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Joint analyses of nitrate transit time distributions and legacy effects in selected mid-European catchements

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We asked for

1. Temporal offset (Time lages) between N input (mainly fertilizer application) and N output (riverine export)
2. Quantitative offset between N in- and N outflux on an annual and cumulative scale
3. Driving parameters for the two

We did:

1. Fit of log-normal transfer functions to derive N travel times (TTs)
2. Legacy estimation
3. Partial least squares regression to determine parameters (for now only for Germany)

We conlude:

- Although catchments with short TTs tend to have less legacy, the quantitative offset (70%) is not explainable with TTs (4a)
⇨ no dominance of hydrological legacy
- 70% legacy poses challenge for system: N either released via denitrification, which is limited and releases harmful N_2O or N stored in a huge soil pool as biogeochemical legacy, which could leach slowly or could be taken up by plants
- Geological settings need to be considered, when aiming at water quality improvement

Background

- Excessive agricultural nitrogen (N) input causes exceeded drinking water limits in groundwater and eutrophication in surface waters
- Nitrate- and Water Framework Directive partly miss their targets
- Reduced N inputs usually do not result in an immediate decrease of riverine concentrations
- Time lags caused by long TTs in soil and groundwater (hydrological legacy) or/and accumulation of N in soils (biogeochemical legacy)
- Need to improve water quality management and assessment of measures by quantifying hydrological and biogeochemical legacy

Materials & Methods

- Long-term time series data from catchments in Germany and France covering ≥20a data for N input (diffuse sources [kg/ha*a]) and N output data (NO_3-N [mg/l] and Q [mm/ha])

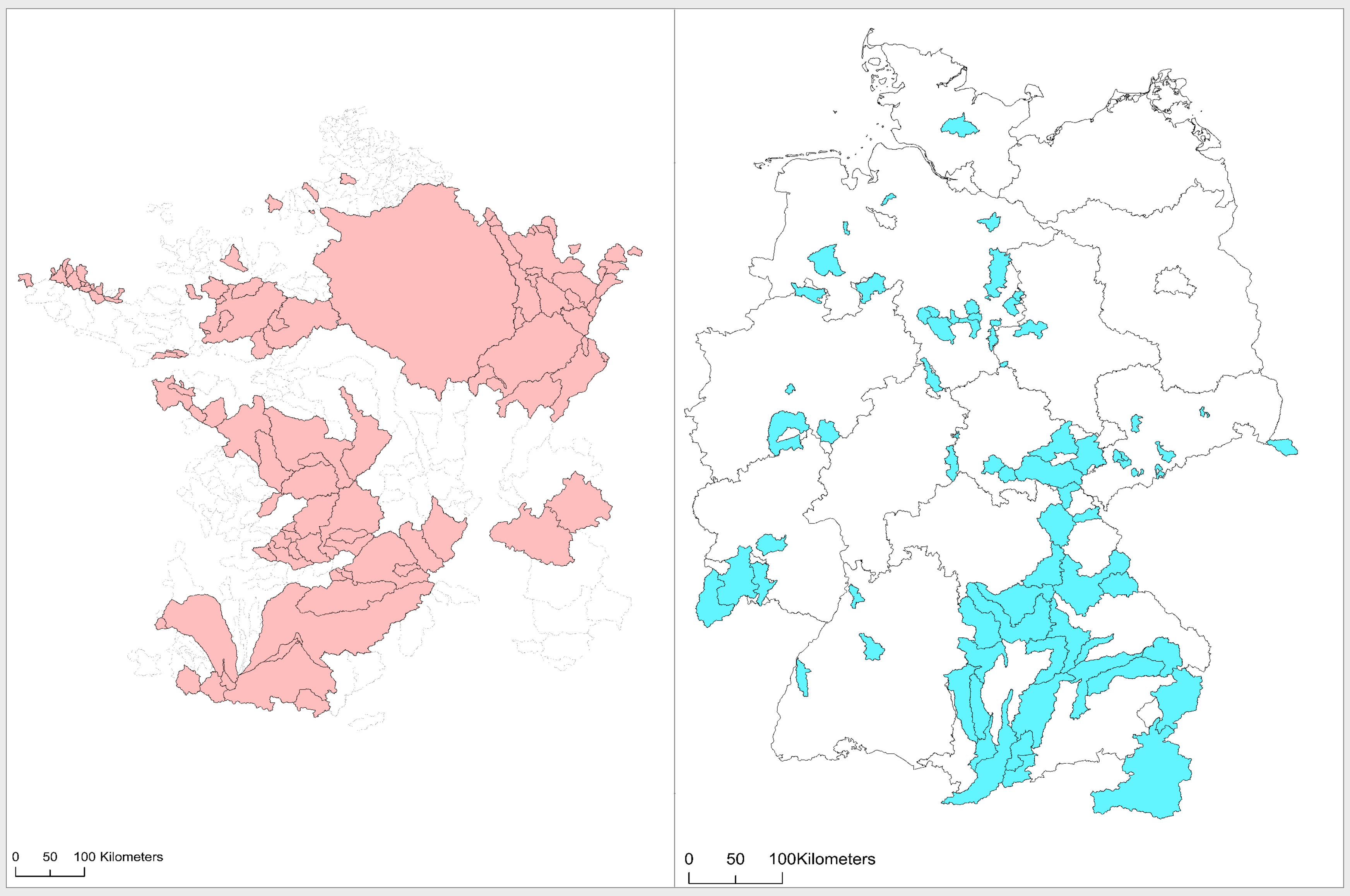

Fig.1: Map of selected catchments in France (left) and Germany (right).

Workflow:

- Data collection of long-term time series for in- and output
- Extending available German Q data base based on filling data gaps by using the mesoscale hydrological model (Kumar et al. 2013, Samaniego et al. 2010)
- Increasing the temporal resolution of N output (concentrations and fluxes) to a daily scale by using the WRTDS (Hirsch et al. 2010)
- Fitting of log-normal effective travel time distributions as transfer function between annual N inputs and annual riverine N-NO_3 concentrations
- Quantitave comparison of the N influx and the N outflux over time
- Finding driving parameters for the derived travel times and N legacy by using a using a partial least squares regression (PLSR) analysis with a ranking according to variable importance (VIP)

Results

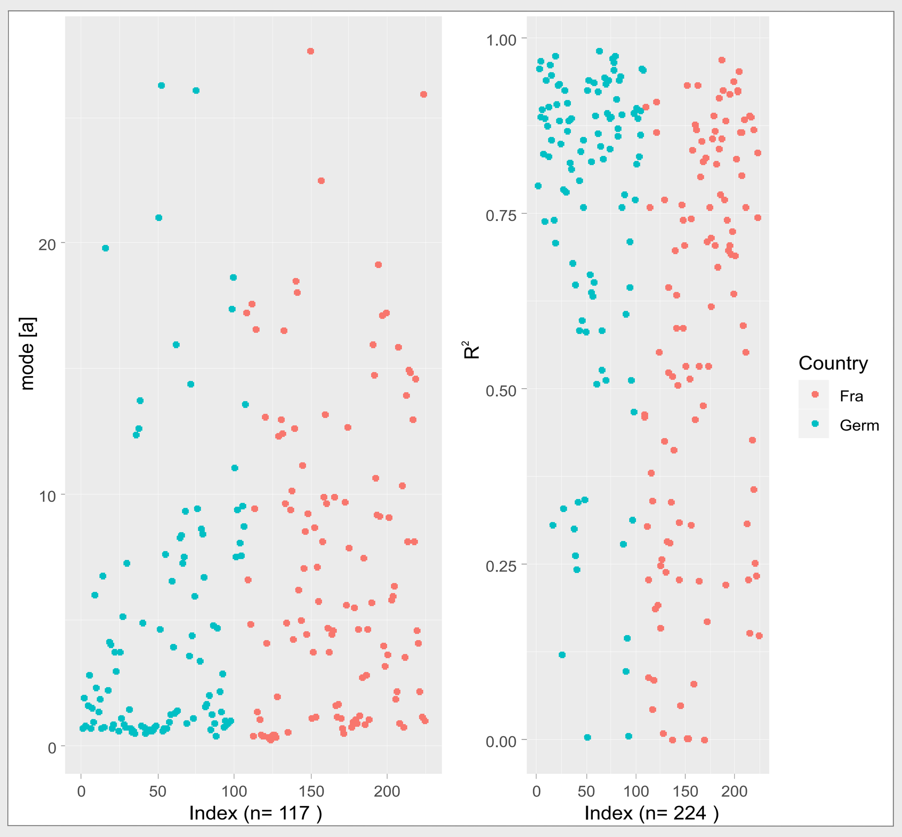

Fig. 2: Results of derived log-normal TTs showing the mode [a] (left) and fit as R² (right) of all stations by index.

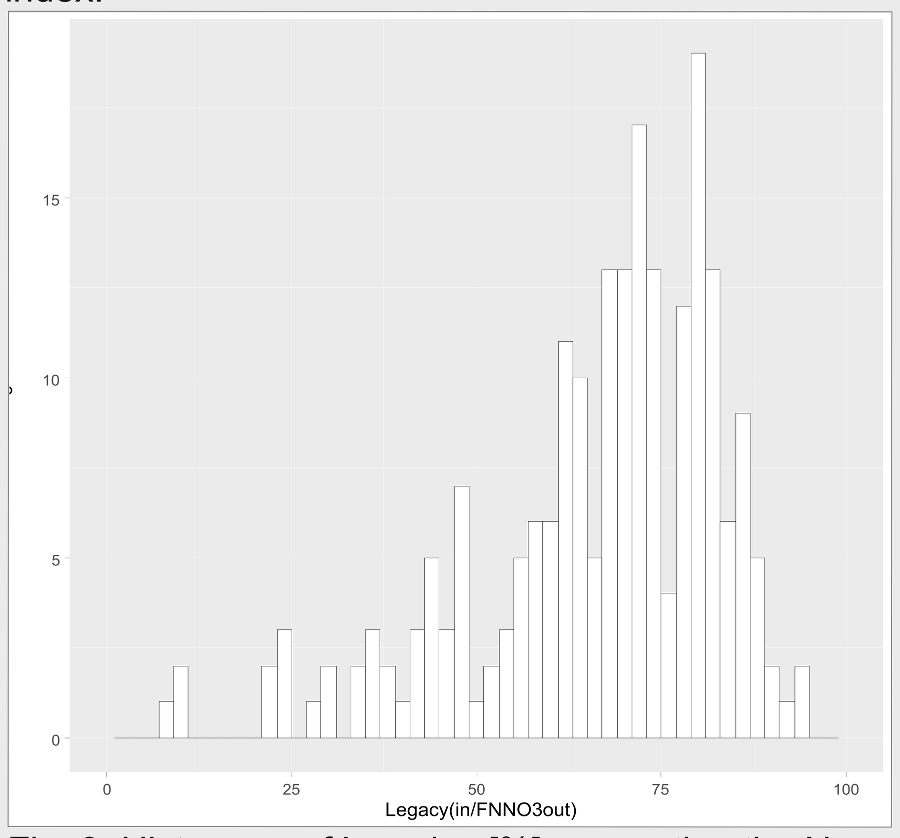

Fig. 3: Histogram of legacies [%] connecting the N influx with the N outflux during the overlapping time.

1. Temporal offset

- Median TT mode of 4a
- Potential p50 (percentile of 50%) TT of 10a (max. 31a)
- Satiyfying fit with a log-normal transfer function for 2/3 of the catchments
- Variable importance in PLSR (VIP): fraction of groundwater impacted soils (+) and fraction of calcareous rocks and sediments (+)

2. Quantitative offset

- Median legacy for the overlapping time of 70%
- Imbalance between N influx and N outflux by a factor of 4
- 88% of the catchments with a p50 TT below median, have also legacy below median
- VIPs: fraction of urban land (-), fraction of metamorphic rocks (+)

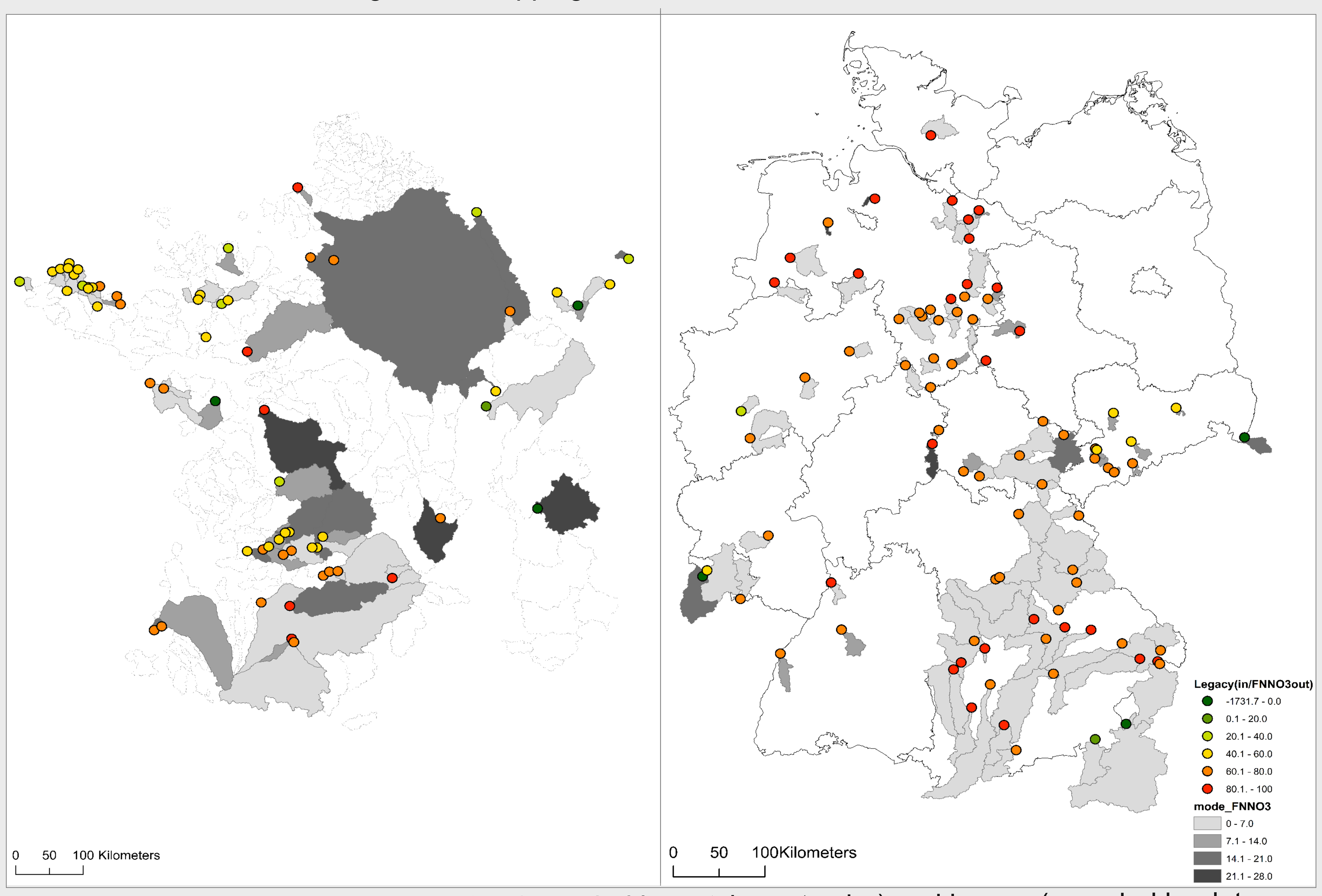

Fig. 4: Maps of the results for TT modes (encoded by catchment color) and legacy (encoded by dot color) for catchments (with fit $R^2 \geq 0.6$) for France (left) and Germany (right).

References:
Kumar, R., Samaniego, L., and Attinger, S.: Implications of distributed hydrologic model parameterization on water fluxes at multiple scales and locations, Water Resour. Res., 49, 360–379, 2013.
Samaniego, L., Kumar, R., and Attinger, S.: Multiscale parameter regionalization of a grid-based hydrologic model at the mesoscale, Water ResourRes., 46, 25 pp. 2010.