

Integrative Isotope Techniques to Evaluate the Fate and Transport of Nitrogen in an Alpine Foothill Catchment



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Motivation

Problem description

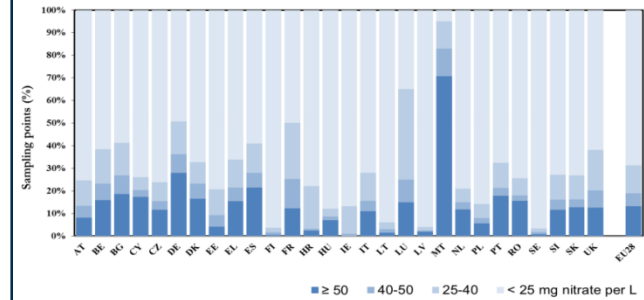
Nitrate (NO_3^-) pollution in EU (2012–2015)

- Groundwater:
 - 13.2% - exceedance of drinking water threshold (50 mg L^{-1})
 - 5.7% - 40 to 50 mg L^{-1}
- Rivers:
 - 12% - eutrophic
 - 7% - hypertrophic

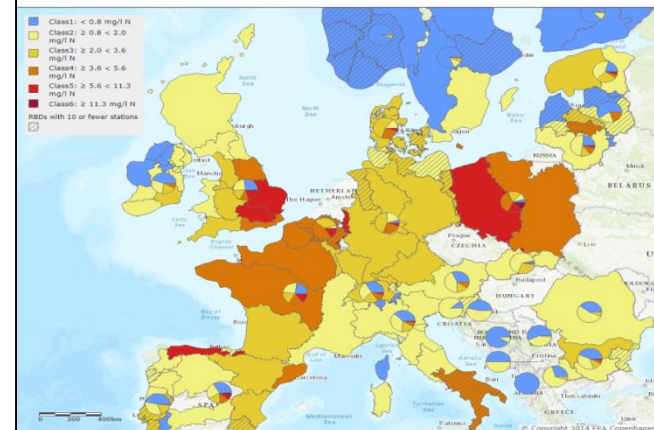
Knowledge gap

Development of effective management strategies requires thorough understanding of the main drivers of nitrate export in large river catchments.

Mean annual NO_3^- concentration in groundwater



Mean annual NO_3^- concentration in rivers



Objective

Our goal

To investigate dynamics of **nitrate** export from a mesoscale river basin impacted by **agriculture** and how it is shaped by different **drivers** using multi-isotope techniques coupled with geo-statistical methods and Bayesian mixing models.

Three drivers controlling NO_3^- export

Driver 1: microbiological N-turnover processes

Driver 2: land-use

Driver 3: hydrological conditions

Methodology

Monitoring

- **high spatial resolution** seasonal surface water monitoring over several years
- event-based monitoring in selected locations
- precipitation
- measured parameters

in field

dissolved oxygen
temperature
EC
pH

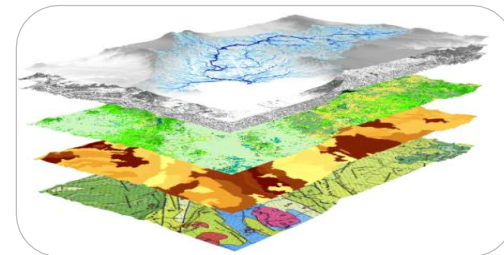
laboratory

nitrate isotopes ($\delta^{15}\text{N}$, $\delta^{18}\text{O}$)
water isotopes ($\delta^2\text{H}$, $\delta^{18}\text{O}$)
 $\delta^{13}\text{C}$ of DIC
major ions
DOC

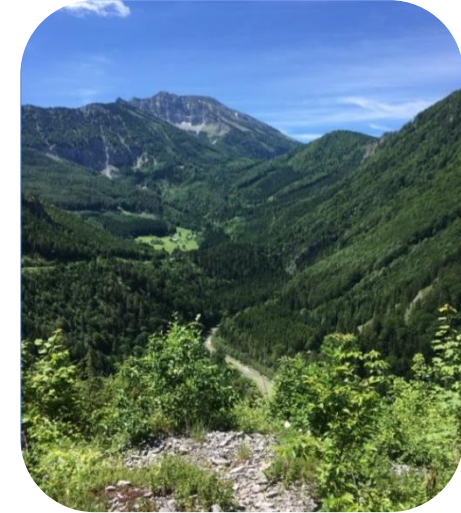
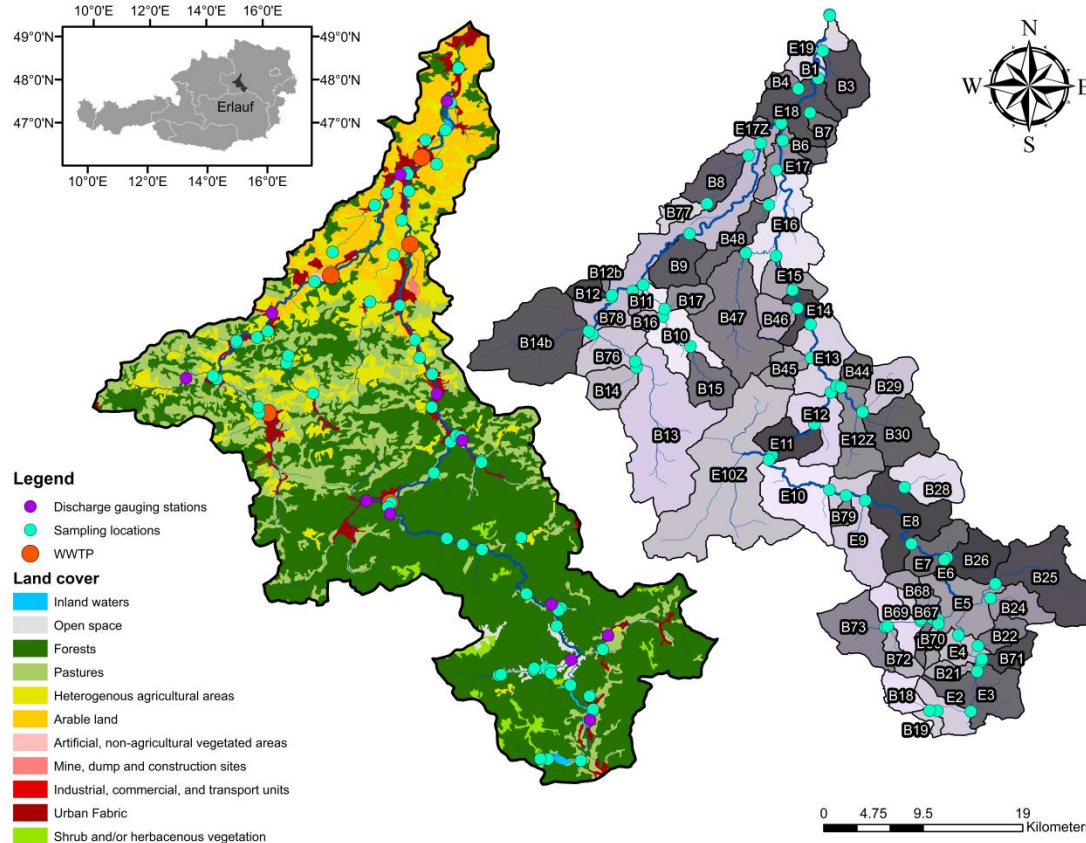


Data analysis and modelling

- spatio-temporal distribution patterns and correlation analysis
- Top-kriging technique & runoff separation
- Bayesian stable isotope mixing model



Study area



Name	Erlauf
Tributary of	Danube
Area	632 km ²
Discharge	14 m ³ s ⁻¹
Elevation min	220 m a.s.l.
Elevation max	1900 m a.s.l.

Results

Driver 1: microbiological N-turnover processes

- **correlations:** very weak for $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$, strong for $\delta^{15}\text{N}_{\text{NO}_3}$ and NO_3^-
- **message:** no signal of NO_3^- degradation

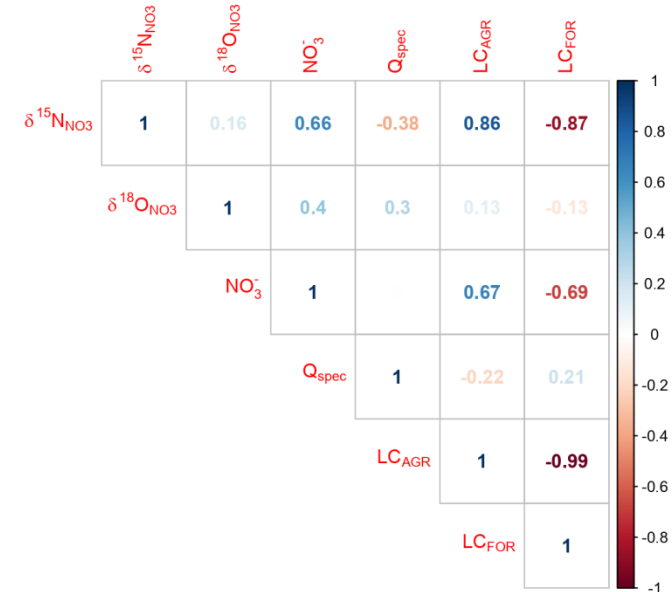
Driver 2: land-use

- **correlations:** very strong to strong between percentage of land cover and $\delta^{15}\text{N}_{\text{NO}_3}$, and NO_3^- but not for $\delta^{18}\text{O}_{\text{NO}_3}$
- **message:** high importance, change in source

Driver 3: hydrological conditions

- **correlations:** weak for Q_{spec} and other parameters
- **message:** low impact of dilution, change in sources/pathways

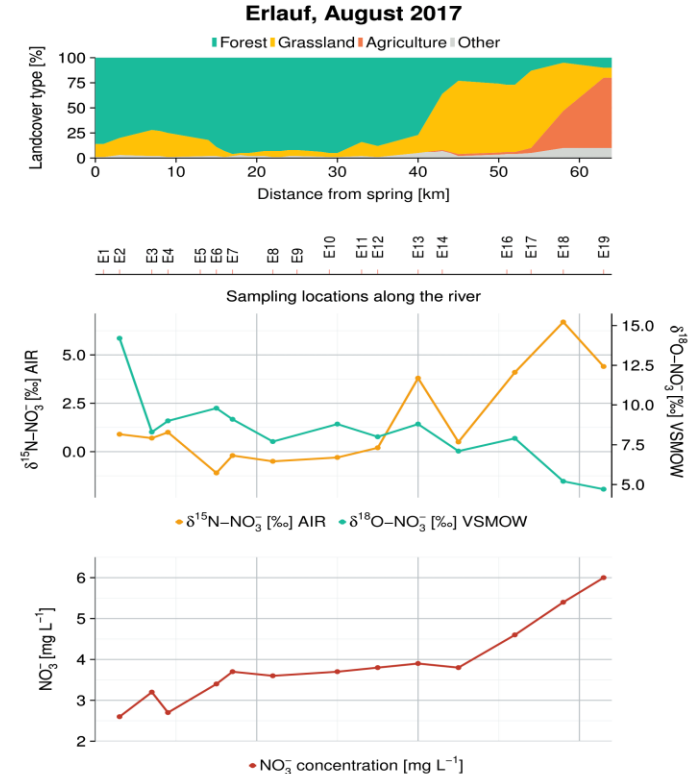
Spearman pairwise correlation matrix



Results

Driver 1: microbiological N-turnover processes

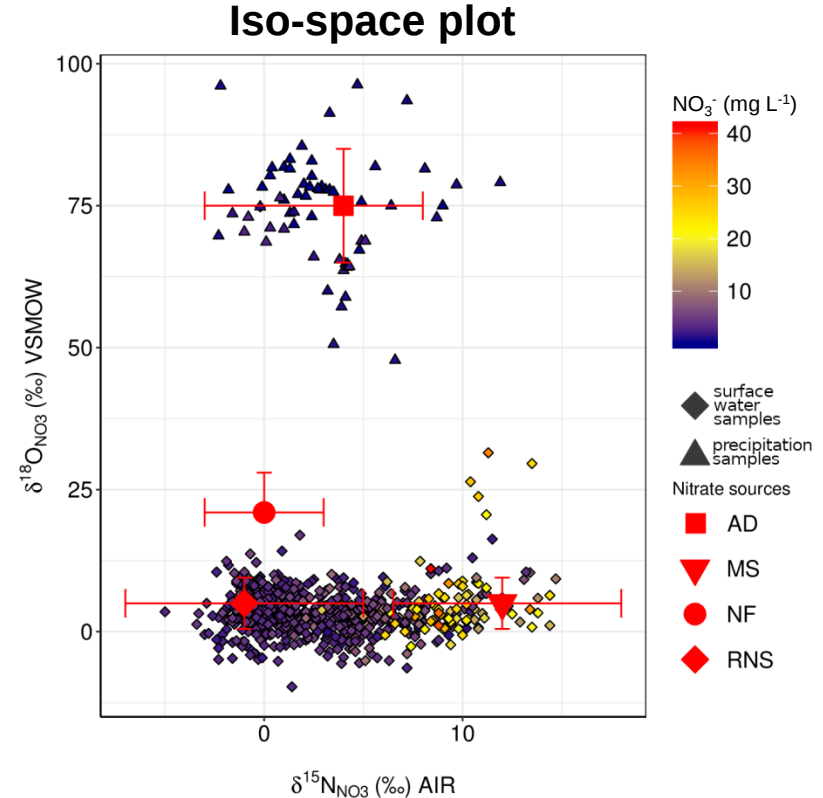
- analysis of changes along the main river
 $\delta^{15}\text{N}_{\text{NO}_3}$, $\delta^{18}\text{O}_{\text{NO}_3}$, NO_3^- , NO_3^- loads
- analysis of correlations location wise
 $\delta^{15}\text{N}_{\text{NO}_3}$ vs $\delta^{18}\text{O}_{\text{NO}_3}$
 $\delta^{15}\text{N}_{\text{NO}_3}$ vs $\ln(\text{NO}_3^-)$
 $\delta^{18}\text{O}_{\text{NO}_3}$ vs $\delta^{18}\text{O}_{\text{H}_2\text{O}}$
- conclusions
in regional scale in-stream denitrification plays only a minor role in Erlauf catchment



Results

Driver 2: land-use

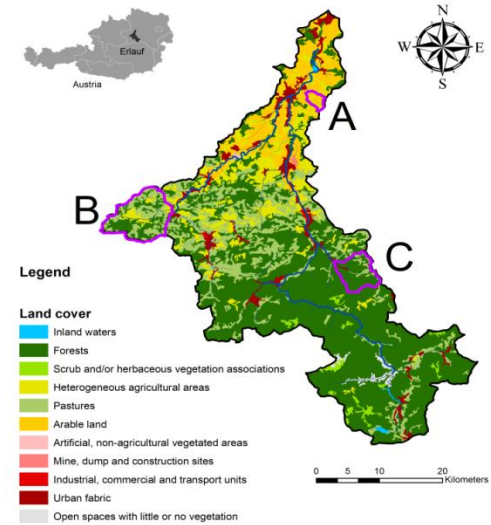
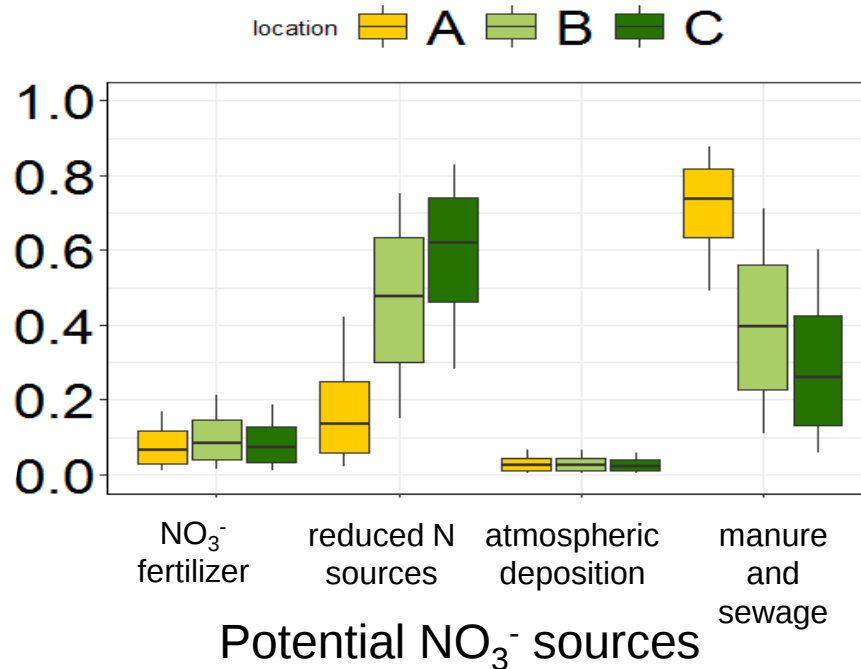
- Bayesian stable isotope mixing model
- potential NO_3^- sources and their isotopic compositions:
 1. atmospheric deposition (**AD**)
 2. manure and sewage (**MS**)
 3. nitrate fertilizer (**NF**)
 4. reduced N sources (**RNS**)



Results

Bayesian stable isotope mixing model

Proportional contribution

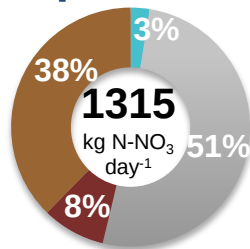


Sub-catchment	A	B	C
Land cover [%]			
Arable land	60	-	-
Heterogeneous agricultural areas	40	13	-
Pastures	-	47	16
Forests	-	39	82
Urban fabric	-	1	2

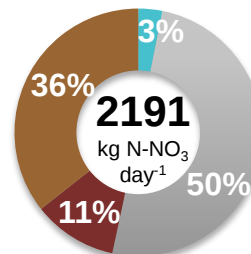
Results

III Outlet

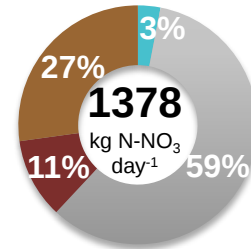
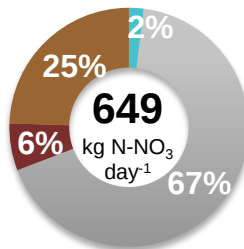
April 2017



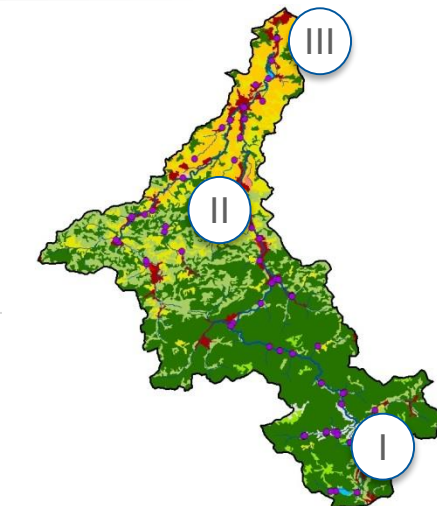
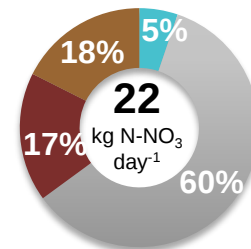
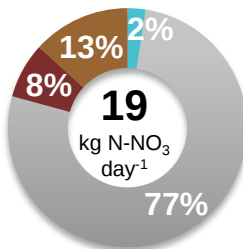
November 2017



II Middle course of the river



I Headwaters



■ Nitrate fertilizer

■ Reduced N sources

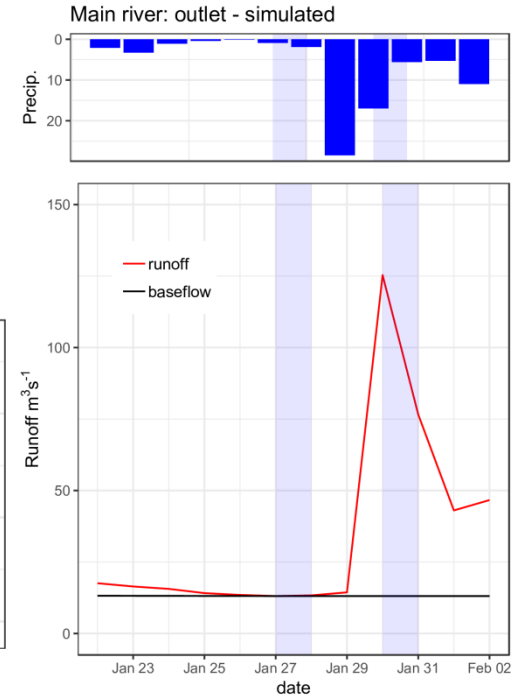
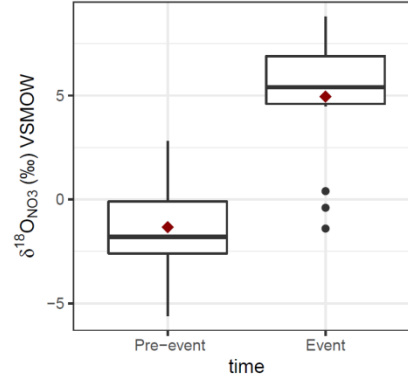
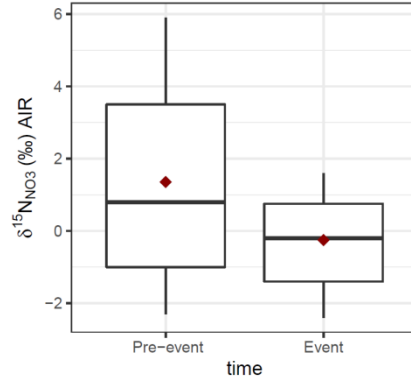
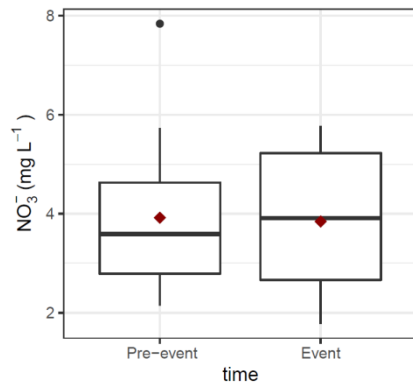
■ Atmospheric deposition

■ Manure & sewage

Results

Driver 3: hydrological conditions

- low impact of dilution
- mobilization of the NO_3^- pools from the unsaturated zone with lower $\delta^{15}\text{N}_{\text{NO}_3}$ coming from RNS and elevated $\delta^{18}\text{O}_{\text{NO}_3}$ caused by the shorter residence time and therefore lower exchange with water $\delta^{18}\text{O}$



Conclusions

Conclusions

- **Driver 1:** NO_3^- degradation potential is not sufficient to control the nitrate export
- **Driver 2:** agriculture is related to a considerable shift in the proportional contribution of manure and sewage and nitrate loads
- **Driver 3:** different NO_3^- export pathways occur during base flow and high flow conditions
- **Methodology:** measurement of NO_3^- alone would not be sufficient to trace all different controls on NO_3^- export

Outlook

Tripple catchment study



Thank you for your attention



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