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Pooled versus fixed-station analyses of stream water quality in Pennsylvania, 2010–2024

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Abstract

Public stream-monitoring archives combine measurements collected at changing sets of stations, which can complicate comparisons over time. We analysed 583,494 quality-controlled records of nitrate as nitrogen (nitrate-N), total phosphorus, pH, dissolved oxygen, specific conductance, and water temperature from 6,451 Pennsylvania stream stations during 2010–2024. We compared record- and station-level exceedance summaries, examined seasonality and station-level trends, contrasted pooled annual series with a long-record station series, separated within- from between-station associations, and assessed spatial clustering. Nitrate-N exceeded 10 mg/L in 0.81% of records and at least once at 4.2% of nitrate-monitoring stations. Total phosphorus exceeded 0.1 mg/L in 15.2% of records and at least once at 25.8% of phosphorus-monitoring stations. Seasonal differences were statistically detectable for all six measures, but effect sizes were substantially larger for temperature and dissolved oxygen. An upward trend in pooled annual nitrate-N medians was not reproduced in the series from long-record stations. Associations among nitrate-N, phosphorus, and conductance predominantly reflected between-station differences, while nitrate-N showed spatial clustering in south-central Pennsylvania. These descriptive findings show that monitoring-network composition and analytical scale affect the interpretation of archived measurements. Streamflow, land use, and sampling-time data are needed to assess potential explanations.

Keywords: stream monitoring; water quality; nitrate; fixed-station trends; spatial autocorrelation; Pennsylvania

Article Highlights

- The pooled nitrate trend was not reproduced when the same long-record stations were followed.
- Record-level and station-level exceedance summaries describe different aspects of the data.
- Higher nitrate measurements were clustered at monitored stations in south-central Pennsylvania.

1 Introduction

Streams integrate processes across their catchments, and a few routine measurements (nutrients, specific conductance, pH, dissolved oxygen, and temperature) provide useful but incomplete descriptions of their condition. In the Chesapeake Bay watershed, which drains much of southern and eastern Pennsylvania, assessments have reported improvements in some locations, with differences among nutrients, tributaries, and

land uses (Oelsner and Stets, 2019; Zhang et al., 2022; Murphy et al., 2022). Basin studies have related nutrient patterns to point-source controls, agricultural practices, and earlier inputs (Fanelli et al., 2019; Ator et al., 2020; Kleinman et al., 2019). Changes in streams can lag behind changes on land because groundwater delivers nitrate for years after inputs fall (Van Meter et al. 2018; Wherry et al. 2021), and phosphorus stored in soils, sediments, and channels is released over years to decades (Stackpoole et al. 2019; Zhang et al. 2016a; Zhang et al. 2016b; Wallington et al. 2024; Dolph et al. 2024). Evaluations of best management practices describe effects that depend on the practice, setting, and monitoring design (Lintern et al., 2020; Kua et al., 2023; Porter, 2025).

The ionic composition, pH, temperature, and oxygen levels also changed over time. Conductivity and chloride levels have increased across much of the eastern United States (Kaushal et al. 2018; Stets et al. 2017; Kaushal et al. 2021; Kaushal et al. 2025), with deicing salts and impervious cover implicated in urban and suburban streams (Moore et al. 2020; Rossi et al. 2022), and increasing riverine conductance reported from 1998 to 2018 (Rumsey et al. 2022). Acid-sensitive streams in the Appalachians and Catskills show rising pH after reductions in acid deposition (Scanlon et al., 2021; Baldigo et al., 2021). Warming has been documented in many streams in the United States (Kaushal et al. 2010; Sadayappan and Li 2025; Ficklin et al. 2023), and a reconstruction found deoxygenation in 70% of nearly 800 rivers (Zhi et al. 2023), although a global compilation reported no consistent trend in hypoxia since 1950 (Blaszczak et al. 2023). Daily oxygen cycles driven by light and flow mean that the time of a grab sample is important (Bernhardt et al. 2022).

Large public archives make statewide analyses possible. The Water Quality Portal pools records from many organisations (Read et al. 2017); however, these records were not collected to a common design. Units, fractions, and detection limits are often inconsistent (Sprague et al. 2017), harmonising multi-source data is a substantial task (Krasovich et al. 2022), and substituting values for non-detects can distort statistics (Helsel 2006). Sampling networks also change over time; therefore, trends calculated from pooled records can partly reflect the locations and sampling schedules that contribute observations in each year. Flow-adjusted methods address part of this problem, where daily discharge and dense sampling exist (Hirsch et al. 2010; Murphy and Sprague 2019; Stets et al. 2020); however, most portal stations do not meet these requirements.

Earlier work has covered much of this ground. Statewide Pennsylvania syntheses report median nitrogen and phosphorus concentrations, their contrast among land uses and seasons, and the share of sites above percentile thresholds (Clune et al. 2020b; Clune et al. 2020a). Regional trend studies rely on flow-normalized loads at fixed networks (Zhang et al. 2022), and panel regressions have been applied to Pennsylvania monitoring records in a study of shale gas development (Olmstead et al. 2013). A national assessment described nitrate above the drinking water standard as relatively uncommon in samples from streams used for drinking water (Dubrovsky et al. 2010). Three comparisons warrant further examination in this application. First, national trend analyses use sites screened for record completeness (Stets et al. 2020; Oelsner and Stets 2019), but we did not identify a directly comparable Pennsylvania study contrasting pooled and fixed-station series with documented quality-control procedures. Second, associations among nutrients and major ion indicators are usually reported across sites (Kaushal et al. 2018), and panel methods that separate site from within site variation (Steinschneider et al. 2013) have, to our knowledge, not been applied to this set of variables. Third, spatial autocorrelation statistics have been used with stream monitoring data elsewhere (Miralha and Kim 2018), but we did not identify directly comparable local indicator maps of station nitrate for Pennsylvania.

Using established statistical tools, this study compares several methods of summarising a documented extract of Pennsylvania stream records from 2010 to 2024. The contribution is an explicit, same-dataset comparison of pooled and fixed-station time series, record- and station-level benchmark summaries, and between- and within-

station associations. These comparisons highlight how the monitoring design and unit of analysis condition interpretation. Three questions guide the analysis. RQ1: How often do six common variables exceed benchmarks, per record and per station, how do they vary seasonally, and do pooled and fixed station series agree on change over time? RQ2: How do the variables co-vary, and do the relationships appear within stations over time or only between stations? RQ3: Is nitrate spatially clustered across the state? The analysis is observational and descriptive and does not identify the causes of water-quality change.

2 Materials and methods

2.1 Data and quality control

Records for Pennsylvania stream stations from January 2010 to December 2024 were obtained from the Water Quality Portal, which combines the United States Geological Survey National Water Information System (NWIS) and the Environmental Protection Agency STORET system (Read et al. 2017). Six variables were analysed: nitrate as nitrogen (nitrate-N), total phosphorus, pH, dissolved oxygen, specific conductance, and grab sample water temperature. Continuous logger series were excluded so that stations were not weighted by logging frequency. Station metadata supplied coordinates and county codes. Fig. 1 shows the monitoring network and annual contributions by data source; Fig. 2 outlines the analytical workflow.

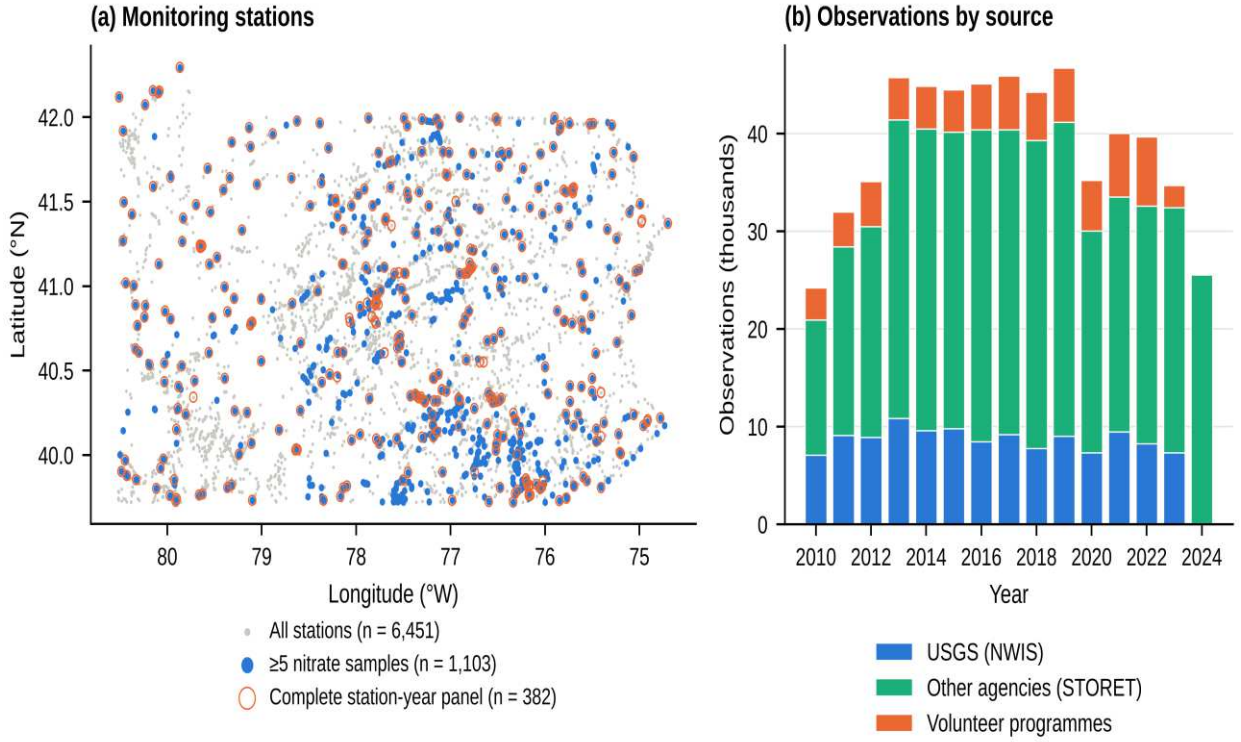

Fig. 1 Monitored stream stations and records by source: (a) 6,451 retained stations, including 1,103 with at least five nitrate measurements and 382 in the complete-case station-year panel; (b) number of records in each year by reporting source

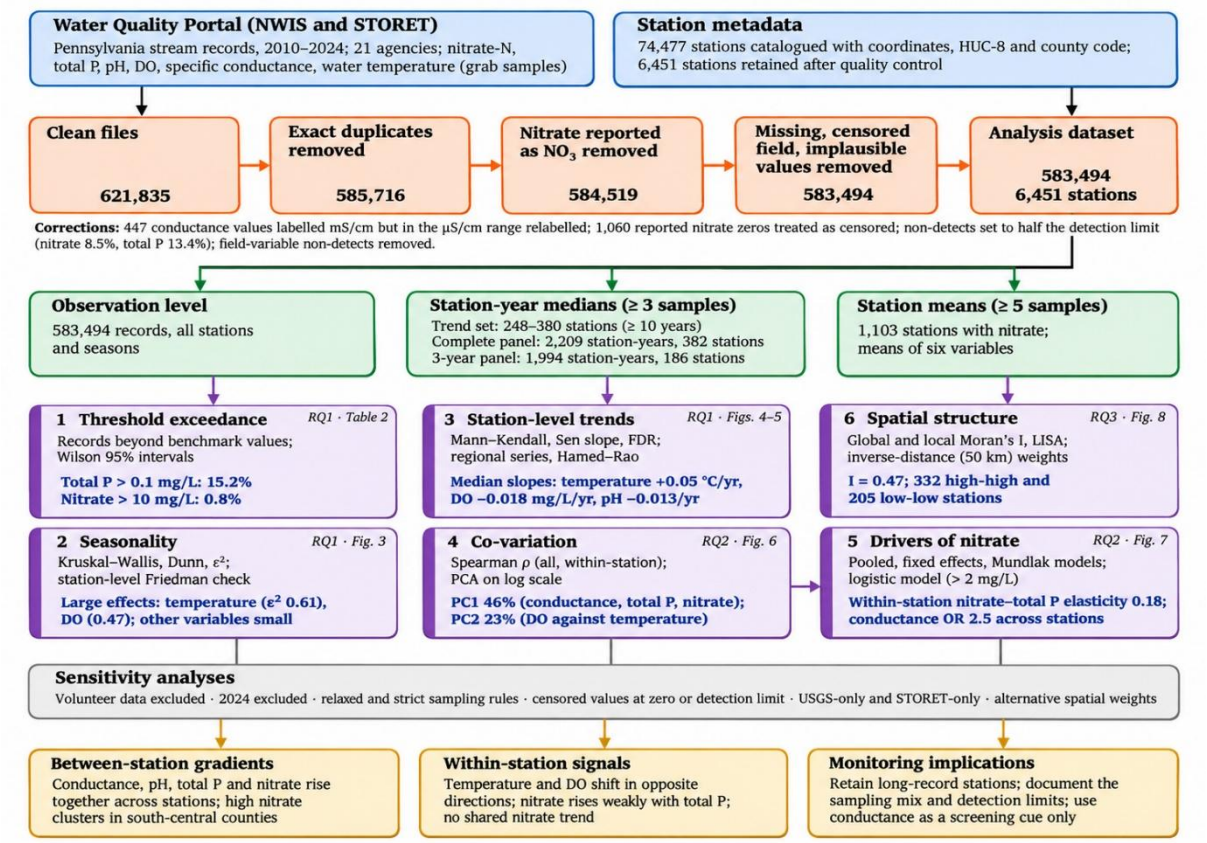

Fig. 2 Analytical framework showing quality-control exclusions, record-, station-, and station-year-level analyses, and the accompanying sensitivity checks.

The cleaned files supplied for the study contained 621,835 records. Five documented filtering steps removed exact duplicates (leaving 585,716 records), nitrate records reported as NO3 that duplicated a nitrate-N value (1,197), results without a numeric value (112), censored results for field variables (627), and physically implausible values (286) from the database. A group of 447 conductance records labelled as millisiemens per centimetre but lying in the microsiemens range was relabeled. The final dataset comprised 583,494 records (Table 1). The processing undertaken before the cleaned source files were supplied was not independently reproduced. Non-detects (8.5% of nitrate-N and 13.4% of total phosphorus records) and reported nitrate zeros (1,060) were set to half the detection limit or half the median nitrate limit for zeros, and trend analysis was repeated with zeros and the full limit (Helsel 2006).

Table 1 Records, station coverage, censoring and medians by variable, 2010–2024 (nitrate-N, total phosphorus and dissolved oxygen in mg/L; specific conductance in µS/cm; temperature in °C)

Variable	Observations	Stations	Censored (%)	Median (interquartile range)
Nitrate-N (mg/L)	47,806	2,580	8.5	0.560 (0.210 to 1.58)
Total phosphorus (mg/L)	75,958	2,877	13.4	0.0240 (0.0110 to 0.0600)
pH (standard units)	144,790	6,200	0.0	7.61 (7.20 to 8.00)
Dissolved oxygen (mg/L)	71,810	4,523	0.0	9.91 (8.60 to 11.8)
Specific conductance (µS/cm)	143,848	6,089	0.0	231 (128 to 372)
Water temperature (°C)	99,282	5,690	0.0	14.2 (7.40 to 19.9)
All variables	583,494	6,451		

2.2 Benchmarks and seasonality

Nitrate-N was compared with 10 mg/L (federal drinking water standard, used as an indicator and not a compliance test) and 2 mg/L (elevated). Total phosphorus was compared with 0.1 mg/L, which is the descriptive screening threshold. Dissolved oxygen was compared with a minimum of 5.0 mg/L and pH with the range of 6.0–9.0, both at 25 Pa. Code §93.7, and with 6.5 to 8.5. Exceedance rates carry Wilson 95% intervals calculated at the record level; these intervals do not consider repeated observations from the same station. The number of stations with at least one exceedance was reported separately. Seasons were followed by calendar months. Differences were tested using the Kruskal-Wallis test and epsilon squared, with Dunn tests (Bonferroni-adjusted) for pairs and a Friedman test on seasonal station medians as a check.

2.3 Station level and regional trends

For each station and variable, annual medians were computed for years with at least three samples. Stations were kept with at least ten annual medians, a first year no later than 2014, and a last year no earlier than 2020. Trends were tested using the Mann–Kendall test (Mann 1945), and the slope was estimated using the Sen estimator (Sen 1968) (Eq. (1)):

$$\beta_i = median\left(\frac{x_j - x_k}{t_j - t_k}\right),\ j > k \tag{1}$$

where x is the annual median measured in year t (reported as a percentage of the station median). Significance across stations was controlled using the Benjamini-Hochberg false discovery rate at 5% (Benjamini and Hochberg 1995). Station slopes were summarised by their median, a bootstrap interval over stations, a Wilcoxon signed rank test, and, among stations with individually significant trends, a sign test of increasing against decreasing. For comparison, two annual series were analysed per variable, the median of station year medians for these long record stations and the annual median of all records, with the variance correction of Hamed and Rao (1998) for 15 values. Flow adjustment was not possible because most stations lacked discharge records.

2.4 Co-variation, panel and logistic models

Associations were measured using Spearman's correlation on station year medians (2,209 station years, 382 stations), with bootstrap intervals that resampled stations, and were split into between-station and within-station parts. Principal component analysis (Jolliffe and Cadima 2016) of the standardised variables (nitrate-N, total phosphorus, and conductance on the log scale) used parallel analysis to set the number of components. For stations with at least three complete station years (186 stations, 1,994 station years), log nitrate-N was modelled as (Eq. (2))

$$\ln N_{it} = \alpha_i + \beta_1 \ln P_{it} + \beta_2 pH_{it} + \beta_3 DO_{it} + \beta_4 \ln C_{it} + \beta_5 T_{it} + \gamma t + \varepsilon_{it} \tag{2}$$

where N is nitrate-N, P total phosphorus, C conductance, T temperature, and αi a station effect. Pooled, station-fixed effects, and two-way fixed effects forms were fitted with station-clustered errors (Cameron and Miller 2015). A correlated random effects form (Mundlak 1978) adds station means x̄i of the predictors (Eq. (3)),

$$\ln N_{it} = \alpha + x_{it}'\beta + \bar{x}_i'\delta + u_i + \varepsilon_{it} \tag{3}$$

and a Wald test of δ = 0 asked whether the relationships between and within the stations differed. A logistic model for annual median nitrate-N above 2 mg/L used five standardised predictors, with discrimination estimated in the sample and by cross-validation that kept each station in one fold (Roberts et al. 2017).

2.5 Spatial analysis, sensitivity and software

The spatial structure was assessed for station means (stations with at least five samples) using inverse distance weights within 50 km, row-standardised. Global Moran's I was calculated using Eq. (4)

$$I = \frac{n}{S_0}\frac{\Sigma_i\Sigma_j w_{ij} z_i z_j}{\Sigma z_i^2} \quad (4)$$

where z is the deviation of the log station mean from its average and S0 is the sum of the weights. Local indicators (Anselin 1995) describe the station-specific spatial association using Eq. (5).

$$I_i = \frac{z_i}{m_2}\Sigma_j w_{ij} z_j \quad (5)$$

with m2 the mean squared deviation. Significance was derived from 999 conditional permutations with false discovery rate control. Distance weights ignore river connectivity and serve here for exploratory mapping (Mainali et al. 2019); 25 km, 100 km, and eight nearest neighbour weights were compared. Nine alternative trend specifications (Supplementary Table S1) varied the station and sampling rules, data source, and treatment of censored values. Analyses were performed using Python with NumPy and SciPy, with the statistical routines written directly.

3 Results

3.1 Dataset, levels and benchmark exceedance

The dataset included 583,494 records from 6,451 stations (Table 1; Fig. 1). Records per year increased from 24,209 in 2010 to 46,700 in 2019 and fell to 25,553 in 2024, when the extracted dataset contained only 88 NWIS records. The cause of this reduced NWIS representation was not established; therefore, 2024 totals should not be interpreted as a verified decline in monitoring activity. Descriptive statistics are given in Table 1 and Supplementary Table S3. Nitrate-N exceeded 10 mg/L in 0.81% of records but at 109 of 2,580 stations (4.2%), and exceeded 2 mg/L in 20.5% of records (Table 2). Total phosphorus exceeded 0.1 mg/L in 15.2% of records and at 743 of 2,877 stations (25.8%). Dissolved oxygen was below 5 mg/L in 2.1% of records at 256 of 4,523 stations (5.7%). The pH was outside 6.0 to 9.0 in 4.1% of records at 1,177 of 6,200 stations (19.0%), mostly below 6.0 (3.4%), and outside 6.5 to 8.5 in 11.6%. Exceedances were concentrated in a minority of stations.

Table 2 Record-level exceedances and numbers of stations with at least one measurement beyond the stated benchmarks

Benchmark	Records beyond benchmark / records	Rate, % (95% Wilson interval)	Stations with at least one record beyond benchmark / stations
Nitrate-N above 10 mg/L	389 / 47,806	0.81 (0.74 to 0.90)	109 / 2,580
Nitrate-N above 2 mg/L	9,805 / 47,806	20.51 (20.15 to 20.87)	863 / 2,580
Total phosphorus above 0.1 mg/L	11,522 / 75,957	15.17 (14.92 to 15.43)	743 / 2,877
Dissolved oxygen below 5 mg/L	1,501 / 71,810	2.09 (1.99 to 2.20)	256 / 4,523
pH outside 6.0 to 9.0	5,959 / 144,790	4.12 (4.01 to 4.22)	1,177 / 6,200
pH outside 6.5 to 8.5	16,828 / 144,790	11.62 (11.46 to 11.79)	2,627 / 6,200

Records whose censored detection limit exceeded the benchmark could not be classified and were excluded from the denominator (one total phosphorus record). Wilson intervals treat records as independent.

3.2 Seasonal behaviour

Kruskal–Wallis tests detected seasonal differences for all six variables (Table 3; Fig. 3; all $p < 0.001$). However, the estimated effect sizes were large for temperature ($\varepsilon^2 = 0.61$) and dissolved oxygen ($\varepsilon^2 = 0.47$), whereas they were small for the other variables ($\varepsilon^2 \leq 0.020$). The median temperature increased from 3.6 °C in winter to 21.0 °C in summer, and the median dissolved oxygen decreased from 13.0 to 8.6 mg/L. For the other four variables, ε^2 was at most 0.020. Nitrate-N was highest in winter (0.74 mg/L, against 0.48 mg/L in summer), total phosphorus in summer (0.029 mg/L), and conductivity in fall (266 µS/cm). The station-level Friedman test agreed (Kendall's W = 0.92 for temperature, 0.89 for dissolved oxygen, and 0.18–0.35 for other variables).

Table 3 Seasonal differences in the monitored water quality (Kruskal–Wallis test). Medians followed by the same Dunn letter are not significantly different at the 5% level; all omnibus p values are < 0.001

Variable	H (3 df)	ε²	Winter median	Spring median	Summer median	Fall median
Nitrate-N (mg/L)	623	0.013	0.74 (a)	0.55 (b)	0.48 (d)	0.5 (c)
Total phosphorus (mg/L)	585	0.008	0.022 (c)	0.021 (d)	0.029 (a)	0.024 (b)
pH (standard units)	2,875	0.020	7.5 (d)	7.54 (c)	7.7 (a)	7.7 (b)
Dissolved oxygen (mg/L)	33,512	0.467	13.01 (a)	10.94 (b)	8.61 (d)	9.93 (c)
Specific conductance (µS/cm)	2,227	0.015	216 (c)	195 (d)	247 (b)	266 (a)
Water temperature (°C)	60,385	0.608	3.55 (d)	11.1 (c)	21 (a)	13.7 (b)

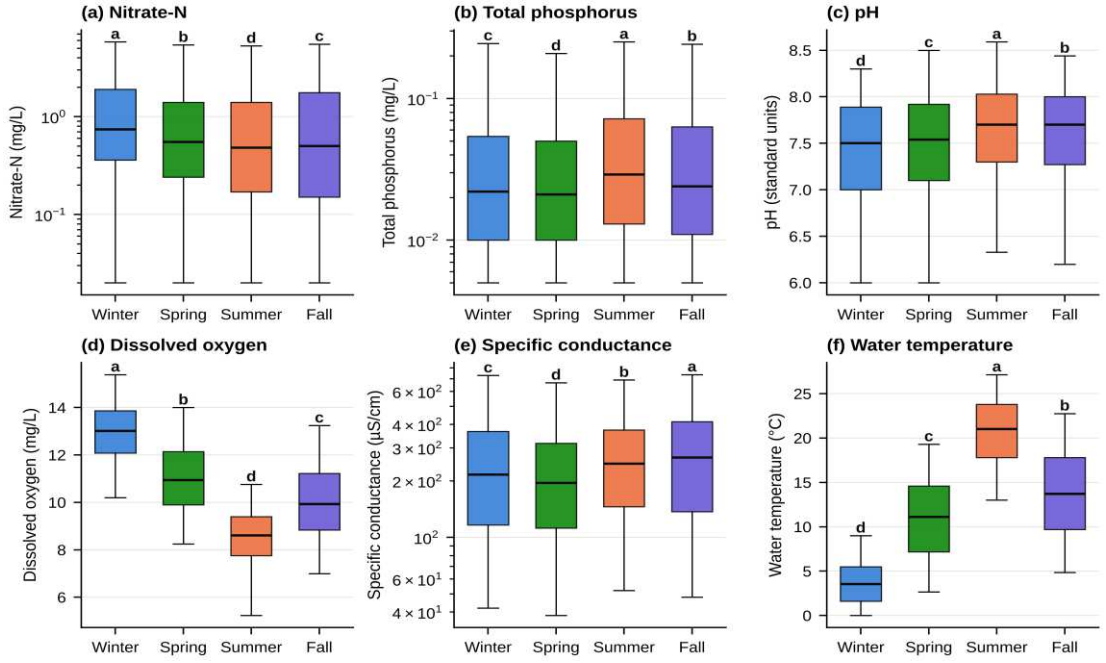

Fig. 3 Seasonal distributions of six monitored variables. Boxes show the medians and interquartile ranges, whiskers show the 5th and 95th percentiles, and letters denote Dunn comparison groups. Nitrate-N, total phosphorus and conductance are shown on log scales

3.3 Station level and regional change

After FDR control, 13 of 285 stations showed increasing and 3 decreasing nitrate-N trends, and no station showed a statistically significant trend for the other variables after FDR control (Table 4; Fig. 4). The available annual time series contained at most 15 values, which limited the precision at individual stations. The median station slopes were small: nitrate-N +0.0017 mg/L per year (+0.35% per year), pH −0.013 units per year (about 0.2 units over the period; 27.9% of 373 stations decreasing and 3.5% increasing before correction), dissolved oxygen −0.018 mg/L per year (sign test p = 0.064), temperature +0.050 °C per year (about 0.7 °C over the period; 19 increasing against 7 decreasing, p = 0.029), conductance −0.43 µS/cm per year with equal numbers of increasing and decreasing stations (sign test p = 0.88), and total phosphorus zero.

Table 4 Station-level trends in annual medians, 2010–2024 Increasing and decreasing percentages refer to unadjusted $p < 0.05$; false-discovery-rate-adjusted counts are reported separately

Variable	Stations	Increasing, % ($p < 0.05$)	Decreasing, % ($p < 0.05$)	Increasing / decreasing after FDR control	Median Sen slope per year (95% CI)	Median change, % per year	Wilcoxon p	Sign test p
Nitrate-N	285	13.0	4.2	13 / 3	0.002 (0.000 to 0.003)	0.35	< 0.001	< 0.001
Total phosphorus	285	7.7	4.6	0 / 0	0 (0 to 0)	0.00	0.27	0.18
pH	373	3.5	27.9	0 / 0	−0.013 (−0.015 to −0.011)	−0.17	< 0.001	< 0.001
Dissolved oxygen	248	2.0	5.6	0 / 0	−0.018 (−0.029 to −0.006)	−0.16	< 0.001	0.064
Specific conductance	342	5.8	6.4	0 / 0	−0.43 (−0.60 to −0.22)	−0.26	< 0.001	0.88
Water temperature	380	5.0	1.8	0 / 0	0.050 (0.029 to 0.068)	0.43	< 0.001	0.029

Sign test: increasing against decreasing among stations with $p < 0.05$. Units of the slope: mg/L per year for nitrate-N, total phosphorus, and dissolved oxygen; pH units per year; µS/cm per year for specific conductance; and °C per year for water temperature.

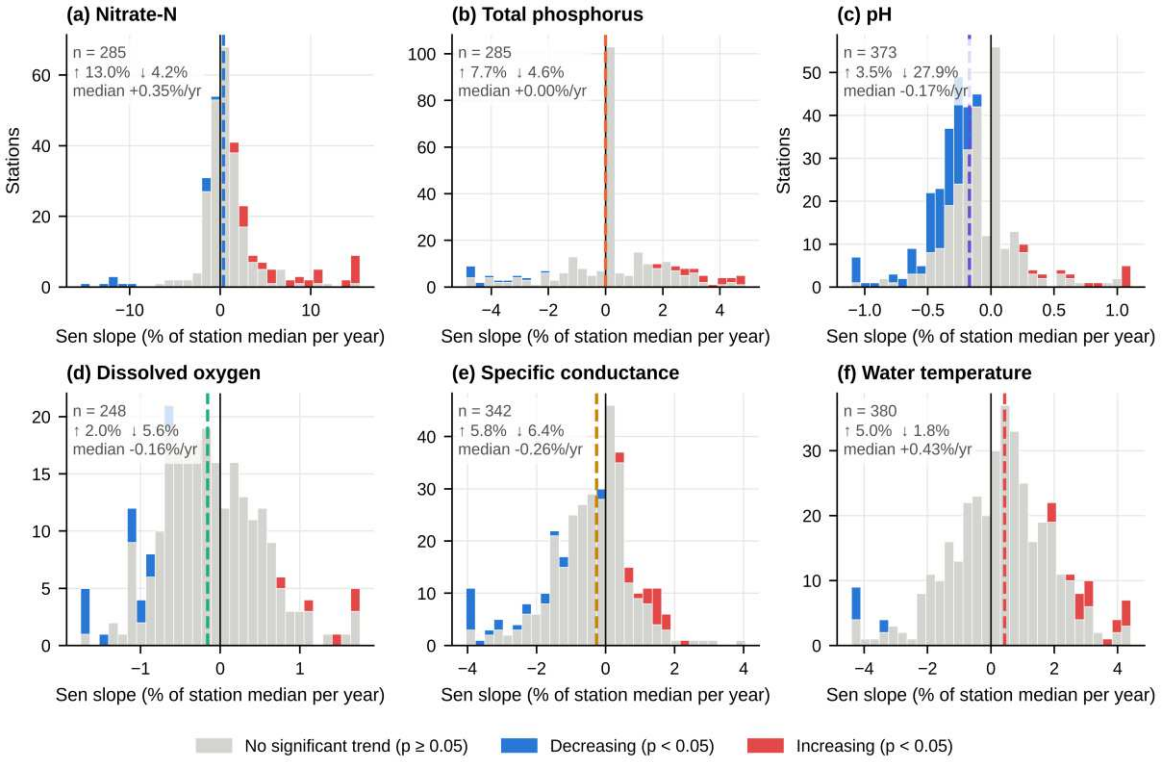

Fig. 4 Station-level Sen slopes as a percentage of the station medians per year. Colours distinguish unadjusted station-level $p < 0.05$; dashed lines indicate median slopes and extremes are grouped in outer bins

The pooled series behaved differently (Fig. 5; Table S6). The annual median of all nitrate-N records rose from 0.56 mg/L in 2010 to 0.89 mg/L in 2022 (Kendall's $\tau = 0.43$, Hamed–Rao $p = 0.015$), but the number of nitrate stations varied from 492 to 703, and the stations changed. The median of station year medians for long record stations stayed between 0.415 and 0.565 mg/L with no trend ($\tau = 0.15$, $p = 0.45$). Apart from pooled nitrate-N, evidence of monotonic change was generally limited; the pH series from long-record stations yielded a

borderline result (τ = −0.34, Hamed–Rao p = 0.049), which should not be interpreted as robust evidence of a regional pH decline. The sign of each median station slope was the same in all nine sensitivity variants (Table S1), pH decreasing shares ranged from 21% to 31%, and the temperature slope was +0.025 °C per year with STORET records (interval including zero) and +0.106 °C per year with NWIS records.

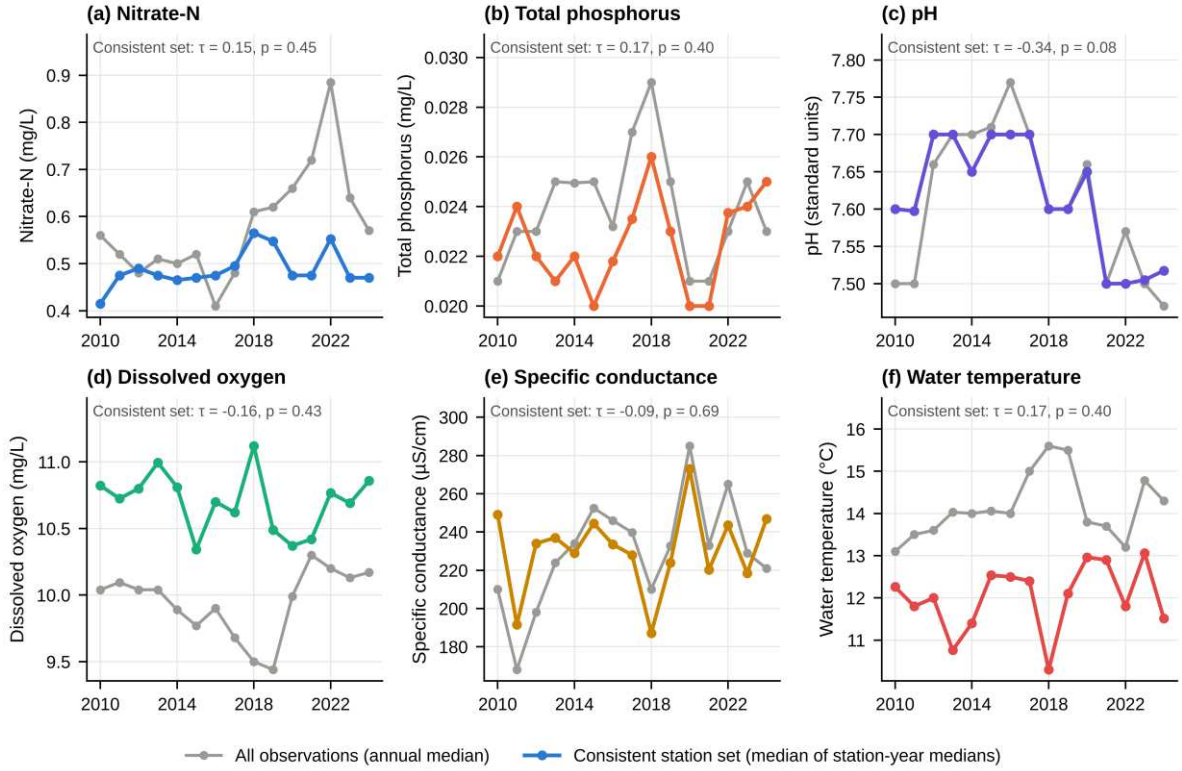

Fig. 5 Annual medians from 2010 to 2024. Grey lines show all observations from the changing network; the coloured lines show the medians among long-record stations. Reported trend tests refer to the consistent-station series

3.4 Co-variation and nitrate models

Rank correlations among station-year medians were largest for pH and conductance (ρ = 0.71), conductance and total phosphorus (0.62), conductance and nitrate-N (0.60), total phosphorus and pH (0.55), nitrate-N and total phosphorus (0.55), and −0.52 for dissolved oxygen and temperature (Fig. 6, panel a; Table S4). Most were between station associations: for nitrate-N and conductance, ρ was 0.62 between and −0.04 within stations, and for nitrate-N and total phosphorus, 0.46 between and 0.11 within. Dissolved oxygen and temperature were related in both settings (−0.57 between, −0.52 within the group). Two components passed parallel analysis (Fig. 6, panel c): 46.0% of the variance for conductance (loading 0.86), total phosphorus (0.81), pH (0.73), and nitrate-N (0.70), and 23.0% for dissolved oxygen (0.84) and temperature (−0.70).

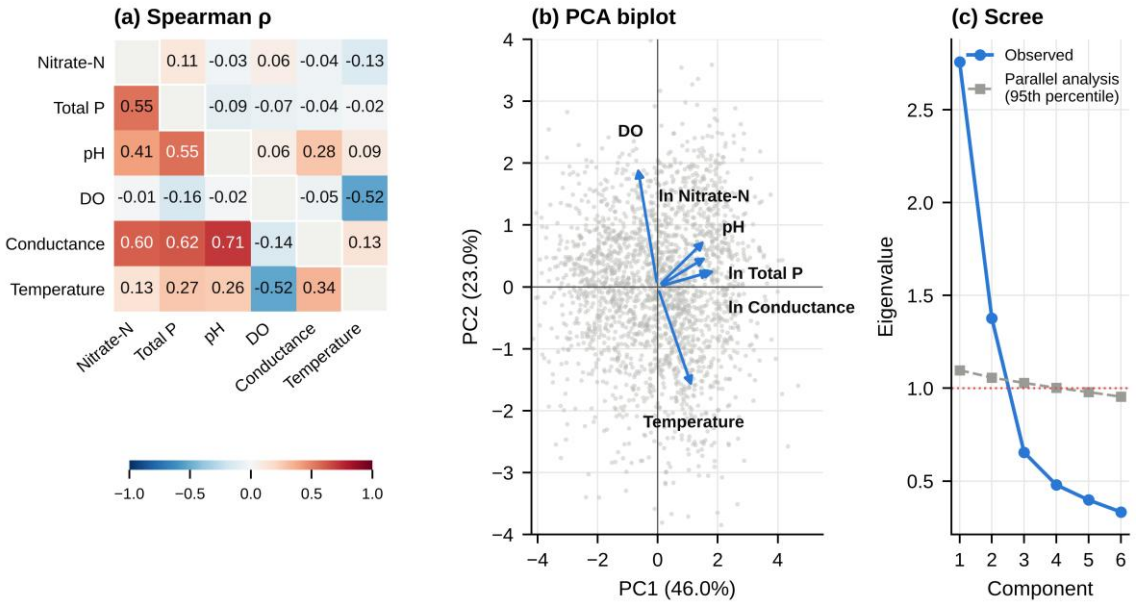

Fig. 6 Multivariate associations: (a) Spearman correlations among station-year medians; (b) principal-component biplot; (c) observed eigenvalues and the parallel-analysis threshold

In the panel models (Table 5), the log total phosphorus coefficient fell from 0.447 (standard error 0.073) when pooled to 0.184 (0.040) with station effects; consistent with a substantial contribution from between-station differences to the pooled association. Temperature had a negative coefficient in the station-fixed-effects model (−0.018 per °C); coefficients for pH, DO, conductance, and year did not differ significantly from zero at the 5% level. The correlated random effects test rejected equal within- and between-relationships (Wald $\chi^2 = 28.8$, $p < 0.001$). Within-station R^2 was 0.049, and the phosphorus and temperature estimates retained their direction across five alternative samples (0.11 to 0.20; −0.014 to −0.022; Table S2). In the logistic model, 342 of 2,209 station years (15.5%) had nitrate-N above 2 mg/L, and odds ratios per standard deviation were 2.48 for log conductance (95% interval 1.39 to 4.41) and 2.12 for log total phosphorus (1.43 to 3.15), against 1.43 for DO, 1.29 for pH, and 1.09 for temperature (Fig. 7). The area under the curve was 0.85, or 0.83 with cross validation grouped by station.

Table 5 Associations with log nitrate-N in pooled and fixed-effects regressions: station-clustered standard errors in parentheses. † p < 0.10; ** p < 0.01; *** p < 0.001

Predictor	M1 pooled OLS	M2 station fixed effects	M3 two-way fixed effects
ln(Total P)	0.447*** (0.073)	0.184*** (0.040)	0.165*** (0.039)
pH	0.016 (0.105)	−0.043 (0.064)	−0.117† (0.069)
DO	0.068 (0.048)	−0.002 (0.013)	0.004 (0.013)
ln(Conductance)	0.477*** (0.130)	0.013 (0.178)	0.159 (0.181)
Temperature	−0.020 (0.014)	−0.018*** (0.004)	−0.012** (0.004)
Year (centred)	−0.006 (0.007)	0.000 (0.003)	n/a
R^2, within	n/a	0.049	0.112
N	1,994	1,994	1,994
Stations	186	186	186

The correlated random effects model yields the same coefficients as M2.

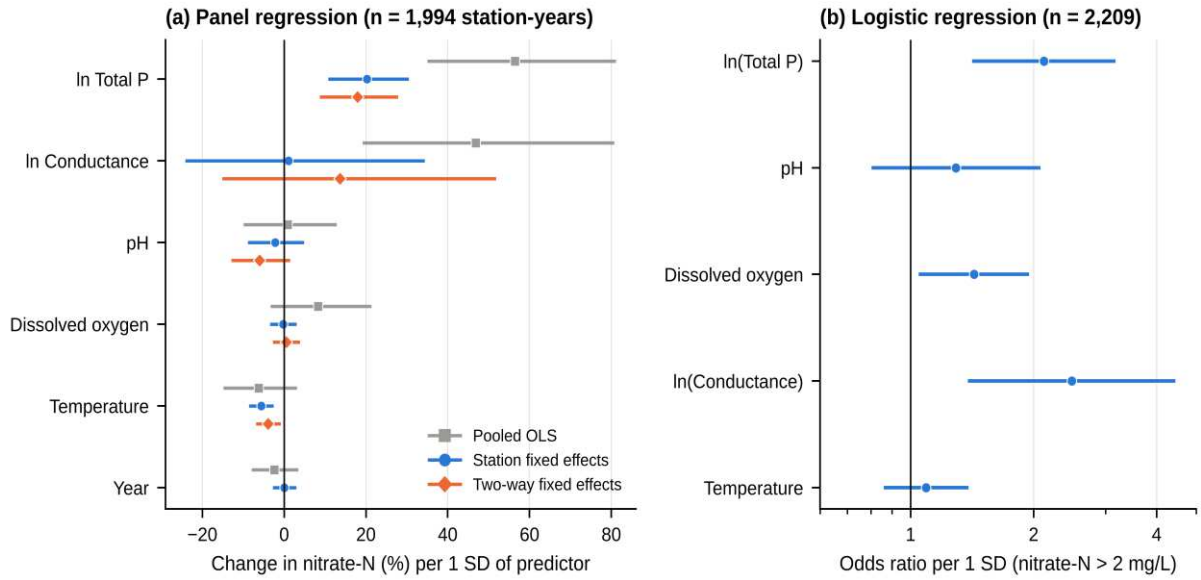

Fig. 7 Estimated associations with nitrate-N: (a) percent differences associated with one standard deviation of each predictor in the pooled and panel models; (b) odds ratios for station-year nitrate-N above 2 mg/L. Bars show 95% intervals

3.5 Spatial structure

Nitrate-N stations showed positive spatial autocorrelation (Moran's I = 0.47, z = 38.0, p = 0.001, 1,103 stations; 0.59 with eight neighbours), and the other variables yielded values from 0.27 to 0.43 (Supplementary Table S5). Local indicators classified 332 stations as high–high, 205 as low–low, 48 as low–high, 18 as high–low, and 500 as not significant (Fig. 8). Stations classified as high–high were concentrated in the south-central counties: Lancaster (86 of 96 stations), Cumberland (52 of 67), York (44 of 49), and Chester (33 of 37). The median station mean nitrate-N was 3.2 mg/L in the high high and 0.15 mg/L in the low low clusters, the latter mostly in the north-central and northern counties. Cluster counts depended on the weights (high high: 267 at 25 km, 332 at 50 km, and 337 at 100 km), whereas Moran's I remained positive (0.54, 0.47, and 0.40, respectively).

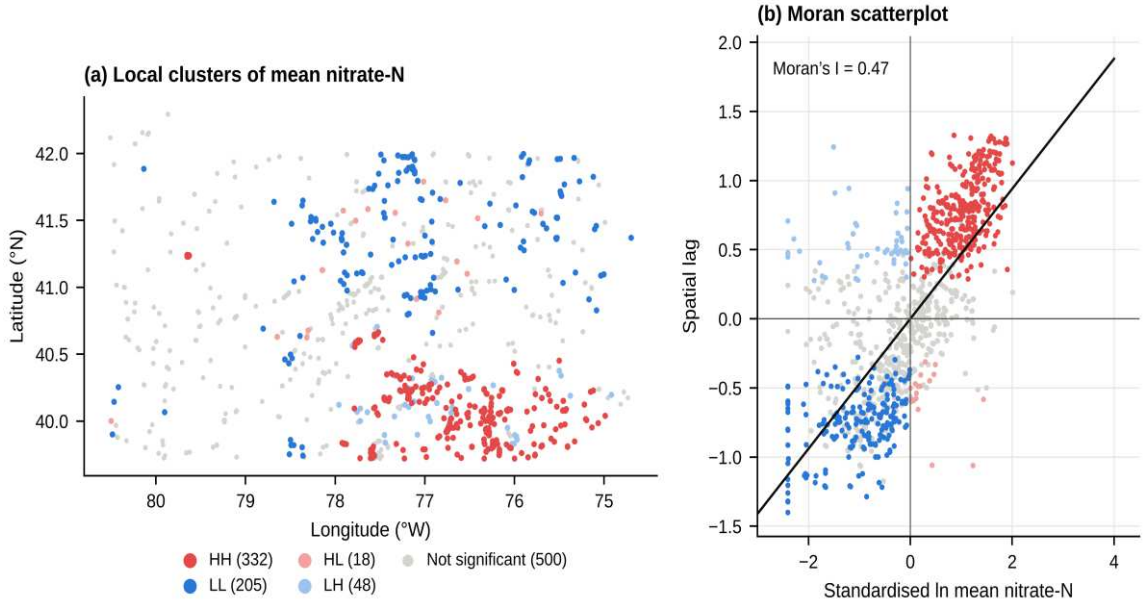

Fig. 8 Spatial analysis of station mean nitrate-N: (a) local Moran cluster classifications, with 50-km weights and false-discovery-rate control (HH, high–high; LL, low–low; HL, high–low; LH, low–high); (b) Moran scatterplot

4 Discussion

Nutrient results showed a clear spatial pattern, with weak temporal evidence. Nitrate-N above 10 mg/L was uncommon among records (0.8%) but occurred at 4% of stations, and elevated values were found in south-central counties, a pattern compatible with previously reported land-use contrasts in stream nitrate (Wherry et

al. 2021). Land use was not analysed here, so this explanation remains untested. The evidence for a statewide nitrate-N increase was thin: a pooled series trended upward, long record stations did not, and station slopes were small. Previous studies have documented delayed responses to historical nitrogen inputs and regional variation in nutrient trends (Van Meter et al. 2018; Zhang et al. 2022; Ator et al. 2020), but the present dataset cannot distinguish these mechanisms. Total phosphorus had a median station slope of zero. Its summer maximum is consistent with reports of in-channel phosphorus release at low flow (Dolph et al. 2024), which these data cannot test. The smaller station-fixed-effects phosphorus coefficient relative to the pooled coefficient (0.184 versus 0.447; Table 5) indicates that the pooled association includes a substantial between-station component.

Several patterns are consistent with earlier observational research. Site-level exceedance of ecoregion percentile thresholds has been reported in Pennsylvania (Clune et al. 2020a). These thresholds are much lower than the benchmarks used here; therefore, the shares cannot be compared. The south-central nitrate cluster is in line with the land use contrasts in Pennsylvania stream nutrients (Clune et al. 2020b) and with high base-flow nitrate in agricultural carbonate settings (Wherry et al. 2021), and the local-indicator analysis provides a complementary description of spatial clustering. The pooled nitrate rise that disappears at long-record stations is consistent with the reason national analyses screen sites for record completeness (Stets et al. 2020; Oelsner and Stets 2019), and this example documents the difference for one state and one monitoring period. Panel methods have been used in hydrology to distinguish associations within and between sites (Steinschneider et al. 2013), and that separation distinguishes the pooled from the station-fixed phosphorus coefficients here.

The median warming of approximately 0.05 °C per year lies within the 0.009–0.077 °C per year reported for long records at 40 sites in the United States (Kaushal et al. 2010). The station-median dissolved oxygen slope (−0.018 mg/L per year) was more negative than the average rate of approximately −0.004 mg/L per year reported in a broader river reconstruction (Zhi et al., 2023). Differences in sampling design and methods limit direct comparison, and the fixed-station regional series did not show a clear trend in the dissolved oxygen. Grab samples reflect the time of day and flow state (Bernhardt et al. 2022); therefore, changes in the time at which the stations were visited could produce apparent trends. The same caution applies to the negative median pH slope (equivalent to roughly 0.2 units over the period; 27.9% of stations declined at unadjusted $p < 0.05$, but none after correction), which differs in direction from pH increases reported for some acid-sensitive Appalachian and Catskill streams (Scanlon et al. 2021; Baldigo et al. 2021) and the rising alkalinity of eastern rivers (Kaushal et al. 2013). Changes in instruments, calibration, or sampling time cannot be excluded, and the dataset does not indicate whether the decline is due to environmental factors. The temperature slope depended on the data source, and all the dissolved oxygen trend stations were STORET stations.

Conductance was strongly related to nitrate-N, total phosphorus, and pH across stations and had the largest reported odds ratio for nitrate-N above 2 mg/L in the fitted logistic model; however, its within-station association with nitrate-N was small and not statistically significant and had no consistent station trend. Reported increases in conductance and chloride (Kaushal et al. 2018; Kaushal et al. 2021; Stets et al. 2017; Moore et al. 2020; Rumsey et al. 2022; Rossi et al. 2022; Kaushal et al. 2025; Hintz and Relyea 2019; Dugan et al. 2017) were not detected at the median station. The annual medians of the grab samples may have missed winter salt pulses. The between-station association could reflect unmeasured site characteristics, including land use or geology. Therefore, conductance may be informative for exploratory screening across monitored locations, but this analysis does not establish an independent or causal indicator of nutrient change. These data neither support nor test the influence of gas development (Bonetti et al. 2021).

Positive spatial autocorrelation persisted across the tested distance-weight specifications, but the cluster counts depended on monitoring density, which was highest in the south-central counties; therefore, the share of stations classified as high within a county (90% in Lancaster and York) provides context beyond the absolute counts. Distance weights ignored river connectivity, and network-based models are required to separate shared streams from shared land (Mainali et al. 2019). Quality control excluded 38,341 of the 621,835 supplied records (6.17%), including 36,119 exact duplicates and 1,197 overlapping nitrate records, consistent with the cautions on metadata (Sprague et al. 2017; Krasovich et al. 2022). Where flow records exist, flow-adjusted methods are preferable (Hirsch et al. 2010; Murphy and Sprague 2019). Because streamflow, catchment land use, point-source inputs, and sampling time were not included in the analysis, the observed associations and temporal differences cannot be attributed to particular environmental drivers. Trend samples (248–380 stations) are long-record stations, and the panel (186 stations) is not a random sample of streams.

5 Conclusions

In 583,494 records from 6,451 Pennsylvania stations (2010 to 2024), benchmark exceedances were concentrated in a minority of stations, seasonality was strong for temperature and dissolved oxygen and weak for other variables, and nitrate-N was spatially clustered in the south-central counties. Median station slopes were positive for nitrate-N and water temperature and negative for pH and dissolved oxygen, but few individual station trends survived multiple-testing adjustment; most consistent-station regional series showed little evidence of change. The associations among nitrate-N, phosphorus, conductance, and pH mainly differed between locations. Pooled trends may differ from fixed-station trends when the sampling network changes, and the choice of pooled or fixed station analysis and record or station-level reporting can change the interpretation of the same data. The study applied established methods, and the findings describe the monitored locations and identify no causes. Future analyses would benefit from harmonised discharge, catchment land use, and sampling time information.

Declarations

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Competing interests.

The authors declare no conflicts of interest.

Data availability.

The monitoring records are available from the United States Geological Survey and Environmental Protection Agency Water Quality Portal (https://doi.org/10.5066/P9QRKUVJ). The cleaned analysis files, tables, and figures are available from the corresponding author upon reasonable request.

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