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Long-term assessment of nutrient dynamics in the Danube River (1996-2021) using flow-normalized indicators: Decoupling hydrological variability from management impacts

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Abstract. Assessing the effectiveness of nutrient management requires distinguishing policy-driven improvements from confounding hydrological variability. This study applies the Weighted Regressions on Time, Discharge, and Season method to analyze 25-year (1996–2021) nutrient dynamics along the Danube River. Results reveal a generalized decrease in total river discharge (streamflow), likely reflecting a combination of hydroclimatic trends, water abstractions, and reservoir operations, which masks underlying water quality trends. Flow normalization analysis confirms the high efficacy of point-source controls, largely driven by the implementation of EU Urban Waste Water Treatment Directive, with flow-normalized ammonium and Total Phosphorus loads declining by ~90% and ~50%, respectively. In contrast, modest nitrate reductions (20–40%) highlight the inertia of diffuse agricultural pollution and catchment legacies. This uneven management success has unintentionally amplified seasonal stoichiometric oscillations: the Total Nitrogen to Total Phosphorus (TN:TP) ratio now fluctuates drastically (from 10–15 to 35–40) within a single year. The magnitude of these seasonal shifts, driven by asynchronous nutrient cycles, exceed the annual nutrient ratio changes achieved in the 25 year period, and point to seasonal windows during which nutrient limitations should be monitored more tightly. We conclude that future management must shift from single nutrient load reduction targets to integrated strategies that address diffuse sources, adapt to climate-induced hydrological changes, and mitigate the ecosystem instability driven by amplified stoichiometric imbalances.

1 Introduction

Widespread surface water degradation from anthropogenic nitrogen (N) and phosphorus (P) enrichment remains a critical challenge for environmental management across Europe, driving eutrophication, harmful algal blooms, and hypoxia that compromise aquatic biodiversity, ecosystem services, and drinking water security (Galloway et al., 2008; Stets et al., 2020). In response, the EU has implemented robust policies for water protection, such as the Nitrates Directive (91/676/EEC), Urban

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Waste Water Treatment Directive (91/271/EEC), and Water Framework Directive (WFD, 2000/60/EC), yet persistent eutrophication in many water bodies signals a gap between policy implementation and ecological outcomes (Grizzetti et al., 2017). A fundamental limitation of current monitoring is its failure to isolate management-driven changes from confounding climate-induced hydrological variability, potentially misattributing water quality improvements to policy success rather than climatic trends.

The Danube River Basin, Europe's second-largest transboundary system, exemplifies this management challenge. Spanning 19 countries and delivering nutrient loads to the eutrophication-sensitive Black Sea, the Danube faces diffuse agricultural pressures and point-source discharges that have compromised its ecological status (Frîncu, 2021; ICPDR, 2015; Malagó et al., 2017; Radu et al., 2020). Legacy effects of intensified agriculture, industrialization, and hydromorphological alteration (dams, reservoirs) since the mid-20th century further complicate recovery (Cozzi et al., 2019; Habersack et al., 2016). Despite efforts coordinated by the International Commission for the Protection of the Danube River (ICPDR), achieving WFD "good status" remains elusive, underscoring the need for analytical frameworks that explicitly separate policy effectiveness from climatic noise (ICPDR, 2021; Mănoiu & Crăciun, 2021).

A critical yet overlooked dimension in nutrient management is stoichiometry. The total nitrogen-to-phosphorus (TN:TP) ratio regulates nutrient limitation, algal community composition, and trophic efficiency, with seasonally-driven shifts potentially favoring harmful algal blooms and degrading food-web nutritional quality (Downing & McCauley, 1992; Frost et al., 2023). Often measures to reduce nutrient pollution in water focus on N or P (loads or concentrations), rather than on their dynamic interaction and the ecological risks of their imbalance. Single-nutrient control success may inadvertently destabilize stoichiometric balance, amplifying seasonal oscillations beyond the thresholds considered in ecologic targets.

Detecting management achievements in nutrient pollution of surface water requires methods that disentangle anthropogenic signals from hydrological variability. Traditional assessments using raw observations are confounded by climate-driven discharge fluctuations, infrequent monitoring, and non-stationary pollutant sources (Choquette et al., 2019; Stets et al., 2020; Wu et al., 2022). The Weighted Regression on Time, Discharge, and Season (WRTDS) method addresses this issue by generating flow-normalized (FN) estimates that isolate long-term water quality evolution from hydrologic "noise" (Hirsch et al., 2010; Hirsch & De Cicco, 2015, Bouraoui et al., 2026). Despite its robustness, WRTDS remains underutilized in large transboundary basins for informing adaptive policy, particularly in linking management interventions to stoichiometric outcomes.

Previous studies in the Danube River Basin have examined nutrient trends in specific reaches, often relying on raw concentration data or annual averages. This study provides the first basin-scale analysis of 25 years (1996–2021) nutrient dynamics across the Danube River network that separates nutrient management impact from hydrological fluctuations. Our objectives are to: (1) quantify FN trends in N and P concentrations and loads at key stations; (2) analyze longitudinal spatial patterns; (3) characterize seasonal stoichiometric (TN:TP) fluctuations; and (4) interpret trends in the context of point-source controls, diffuse-source legacies, and climate-driven hydrological change.

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2 Materials and methods

2.1 Watershed description

The Danube River Basin (DRB) covers ~800,000 km² across 19 countries (Figure 1). A detailed description of the basin's hydrology, land use, and major tributaries is provided in the Supplementary Material (Section SM.1).

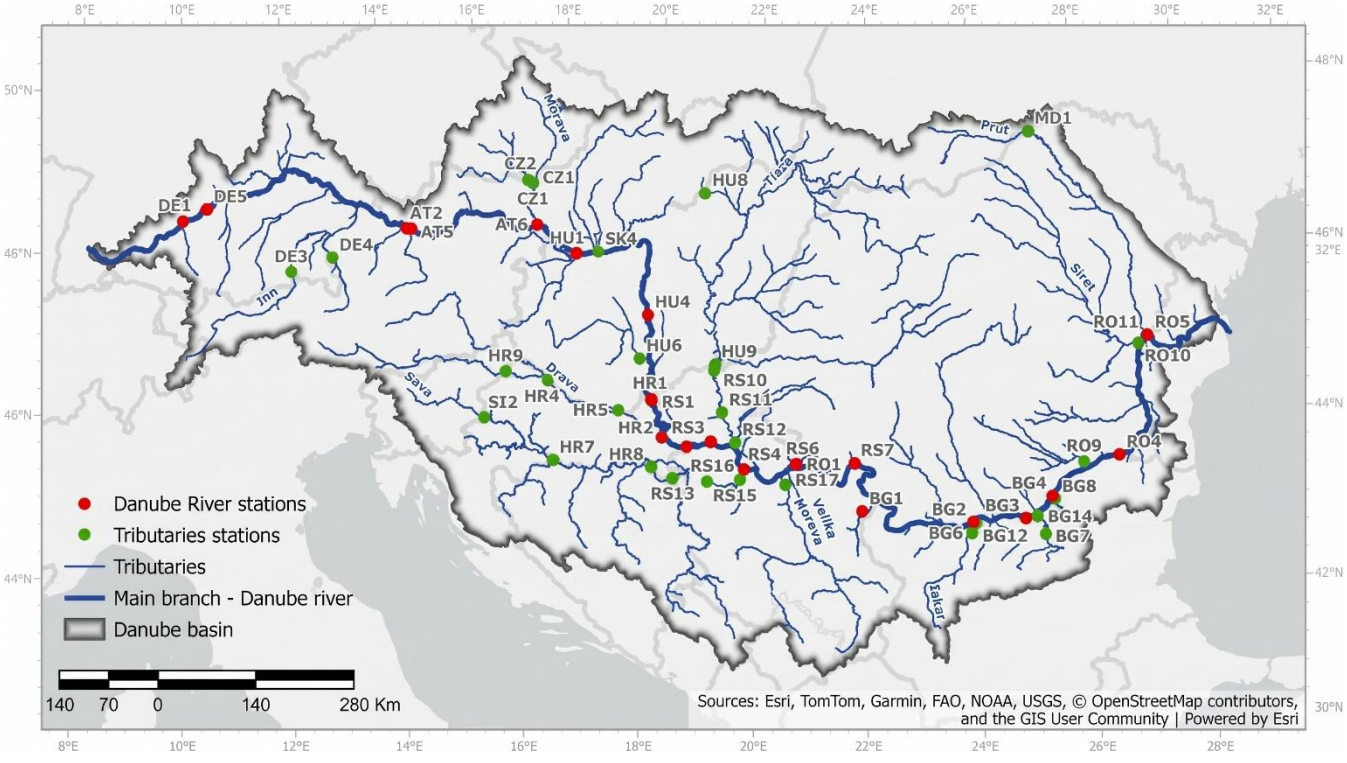


Figure 1: Geographic overview of the Danube River Basin, delineating the main stem, primary tributaries, and the spatial distribution of the water quality monitoring network analyzed in this work. Red dots denote main-channel monitoring sites along the Danube, whereas green dots represent stations situated on major tributaries.

2.2 Water quality data

Water quality data for the 25-year study period (1996-2021) were sourced from the Transnational Monitoring Network (TNMN) database managed by the International Commission for the Protection of the Danube River (ICPDR) and is publicly accessible (at: https://wq-db.icpdr.org/wq/static/stations?context=TNMN; see also ICPDR, 2015, 2017 for TNMN Yearbooks and related publications). The TNMN provides monitoring data from stations strategically located along the Danube River and its major tributaries. The sampling frequency is typically monthly, although this could vary with station, constituent, and period.

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This study focused on key nitrogen and phosphorus constituents: Nitrate (NO3-N), Nitrite (NO2-N), Ammonium (NH4-N), Total Nitrogen (TN), Total Phosphorus (TP), and Orthophosphate-Phosphorus (PO4-P).

An initial dataset was compiled, comprising information from 101 sampling stations, with 49 stations located on the Danube and 52 on its tributaries (Table SM_NS1 and Table SM_NS2 in supplementary material SM.2). We conducted an extensive data quality control comprising: initial screening, visual inspection, anomaly identification and correction, identification and removal of outliers.

Following this initial step, the dataset was further refined to ensure its suitability for long-term trend analysis over the target period (1996-2021) through the following steps:

- Temporal Coverage: Stations or specific nutrient time series were excluded if the available data series was too short (typically less than 15 years) or contained gaps (exceeding 3 consecutive years without observations).
- Spatial Aggregation: To obtain longer time series for trend analysis, data from nearby stations (typically located on the same river stretch, less than 50 km apart and without significant major tributary confluences in between) with complementary but individually incomplete records were merged, ensuring hydrological and water quality representativeness.
- Handling of Limit of Detection (LOD) Values: Concentration values reported as below half the limit of detection (LOD) were substituted with the LOD value itself.
- Cross-Sectional Averaging: Multiple samples taken at a river cross-section (e.g., left bank, middle, right bank) on the same sampling date were averaged into a single representative concentration value for that date.

As a result of this selection, a final set of 34 stations on the Danube and 33 on the tributaries was obtained. The Danube River stations are well-distributed along the river's course (see table SM_PERF1 in SM), with 6 stations located in the Upper Danube (upstream of rkm 1870, Devin Gate), 15 in the Middle Danube (rkm 1870–930, Iron Gate), and 12 in the Lower Danube and Delta (downstream of rkm 930).

2.3 River discharge data

Daily river discharge (flow) data are essential for calculating nutrient fluxes and applying the flow-normalization procedure (see Section 2.4). Daily discharge time series at the water quality monitoring location were compiled using the best available source, prioritized as follows:

1. Measured Discharge: Where reliable records existed from co-located or nearby gauging stations, daily measured discharge data were obtained from the Global Runoff Data Centre (GRDC) portal (https://grdc.bafg.de/data/data_portal/) and the Transnational Monitoring Network (TNMN) database.
2. Modeled Discharge: For water quality stations where measured discharge series were incomplete, had significant gaps, or were entirely missing, daily modeled flow estimates were utilized. These modeled data were extracted from

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the Copernicus Emergency Management Service (CEMS) European Flood Awareness System (EFAS) historical dataset (available at: https://ewds.climate.copernicus.eu/datasets/efas-historical?tab=overview). This dataset provides spatially consistent discharge time series across Europe, for 1992-2024.

Modeled discharge data were utilized for approximately 25% of the monitoring stations where observed records were partially or entirely missing. For these stations, the modeled series were verified and adjusted, as necessary, to correct for inconsistencies by comparing them with measured discharge series from upstream stations. The overall reliability of the modeled discharge was assessed at the stations where hydrometric data was available by means of performance metrics, such as Kling-Gupta Efficiency (KGE), Nash-Sutcliffe Efficiency (NSE), and Percent Bias (PBIAS). Furthermore, to ensure the accuracy of flux calculations across hydrological extremes, model performance was specifically analyzed for low-flow (PBIAS-L, lowest 25%) and high-flow (PBIAS-H, highest 25%) regimes. Although direct local validation was not feasible at the specific stations lacking observed records, performance metrics were successfully calculated for nearly half of the total study stations where concurrent data existed. This provided reasonable spatial representativeness across the basin to validate the model's performance. The detailed results, presented in Supplementary Material (Section SM.3) Tables SM_SF1 and SM_SF2, confirmed the general good agreement between modeled and observed series (e.g., KGE > 0.5 at most stations), confirming the suitability of the dataset for WRTDS flux estimation.

2.4 Flow trends estimation

Long-term trends in daily streamflow were assessed over the 25-year study period (1996-2021) at the 67 selected stations along the Danube River and its major tributaries. The analysis focused on trends in key annual hydrological metrics of the flow regime: 7-day minimum flow, daily median flow, daily mean flow, and 7-day maximum flow.

Trend magnitude for each hydrological metric was calculated using the non-parametric Theil-Sen slope estimator (Helsel and Hirsch, 2002). This method is robust to outliers and provides an unbiased estimate of the linear rate of change. Trend slopes were expressed as a percent change per year relative to the median value over the entire study period. The statistical significance of the trends was determined using the Mann-Kendall non-parametric test (Kendall, 1975; Hirsch et al., 1982). To account for potential serial correlation, which is often present in hydrological time series and can affect the outcome of the Mann-Kendall test, p-values were adjusted using the prewhitening method implemented in standard statistical packages (zyp R package; Bronaugh and Werner, 2009).

Furthermore, to explore trends in daily flow values, rather than just annual summary statistics, Quantile-Kendall plots were generated (Hirsch, 2018). These plots display Mann-Kendall trend test values and associated Theil-Sen slope estimates for various quantiles (from the annual minimum to the maximum daily discharge) of the daily flow distribution over the specified period. This approach allows visualizing trends for low, median, and high flows.

All trend analyses were conducted using the R statistical computing environment (R Core Team, 2014).

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2.5 Nutrient trend analysis using WRTDS

Nutrient trends were analyzed using the Weighted Regressions on Time, Discharge, and Season (WRTDS) method (Hirsch et al., 2010). WRTDS uses flexible regressions to estimate daily concentrations based on time, discharge, and season, allowing for the calculation of flow-normalized (FN) trends that isolate management impacts from hydrological variability. A detailed description of the model formulation, calibration procedures, and error estimation is provided in the Supplementary Material (Section SM.6). WRTDS was applied to NO3-N, NH4-N, TN, TP, and PO4-P time series. Statistical significance of trends was assessed using bootstrap methods (Hirsch et al., 2015).

3 Results

3.1 Trend and variability in streamflow

Insights into stream discharge changes, driven by factors such as climate and precipitation regime, are provided by Quantile-Kendall plots (e.g. Figure SM_SF1 in section SM.3), which were generated for all analyzed stations. These plots depict trend slopes for the full spectrum of daily flow quantiles. For instance, the plot of station 2113-AT5 in the upper Danube (Figure SM_SF1 left) reveals a general decrease of streamflow over all quantiles over 1996-2021; the median streamflow is decreasing at an approximate rate of 0.5% per year. This downward trend in the upper reaches of the Danube River is less marked in the downstream parts of the basin. Downstream the confluence of major tributaries, the Quantile-Kendall plots show nuanced patterns, sometimes indicating slight reductions in flows below the median and slight increases above it.

In the lower Danube reaches, where reservoir regulation likely influences flow dynamics, the plots reveal decreases in very low flows (below the 10th percentile) on the order of 0.2% per year. In contrast, above the 10th percentile flow trends are mostly upward, with increments around 0.1% at medium flow regime, and even higher increases for the highest daily flows, where annual increases may exceed 0.5% (e.g., station 554-BG3, Figure SM_SF1, right).

These general patterns are corroborated by analyses of annual hydrological metrics (7-day minimum, median, mean, and 7-day maximum flows), for which Theil-Sen slope estimates and Mann-Kendall p-values are presented in the supplementary information (Table SM_SF3).

The Quantile-Kendall analysis applied to major tributaries reveals varied responses (statistics of annual metrics are in Table SM_SF4). For example, an annual decrease in median flows of approximately -0.4% was consistent along the Sava River. In contrast, slight increases of around 0.2% were observed for the Tisza River, and small increases for the Drava River across many flow quantiles.

3.2 WRTDS performance assessment

The WRTDS model performance changed with constituent and river section (Tables SM_Perf1 and SM_Perf2 in section SM.6). For Nitrate (NO3-N), the model generally captured the seasonal dynamics well, with R^2 values for simulated

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concentrations typically ranging between 0.50 and 0.80 in the upper and middle Danube, though decreasing to 0.30–0.45 in the lower reaches. Flux estimates for nitrogen remained consistently robust (R^2 frequently > 0.80).

For Total Phosphorus (TP) and Ammonium (NH4-N), WRTDS models resulted in lower explanatory power for daily concentrations (R^2 values frequently below 0.40). The lower predictability reflects the nature of these constituents: TP is affected by episodic particulate transport during storm events, while NH4-N is heavily influenced by discrete point-source discharges. Both processes introduce high-frequency variability that cannot be fully captured by smooth, discharge-based regressions. To avoid selection bias, no stations or time periods were retrospectively excluded due to low concentration R^2 values; all exclusions were solely based on data density and continuity criteria (Section 2.2). Despite the low daily concentration performance, the flux estimates remained highly reliable (R^2 typically > 0.70-0.80), as mass transport depends on discharge volumes. Furthermore, the WRTDS flow-normalization technique fundamentally acts as a low-pass filter: by integrating daily estimates across the entire historical probability distribution of streamflow, it mathematically smooths out unmodeled short-term variability. This process effectively isolates the underlying multi-year management signal from the daily stoichiometric noise (Hirsch et al., 2010; Chanat et al., 2016)

3.3 Trends in nitrogen concentration and loads

NO3-N data from up to 34 stations along the Danube River were utilized (Figure 2), complemented by data from 28 stations on major tributaries. The Total Nitrogen (TN) dataset was less comprehensive, with 19 stations on the Danube and 24 stations on tributaries, having approximately 20 years of data.

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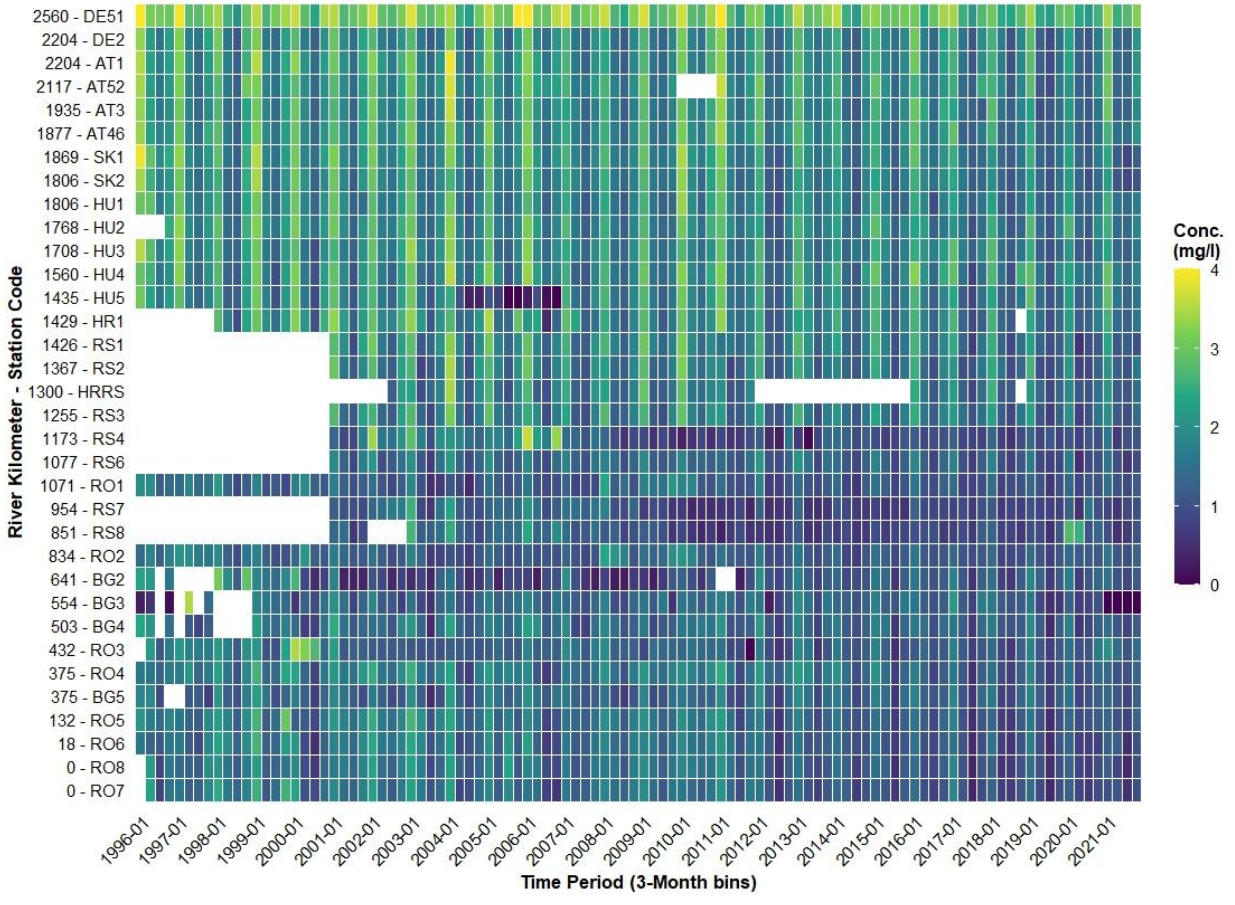


Figure 2: Spatio-temporal distribution of raw quarterly (3-month) mean NO3-N concentrations across Danube main-stem monitoring sites over the 1996–2021 period. Stations are arranged along the vertical axis following the longitudinal river gradient, from the headwaters in Germany and Austria (top) to the delta in Romania and Ukraine (bottom), with horizontal dividers delineating the Upper, Middle, and Lower reaches. Each site label combines its river kilometer (distance upstream from the Black Sea) with its two-letter country code (DE: Germany, AT: Austria, SK: Slovakia, HU: Hungary, HR: Croatia, RS: Serbia, BG: Bulgaria, RO: Romania; see Table SM_SF3).

3.3.1 Spatio-temporal trends in Nitrate (NO3-N)

Raw NO3-N concentration observations along the Danube River, illustrated via the heatmap (Fig. 2) and boxplots (Fig. SM_BP1), exhibit a clear longitudinal decrease from the headwaters down to the Iron Gate impoundment (rkm 940), with median concentrations dropping from roughly 3 mg/L to 0.9 mg/L. Downstream of the reservoir, concentrations show a modest rebound. Over the full 25-year record, a general temporal decline is also visually apparent across the monitoring network (Fig. 2).

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Nevertheless, drawing definitive conclusions from raw monitoring records is complicated by substantial measurement scatter and pronounced streamflow variations operating across daily, seasonal, and interannual timescales.

Once discharge-driven variability is filtered out through WRTDS flow normalization, a consistent downward trajectory in both NO3-N concentrations and loads emerges throughout the entire main channel (Fig. 3). Across the study period, flow-normalized fluxes declined by roughly 13% in the Upper Danube and by more than 20% approaching the delta. In terms of mass export to the Black Sea, these model estimates translate into a reduction from approximately 330,000 t/yr in 1996 to about 270,000 t/yr by 2021.

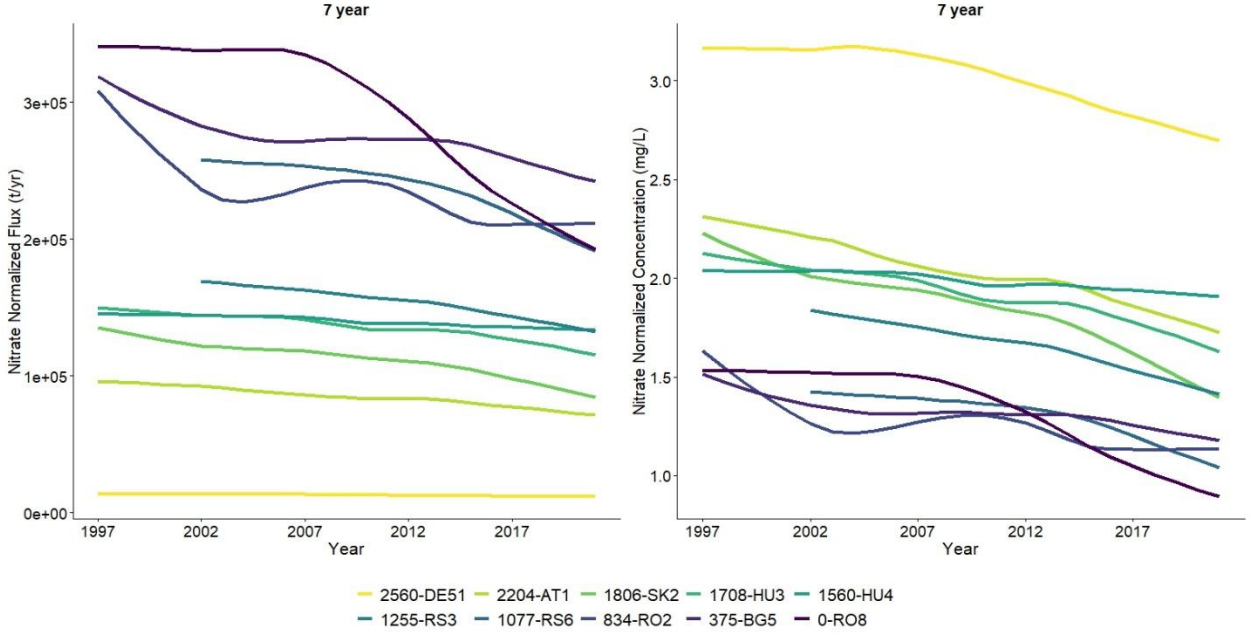


Figure 3: Multi-year trajectories (1996–2021) of WRTDS flow-normalized NO3-N loads (left panel) and concentrations (right panel) at representative monitoring sites along the Danube main channel

Extending the WRTDS evaluation to 28 monitoring sites across the principal tributaries reveals marked spatial differences in baseline concentrations: in 1996, NO3-N averaged roughly 3.9 mg/L in the Morava River, whereas levels in the Drava, Tisza, and Sava Rivers stood near 1.3 mg/L. Despite these differing starting points, downward trajectories are evident in every tributary, both in the raw observations (Figs. SM_BP2 and SM_HM2 in Sects. SM.4 and SM.5) and in the flow-normalized series (Sect. SM.7). Between 1996 and 2021, statistically significant ($p < 0.05$) flow-normalized concentration declines reached approximately 25% in the Drava (Fig. SM_FN2) and Morava (Fig. SM_FN4) Rivers, and up to 30% in the Tisza River (Fig. SM_FN3). Along the Sava River (seven monitoring sites; Fig. SM_FN1), concentrations also fell by roughly 15%, although with weaker statistical significance.

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3.3.2 Spatio-temporal trends in Nitrite (NO2-N) and Total Nitrogen (TN)

Across the monitoring network, NO2-N levels remained consistently low, typically below 0.08 mg/L, and exhibited a gradual decline over the 25-year record. Spatially, concentrations tend to rise moving downstream along the main channel (Fig. SM_HM5 in Sect. SM.5). Within the tributary network, NO2-N values were likewise low, with the Drava River recording slightly lower concentrations than the main stem and the Morava River exhibiting somewhat higher levels (Figs. SM_BP6 and SM_HM6).

Although Total Nitrogen (TN) monitoring records were less extensive than those available for nitrate, the spatio-temporal trajectories of TN closely mirrored those of NO3-N across both the main river and its tributaries

3.3.3 Spatio-temporal trends in Ammonium (NH4-N)

Raw ammonium (NH4-N) concentration reveal a marked longitudinal rise moving downstream (Figs. SM_BP7 and SM_HM7 in Sects. SM.4 and SM.5). This spatial escalation is most evident near the confluences of major tributaries, including the Drava, Tisza, and Sava, where surrounding population densities are high. Temporally, however, raw NH4-N levels declined broadly across the 1996–2021 period (Fig. SM_HM7).

Flow-normalized WRTDS estimates confirm substantial basin-wide declines in both NH4-N concentrations and loads between 1996 and 2021 (Fig. 4). The steepest reductions took place prior to 2013, coinciding with the progressive rollout of the EU Urban Waste Water Treatment Directive (Council Directive 91/271/EEC). Improvements were most pronounced in the Lower Danube, where baseline pollution was highest: mean flow-normalized NH4-N concentrations fell from roughly 0.32 mg/L in 1996 to nearly 0.07 mg/L in 2021 (Fig. 4, right panel). Correspondingly, the flow-normalized ammonium load exported to the Black Sea dropped sharply from approximately 80,000 t/yr in 1996 to 15,000 t/yr by 2021 (Fig. 4, left panel).

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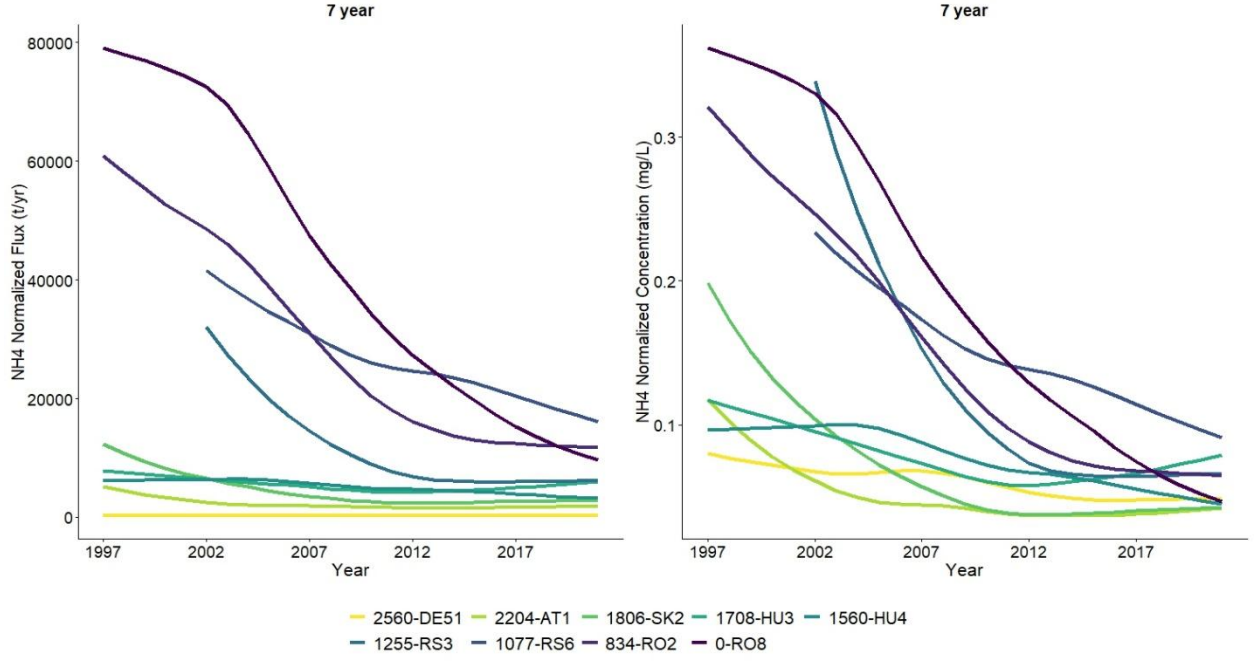


Figure 4: Multi-year trajectories (1996–2021) of WRTDS flow-normalized NH4-N loads (left panel) and concentrations (right panel) across selected Danube main-stem monitoring sites.

Similar decreasing NH4-N trends occurred were observed across most major tributaries, again with the strongest reduction occurring before 2012 (Sect. SM.8). In the Sava River (Fig. SM_FN8), concentrations tracked the main-stem pattern closely, dropping from 0.3 mg/L in 1996 to around 0.04 mg/L in 2021. Rivers with more moderate initial levels, the Drava (Fig. SM_FN9), Tisza (Fig. SM_FN10), and Inn (Fig. SM_FN12), declined from roughly 0.1 mg/L in 1996 to about 0.06 mg/L in 2021. By contrast, the heavily impacted Morava (Fig. SM_FN11) and Prut (Fig. SM_FN13) Rivers experienced steep drops from approximately 0.6 mg/L to 0.08 mg/L over the same timeframe. The Velika Morava River (Fig. SM_FN11) stands out as an exception to this basin-wide improvement, exhibiting an upward trend in NH4-N from roughly 0.09 mg/L in 1996 to about 0.2 mg/L in 2021.

3.4 Trends in phosphorus concentration and loads

The analysis of Total Phosphorus (TP) and Orthophosphate-Phosphorus (PO4-P) reveals significant changes over the 1996-2021 study period.

Analysis of raw TP concentration samples from the Danube River stations (Figure SM_HM 9 and figure SM_BP9 in sections SM.4 & SM.5 of) suggests an increase in concentrations downstream towards the central reaches, followed by a decrease closer to the mouth. Improvements are evident over the observation period (1996 to 2021), particularly in the upper and lower

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sections of the Danube, though less pronounced in the middle section. Specific stations in the Lower Danube (e.g. 851-RS58, 834—BG1, 554-BG1) indicated higher raw TP concentrations compared to others.

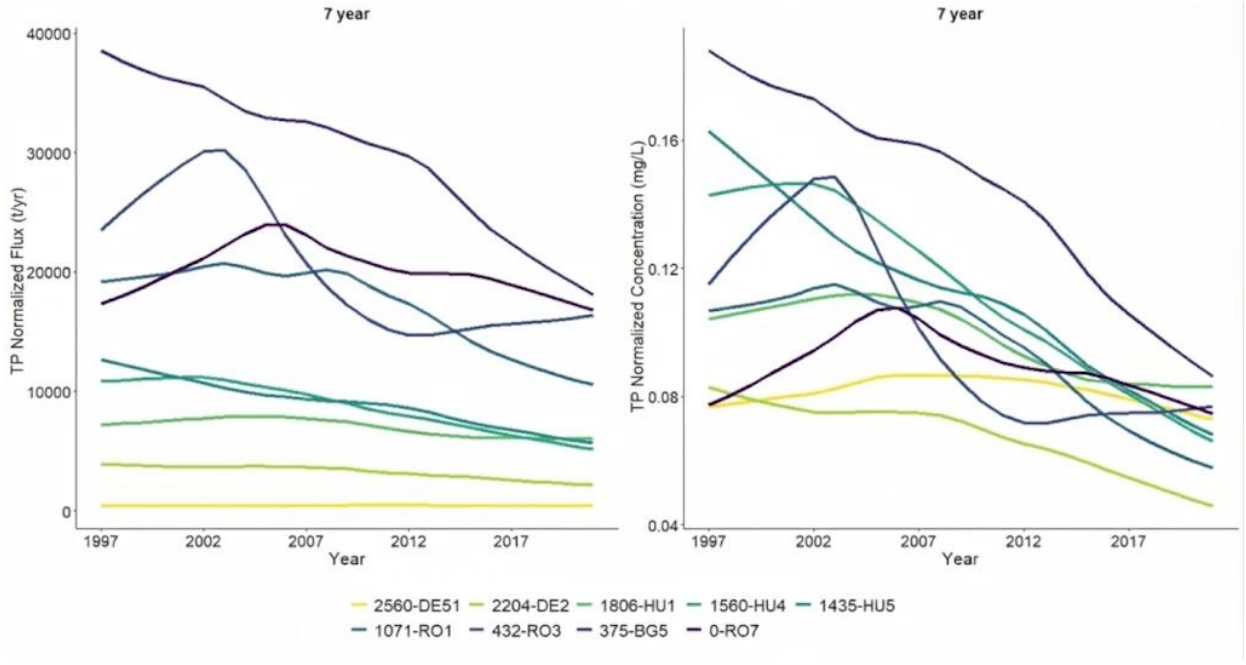


Figure 5: Multi-year trajectories (1996–2021) of WRTDS flow-normalized TP loads (left panel) and concentrations (right panel) across selected Danube main-stem monitoring sites

WRTDS flow-normalized trajectories (Fig. 5) confirm pronounced declines in both TP concentrations and fluxes, with reductions reaching roughly 40% across numerous sites between 1996 and 2021. These gains are primarily driven by upgraded municipal wastewater infrastructure, specifically enhanced phosphorus removal, alongside regulatory restrictions and bans on phosphate-based detergents (Grizzetti et al., 2025), and increased trapping of particulate phosphorus behind major impoundments. Spatially, mean flow-normalized TP concentrations display an upward gradient moving downstream; in 2008, for instance, values rose from roughly 0.07 mg/L in the Upper Danube (station 2560-DE51; Fig. 5, right panel) to nearly 0.16 mg/L near the lower reaches (station 375-BG5). At the river mouth (0-RO7), the estimated flow-normalized TP load exported to the Black Sea was halved over the study period, dropping from roughly 40,000 t/yr in 1996 to 20,000 t/yr in 2021.

Orthophosphate (PO4-P) trends generally followed those observed for TP, although a cautious interpretation of the flow-normalized (FN) results is required, particularly in the lower Danube where WRTDS model uncertainty is high. While raw PO4-P data (Figures SM_BP11 and SM_HM11 BP9 in sections 4 & 5 of SM) indicate a spatial pattern of increasing concentrations into the middle section before declining towards the mouth, the FN results appear to support a slight increase

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in concentrations along the river's course. However, the high model uncertainty in the downstream reaches precludes a robust quantification of this spatial pattern.

Despite these spatial complexities, a clear temporal trend is evident: a significant reduction of approximately 25% in FN PO4-P concentrations was observed over the 1996-2021 period across the more reliable stations (Figure SM-PO4 in section 3 of SM). While model uncertainty in the Lower Danube limits precise estimation of the load to the sea, the trajectory of the flow-normalized trends suggests that the FN PO4-P load delivered to the Black Sea in 2021 was likely below 10,000 t/year.

3.5 Seasonal variations in nutrient dynamics and stoichiometry

3.5.1 Contrasting seasonal dynamics in raw nutrient concentration

The examination of raw concentration data reveals contrasting seasonal behaviors for nitrogen and phosphorus, highlighting the complexity of nutrient dynamics in the Danube basin (Figures in section 11 of SM). Nitrogen species (TN and NO_3-N) exhibit a consistent seasonal pattern throughout the Danube River Basin. Concentrations consistently peak during the low-flow winter months and are typically halved during the high-flow period from April to August. This clear and consistent inverse relationship with discharge, observed across multiple upstream and downstream stations in the Supplementary Material (Figures SM_TN&TP 1, 3, 5, and 9 in section SM.11), points to dilution as the dominant process controlling nitrogen concentrations.

In contrast, along the Danube River, raw TP concentrations show very little to no discernible seasonality, and their relationship with streamflow is inconsistent, varying between seasons (e.g., Figure SM_TN&TP 7 in SM). Conversely, in major tributaries the seasonality is markedly different.

In agriculturally dominated tributaries (e.g., Morava, Tisza), a positive concentration-discharge relationship provides empirical evidence of a transport mechanism driven by surface runoff and erosion. Unlike the dilution pattern seen for nitrate (indicative of groundwater sources), TP peaks coincide with hydrological events, consistent with mobilization of particulate-bound phosphorus and sediment resuspension documented in similar agricultural catchments (Bowes et al., 2003; Vigiak et al., 2017)

3.5.2 Long-trends in flow-normalized nutrient concentration stoichiometry

Direct stoichiometric analysis of raw data is unreliable due to the confounding influence of hydrological variability. Apparent shifts in raw TN:TP ratios often reflect short-term discharge events rather than biogeochemical trends.

To isolate stoichiometric trends from hydrological variability, we analyzed flow-normalized (FN) time series. Because simultaneous, long-term (>20 years) TN and TP records were limited, flow-normalized NO_3-N was used as a proxy for TN. While useful for tracking general multi-year trajectories, this proxy should be interpreted with caution, as NO_3-N does not capture seasonal changes in the contribution of organic nitrogen to TN.

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A comprehensive validation (Section SM.12) confirms that NO3-N constitutes the dominant fraction of TN. While the relationship is stable in the Upper Danube (TN≈1.2×NO3-N), organic nitrogen inputs in the Lower Danube alter the seasonal NO3-N contribution to TN (from ~1.35 in winter to ~1.63 in summer). This seasonal shift in the organic fraction introduces a systematic underestimation of the true TN mass during the summer months. Nevertheless, the proxy robustly captures the directional trajectory and the extreme magnitude of the stoichiometric shifts.

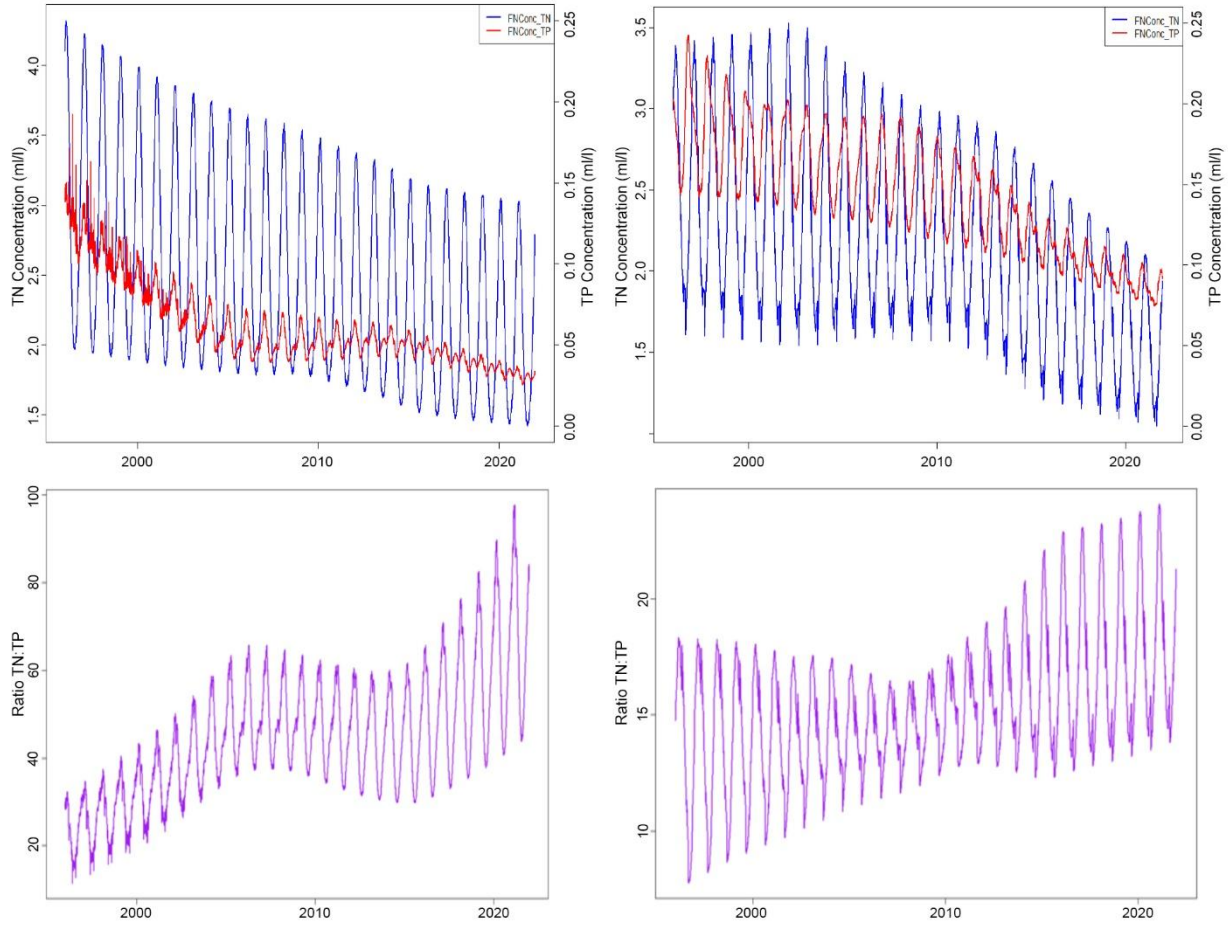


Figure 6: Panel of four figures displaying temporal trends. The top row shows the temporal evolution of flow-normalized (FN) concentrations of NO_3-N (blue line) and TP (red line) from 1996 to 2021. The bottom row illustrates the temporal evolution of the flow-normalized (FN) TN/TP ratio for the same period. The left column represents the upstream station (1935-AT3), while the right column represents the downstream station (375-BG5). Note that the y-axis scales for the TN:TP ratio differ between the left and right panels to highlight the specific seasonal amplitude and stoichiometric dynamics at each station.

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This flow-normalized approach analysis reveals three management-relevant trends in the Danube's nutrient stoichiometry, all of which are illustrated in Figure 6 and corroborated by a broader analysis of five key stations presented in section 13 of the Supplementary Material.

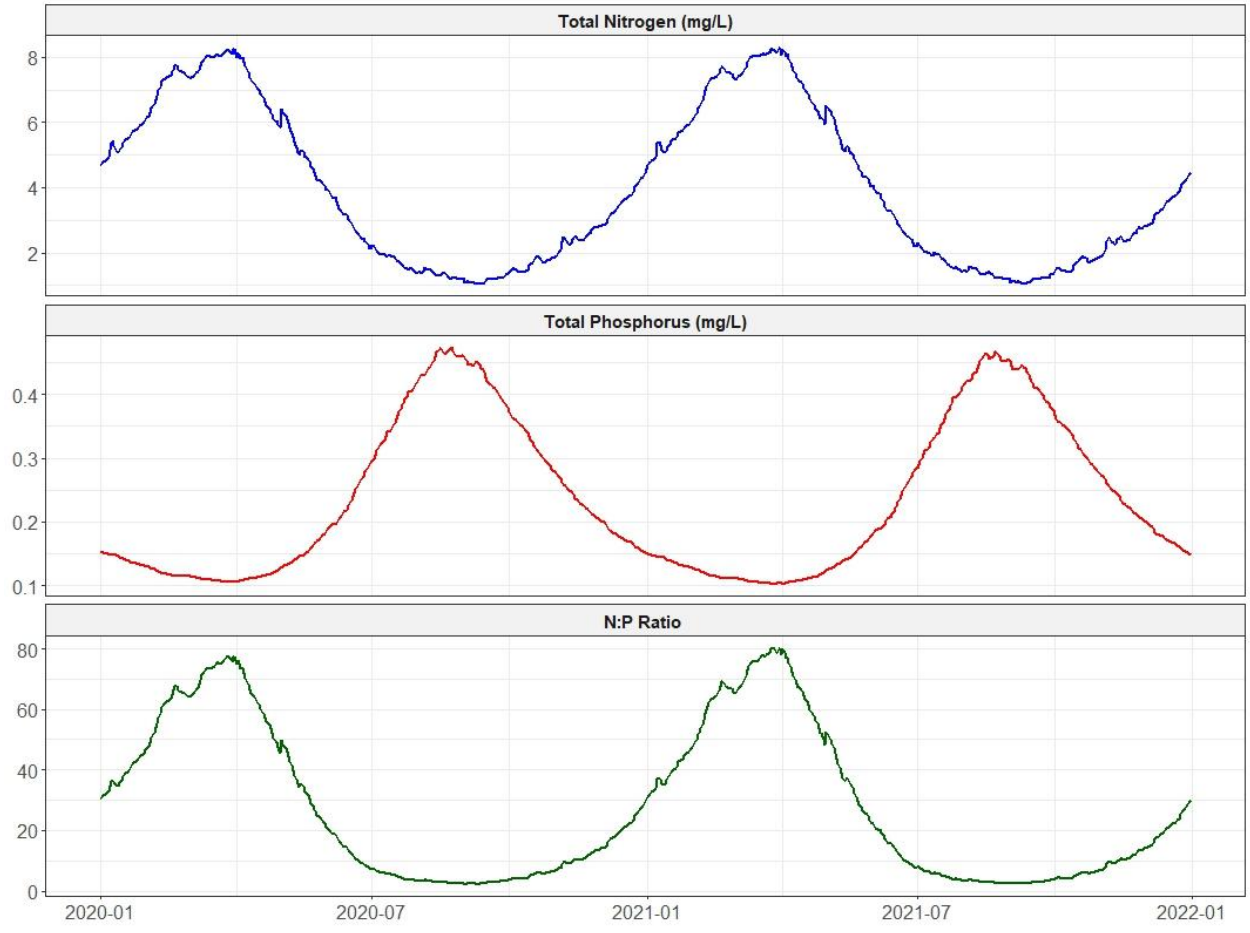
1. Strong longitudinal gradient: A pronounced longitudinal decline in the mean annual TN:TP ratio is evident across the basin (Figure SM_TN/TP 1 & Figure SM_TN/TP 2 in Section SM.13). The high upstream ratios decrease by up to three-fold in downstream sections. This gradient results from the combined effect of decreasing nitrogen concentrations and proportionally higher phosphorus levels along the river continuum.
2. Basin-wide long-term increase: A significant, consistent increase in the mean annual TN:TP ratio was observed across all stations over the 1996–2021 period (Section SM.13). This upward trend is driven by differential abatement rates, where FN TP concentrations have declined significantly faster than FN TN concentrations.
3. Dominant seasonality and longitudinally diverging trends: Superimposed on the long-term trend is a distinct seasonal oscillation (Figure 6). However, the long-term evolution of this seasonal dynamic differs notably along the river continuum:
    - Upper Danube (Station 1935-AT3): The seasonal amplitude has intensified significantly. While the ratio fluctuated between ~10 and 30 in the late 1990s, by 2020–2021 it oscillated from a summer low of ~40 to a spring peak near 100, effectively tripling the seasonal range.
    - Lower Danube (Station 375-BG5): In contrast, the absolute seasonal amplitude has remained relatively stable (maintaining a peak-to-trough difference of ~10 to 13). Instead of an amplitude expansion, this station exhibits a clear upward shift in the entire seasonal window, moving from a 7–17 range in 1997 to a 12–25 range in 2020–2021

Thus, flow-normalized (FN) analysis reveals a strong seasonal TN:TP oscillation previously masked in raw data by hydrological variability (Figures in section SM.11). Rescaling the FN series reveals opposing nutrient cycles across the basin, exemplified by the Morava River (Figure 7) and stations of the Danube (Figure SM_ST 2 in section SM.14).

The seasonal TN:TP pattern is primarily driven by FN TN fluctuations, which exhibit a much larger amplitude than TP. However, the inverse phasing of TP plays a critical amplifying role: FN TN peaks coincide with FN TP minima, driving the ratio to extreme highs, while TN minima align with TP peaks, suppressing the ratio.

This pattern is consistent basin-wide (Figure 7; Section SM.14). Peaks in TN and the TN:TP ratio typically occur in late February or early March (end of winter low-flow), while minima occur between August and September (waning summer high-flow). A minor spatial lag exists in the Lower Danube, where delayed TP cycles shift the stoichiometric peak to late March (Figure SM_ST 2 in section SM.14).

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Figure 7: Flow-normalized nutrient cycles in the Morava River (Station MORA17_CZ2) for 2020-2021. Panels show TN concentration, TP concentration and TN:TP ratio

3.5.3 Estimated nutrient fluxes to the Black Sea

380 To estimate actual historical loads delivered to the Black Sea, we utilized WRTDS flux estimates based on daily discharge records, as Flow-Normalized (FN) fluxes are designed solely for trend diagnosis. Station 375-BG5 was selected for this analysis to minimize uncertainties associated with model degradation in the final deltaic reaches, while maintaining consistency with upstream trends (Figure 5). Table 1 summarizes these annual loads.

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Total Nitrogen (TN) loads decreased by approximately 39%, dropping from a median of 517,500 t/year (1996–2001) to 317,400 t/year (2016–2021; Table 1). This estimate confirms continued abatement progress, falling well below the historical benchmark of ~400,000 t/year reported for the 1988–2005 period (ICPDR, 2015).

Total Phosphorus (TP) loads declined more sharply, with median values decreasing from 37,500 t/year to 18,200 t/year, corresponding to a reduction of over 51% during the same period. These results align closely with independent modeling, including SWAT estimates of ~25,000 t/year for 1995–2009 (Malagó et al., 2017). They are also consistent with recent ICPDR (2021) reports of 31,000 t/year in basin-wide emissions. The significantly lower export load observed at the river mouth (e.g., around 18,200 t/year) is expected, as total basin emissions are substantially attenuated by in-stream retention processes along the river continuum. This attenuation is primarily driven by particulate phosphorus settling within large reservoirs (such as the Iron Gate) and, to a lesser extent, biological uptake during the vegetative season.

Table 1: Comparison of WRTDS-estimated annual nutrient loads at station 375-BG5 between two periods.

		WRTDS flux (10^3 t/year)			FN flux (10^3 t/year)		
	Period	Min	Median	Max	Min	Median	Max
TN	1996-2001	463.0	517.5	652	496.0	504.0	509.0
	2016-2021	274.0	317.4	387.0	315.0	339.6	366.0
TP	1996-2001	33.9	37.5	46.4	35.1	36.6	38.5
	2016-2021	15.6	18.2	22.5	17.6	19.7	21.8

Note: 'WRTDS flux' represents the actual estimated mass transport driven by the specific hydrological conditions of each year. In contrast, 'FN flux' (Flow-Normalized flux) is a theoretical metric that removes the influence of year-to-year streamflow variability, isolating the underlying trend driven by anthropogenic management and source changes

While the long-term decrease in Danube discharge contributed approximately 5% to these reductions, the vast majority of the decline is attributable to successful nutrient source management rather than hydrological variability. Similarly, the Flow-Normalized (FN) loads, which isolate the management signal from hydrological variability, demonstrated substantial decreases for both TN and TP (Table 1), confirming the effectiveness of pollution control measures

4 Discussion

This study applies the Weighted Regressions on Time, Discharge, and Season (WRTDS) method to assess nutrient dynamics in the Danube River (1996–2021). By robustly separating management-driven changes from hydrological variability, the analysis reveals a generalized decrease in streamflow, particularly in the upper reaches. This observation underscores the

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critical importance of utilizing flow-normalization methods; without accounting for declining discharge, observed decreases in nutrient fluxes could be misattributed solely to improved source control.

Our flow-normalized trends corroborate and refine findings from previous investigations employing different analytical techniques. The significant nutrient reductions observed in the Lower Danube align with rank-correlation analyses by Frîncu & Iulian (2020) and Țuchiu (2019), who reported temporal decreases in ammonium and nitrate concentrations at key Romanian stations. Similarly, our results confirm the downward nitrate trends identified by Salvai et al. (2022) in the Serbian Middle Danube. Conversely, discrepancies with studies reporting invariant concentrations based on raw data averages (e.g., Mănoiu & Crăciun, 2021) highlight the confounding influence of hydrological variability and demonstrate the capability of WRTDS to detect underlying water quality improvements that are masked by flow fluctuations.

The results demonstrate a clear dichotomy in management effectiveness. The dramatic reductions in ammonium (~90%) and Total Phosphorus (~50%) are largely attributable to the EU Urban Wastewater Treatment Directive (91/271/EEC) and phosphate restrictions (Pistocchi et al., 2019). In contrast, nitrate reductions were more modest (20–40%) and spatially heterogeneous. The Upper Basin, where upstream countries exhibit the highest nitrogen inputs to agricultural land (FAO, 2023; ICPDR, 2021; Figure SM_TN&TP), showed only gradual declines. This slow response is driven by a complex combination of catchment legacies (Van Meter & Basu, 2017; Liu et al., 2024). Nitrogen applied during periods of high surplus before the 1990s accumulated in soil and groundwater (Van Meter et al., 2016; Wang et al., 2025), creating a legacy pool that releases nitrate into rivers with time lags spanning decades (Meals et al., 2010; Vero et al., 2018).

Concurrently, the implementation of the EU Nitrates Directive (91/676/EEC) has fostered better agricultural practices (e.g., balanced fertilization), playing a role in the gradual reduction in N surpluses entering groundwater systems (Grizzetti et al., 2021; Grizzetti et al. 2025). Therefore, the observed nitrate trends reflect a multifaceted response: the lagged impact of past reductions compounded by continuous improvements in nutrient management strategies over the last decades (ICPDR, 2022; Batool et al., 2025).

Furthermore, the interpretation of these long-term nutrient patterns must account for the basin's extensive hydromorphological alterations (Habersack et al., 2016). Historical channel deepening and reduced floodplain connectivity have progressively restricted lateral nutrient exchanges between the river and its surrounding landscape. Most crucially, dams, particularly the Iron Gate cascade, act as major physical barriers to nutrient transport. These large impoundments significantly increase water residence time and function as massive sinks for particulate matter. This enhanced phosphorus storage in reservoir sediments partially explains the pronounced spatial gradients and the significant downstream stabilization of TP loads observed in our flow-normalized estimates.

Beyond these long-term trends, a distinction between dissolved and particulate forms is crucial for interpreting the opposing seasonal dynamics observed for nitrogen and phosphorus. The dominant dilution pattern of nitrate during high-flow periods aligns with the chemostatic behavior reported for dissolved solutes in agricultural catchments (Basu et al., 2011; Moatar et al., 2017). In contrast, the increase in TP concentrations during high discharge events, particularly in tributaries, confirms the mobilization of particulate phosphorus. This mechanism is consistent with in-stream processes, where hydrological peaks

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trigger soil erosion and the resuspension of in-stream sediments, effectively overriding dilution effects (Bowes et al., 2003; Vigiak et al., 2017).

The asynchronous cycles—chemostatic nitrogen versus episodic particulate phosphorus create an intense seasonal stoichiometric oscillation. The TN:TP ratio is dominated by the large winter-to-summer fluctuation in nitrogen, amplified by the opposing cycle of phosphorus. This dynamic creates seasonal shifts in nutrient limitations that impact aquatic primary producers. While high TN:TP ratios in late winter suggest strong potential for phosphorus limitation, the lower ratios in summer could shift the system towards nitrogen limitation in certain reaches. Specifically, TN:TP mass ratios falling below 15–20 during the warm vegetative season, as observed in the Lower Danube, represent ecologically critical thresholds. As biological data were not analyzed in this chemical assessment, the ecological consequences remain a hypothesis derived from established stoichiometric principles. The summer low TN:TP ratio create potential favorable conditions for toxin-producing cyanobacterial bloomsin lentic and slow-flowing waters, such as in the Iron Gate reservoirs, lateral standing waters, and at the coastal waters of the Black Sea (Smith, 1983; Paerl et al., 2016). These blooms are unlikely to develop in the fast-flowing, turbulent waters of the Danube river; along the main river the primary potential impact may be a shift in phytoplankton community composition (e.g., reduced diatom dominance) that could alter the nutritional quality of the base of the food web (Abonyi et al.,2018).. These seasonal shifts align with recent findings in the interconnected Danube-Tisza-Danube hydrosystem, where Savic et al. (2022) identified a similar pattern of N-limitation predominantly during the vegetation season and P-limitation or co-limitation in colder months.

Consequently, the ecosystem response to nutrient management has become more complex than a simple reduction in algal biomass. While the successful control of Total Phosphorus has likely capped the potential for massive hypertrophic blooms (Lürling et al., 2016), it has inadvertently unmasked ecological risks driven by stoichiometry imbalance. As highlighted by Glibert (2017), the intensified oscillation of the N:P ratio creates a dual threat: the extreme spring peaks result in poor-quality food resources ('stoichiometric mismatch') that suppress zooplankton grazing and energy transfer (Frost et al., 2023), while the subsequent summer drops alter the competitive balance, potentially favoring opportunistic cyanobacteria in impounded or coastal waters.

4.1. Implications for River Basin management

These findings suggest three critical elements for future management planning in the Danube Basin:

- Targeted diffuse pollution control: Given the dominance of diffuse sources of nutrient pollution and legacy effects, besides reducing nutrient surplus in agricultural fields , future management should focus on targeted landscape-scale interventions (e.g., riparian buffer zones, wetland restoration) to intercept diffuse fluxes, aligning with the EU 'Farm to Fork' strategy objectives.

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- Operationalizing stoichiometric-informed early warning systems: Management plans should complement static, annual-average nutrient targets with seasonal-specific nutrient criteria to leverage the amplified TN:TP oscillation as a functional early warning indicator. This indicator serves a dual operational purpose for water managers: (a) spring peaks exceeding a mass ratio of 50–60 warn against severe phosphorus limitation and subsequent 'stoichiometric mismatch' that degrades food-web nutritional quality along the river continuum; and (b) summer drops below 15–20 signal an immediate risk window for nitrogen co-limitation and opportunistic cyanobacterial shifts in vulnerable lentic zones (e.g., the Iron Gate reservoirs) and in the receiving Black Sea coastal plume. To operationalize this tool, traditional monthly monitoring frameworks must transition toward bi-weekly or high-frequency sampling during the critical seasonal windows (late winter-spring and mid-summer). This would enable authorities to implement countermeasures, such as dynamically tightening emission limits for wastewater discharges during low-flow periods or optimizing reservoir flushing regimes.

Regarding study limitations, the reliance on NO3-N as a proxy for TN implies an underestimation of the summer nitrogen pool due to peak organic N inputs. As demonstrated by the validation analysis in the Supplementary Material (Section SM.12), the organic fraction increases the TN: NO3-N ratio from about 1.35 in winter to approximately 1.63 in summer. However, the impact of applying this range of correction factors to the time series is minor relative to the massive 3-to-5-fold seasonal oscillations driven by discharge and management. This proxy-induced bias does not alter the fundamental ecological diagnosis. Applying the maximum summer correction factor to the lowest flow-normalized proxy ratios (which drop to around 12 in the Lower Danube) yields a corrected TN:TP mass ratio of approximately 19.5, which still falls within the ecologically critical threshold window of 15–20. Therefore, the proxy provides a conservative lower bound for nitrogen availability and it reliably captures the severe seasonal narrowing of stoichiometric ratios during the vegetative period.

Additionally, while daily TP concentrations exhibit high modeling uncertainty due to unmodeled episodic variability, the amplitude of the seasonal TN:TP shift is governed by the highly predictable, dilution-driven fluctuations in TN. Consequently, the long-term stoichiometric trends remain robust despite the inherent noise in daily particulate phosphorus transport.

5 Conclusions

This 25-year assessment (1996–2021) provides a robust evaluation of nutrient management effectiveness in the Danube River Basin. The application of WRTDS flow-normalization proved decisive in decoupling management-driven water quality improvements from the confounding signal of a generalized, climate-driven decline in streamflow. By treating discharge as an independent variable, the method successfully isolates the water quality signal regardless of whether the flow reductions are driven by climate change, increasing water abstractions, or hydromorphological alterations. This distinction is critical for understanding valid progress in reducing nutrient pollution and achieving water quality objectives.

This study provides insights on the effectiveness of EU and national policies addressing nutrients in the Danube region in the last 25 years: the EU Urban Waste Water Treatment Directive has been highly successful. Point-source control measures have

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driven important reductions in flow-normalized ammonium loads (~90%) and Total Phosphorus (~50%), significantly lowering the pressure on the riverine ecosystem. However, the more modest reductions in nitrate (20–40%) highlight the persistent inertia of diffuse pollution. The slow response of nitrate loads underscores that current agricultural measures are struggling to counterbalance catchment legacies, necessitating a shift towards more targeted landscape interventions.

This study reveals an unintended ecological consequence of these management successes: an amplified seasonal stoichiometric oscillation. The asynchronous seasonal variation of nitrogen and phosphorus concentrations have paradoxically intensified the fluctuation of the TN:TP ratio, creating highly dynamic nutrient regime that shifts rapidly from phosphorus to nitrogen limitation, complicating eutrophication management in the receiving Black Sea. Tracking these amplified oscillations offers a potential early warning tool, enabling water managers to anticipate seasonal ecosystem instability—ranging from main-channel food-web decoupling to localized lentic proliferation—and transition from reactive chemical monitoring to proactive, adaptive river basin intervention.

In conclusion, while the first phase of nutrient management (point-source control) has been effective, the Danube Basin now faces "second-generation" challenges. Future management cannot rely solely on hydraulic dilution, given the declining discharge trends. Strategies must now focus on: (1) mitigating diffuse nitrogen pollution through clearer integration of the agricultural practices with water objectives; (2) addressing the new risks posed by intensified stoichiometric imbalances; and (3) leveraging synergies with the Industrial Emissions Directive (IED) to further curb remaining point sources. Such adaptive and policy-integrated management can improve the ecological integrity of this vital transboundary river system.

Code and data availability

All data used in this study are available from public repositories. Water quality data from the Transnational Monitoring Network (TNMN) can be accessed at https://wq-db.icpdr.org/wq/static/stations?context=TNMN. Measured daily river discharge data are available from the Global Runoff Data Centre (GRDC) portal at https://grdc.bafg.de/data/data_portal/. Modeled daily river discharge estimates from the Copernicus Emergency Management Service (CEMS) European Flood Awareness System (EFAS) historical dataset are available at https://ewds.climate.copernicus.eu/datasets/efas-historical?tab=overview. Additionally, the processed discharge time series used in this analysis have been deposited in Zenodo and can be accessed at https://doi.org/10.5281/zenodo.24308438. The code used in this study is available from the corresponding author upon reasonable request.

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Author contributions

AU: Conceptualization, Methodology, Data curation, Implementation, Validation, Visualization, Writing – original draft; FB: Conceptualization, Methodology, Implementation, Validation; OV: Conceptualization, Methodology, Writing—review and editing; FM: Data curation; BG: Conceptualization, Writing—review, Supervision.

Competing interests

The contact author has declared that none of the authors has any competing interests.

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