification models with the N2/Ar-method.
Results for groups of monitoring wells of different hydrogeologic units showed that DENUZ and N2/Ar-method where in good agreement for glacial outwash plains and moraine deposits. In lowland regions however, where hydromorphic soils are more widespread, DENUZ modelled systematically 3 to 27 % higher NO_3- emissions to the groundwater than the N2/Ar-method. There, denitrification processes in soil and groundwater may interfere with each other. Differences between modelled and measured NO_3- at the groundwater surface at individual monitoring wells indicated that about 100 monitoring wells are needed to capture a possible bias between the N2/Ar-method and DENUZ with sufficient precision (i.e. narrow 95% confidence intervals).

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