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

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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 input and N output 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 conclude:
• 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 N₂O 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

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 (NO₃-N [mg/l] and Q [mm/ha])

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-NO₃ concentrations
• Quantitative comparison of the N influx and the N outflux on an annual and cumulative scale
• 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)

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

Results
1. Temporal offset
• Median TT mode of 4a
• Potential p50 (percentile of 50%) TT of 10a (max. 31a)
• Satisfying fit with a log-normal transfer function for 2/3 of the catchments

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 and sediments (+)

References:
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