



## **A new method for tracing denitrification and CO<sub>2</sub> production in riparian groundwater**

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Globally, nitrate is among the most common groundwater pollutants. Although, denitrification—the process eliminating nitrate to nitrogen gas—has been studied intensively for a long time, we still lack a comprehensive understanding of its spatio-temporal dynamics. Despite recent advances in analytical tools, measuring denitrification in groundwater is still labour intensive, thus, time series data to study denitrification dynamics are scarce. We present a new method to quantify denitrification dynamics in groundwater in a comparatively fast and cheap way. To this end, we continuously analysed in the field dissolved N<sub>2</sub>—the product of complete denitrification—together with other dissolved (noble) gases (<sup>4</sup>He, <sup>40</sup>Ar, <sup>84</sup>Kr, CO<sub>2</sub>) using a newly developed portable mass spectrometry system in three riparian groundwater observation wells from January until June 2018. Riparian zones are well known hot spots for nitrogen cycling, thus, we expect to detect a signal of N<sub>2</sub> stemming from denitrification as well as elevated pCO<sub>2</sub>. Our aim is to quantify spatio-temporal dynamics of N<sub>2</sub> production by disentangling the N<sub>2</sub> we measure into its three major sources: (1) atmospheric N<sub>2</sub> (due to air-water gas exchange), (2) excess air (the dissolution of entrapped air bubbles) and (3) denitrification. The theoretical amount of atmospheric N<sub>2</sub> (1) can be estimated based on the water temperature at recharge. The inert noble gases serve as conservative proxies for gas exchange in groundwater which allow us to model the amount of excess air (2). Consequently, the remainder can be attributed to N<sub>2</sub> stemming from denitrification (3). Our results show a strong signal of N<sub>2</sub> stemming from denitrification which exceeds the natural background concentration (i.e., atmospheric N<sub>2</sub> due to air-water gas exchange and excess air) of up to 20%. Moreover, at one observation well we see a correlation (R<sup>2</sup>=0.75) between N<sub>2</sub> and pCO<sub>2</sub> concentrations—a phenomenon not observed at the other two observation wells. We can link and explain these discrepancies in denitrification and pCO<sub>2</sub> patterns to different hydraulic conductivities at the study site. Our work shows that continuous (noble) gas measurements in the field allow to study the dynamics of spatio-temporal denitrification patterns in riparian groundwater. Moreover, the method can be used for extensive sampling of larger areas (e.g., catchments) with a high spatial resolution, and thus, further advance our understanding of denitrification dynamics on larger scales.