

# Supporting Information for “A New in Situ Method for Tracing Denitrification in Riparian Groundwater”

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**Introduction.** This Supplementary Material includes

- Text S1 providing background information on dissolved (noble) gas theory;
- Text S2 explaining assumptions and limitations of this study;
- Text S3 stating some field work issues;
- Code S1 providing links to the noble gas data processing scripts;
- Figure S1 showing Nitrite and Ammonium data of P1, P4, P5 and the stream (weekly sampling);
- Figure S2 showing the recorded stream water temperature and estimated NGTs for all piezometers;
- Figure S3 showing a picture of the study site including the stream, the piezometers and the location of the GE-MIMS;
- Table S1 containing information about instruments used, limits of quantification and uncertainties for the data shown in Figure 3 (manuscript);
- Dataset S1 contains (noble) gas data obtained at piezometer P1, P4 and P5;
- Dataset S2 contains the CE-model results and subsequent calculations for piezometer P1, P4 and P5;
- Dataset S3 contains the data for Figure 3 (except for oxygen, which can be found in Dataset\_S2), Figure 2 (microbial activity) and Figure S1 for all piezometers;
- Dataset S4 contains the hydraulic conductivity (k) data for all piezometers;
- Dataset S5 contains the stream (Chriesbach) water level data (data source: <http://www.hydrometrie.ch/KundenDaten/EAWAG/HBZHa-558.htm>);
- Dataset S6 contains the groundwater level data of P4 and P5;

- Dataset S7 contains precipitation and air temperature data (data source: <https://bafu.meteotest.ch/nabel/index.php/abfrage/start/english> recorded at station "Dübendorf-Empa").

Datasets S1 to S7 are available online: <https://doi.org/10.25678/0001JD>.

**Text S1: Dissolved (Noble) Gas Theory.** In surface waters, gas exchange occurs at the interface between the atmosphere and water bodies.<sup>1</sup> Commonly, dissolved gases in well mixed surface waters reach an equilibrium with atmospheric gases according to Henry’s Law (assuming that gases are neither produced nor consumed):

$$C_{gas}^{ASW} = \frac{p_{gas}^{atm}}{H_{gas}(T_w, S_w)}, \quad (1)$$

where  $C_{gas}^{ASW}$  (cm<sup>3</sup>STP/g<sub>water</sub>) is the gas concentration of a gas species (e.g., N<sub>2</sub>) in air-saturated water (ASW),  $p_{gas}^{atm}$  is the partial pressure (atm) of a gas species in dry air, and  $H_{gas}$  is the Henry coefficient (atm) of a gas species at a specific temperature ( $T_w$ , °C) and salinity ( $S_w$ , ‰) of the water.<sup>1</sup> Once surface water infiltrates, the abundance of gases in shallow groundwater changes: reactive gas species typically increase due to gas production (e.g., N<sub>2</sub> or CO<sub>2</sub>) or decrease due to gas depletion (e.g., O<sub>2</sub>); excess air—the dissolution of entrapped air bubbles due to water table fluctuations and groundwater recharge—affects both reactive and noble gases and can supersaturate groundwater in dissolved gases by up to 50%.<sup>1,2</sup> Moreover, excess air is typically fractionated,<sup>1,3,4</sup> which means that during excess air formation the composition of the dissolved gas and the remaining gas phase differs from that of pure atmospheric air. Thus, to reliably study N<sub>2</sub> production due to denitrification, excess air formation including fractionation patterns need to be quantified accurately.

Aeschbach-Hertig et al.<sup>5</sup> introduced a widely accepted excess air model (CE model), which assumes that the gas composition in the entrapped gas bubbles and the dissolved gases are in solubility equilibrium with respect to the elevated pressure in the gas phase. Thus, the dissolved gas concentration in groundwater ( $C_{gas}$ , cm<sup>3</sup>STP/g<sub>water</sub>) of a gas at a given temperature ( $T_w$ ; assuming salinity to be zero) and ambient atmospheric pressure ( $P$ , atm) can be described by the CE model as follows:

$$C_{gas}(T_w, P, A, F) = C_{gas}^{ASW}(T_w, P) + \frac{(1 - F)Az_{gas}}{1 + F \frac{Az_{gas}}{C_{gas}^{ASW}(T_w)}}, \quad (2)$$

where  $A$  ( $\text{cm}^3\text{STP}/\text{g}_{\text{water}}$ ) represents the amount of dry air per unit mass of water initially entrapped in the water and  $z_{\text{gas}}$  is the volume fraction of the gas in dry air;  $F$  (-) describes the degree of fractionation of bubble dissolution, with  $F \approx 0$  implying that all air bubbles are completely dissolved and  $F \approx 1$  implying that basically no entrapped gas is dissolved in the surrounding groundwater;  $F > 0$  means that only a partial dissolution of entrapped air occurred, which favors the more soluble gases causing a fractionation with respect to the complete dissolution of air in which case the heavier, more soluble gases are enriched in the water phase.

## **Text S2: Assumptions and Limitations.**

In this study, we assume that nitrate is fully reduced to  $\text{N}_2$  and we neglect other processes that potentially contribute to  $\text{N}_2$  dissolved in groundwater such as Anammox. During weekly measurements, we analyzed nitrite and ammonium, but found only very low concentrations (see Fig. S1). These data suggest that nitrification, Anammox, ammonification or nitrate reduction to  $\text{NH}_4^+$  (i.e., DNRA) play no important role at our study site. We also checked if nitrogen is bound in intermediate N-species: During sporadic checks the GE-MIMS did not detect any elevated peaks for NO and  $\text{NO}_2$ , which shows that denitrification appears to be complete.  $\text{N}_2\text{O}$  could not be analyzed as it has the same mass as  $\text{CO}_2$ .

Moreover, we assume that the helium content of our samples is purely atmospheric (i.e., no terrigenic helium is present) due to the shallow groundwater fed by the stream and the absence of a deep aquifer within the study area. The estimated groundwater thickness at the study location is between 2-20m and the riparian aquifer is unconfined, consisting of unconsolidated rocks.; information source: <https://maps.zh.ch/?topic=AwelGrundWaMwwwZH&offlayers=bezirkslabels&scale=310000&x=692000&y=252000>, Baudirektion, Amt für Abfall, Wasser, Energie und Luft Abteilung Gewässerschutz, Zürich, CH). We thus use He as input parameter (together with Ar and Kr) to estimate A, F and NGTs.

Figure 6 shows rainfall patterns and the water heads recorded in the stream and the groundwater at our study location. The latter indicates that the stream is indeed a losing

stream for the duration of our experiment. Precipitation was recorded at the BAFU station “Dübendorf-Empa”, which is  $\sim 450\text{m}$  away from our study site (data source: <https://bafu.meteotest.ch/nabel/index.php/abfrage/start/english>). Stream water heads were recorded  $\sim 200\text{m}$  upstream of our study site (data source: <http://www.hydrometrie.ch/KundenDaten/EAWAG/HBZHa-558.htm>). All water levels of the piezometers were recorded using Ott CTD probes.

With the methods used in this study we cannot estimate infiltration flow paths or travel times. This would require a hydrogeological model, which is beyond the purpose of this study. However, several factors indicate that the analyzed groundwater is indeed recently infiltrated stream water: e.g., the microbial activity is unusually high for groundwater (Fig. 2b), NGTs correspond well with the recorded stream water temperature (Fig. S2) and groundwater levels respond fast to increases in stream discharge (Fig. S1 b and c). Thus, we can assume that groundwater flow paths and travel times from the stream to the riparian groundwater are relatively short.

**Text S3: Issues during Field Work.** We first intended to analyze dissolved (noble) gases in the stream water as well. However, due to the high load of suspended matter in the stream, which immediately clogged the pump and the water filter, we were unable to proceed with the stream water analysis. Consequently, we could not test whether denitrification already occurs through hyporheic exchange, which would lead to an increase in dissolved  $\text{N}_2$  in the stream water. The used filters and membranes for groundwater analyses had to be cleaned or exchanged weekly due to clogging.

Due to the temperature difference of the ambient air (relatively cold) and groundwater (relatively warm) in the colder weeks of our sampling period (mainly February), water condensed inside the membrane module. This does not at first affect the gas measurements, but extensive water condensation inside the membrane module does eventually clog the attached capillary. Under cold ambient air temperatures, we therefore suggest to heat the membrane module and the attached capillary (to decrease the temperature difference between ambient

air and sampling water), thus reduce water condensation.

**Code S1.** All processing scripts necessary to convert raw data to partial pressure of gas species and gas concentrations are available online (<https://github.com/brennmat/ruediPy>). GNU Octave can be used to run the scripts. The software package NOBLEFIT (<https://github.com/brennmat/noblefit>), containing a  $\chi^2$  regression model to estimate the amount of excess air and the noble gas recharge temperature, are also publicly available. Both software packages include examples and manuals to facilitate reproducing our results.

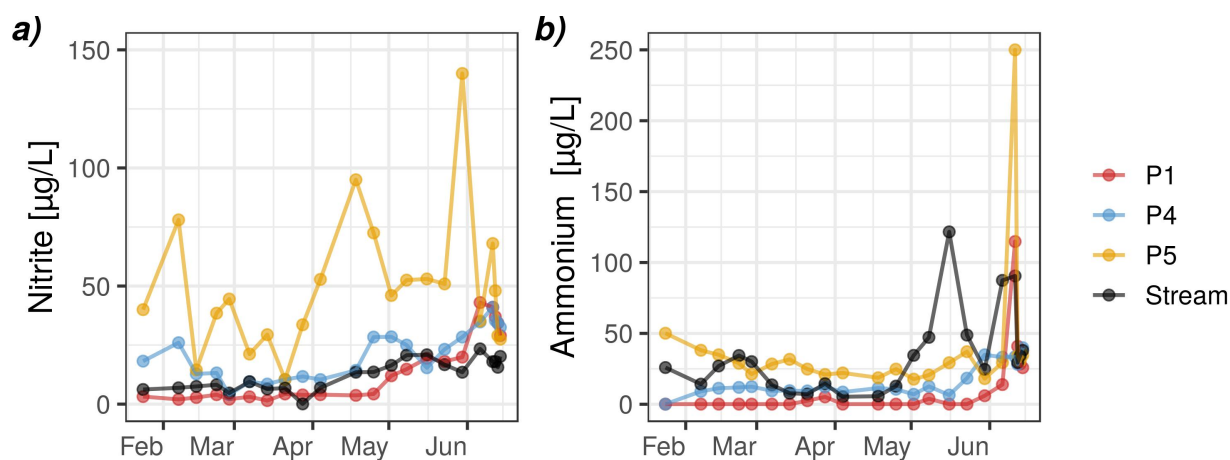


Figure S1: Nitrite (a) and ammonium (b) concentrations of P1, P4, P5 and the stream from weekly sampling.



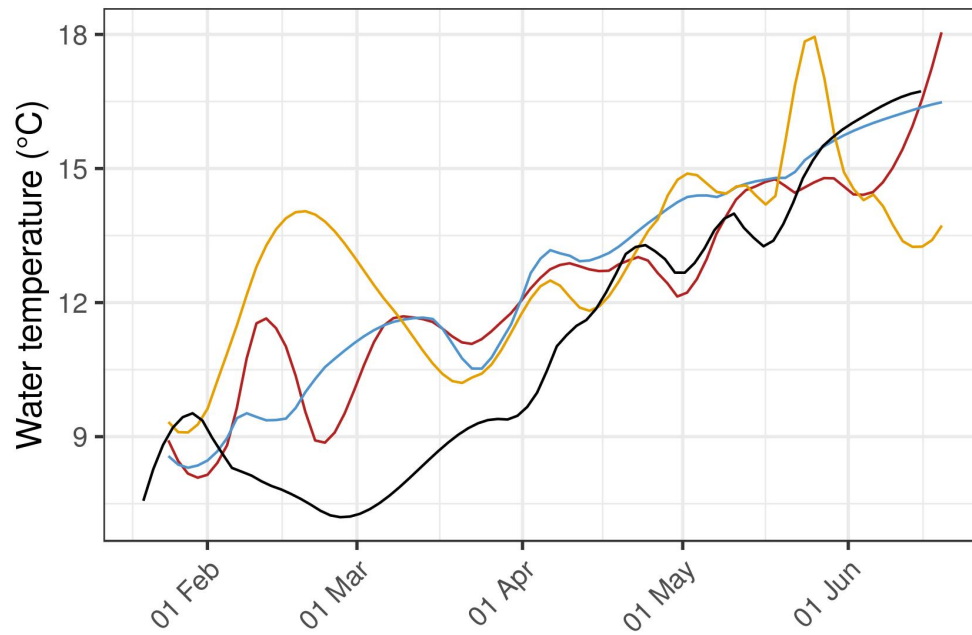


Figure S2: Recorded stream water temperature (black; data source: <http://www.hydrometrie.ch/KundenDaten/EAWAG/HBZHa-558.htm>) and estimated NGTs of P1 (red), P4 (blue) and P5 (orange).

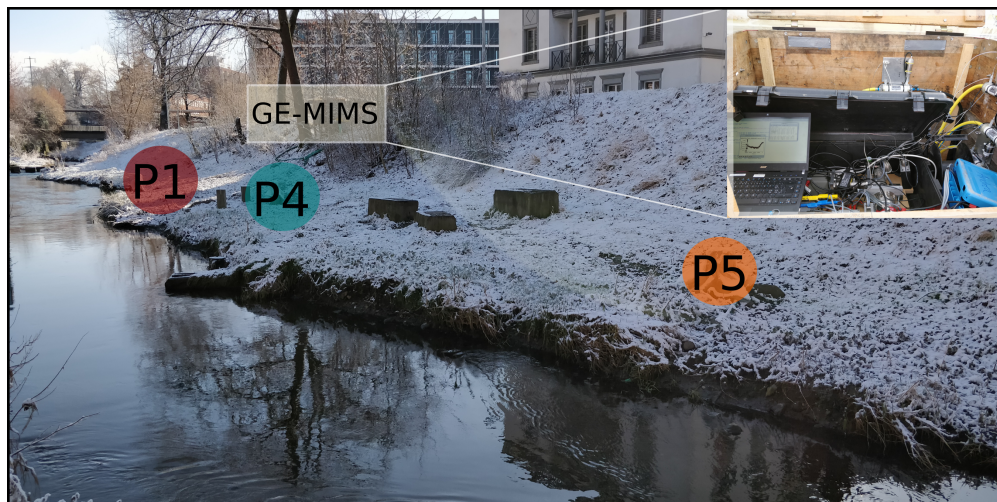


Figure S3: Picture of the study site in February 2018 showing the stream, the piezometers as well as the location of the GE-MIMS.

Table S1: Information about instruments used, parameter units, LOQ and measurement uncertainties for nitrate, sulfate, alkalinity, DOC and TCC concentration data. LOQ and measurement uncertainties are given in the respective parameter unit.

Parameter	Instrument	Method	Units	LOQ	Uncertainty $\pm$
Nitrate	Metrohm 761 Compact IC	Column: Metrohm Metrosep A Supp 5 100/4 mm	mg/L	0.25	0.1
Sulfate	Metrohm 761 Compact IC	Column: Metrohm Metrosep A Supp 5 100/4 mm	mg/L	5	2
Alkalinity	Metrohm 809 Titrand	Metrohm pH-electrode	mmol/L	0.2	0.1
DOC	shimadzu TOC-L CSH	Catalytic incinerator 720 °C (analysis of CO <sub>2</sub> via IR)	mg/L	0.5	0.2
TCC	BD Accuri cytometers, Belgium; 6	Flow cytometric cell counting (not diluted)	cells/ $\mu$ L	–	–

## References

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