

Dynamics of nitrous oxide in groundwater under agricultural areas: insights from multi-isotopic studies (15N, 34S, 18O, 13C, 3H)

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In the last two decades the biogeochemistry of nitrous oxide (N₂O), one of the most important greenhouse gases, in the subsurface has started to draw significant research attention due to the rising concern about climate change (Clough et al., 2005). The increase in the concentration of N₂O in the atmosphere reflects the increase in amount of N₂O derived from the anthropogenic sources (Robertson & Vitousek, 2009). Among these sources it is agriculture that contributes nearly 60% of the total anthropogenic emission of N₂O (Syakila & Kroeze, 2011). Agricultural N₂O emission to the atmosphere could be divided into direct (occurring from soils) and indirect (occurring from groundwater and surface water as a result of N input to aquatic systems) contributions. While the former one has been intensively studied and is relatively well constrained, the latter one requires additional investigations (Beaulieu et al., 2011; Jurado et al., 2017). Our study attempts to acquire additional evidence about the N₂O dynamics in the subsurface by studying its distribution across the chalk aquifer of the Geer catchment in Belgium (the area of the basin 480 km²), where previous studies detected the pronounced impact of the agricultural activities on the groundwater chemistry (Brouyère et al., 2004). To this end, the groundwater samples from 32 locations in confined and unconfined parts of the aquifer were collected in order to examine the spatial variability of N₂O along the lateral and vertical dimensions of the studied aquifer. The results of the study revealed that the concentration of dissolved N₂O in groundwater varied from 0.03 µgN/L to 19 µgN/L. The majority of groundwater samples collected in the unconfined part of the chalk aquifer, were supersaturated with N₂O (above 0.3 µgN/L), while confined area was characterized with lower values of N₂O concentration (0.02 – 0.12 µgN/L). In order to identify the biogeochemical pathways of N₂O, the multiple isotope analysis of NO₃⁻, N₂O, SO₄²⁻, B, DOC and 3H were conducted. In addition, the dynamics of N₂O production/consumption processes was further explored using data about intramolecular distribution of ¹⁵N in N₂O. Analysis of information about isotopic signals of compounds of interest and isotopomer maps of N₂O helps to elucidate the causes of shifting N₂O occurrence in the subsurface. Beaulieu, J. J., Tank, J. L., Hamilton, S. K., Wollheim, W. M., Hall, R. O., Mulholland, P. J., ... & Dodds, W. K. (2011). Nitrous oxide emission from denitrification in stream and river networks. *Proceedings of the National Academy of Sciences*, 108(1), 214-219.