Appendix 2: Analysis of spatial, seasonal, and temporal variability, and long-term trends in nutrient concentrations in the Sacramento – San Joaquin Delta and Suisun Bay during the period 1975 - 2013

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Summary

The goal of this study was to characterize seasonal, spatial, and long-term variability in nutrient concentrations and proportions in the Sacramento – San Joaquin Delta and Suisun Bay during the period 1975 – 2013. The study was structured in accordance with a basic conceptual model that suggests that nutrient variability in the Delta is shaped by five main factors: 1) source waters; 2) seasonal nutrient cycles; 3) long-term trends, 4) climate variability, and 5) local influencing factors. To better understand the factors influencing observed N concentrations at stations throughout the Delta, we explored how water sources varied among stations; seasonal variability of key parameters at several diverse and hydrologically important sites; and the spatial and temporal variations in nutrient concentrations.

Water sources

Volumetric fingerprint time series derived from hydrologic model output revealed substantial spatial, seasonal, and interannual variability in water sources over the period 2000-2011. Waters at nine of eleven stations were mixtures of multiple sources in proportions that varied seasonally and interannually. The exceptions were the upstream stations Sacramento River at Hood (C3) and San Joaquin River at Vernalis (C10), which were comprised almost entirely (>97%) of Sacramento River water (C3) and entirely (100%) of San Joaquin River water.

Seasonal and temporal changes in nutrient concentrations

Nutrients and nutrient-related variables display a range of seasonal patterns across stations. In-Delta stations can have typical summertime dissolved inorganic nitrogen (DIN) depletion, whereas seasonal variability at upstream stations on the Sacramento and San Joaquin rivers does not follow this pattern because it is affected by upstream loadings and local sources. No systemic changes in seasonality of nutrient concentrations over time were apparent. However, there were some more localized changes in seasonal patterns at specific stations.

A trend analysis of the entire 38 yr data record from 1975 – 2013 showed significant increasing trends for nitrogen species and significant decreasing trends for PO4 at most of the stations. However, if only the data from the most recent 15 yr period from 1998 to 2013 are analyzed, there is a change in the direction of trends for the nitrogen species. For the period from 1998 to 2013, there are significant decreasing trends in ammonium at six of 11 stations, and no trends at the remaining five stations (Table 2.1). Similarly, there are significant decreasing trends for nitrate at two stations, and no trends for nitrate at the other stations for the period from 1998 to 2013. Phosphate declined during the 38 yr period from 1975 – 2013 at 9 of 11 sites and also declined at 4 sites during the period from 1998 to 2013, but there was also an increasing trend at one of the stations (MD10 – Disappointment Slough) for the period from 1998 to 2013. Generally, and not surprisingly, the trends are more consistent across stations as the length of the analyzed period increases.

The trend analysis revealed that extrapolation across space may be problematic. For the shorter period of 1998 – 2013, seven of the eleven stations did not have any significant correlations in trends across multiple variables with any other station. More specifically, variables exhibit rather unique patterns of trends at each of these stations. This implies that, with the exception of the synchronous Suisun stations, all of the other stations fill rather unique spatial niches in the nutrient-monitoring network.

The observed trends in nutrients in this study most likely correspond to anthropogenic events. Increased concentrations of nitrogen species over the 36-year period correspond to increased loadings from urban sources (runoff and, mostly, wastewater discharges) associated with population growth and increased urbanization of the watershed. The reversal of these trends in the most recent period (1998 – 2013) suggests that certain management efforts are successful at controlling and reducing N loadings. Decreasing trends in phosphorus correspond to phosphorus loading reductions in the watershed, mainly by reducing point source loadings (Kratzer et al. 2011). Local factors, including local sources and concentrations of nutrients in source water, can also affect how nutrients are transported and processed locally, and ultimately, influence trends in concentrations. For example, there is an increasing trend in phosphate (PO4) during the most recent period (1998 – 2013) at MD10, which is the station with the largest relative contribution of tailwater from irrigated lands. There is also an increase in DIN at both stations during the same period, but it is not a significant trend for Grizzly Bay. The increase in DIN could be associated with local sources.

Which stations and which parameters behave similarly?

Empirical Orthogonal Function (EOF) analysis was performed to further examine the seasonal, interannual, and spatial variability in N concentrations across the Delta. The EOF analyses determined that time series for NH4 and NO3 can be reasonably well-explained by 2 modes of variability across stations, suggesting that a common set of dominant underlying processes influence N cycling, helping to simplify the explanation of what is otherwise a large and complex system. For PO4, three EOFs explain 78% of all variability.

Summary

This report documents a large degree of temporal and spatial variability across stations. The existing stations are not redundant (with the exception of the Suisun Bay stations), because trends for several stations were not consistent with each other over time and variables exhibit rather unique patterns of trends and variability. It follows that conditions and trends at the currently monitored stations cannot be extrapolated to areas of the Delta that are not currently monitored, such as the North Delta, the South Delta, and contributions from Eastside tributaries. Additional stations would be needed, if the goal were to evaluate conditions and trends across all regions of the Delta. Given the large amount of variability associated with flow and temperature, these ancillary variables should also be measured at water quality stations.

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Glossary

AG	In-Delta agricultural drain inflows volumetric fingerprint
CALAVERAS	Calaveras River volumetric fingerprint
Chl	chlorophyll
Chl-a	chlorophyll *a*
C3	San Joaquin River at Vernalis (monitoring station)
C10	Sacramento River at Hood (monitoring station)
DIABLOWW	Diablo Range Sanitation District wastewater input volumetric fingerprint
DIN	dissolved inorganic nitrogen
DO	dissolved oxygen
DON	dissolved organic nitrogen
DSM2	Delta Simulation Model 2
DWR	California Department of Water Resources
D4	Sacramento River above Point Sacramento (monitoring station)
D6	Suisun Bay near Martinez (monitoring station)
D7	Grizzly Bay (monitoring station)
D8	Suisun Bay off Middle Point (monitoring station)
D19	Frank's Tract (monitoring station)
D26	San Joaquin River at Potato Point (monitoring station)
D28	Old River (monitoring station)
EAST	eastside tributaries volumetric fingerprint
EMP	Environmental Monitoring Program
EOF	Empirical Orthogonal Function
EOF 1	first EOF mode
EOF 2	second EOF mode
EOF 3	third EOF mode
Era 1	1975-1986
Era 2	1987-1997
Era 3	1998 - 2013
IEP	Interagency Ecological Program
JONES	Jones Tract volumetric fingerprint
LODIWW	LODI Wastewater Treatment Plant volumetric fingerprint
MD10	Disappointment Slough (monitoring station)
MTZ	Suisun Bay near Martinez volumetric fingerprint
N	nitrogen
n	number of observations
nn	nitrate nitrogen (*R* programming language)
NAWQA	National Water Quality Assessment program
nh	ammonium nitrogen (*R* programming language)
nh2nn	ammonium nitrogen : nitrate nitrogen ratio (*R* programming language)
NH4	ammonium
NH4-N	ammonium nitrogen
NO3	nitrate
NO3-N	nitrate nitrogen
n2p	nitrogen:phosphorus ratio (*R* programming language)
N:P	nitrogen:phosphorus ratio
o-PO4	orthophosphate
Phe	phaeophytin

PO4	phosphate
P8	San Joaquin River at Buckley Cove (monitoring station)
SAC	Sacramento River volumetric fingerprint
SJR	San Joaquin River
SJRWW	Stockton and Manteca wastewater input volumetric fingerprint
SKT	Seasonal Kendall test
SOUTHWW	South Delta (Discovery Bay, Mountain House, and Tracy) wastewater volumetric fingerprint
SPM	suspended particulate matter
SRWWTP	Sacramento Regional Wastewater Treatment Plant
TN	total nitrogen
TP	total phosphorus
vs.	versus
WESTWW	western wastewater input (Fairfield, Suisun City, Valero, Central San, Martinez-Tesoro) volumetric fingerprint
WWTP	Wastewater Treatment Plant
YOLO	Yolo Bypass volumetric fingerprint
yr	year
yrs	years

2.1 Introduction

The Sacramento-San Joaquin Delta is a heavily altered ecosystem. The Sacramento and San Joaquin Rivers have been recognized to carry elevated loads of nitrogen and phosphorus, but with one exception (decreased dissolved oxygen concentrations in the Stockton Deep Water Ship Channel), these were not thought to cause water quality problems in the Delta. However, the paradigm that the Delta is resilient to high nutrient concentrations is being challenged. The combination of altered nutrient inputs and changes in other environmental factors that regulate the Delta's response to nutrients has generated growing concern that the Delta is trending, or may already be experiencing, adverse impacts from nutrients. Thus, altered nutrient inputs are investigated as one of the co-factors contributing to several undesirable conditions in and downstream of the Delta.

The Environmental Monitoring Program (EMP), managed by the California Department of Water Resources, has been monitoring water quality at a network of stations in the Delta since 1975. This dataset has provided a resource for numerous studies of the seasonal, temporal, and spatial variations in water quality conditions and the controlling drivers in the northern estuary. Previous analyses of this dataset have provided valuable insights into the fundamental pattern and mechanisms of long-term changes and interannual variability in nutrient concentrations and pelagic primary production. These studies have mostly focused on regional characterization of trends. However, the variability within the Delta has been less well characterized. To inform important management decisions in the Delta, improved understanding of nutrient-related ambient conditions and dynamics in the Delta are needed. Toward that goal, we analyzed EMP data across its network of stations to

1. Characterize seasonal, spatial, and long-term variability in nutrient concentrations and proportions
2. Identify important data gaps in the ongoing monitoring program for nutrients and nutrient related parameters

2.2 Approach

2.2.1 Study Area

Attention is focused on the Delta and Suisun Bay regions of the Northern San Francisco Estuary, which is strongly influenced by tidal mixing as well as annual and seasonal variations in river flows from the Sacramento, San Joaquin, and several eastside tributaries. The analysis focuses on 11 sites in the Delta and Suisun Bay (Figure 2.1) that were sampled monthly for nutrients and nutrient-associated variables since 1975. Nutrient and associated data are available for additional stations but sampling at these stations does not cover the entire period of data collection. The study area is characterized by high variability in flows and salinity. The two subregions of the study area have in common that they are characterized by high nutrient concentrations. They are highly interconnected but are hydrologically very distinct. Suisun Bay is a shallow, turbid, low-salinity embayment incised by a remnant river channel. The Delta is primarily a freshwater system comprised of a complex channel network that is hydrologically strongly influenced by river flows, tidal exchange, and water exports. Delta nutrient concentrations are strongly influenced by riverine inputs. Loadings from the Sacramento and San Joaquin river watersheds have been well characterized by the National Water Quality Assessment (NAWQA) program. Suisun Bay receives most of its nutrient loadings from the Sacramento and San Joaquin watersheds via the Delta, but also receives significant contributions from local anthropogenic sources and by tidal mixing from San Pablo Bay.

2.2.2 Conceptual Model for Variability in Nutrient Concentrations in the Delta

The study is based on the conceptual model depicted in Figure 2.2. This model hypothesizes that nutrient variability in the Delta is a function of:

- Relative contributions and chemical composition of source waters
- Seasonal nutrient cycles
- Long-term trends
- Climate variability
- Local influencing factors

The different components of the conceptual model are discussed more in Section 2.3.2, in relation to the analyses that were used to explore different aspects of variability.

2.2.3 IEP-EMP Discrete Water Quality Monitoring

The data used for this analysis were collected by the DWR-EMP, which is part of the Interagency Ecological Program. The EMP conducts discrete physical-chemical monitoring (near-monthly) of macronutrients (inorganic forms of nitrogen, phosphorus, and silicon); total suspended solids; total dissolved solids; total, particulate and dissolved organic nitrogen and carbon; chlorophyll a, DO, EC (specific conductance), turbidity, Secchi depth, and water temperature. The dataset spans 36 years from 1975 to 2013. For more information about the monitoring program see the program website: http://www.water.ca.gov/iep/activities/emp.cfm. Appendix A1 provides a data summary description.

2.2.4 Analysis

Different non-parametric statistical tests were used to characterize seasonal, temporal, and spatial variance. During initial exploratory data analysis, a number of statistical tests were employed, not all of which are presented here. This appendix summarizes the main tests we decided to pursue after completing a critical review of the initial data exploration results.

Seasonality. The distribution of average nutrient concentrations at each station across months and across eras served as a basis for a discussion of seasonal patterns at representative stations. Data were visualized as seasonal plots across stations and long-term monthly concentrations across the entire data record.

Spatial Variance: Empirical Orthogonal Function (EOF) analysis was used to explain the maximum amount of spatial variance in the dataset. EOF analysis is an approach to data exploration that is primarily applied to simultaneous time series at different spatial locations. The analysis is a component of the *wq* package for the R computing environment (Jassby and Cloern 2013. Detected EOFs represent modes of relative (i.e. dimensionless) variability and allow identifying common patterns among stations or parameters, regardless of differences in units of measurement or absolute values. Thus, EOF analysis involves standardization of time-series data to the mean. For example, the NH4 time series at station X used in the EOF analysis would be determined as:

$$[NH4_{standardized}]_X = [(NH4(t)_X - NH4_{X,mean}) / NH4_{X,s.d.}]$$

where $NH4(t)_X$ is the measured value for a given date at X; $NH4_{X,mean}$ and $NH4_{X,s.d}$. are the mean and standard deviations, respectively for the NH4 time series at X.

The EOF analyses were run on a subset of the data (2000 – 2012), with a focus on NH4 and NO3. Station 19 was not included in the EOF analyses, because of large data gaps prior to 2004. The observed patterns in spatial variance were related to possible drivers to evaluate potential mechanistic explanations, by comparison of EOF time series with time-series for inflows, temperature, and volumetric fingerprints.

Temporal Variability (Trends). The Seasonal Kendall test (SKT, Hirsch *et al* 1982) test was used to test for long-term trends in the data. It is a non-parametric rank test that has been proven robust in evaluating trends in time series that have strong seasonality. The SKT does not make assumptions about the distribution of the data and allows missing values and censored data without biasing the analysis (Helsel 2005). It is an extension of Mann-Kendall test. More specifically, it accounts for seasonality by computing the Mann-Kendall test on each month separately, and then combining the results. As described by Jassby (2008), long-term trends were estimated after adjusting for total river inflow using locally weighted regression with a span of 0.5 and a locally linear fit. Trends were tested and compared for three different periods (calendar years from 1998 to 2013, 1987 to 2013, and 1975 to 2013).

2.3 Results

2.3.1 Overview of data

Most of the discussion below focuses on data related to concentrations of nitrogen and phosphorus in their various forms (i.e., NH4, NO3, DIN, TN, PO4, TP), while figures for other variables (nitrogen:phosphorus, chl-a, and SPM) are also included for completeness. The reader is referred to previous studies for more detailed explorations of chl-a (Jassby et al. 2002; Jassby 2008) and SPM. There are abundant data for the nutrient and nutrient-associated parameters of interest across the 11 stations considered. The number of data points for each variable for the timeframe considered are n = 467 for NH4, PO4, and TP; and n = 465 for NO3.

Monthly time-series are presented for nutrients, chl-a, and other water quality parameters (Figures 2.3-2.10), and overall summaries for the 38-year record presented in Figure 2.11. Overall, the figures illustrate that a) there are substantial differences across sites, and that b) concentrations of all parameters varied with strong periodic signals (Figures 2.3-2.10) that generally correspond with the seasonal pattern of the wet/dry and warm/cool Mediterranean climate of this region. These seasonal variations appear superimposed upon substantial spatial differences in concentrations (as illustrated in Figure 2.11), in addition to both interannual variability (e.g., occasional concentration jumps) and apparently increasing or decreasing trends for some parameters and stations. Subsequent sections have the goal of examining and explaining these various aspects of variability (seasonal patterns, long-term trends, and spatial differences) separately, to the extent possible.

Figures 2.12 and 2.13 provide insight into the proportion of TN present as DIN (Figure 2.12) and TP present as o-PO4 (Figure 2.13). Across all data, the majority of TN was present as DIN, with DIN generally comprising 50-75% (Figure 2.12). By visual inspection, the ratio of TN:DIN appears to have varied both spatially and seasonally, and TN:DIN increased as DIN decreased (Figure 2.12). Across all the data, o-PO4 also generally comprised > 50% of TP (Figure 2.14). However, a greater number of samples appeared to have TP:o-PO4 > 2, especially at low o-PO4 concentrations, perhaps due to the potential for inorganic phosphorus complexes to form (e.g, o-PO4 binding to the surfaces of particulate iron-oxides).

2.3.2 Application of conceptual model

The conceptual model introduced in Section 2.2.2 and depicted in Figure 2.2 implies that nutrient variability in the Delta is shaped by five main factors: 1) source waters; 2) seasonal nutrient cycles; 3) long-term trends, 4) climate variability, and 5) local influencing factors.

1. *Source waters.* Relative contributions and chemical composition of source waters are considered a key factor shaping overall nutrient variability. The Delta receives multiple hydrologic inputs that have diverse water quality characteristics, including different concentrations and forms of N. Volumetric fingerprints provide an estimate of the relative contribution of different water sources at a site. Therefore, volumetric fingerprints were generated to evaluate spatial, seasonal, and interannual variability in water sources (Section 2.3.3).
2. *Seasonal Nutrient Cycles.* Seasonality is a main factor in shaping overall nutrient variability in the Delta. Main factors affecting seasonality in nutrient concentrations include seasonal variability in loads; transformations and losses within the system, with seasonally-varying rates; as well as flow rates (dilution, residence time) and flow routing (withdrawals). Monthly nutrient concentrations at each station were examined across three eras to identify typical seasonal patterns, evaluate changes in these patterns over time, and to develop hypotheses to explain seasonal variability (Section 2.3.4)
3. *Long-term trends.* Changes in nutrients over time can reflect change in climatic drivers, such as hydrology and temperature trends, or in anthropogenic influences. Long-term trends where tested and compared across time intervals, to generally examine long-term changes and evaluate how they influence the overall variability (Section 2.3.6)
4. *Climate Variability.* Climate variability plays an important role in nutrient variability, by affecting influencing factors such as flow and temperature (Figure 2.2).
5. *Local Influencing Factors.* The potential role of site-specific factors (e.g., local sources or residence times at a site) is considered throughout in the interpretation of results.

2.3.3 Estimated water sources: Volumetric fingerprints

Substantial spatial, seasonal, and interannual variability in water sources is evident in the volumetric fingerprint time series, derived from hydrologic model output, over the period 2000-2011(Figures 2.14 and 2.15):

Upstream Stations (C3 and C10): Water at station C3 is comprised almost entirely (>97%) of Sacramento River water, and water at C10 is comprised entirely (100%) of San Joaquin River water. Waters at all other stations were mixtures of multiple sources in proportions that varied seasonally and interannually.

Central-South Delta stations (D26, D19, and D28): Water composition is similar at these stations, both on average and in their seasonal and interannual shifts. The Sacramento River is the dominant source throughout most of the year. There are brief spring pulses during which San Joaquin and Cosumnes/Mokelumne Rivers account for non-trivial amounts of source water. The San Joaquin River is the dominant water source for extended periods in 2006 and 2011, the two wettest years during this period, and to a lesser extent during 2005, which was also a wet year. There are also minor contributions from agricultural return flows. In addition, D19 and D26 received minor contributions from estuary waters and the Yolo Bypass.

Suisun Bay stations (D4, D6, D7, D8): Water composition is characterized primarily by seasonally-varying proportions of Sacramento and estuarine sources, with the estuarine influence greatest during low flow periods, and a pronounced east-west gradient from mostly Sacramento (D4) to Sacramento-estuarine (D8, D7), and mostly estuarine sources (D6). Flows from the Yolo Bypass contributed to Suisun stations at low levels (<10%, except for short spikes) during winter/spring.

Central Delta – Eastside (MD10): MD10 exhibited the greatest diversity in its volumetric fingerprint. San Joaquin flows water contributed substantially during late-winter/early-spring, with the broadest peaks occurring during the wettest years (2005, 2006, 2011) and fall peaks during some years. Sacramento waters became dominant, on average, during summer and fall. Cosumnes/Mokelumne Rivers were also an important source during short periods, typically at its greatest in winter (January/February). Compared to all other sites, agricultural return flows contributed to the greatest extent at MD10. The peak seasonal contribution from the Sacramento River may be driven in part by water exports inducing the southward movement of Sacramento River water during summer.

San Joaquin River, upstream of Central Delta (P8): San Joaquin was the dominant water source at P8. Contributions from the Sacramento and Calaveras rivers peaked in summer, and were most pronounced during three of the driest years of the decade (2007, 2008, 2009). Agricultural return flows contributed seasonally (up to ~15%), following a similar pattern as contributions from the Sacramento and Calaveras rivers.

2.3.4 Seasonal and temporal changes in nutrient concentrations

The following narrative summarizes key observations in seasonal variation at five stations that are reasonably representative of the range in patterns of seasonal variation observed in the Delta: C3 (Sacramento River as it enters the Delta), D7 (Suisun Bay), C10 (San Joaquin River as it enters the Delta), P8 (San Joaquin River below Stockton as it enters the Central Delta), and D28 (representing the Central Delta stations).

As a first step toward examining both seasonal and temporal trends in water quality, we plotted monthly median and interquartile concentrations ranges for each station, with data divided into three eras (Figures 2.16-2.27). While plots are presented for all 11 stations, the discussion focuses primarily on a subset of stations organized on a qualitative and a priori basis on their geographic distribution (upstream: C3 and C10; downstream: D4; central Delta: D19, D26, and 28; internal/eastern: MD10, P8).

The seasonal and temporal trends are organized first by brief semi-quantitative descriptions of major features at upstream, internal, and downstream stations, followed by several statistical tests and data analysis approaches for examining similarity and differences in variability.

2.3.4.1 Nutrient observations at individual stations

C3– Sacramento River at Hood (Figure 2.16)

Monitoring at C3 characterizes water quality in the Sacramento River as it enters the Delta. It is situated at the terminus of the Sacramento River watershed, just downstream of the Sacramento metropolitan area and the SRWWTP. The station integrates the influences from an agricultural watershed, an urban area, and a major wastewater treatment facility (SRWWTP). The SRWWTP is known as the single-largest source of ammonium to the Delta. Therefore, C3 is the station with the highest NH4 concentrations and at this station is dominated by NH4. The average NH3:NO3 ratio (2000-2013) was 2.03; C3 is unique in this regard in comparison with the other station.

Figure 2.16 shows 1) an increase in DIN and TN over time in all months and 2) limited seasonality in most variables during the most recent era (1998-2013). Most of the increase in DIN and TN is due to NH4. NH4 concentrations at C3 showed limited seasonality; except for slightly lower concentrations in January and February (Figure 2.16), likely caused by dilution during seasonally higher flows. NH4 concentrations at C3 do not, on average, decrease during summer months, which is not surprising given the short distance between the SRWWTP input and C3's location xxx km downstream, and limited time for nitrification or NH4 uptake to influence concentration. NO3 at C3 exhibited some seasonal variability, with winter median concentrations that were ~2x higher than other times of year and lowest concentrations in late summer (July, August, September). This pattern is consistent with the cyclical annual pattern of nutrient loadings from the Sacramento River basin (Kratzer et al. 2011).

For TP and PO4, Figure 2.16 indicates limited seasonality and substantial decreases in PO4 and TP between era 2 (1987-1997) and era 3 (1998 – 2013). There is an increase in the N:P ratio, as the result of decreasing P and increasing N.

C10– San Joaquin River at Vernalis (Figure 2.17)

Observations at C10 show considerably different patterns as compared to those at C3. At station C10, NO3 was the dominant form of inorganic nitrogen in all months, accounting for more than 95% of DIN on average. NH3 concentrations at station C10 in Era 3 (1998-2013) are reduced by approximately 80% compared to Era 1 (1975-1986). C10 had the lowest peak NH4 concentrations of all stations, observed during winter months, and reached the lowest NH4 levels of all stations in spring, summer, and early fall. In contrast, nitrate concentrations have increased over time. DIN concentrations at C10 are among the highest of all stations (Figure 2.11). The average DIN concentration from 1998 to 2013 was 1.43 mg/L (second-highest of all stations), compared to an average of 0.70 mg/L across all stations. Both upstream sites have in common that here is limited seasonality, with concentrations of nutrients being generally lowest in the summer.

D4 – Sacramento Point (Figure 2.18)

Station D4 exhibits a flattened seasonal profile as compared to C3, particularly for DIN and NH4. The station is situated along a gradient of change in seasonal patterns along the Sacramento River between C3 and D6 (Suisun Bay at Martinez, compare Figures 2.16, 2.18, 2.19, and 2.20). The gradual change in seasonal patterns corresponds to a gradual change in volumetric fingerprints from C3, which is completely dominated by the Sacramento River as a water source, to D6, which is dominated by the estuarine contribution (Figure 2.16).

D19– Frank's Tract (Figure 2.22)

Station D19 exhibits several seasonal patterns that are typical for stations in the Central Delta, which include D19, D26, D28, MD10, and seasonally D4. Sacramento River water constitutes the dominant water source at these sites for most of the time. However unlike C3, these stations exhibit pronounced seasonality with a drawdown of DIN extending from early spring to late summer. Maximum NH4 concentrations at these stations are >2x lower than at C3, and, unlike C3, exhibit strong seasonal variations, with 4-5 fold lower NH4 concentrations in summer than winter. In addition to these more general trends, there are a number of differences among the Central Delta stations. These differences do not always seem to have an obvious relationship to volumetric patterns. For example, Station D19 exhibits the strongest seasonal signal for NH3-N but there are no visible relationships of NH3-N concentrations with either the SAC or SJR volumetric fingerprint (see Figures 2.14 and 2.15). The more likely explanation is that Station D19 is located in Frank's Tract, which is a lake-like environment with longer retention times.

P8 – San Joaquin River at Buckley Cove (Figure 2.26)

P8 has the highest DIN concentrations of all stations (1.99 mg/L). DIN here exhibits a more pronounced seasonal "U" pattern for both DIN and NH3 (Figure 2.26) and a less pronounced seasonal pattern for NO3, indicative of local sources of NO3. The representation of long-term trends by comparison of the eras as chosen doe not capture the switching of the Stockton WWTP to tertiary treatment in the mid-2000s (middle of 1998-2013 era) and the associated marked decrease in NH3 and increase of NO3 signal, which is clearly visible in the long-term time series (Figures 2.4 and 2.5).

2.3.5 Which stations and which parameters behave similarly?

EOF analysis was employed to summarize the dominant spatial and temporal patterns in nutrient variables (Figure 2.27). The EOF analyses determined that the 20 time series for NH4 and NO3 (2 parameters x 10 stations) can be reasonably well-explained by 4 modes of variability, suggesting that a common set of dominant underlying processes influence N cycling, helping to simplify the explanation of what is otherwise a large and complex system.

Analysis of the 10 NH4 time series identified 2 significant EOFs that explained 73% of the variability over time and space (Figure 2.27a). NH4 concentrations at the Suisun Bay stations (D4, D6, D7, and D8) and at D26 varied in a manner captured by NH4-EOF1. The substantial and consistently timed peaks in October-December/January are an important feature of NH4-EOF1. Those peaks pre-date the timing of large changes in flow rates; it is therefore unlikely that they resulted from changing NH4 loads or concentrations in runoff; instead, they are likely result from the system-wide slow-down in either nitrification (conversion of NH4 to NO3) or NH4 assimilation during primary production. In 2006 and 2011, the NH4-EOF peaks are followed by sharp and sustained decreases, suggesting that NH4 concentrations at Suisun stations and D26 were similarly influenced by high-flow dilution, in particular during the wettest years. The moderately negative amplitude of NH4-EOF1 during spring and summer of other years captures the seasonal NH4 decreases at these sites, due to either nitrification or uptake.

The EOF analysis for NH4 also identified NH4-EOF2, which explained a large portion of the variability at MD10, C10, and P8. The NH4-EOF2 peaks lag behind those from NH4-EOF1 by 1-2 months in most years. For stations MD10, C10, and P8, this may be due to a slightly lagged temperature response due to warmer conditions and longer residence within the Delta prior to the wet season, compared to the Suisun stations and D26. While the NH4 time series at P8 (Figure 2.28) is well-explained by NH4-EOF1 prior to 2006, peak NH4 concentration at P8 decrease sharply after 2006, which corresponds to the timing of an upgrade to nitrification at Stockton's wastewater treatment plant that discharges near P8. D28 was only marginally explained by NH4-EOF2; however, this suggests that NH4 concentrations at D28 were regulated by a combination of factors more similar to the central/southern Delta stations than to Suisun stations and D26. The decreasing NH4 concentrations at P8 after 2006 are likely a main driver of the decreasing amplitude for NH4-EOF2, although NH4 concentrations at MD10 also appear to decline after 2006. The NH4 time series at C3 is also well explained by NH4-EOF2; however, the coefficient for C3 was negative (i.e., peaks in NH4-EOF1 as shown in Figure 2.27a are aligned with troughs in C3's NH4 time series as shown in Figure 2.28). The sharp decreases in NH4 may be due to the beginning of higher flows in January-February, an effect that only becomes evident at downstream sites 1-2 months later (i.e., minima in NH4-EOF1). Thus, although the underlying mechanisms were different, the timing and the relative influence on NH4 concentrations detected by the EOF analysis were similar for C3 and MD10, C10, and P8.

Analysis of the 10 NO3 time series also identified 2 significant EOFs that explained 75% of the variability (Figure 2.27b), with some interesting differences from the EOFs for NH4. NO3-EOF1 captures much of the variability in NO3 concentrations at the Suisun stations. Interestingly, NO3 concentrations at P8 and C10 are also well aligned with NO3-EOF1, despite the substantial distance between them and the Suisun stations, and the fact that they are hydrologically distinct. NO3-EOF1 exhibits less of the clear seasonal variability of NH4-EOF1, but captures the large drops in winter 2006 and winter 2011; NH4-EOF1 may therefore be capturing major event-driven responses. NO3-EOF2 identifies more of the strong seasonal responses than NO3-EOF1, showing the similar patterns of strong seasonality for NO3 at stations MD10, D28, and D26, including late fall/early-winter peaks in NO3 and spring and summer minima.

Analysis of the 10 o-PO4 time series identified three significant EOFs that explained 78% of the variability (Figure 2.29). NO3-EOF1 captures much of the variability in PO4 concentrations at C3 and the Suisun stations. D26 is moderately aligned with PO4-EOF1. The PO4-EOFs exhibit a much weaker seasonal signal than those for the N species NH4 and NO3. As for the N species, EOF1 for PO4 shows large negative amplitudes in the wet winters of 2006 and winter 2011; suggesting that it does capture major event-driven responses. EOF2 shows clearer winter peaks than other stations, corresponding to increased winter loads, particularly at stations C10, P8, and MD10. There is a third significant EOF mode for o-PO4 that aligns with stations MD10, D26, and D28, with little evidence for seasonality. EOF 3 explains less than 13% of variance in o-PO4 and its pattern could not be readily explained without more detailed follow-up analyses and was not further diagnosed.

2.4 Discussion

The DWR-EMP long-term data provide a unique opportunity to evaluate complex patterns of nutrient concentrations over four decades in the Delta. Overall, the data present considerable spatial and temporal variability.

2.4.1 Seasonal and temporal changes in nutrient concentrations

The various stations display a range of seasonal patterns across the examined variables. To describe the range of observed seasonal patterns, the stations were subjectively grouped based on visual comparison of these seasonal patterns. As discussed in a subsequent section, there is some justification to these groupings based on trend analyses and correlations among stations. The groupings are: Sacramento River (C3), Suisun Bay (D4, D6, D7, D8), Central Delta (D19, D26, D28A, MD10), and San Joaquin River (C10, P8) (Figure 2.1).

The Sacramento River station C3 integrates and represents inputs from the Sacramento River watershed and does not display strong seasonality in any of the examined variables. There is a muted seasonal pattern for DIN and NO3 with lowest concentrations in late summer (July, August, September) and highest concentrations in the winter (Figure 2.15), which is consistent with the cyclical annual pattern of nutrient loadings from the Sacramento River basin.

The Suisun Bay stations have very pronounced seasonality in DIN and NH3, with significant drawdown in the summer (Figures 2.18 to 2.21). Changes in seasonal patterns along the Sac Pathway between C3 and D6 are gradual and correspond to a gradual change in volumetric fingerprints from C3, which is completely dominated by the Sacramento River volumetric fingerprint, to D6, which is dominated by the estuarine volumetric fingerprint (Figure 2.20). Chl-a blooms at Suisun stations have increased in the “post-clam” era from 1987-1997 to 1997-2013 but remain much smaller than prior to the invasion by the Asian clam (*Corbula amurensis*) in 1986 (Figure 2.9).

A typical feature of the Central Delta stations is strong seasonality with a drawdown of DIN extending from early spring to late summer. Aside of this more general trend, there are numerous differences in seasonal patterns among the Central Delta stations. These differences do not always seem to have an obvious relationship to volumetric patterns.

The SJR stations C10 (Vernalis) and P8 (Buckley Cove) integrate and represent inputs to the Delta coming from the San Joaquin River. They are characterized by having the highest DIN/NO3 and PO4 concentrations of all stations (Figure 2.11). However, the two stations integrate different sources: C10 represents inputs from the San Joaquin watershed to the Delta, and P8 represents inputs from the Stockton urban area to the Central Delta. Overall, there is more seasonality in N-related variables at P8 than at C10 (Figures 2.17 and 2.26). However, there is some weak seasonality at C10. Somewhat lower nutrient concentrations at C10 during the summer period are consistent with the seasonal patterns described for nutrient loads from the San Joaquin Basin, with maximum in winter/spring during high flow and minimums during summer/fall during low flows (Kratzer et al. 2011). The amplitude of the seasonal variation in NH4 at C10 has decreased over time for the time period 1975 - 2013, due to load reductions from the watershed (Figure 2.4). The amplitude in NH4 at P8 has increased over time, due to the increase in NH4 loadings from the Stockton WWTP up until the 2000s (Figure 2.4). (The plant has since switched to tertiary treatment and stopped discharging NH4 into the SJR).

Analysis of the entire 38 yr data record from 1975 – 2013 showed significant increasing trends for nitrogen species and significant decreasing trends for PO4 and Chl at most of the stations. However, if only the data from the most recent 15 yr period from 1998 to 2013 are analyzed, there is a change in the direction of trends for the nitrogen species. For the period from 1998 to 2013, there are significant decreasing trends in ammonium at six of 11 stations, and no trends at the remaining five stations (**Table 2.1**). Similarly, there are significant decreasing trends for nitrate at two stations, and no trends for nitrate at the other stations for the period from 1998 to 2013. Phosphate declined during the 38 yr period from 1975 – 2013 at 9 of 11 sites and also declined at 4 sites during the period from 1998 to 2013, but there was also an increasing trend at one of the stations (MD10) for the period from 1998 to 2013. Generally, and not surprisingly, the trends are more consistent across stations as the length of the analyzed period increases.

Trends for several stations were not consistent over time, and there is need for caution in extrapolating trends over time. On one hand, trends for short periods may not necessarily be indicative for longer-term patterns but on the other hand, and equally important for an adaptively managed system such as the Delta, focusing on the long-term trends alone may mask the outcomes of recent impacts or management actions. For example, the analysis shows a significant increasing trend in NH4 at C3 for the 38 yr period from 1975 – 2013, but a significant deceasing trend for the shorter period from 1998 to 2013 indicative of current trends.

There is also an increase in the correlation of trends across variables between stations as the length of the analyzed data record increases, which is also not surprising. For example, trends across the examined variables during the period from 1998 to 2013 were synchronous across the Suisun Bay stations (D4, D6, D7, D8). Over the longest time scale (1975 – 2013), C3 (Sacramento River at Hood) and D19 (Frank's Tract) also correlated with D4 (Sacramento River above Point Sacramento, which behaves like a Suisun station). Additionally, D19 correlated with D26 (a San Joaquin River station in the Central Delta) during the 1987 – 2013 period and the 1975 and 2013 period. The results of the correlation analysis suggest that trends at all of the Suisun Bay stations (D4, D6, D7, D8) were similar.

Other than for the Suisun Bay stations, extrapolation across space may be problematic. For the shorter period of 1998 – 2013, seven of the eleven stations did not have any significant correlations in trends across multiple variables with any other station. More specifically, variables exhibit rather unique patterns of trends at each of these stations. This implies that, with the exception of the synchronous Suisun stations, all of the other stations fill rather unique spatial niches in the nutrient-monitoring network.

2.4.2 Which stations and which parameters behave similarly?

Empirical Orthogonal Function (EOF) analysis was performed to further examine the seasonal, interannual, and spatial variability in N concentrations across the Delta. The EOF analyses determined that time series for NH4 and NO3 can be reasonably well-explained by 2 modes of variability across stations, suggesting that a common set of dominant underlying processes influence N cycling, helping to simplify the explanation of what is otherwise a large and complex system. For PO4, three EOFs explain 78% of all variability.

For spatial variance, the analyses suggest that nutrient variables and Delta stations load to different degrees onto different modes of variability. For most analyses, the ability to extrapolate may be limited to the Suisun Bay stations (D4, D6, D7, D8) which all behave similarly across the three variables over the 2000 – 2011 timeframe considered in the analyses. Other than that, most of the stations behave uniquely across variables and modes of variation and, therefore, conditions and trends at these stations may not be readily extrapolated based on observations from other stations.

2.4.3 Data gaps

The analysis documents a large degree of temporal and spatial variability across stations. The results demonstrate that extrapolation across space may be problematic (with the exception of the Suisun Bay stations), because trends for several stations were not consistent with each other over time and variables exhibit rather unique patterns of trends and variability at each of these stations. It follows that conditions and trends at the currently monitored stations cannot be extrapolated to areas of the Delta that are not currently monitored, such as the North Delta, the South Delta, and contributions from Eastside tributaries. Additional stations would be needed to evaluate conditions and trends in these regions. Given the large amount of variability, additional stations will also increase the power for detecting significant larger-scale and longer-term trends.

2.5 Conclusions

The DWR-EMP long-term data document large spatial and temporal variability of nutrient concentrations in the Delta. Most of the currently sampled stations behave uniquely across the range of variables and conditions, and trends may not be readily extrapolated from one station to the other. It follows that conditions and trends at the currently monitored stations cannot be extrapolated to areas of the Delta that are not currently monitored, such as the North Delta, the South Delta, and contributions from Eastside tributaries. Additional stations would be needed, if the goal were to evaluate conditions and trends across all regions of the Delta.

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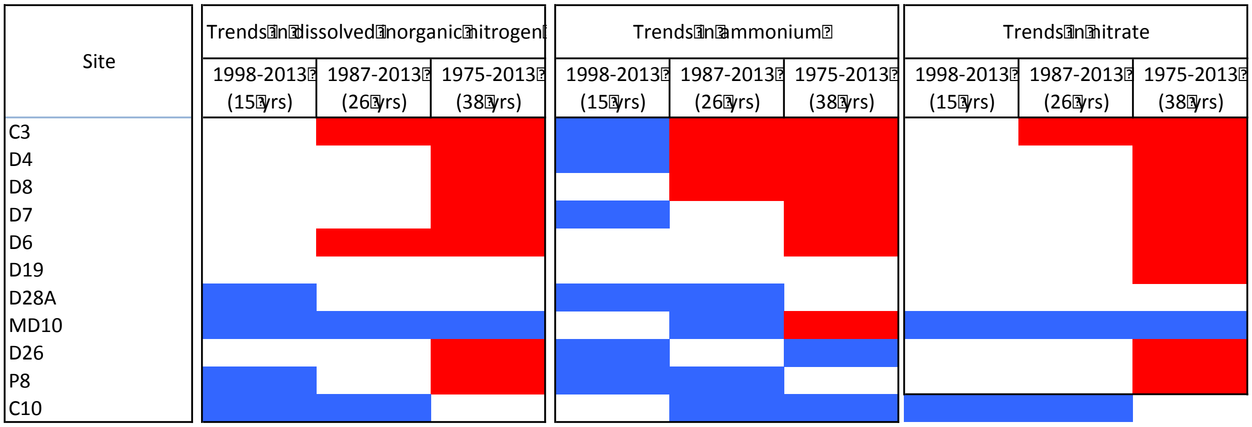
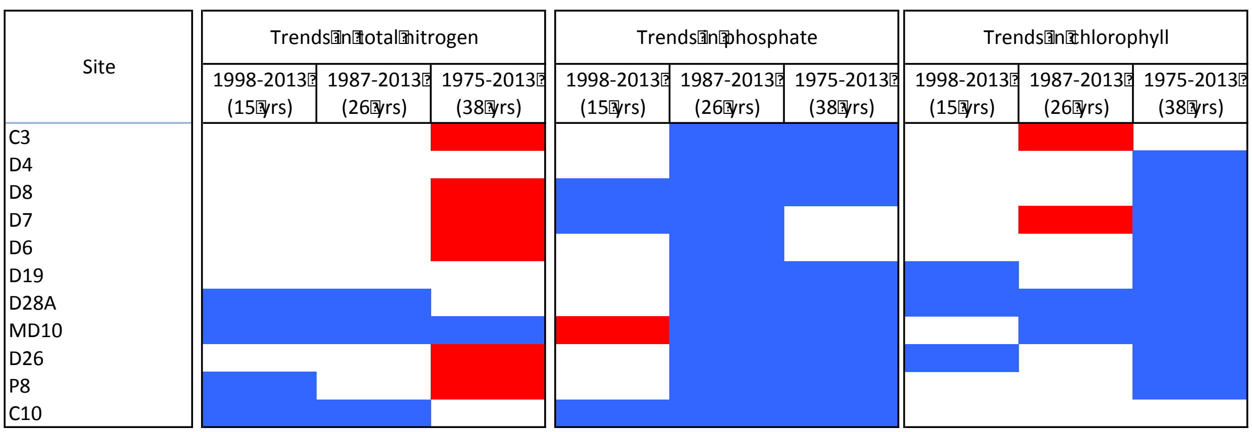
Tables

Table 2.1 Observed trends in inflow-adjusted concentrations of DIN, NH4, NO3, TN, PO4, and Chl for three time periods, calculated using Seasonal Mann–Kendall. Red denotes increasing trends, white denotes no significant trends, and blue denotes decreasing trends for that period of time and station.



	Trends in dissolved inorganic nitrogen 1998-2013 (15 yrs)	Trends in dissolved inorganic nitrogen 1987-2013 (26 yrs)	Trends in dissolved inorganic nitrogen 1975-2013 (38 yrs)	Trends in ammonium 1998-2013 (15 yrs)	Trends in ammonium 1987-2013 (26 yrs)	Trends in ammonium 1975-2013 (38 yrs)	Trends in nitrate 1998-2013 (15 yrs)	Trends in nitrate 1987-2013 (26 yrs)	Trends in nitrate 1975-2013 (38 yrs)
Increasing trends	0 (0.0%)	2 (18.2%)	7 (63.6%)	0 (0.0%)	4 (36.4%)	6 (54.6%)	0 (0.0%)	1 (9.1%)	8 (72.7%)
No trends	7 (63.6%)	7 (63.6%)	3 (27.3%)	6 (54.6%)	3 (27.3%)	3 (27.3%)	9 (81.8%)	8 (72.7%)	2 (18.2%)
Decreasing trends	4 (36.4%)	2 (18.2%)	1 (9.1%)	5 (45.5%)	4 (36.4%)	2 (18.2%)	2 (18.2%)	2 (18.2%)	1 (9.1%)



	Trends in total nitrogen 1998-2013 (15 yrs)	Trends in total nitrogen 1987-2013 (26 yrs)	Trends in total nitrogen 1975-2013 (38 yrs)	Trends in phosphate 1998-2013 (15 yrs)	Trends in phosphate 1987-2013 (26 yrs)	Trends in phosphate 1975-2013 (38 yrs)	Trends in chlorophyll 1998-2013 (15 yrs)	Trends in chlorophyll 1987-2013 (26 yrs)	Trends in chlorophyll 1975-2013 (38 yrs)
Increasing trends	0 (0.0%)	0 (0.0%)	6 (54.6%)	1 (9.1%)	0 (0.0%)	0 (0.0%)	0 (0.0%)	2 (18.2%)	0 (0.0%)
No trends	7 (63.6%)	8 (72.7%)	4 (36.4%)	7 (63.6%)	0 (0.0%)	2 (18.2%)	8 (72.7%)	7 (63.6%)	2 (18.2%)
Decreasing trends	4 (36.4%)	3 (27.3%)	1 (9.1%)	3 (27.3%)	11 (100.0%)	9 (81.8%)	3 (27.3%)	2 (18.2%)	9 (81.8%)

Figures

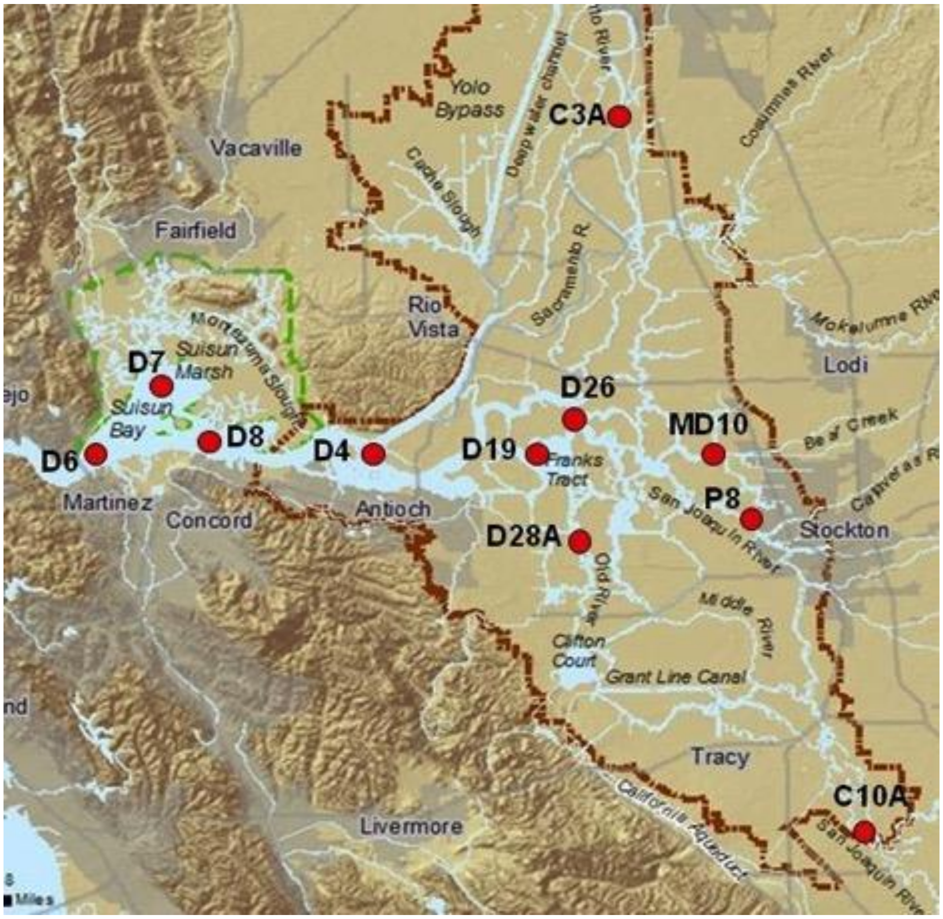


Figure 2.1 Map showing IEP-EMP discrete water quality sampling stations from which data were used in the analysis.

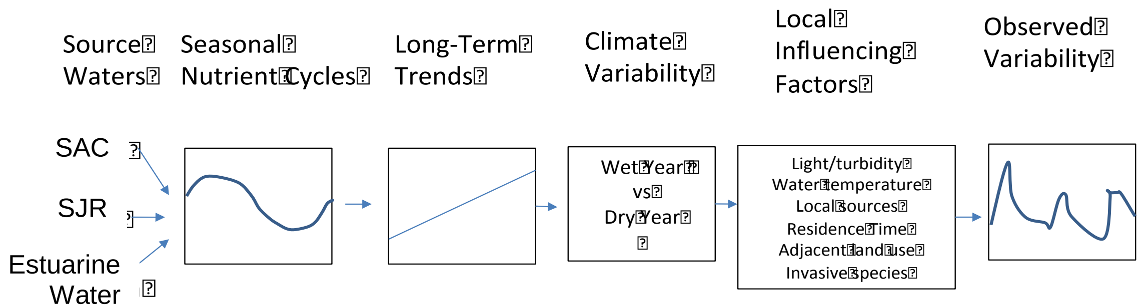


Figure 2.2 Conceptual model for nutrient variability in the Sacramento-San Joaquin Delta.

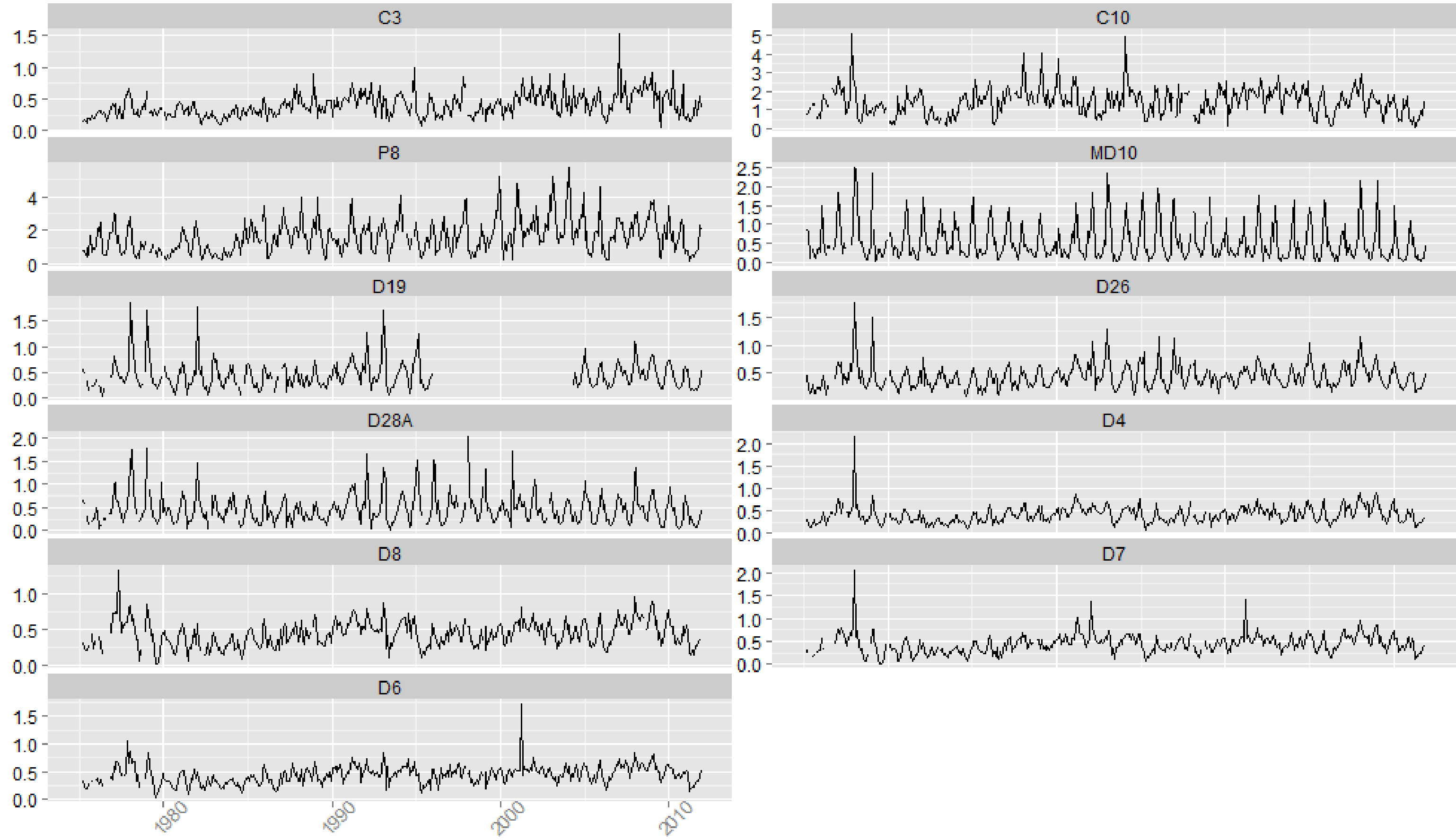


Figure 2.3 Mean monthly DIN concentrations at IEP/DWR-EMP stations C3, D4, D8, D7, D6, C10, P8, D26, MD10, D28, and D19.

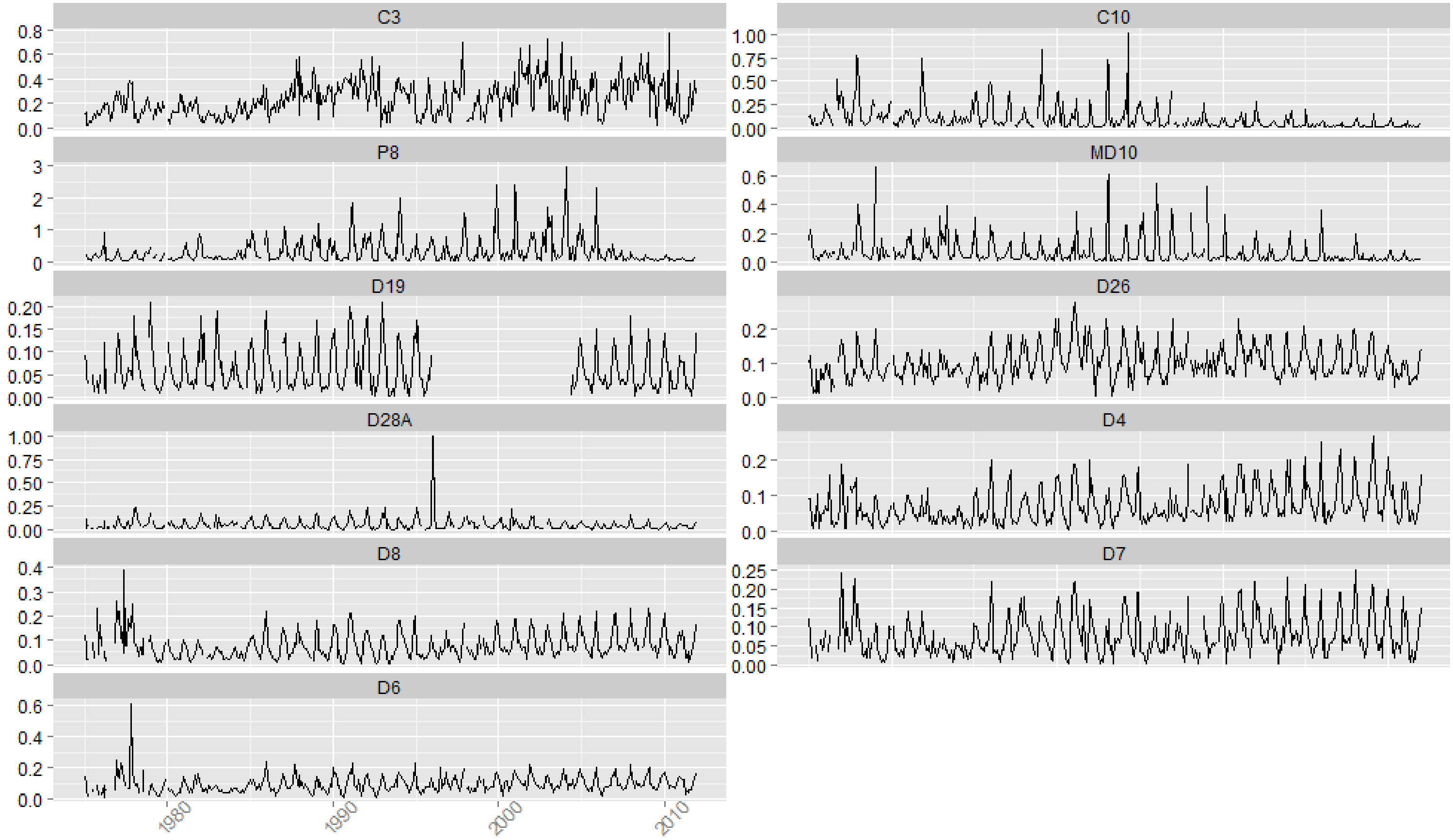


Figure 2.4 Mean monthly NH3-N concentrations at IEP/DWR-EMP stations C3, D4, D8, D7, D6, C10, P8, D26, MD10, D28, and D19.

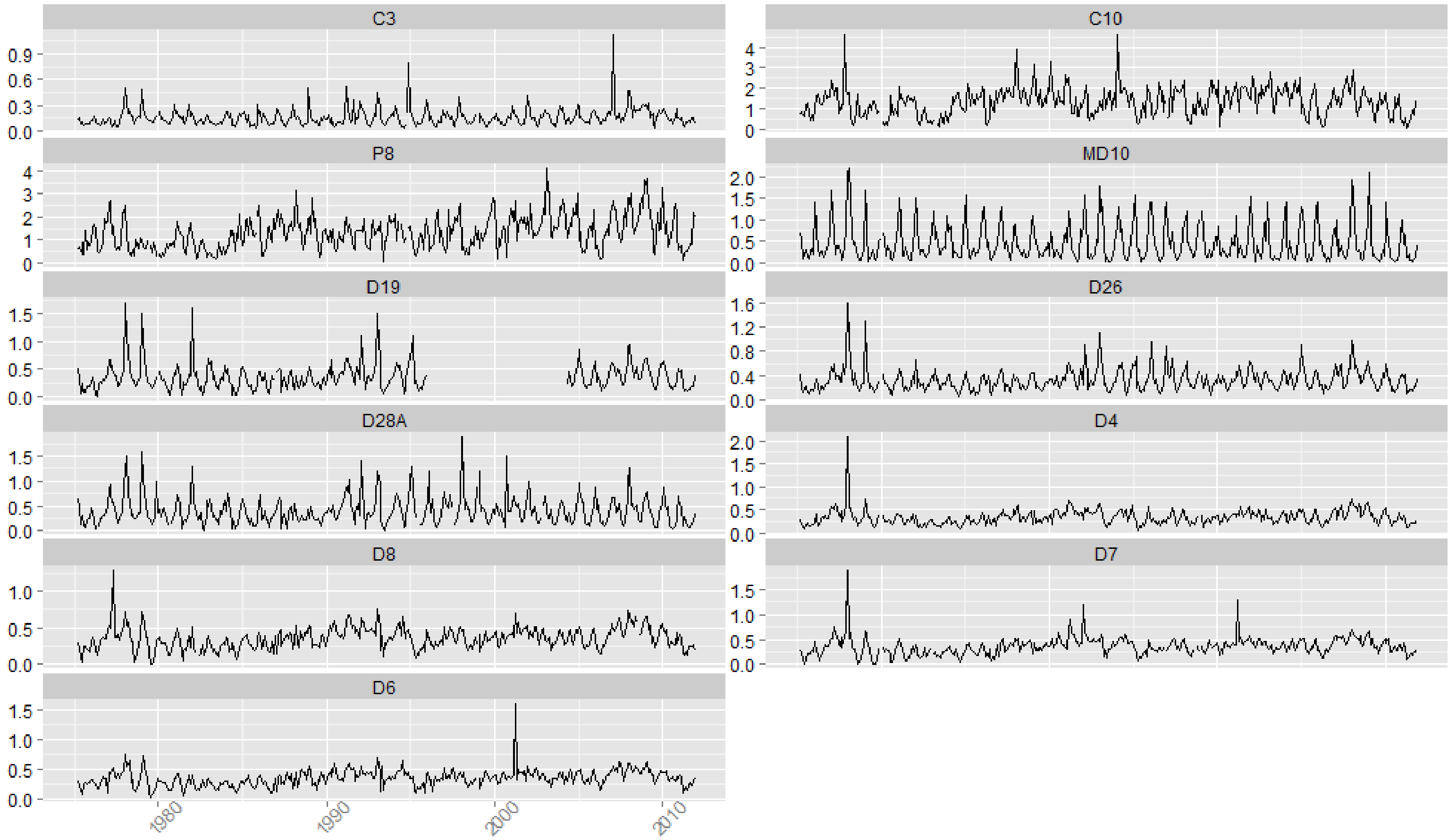


Figure 2.5 Mean monthly NO3-N concentrations at IEP/DWR-EMP stations C3, D4, D8, D7, D6, C10, P8, D26, MD10, D28, and D19.

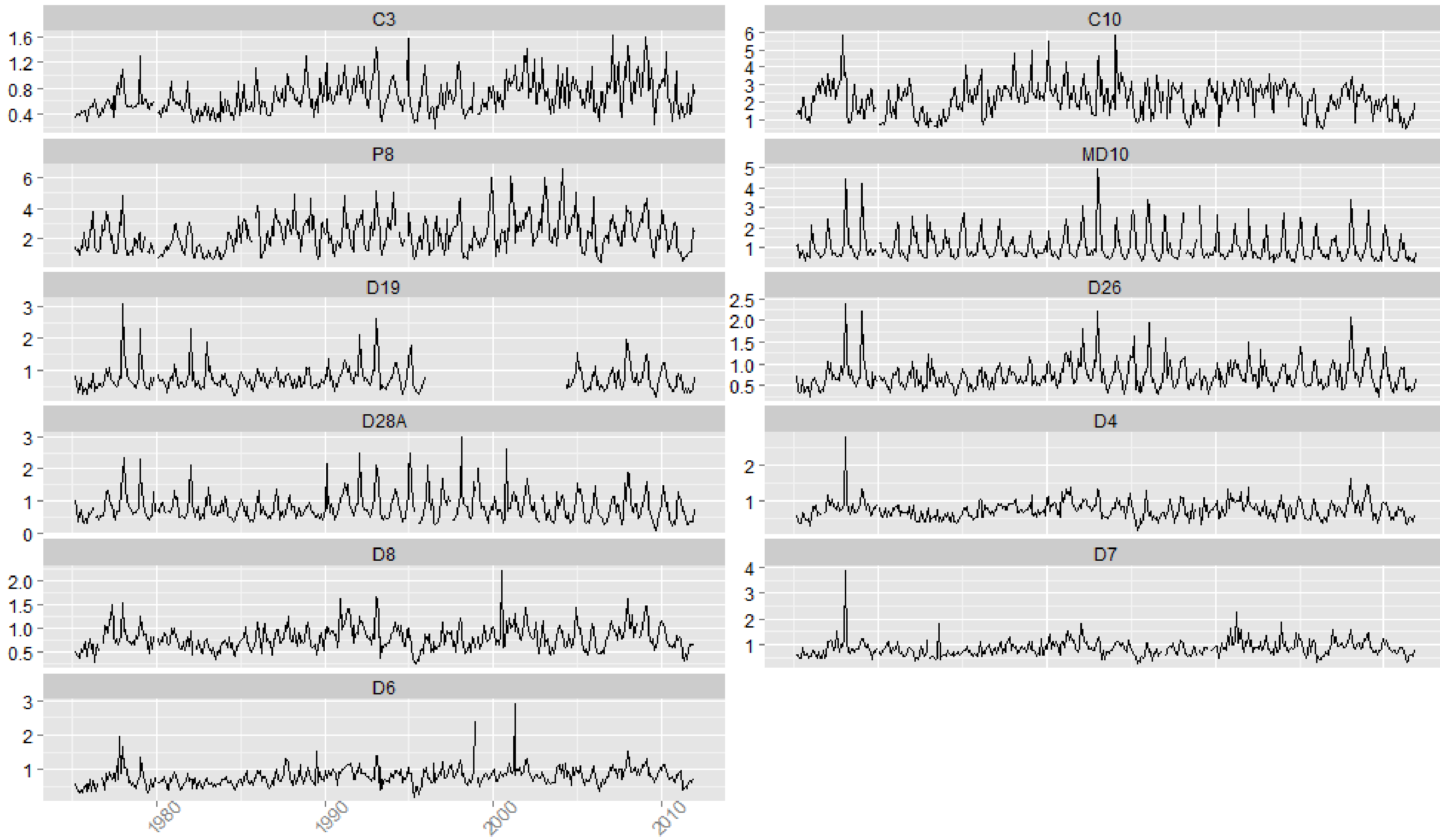


Figure 2.6 Mean monthly TN concentrations at IEP/DWR-EMP stations C3, D4, D8, D7, D6, C10, P8, D26, MD10, D28, and D19.

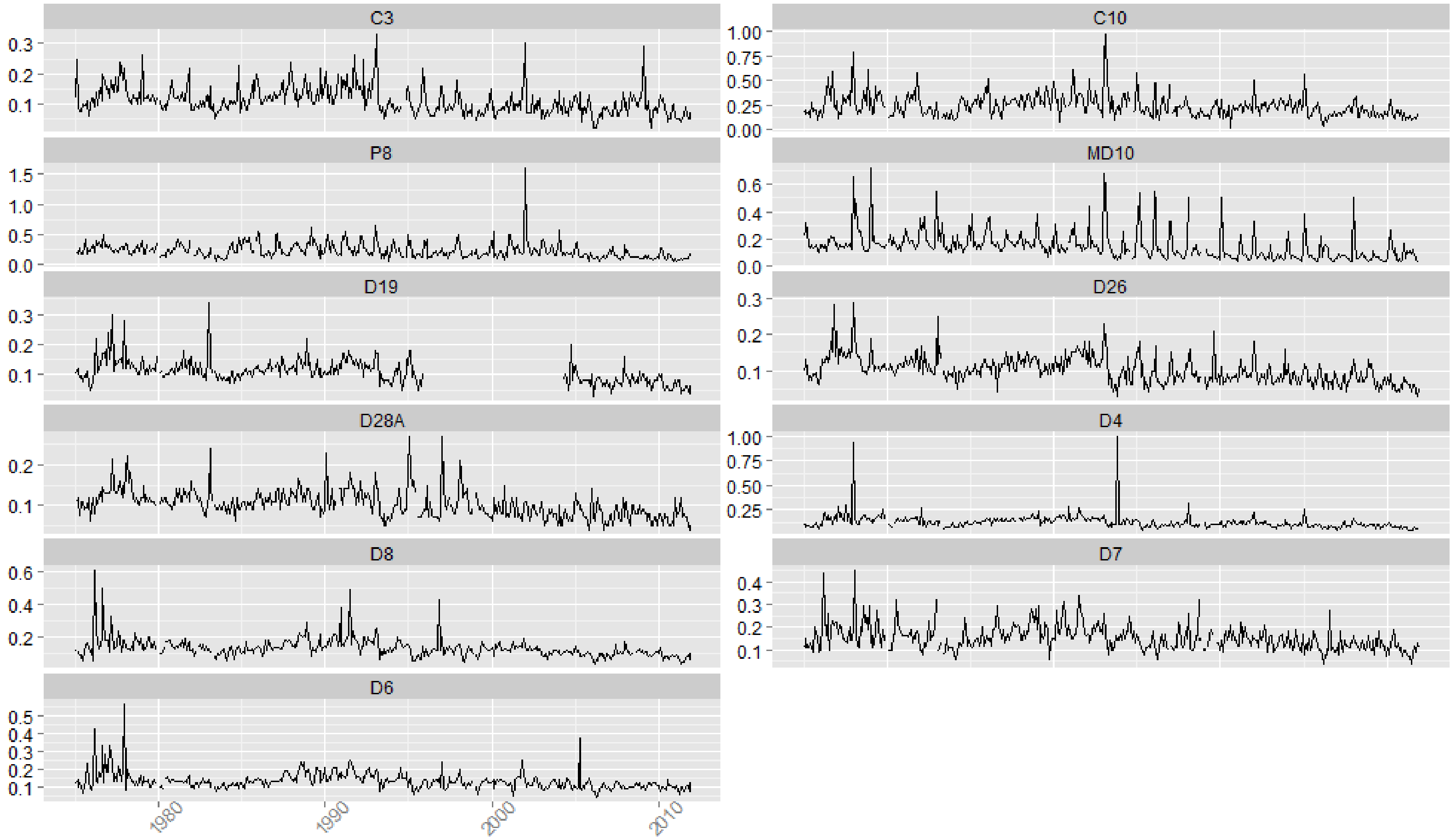


Figure 2.7 Mean monthly TP concentrations at IEP/DWR-EMP stations C3, D4, D8, D7, D6, C10, P8, D26, MD10, D28, and D19.

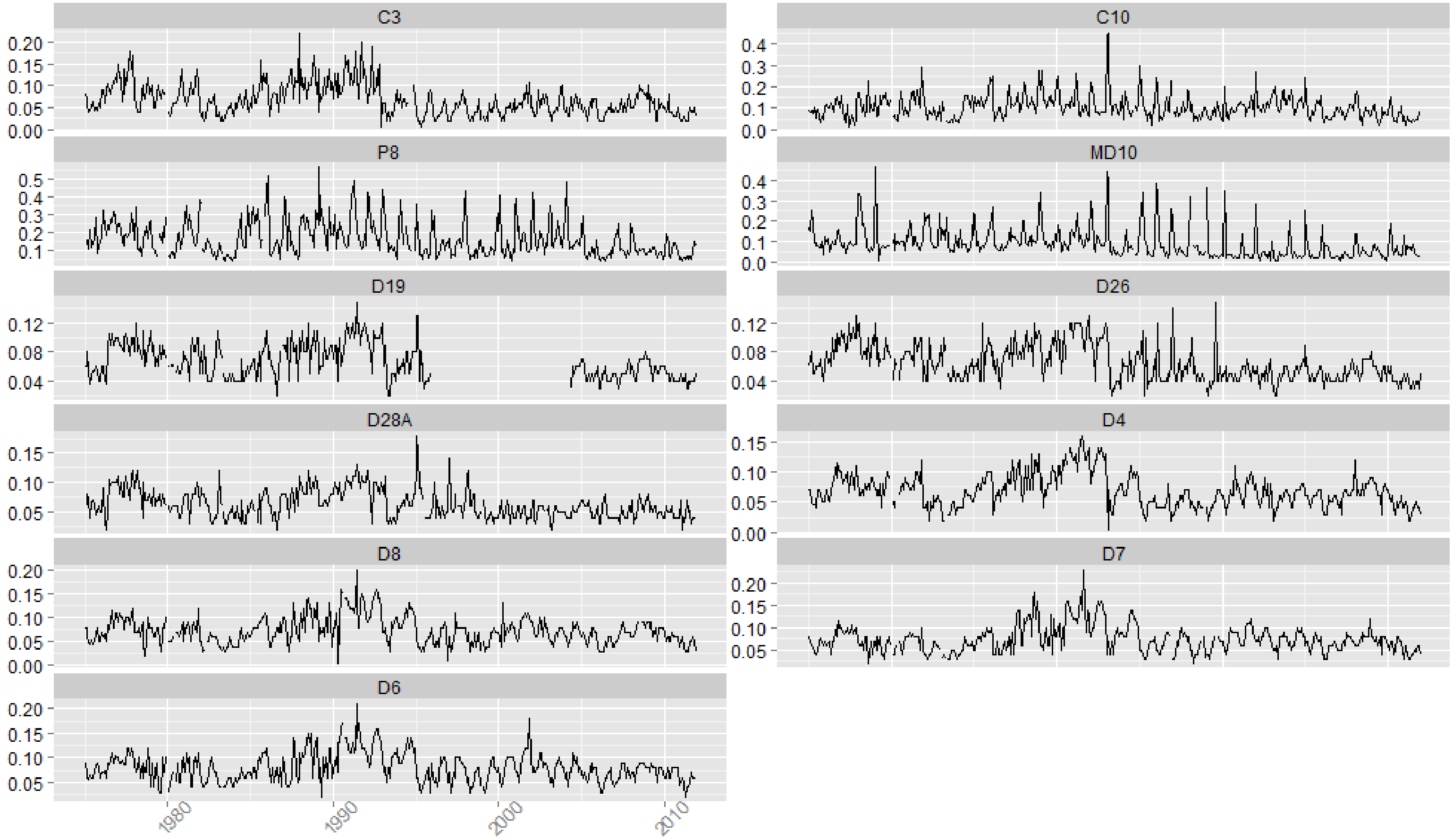


Figure 2.8 Mean monthly PO4 concentrations at IEP/DWR-EMP stations C3, D4, D8, D7, D6, C10, P8, D26, MD10, D28, and D19.

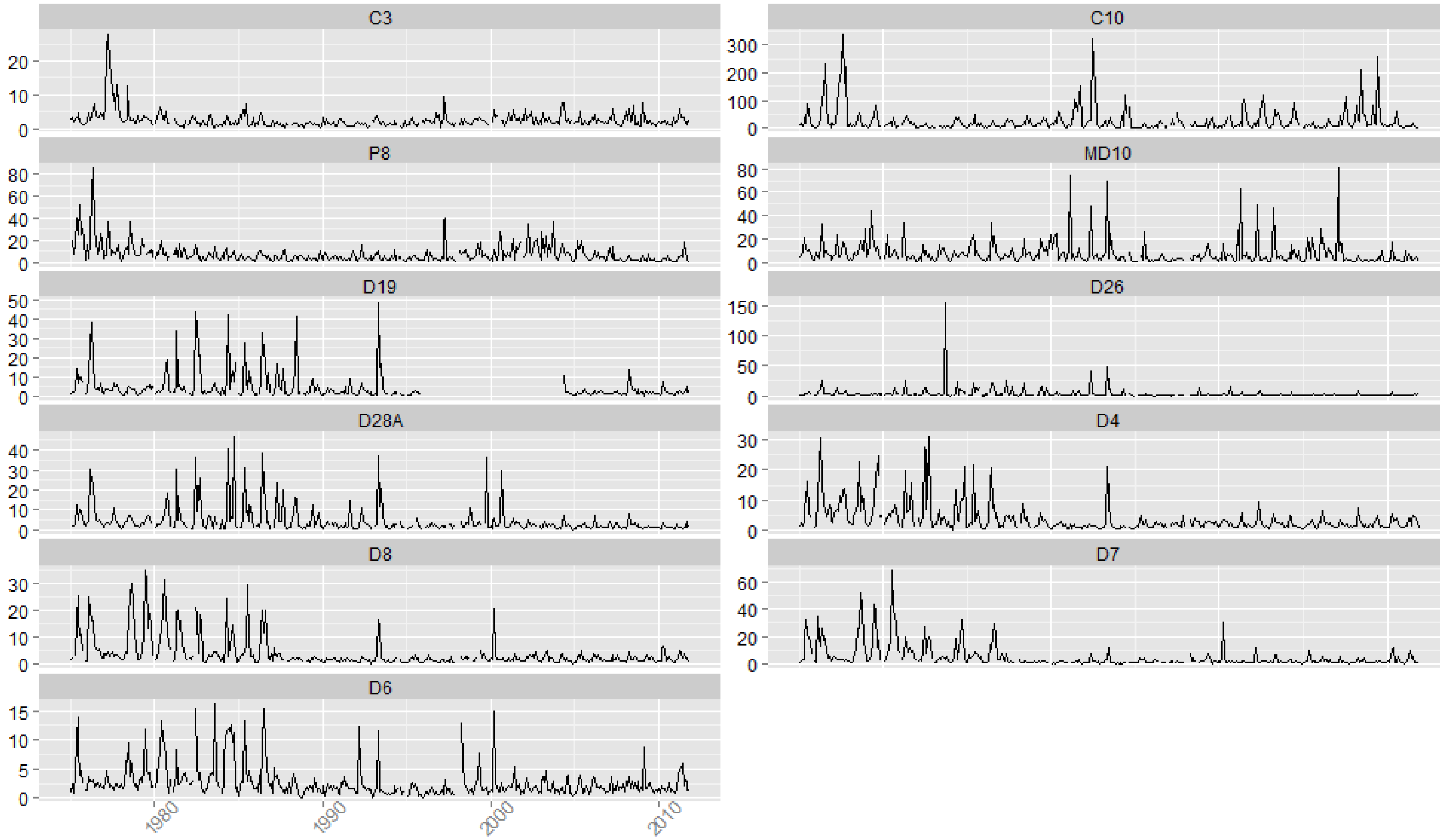


Figure 2.9 Mean monthly chl-a concentrations at IEP/DWR-EMP stations C3, D4, D8, D7, D6, C10, P8, D26, MD10, D28, and D19.

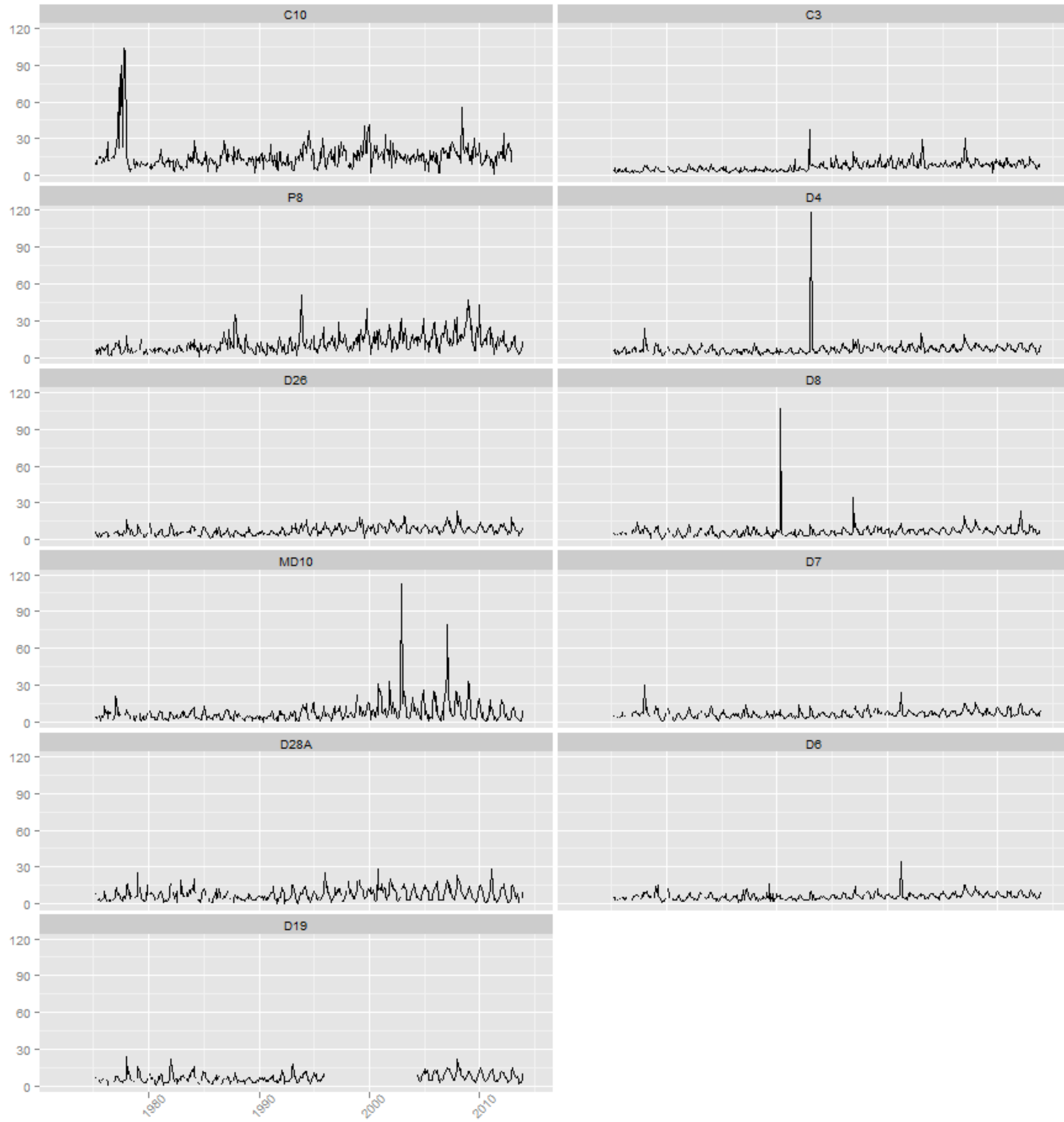


Figure 2.10 Mean monthly nitrogen:phosphorus ratios at IEP/DWR-EMP stations C3, D4, D8, D7, D6, C10, P8, D26, MD10, D28, and D19.

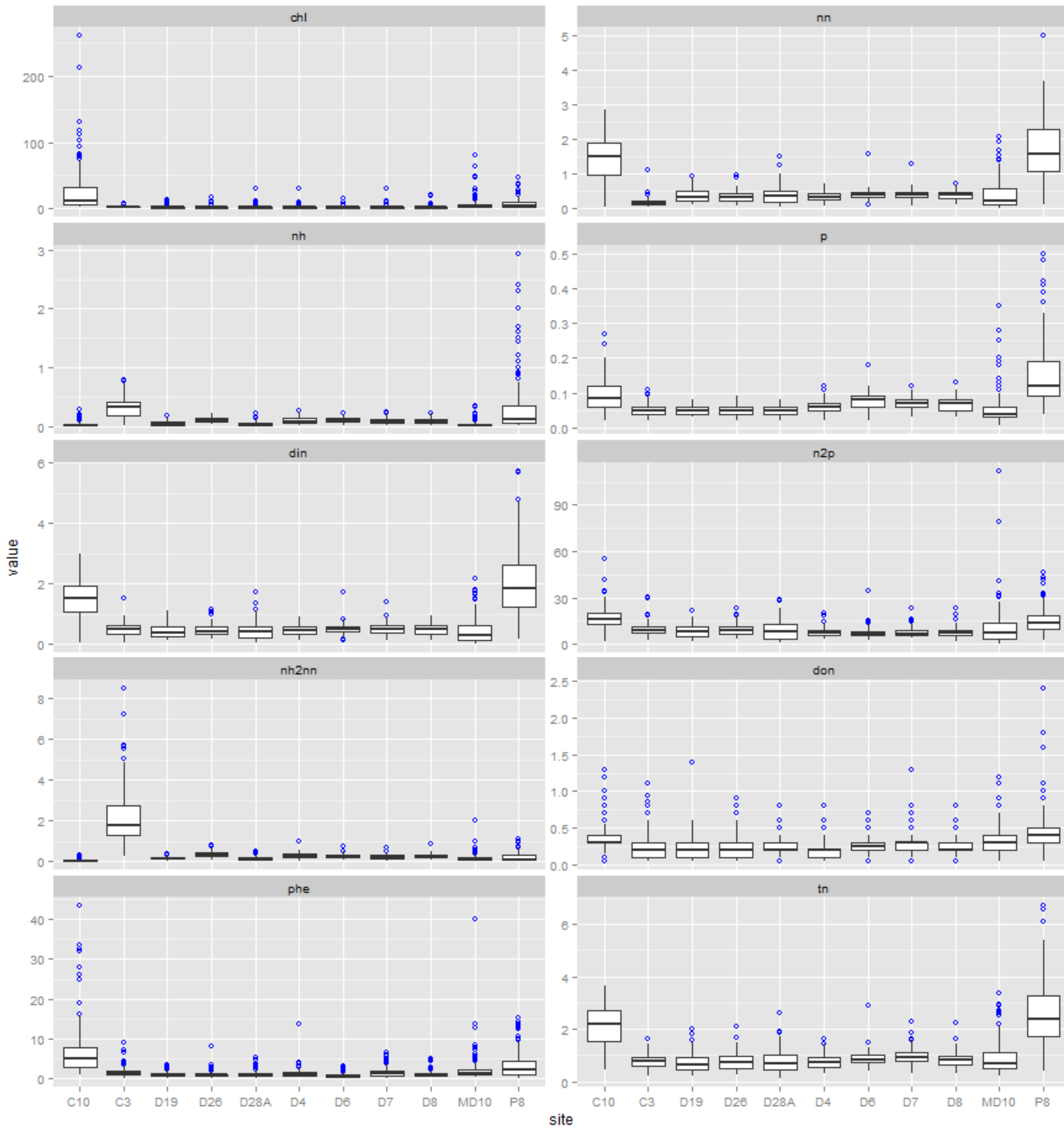


Figure 2.11 Distribution of concentrations (1998 – 2013) of DIN, NO3, NH4, TN, TP, PO4, chl-a, and N:P at IEP-EMP discrete sampling stations.

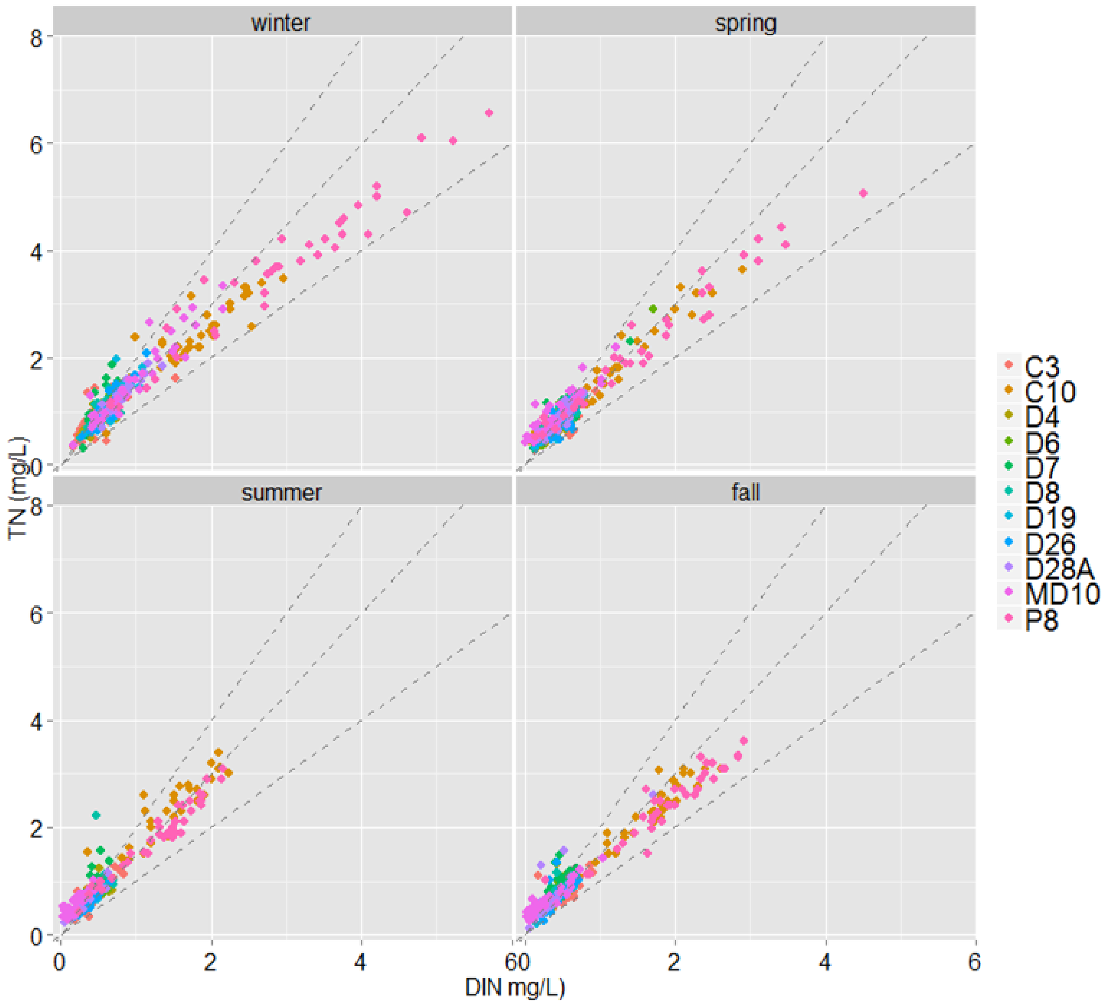


Figure 2.12 DIN (mg N/L) vs. TN (mg N/L), grouped by season and colored by stations.

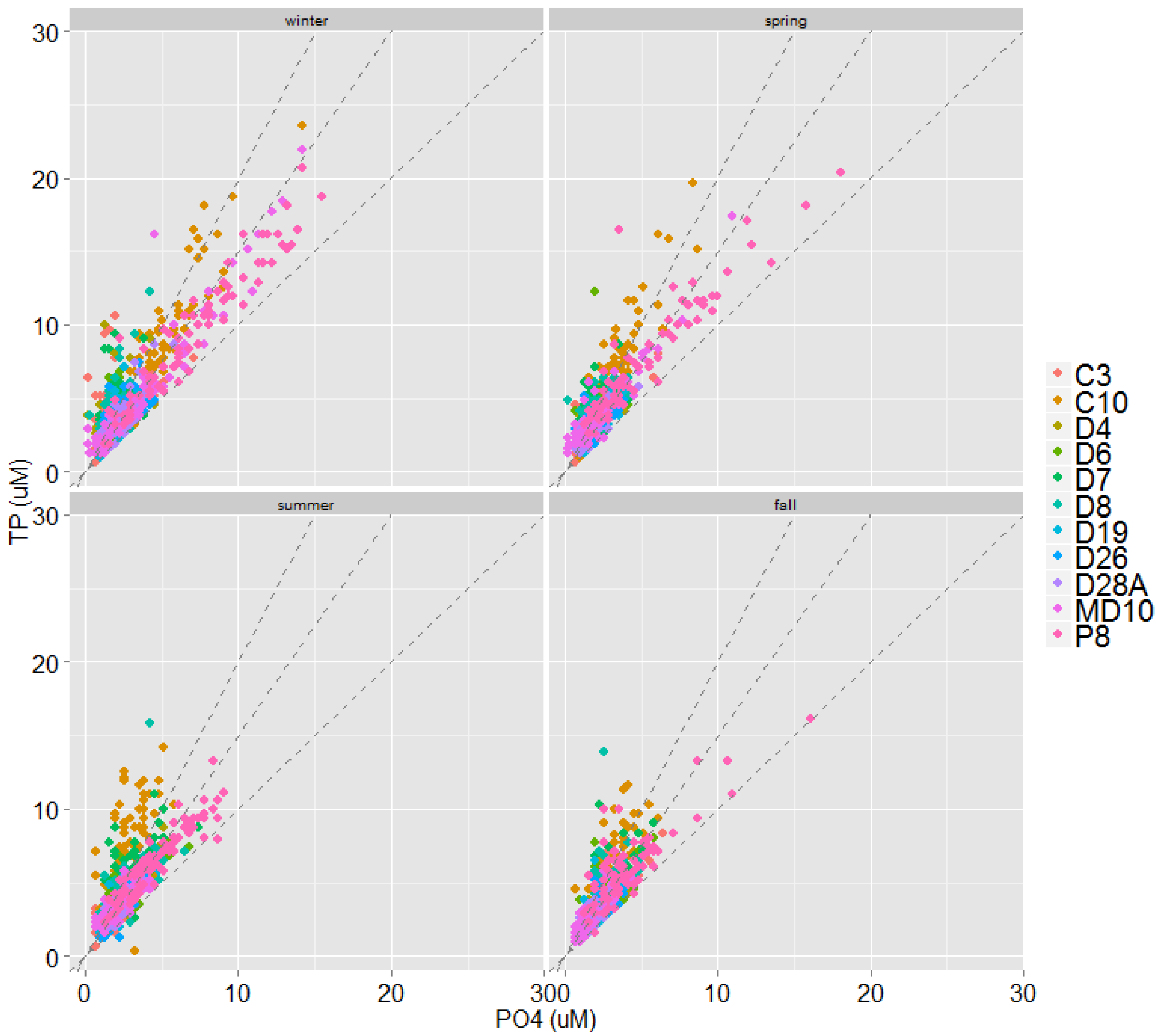


Figure 2.13 o-PO4 (uM) vs. TP (uM), grouped by season and colored by stations.

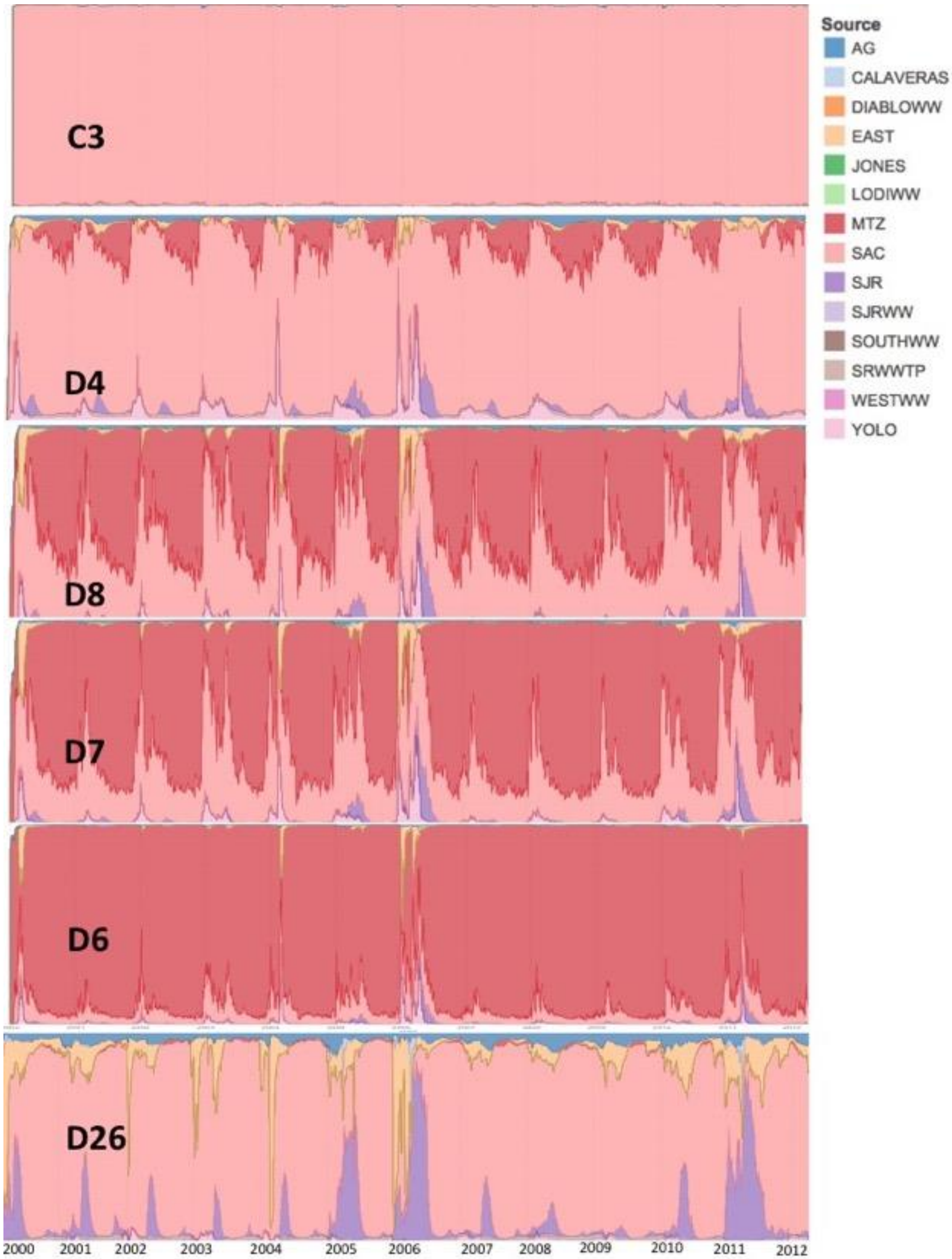


Figure 2.14 DSM2 volumetric fingerprints for Sacramento River and Suisun "mode" stations.

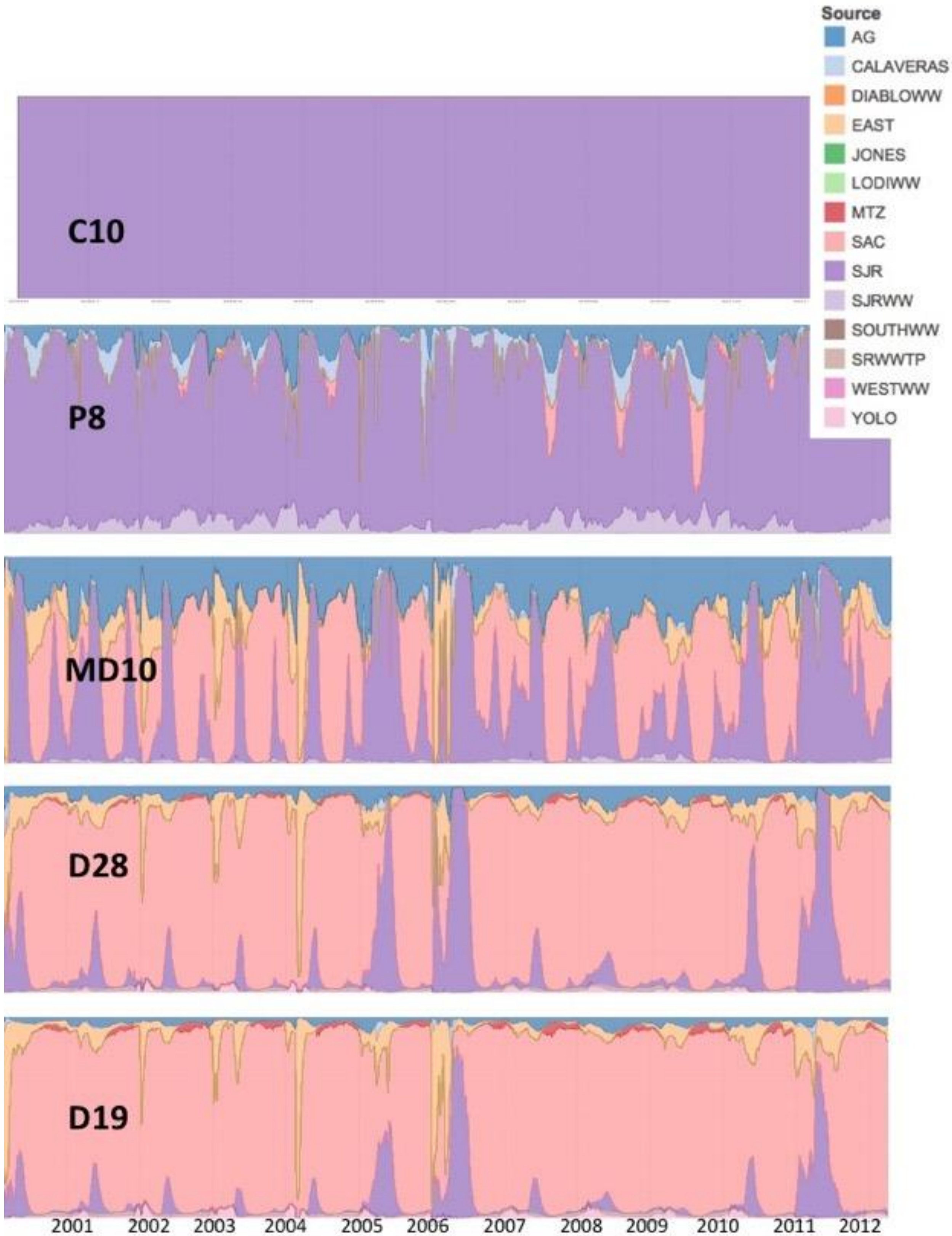


Figure 2.15 DSM2 volumetric fingerprints for San Joaquin River and Central Delta "mode" stations.

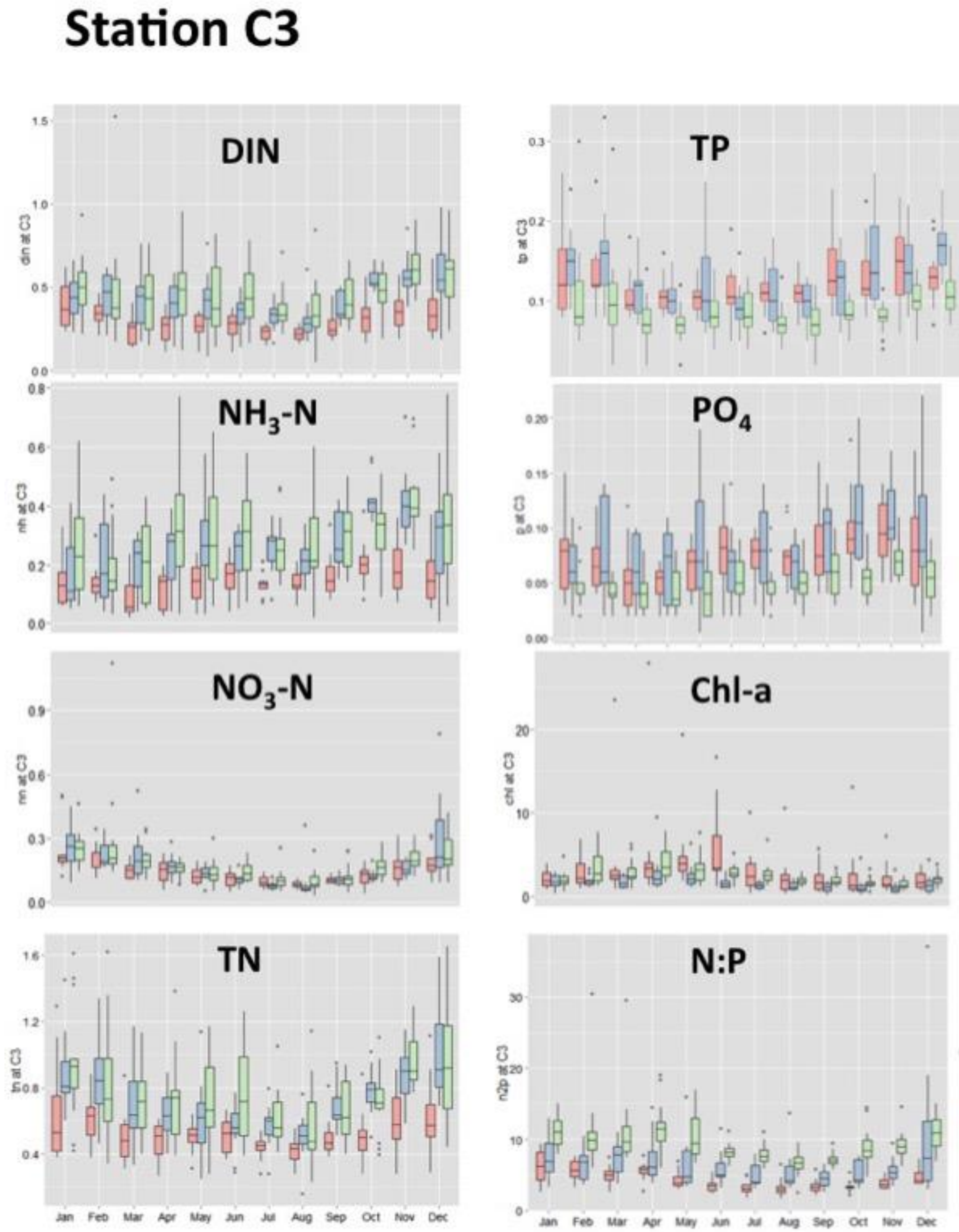


Figure 2.16 Seasonal and temporal variation in DIN, NH3-N, NO3-N, TN, TP, PO4, chl-a, and N:P at station C3 (Sacramento River at Hood).

Station C10

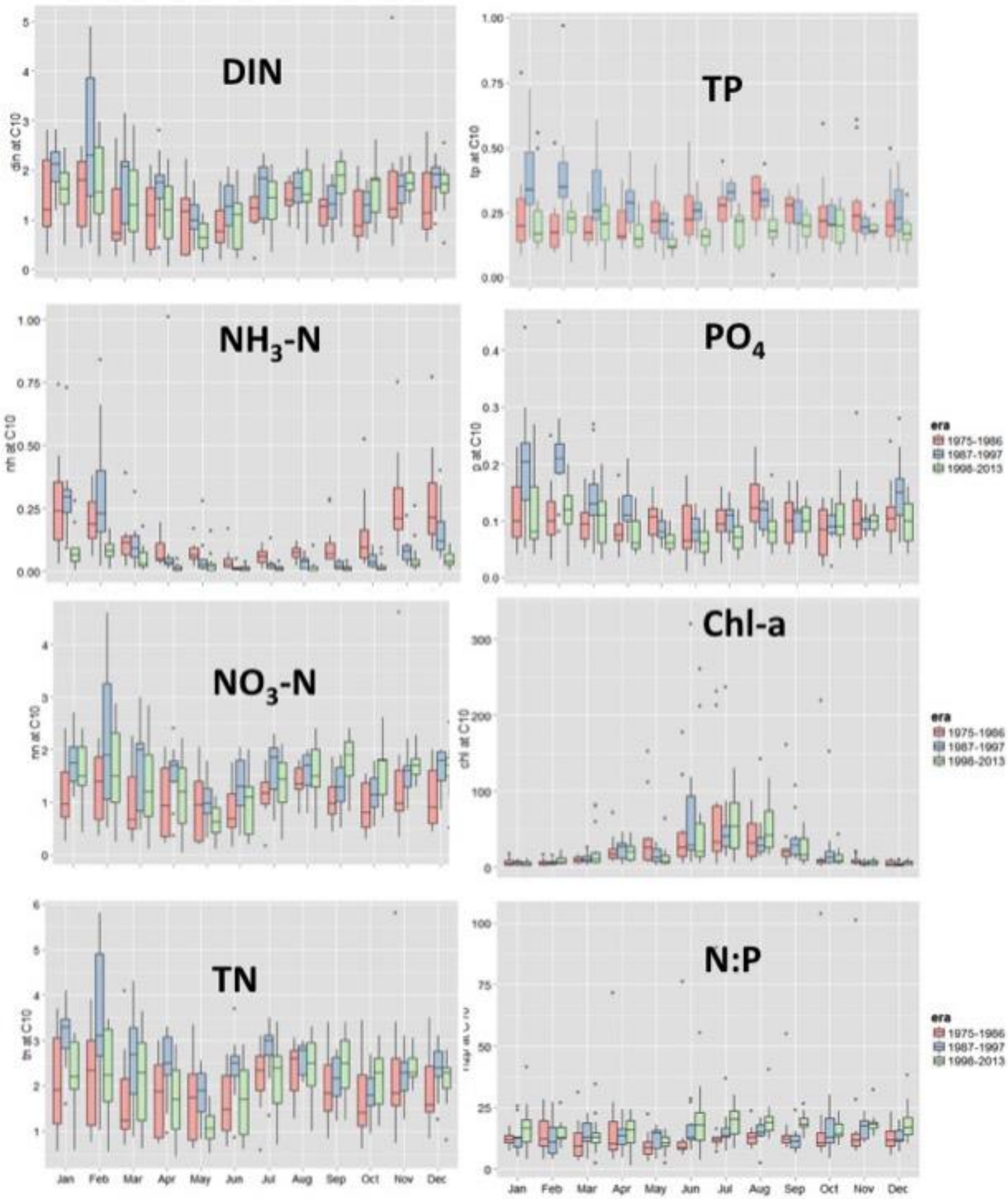


Figure 2.17 Seasonal and temporal variation in DIN, NH3-N, NO3-N, TN, TP, PO4, chl-a, and nitrogen:phosphorus (N:P) at Station C10 (San Joaquin River at Vernalis).

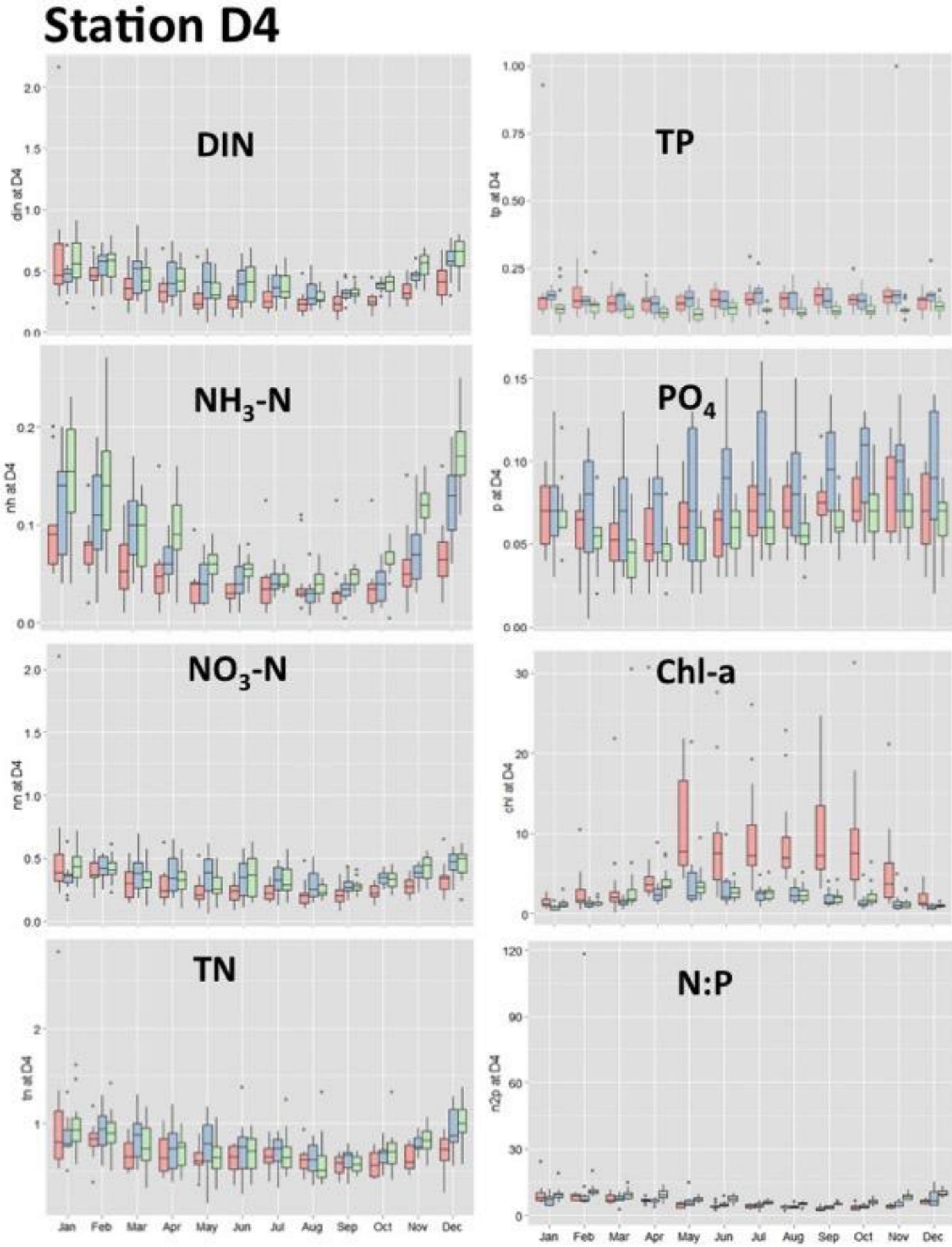


Figure 2.18 Seasonal and temporal variation in DIN, NH3-N, NO3-N, TN, TP, PO4, chl-a, and nitrogen:phosphorus (N:P) at Station D4 (Sacramento River above Point Sacramento).

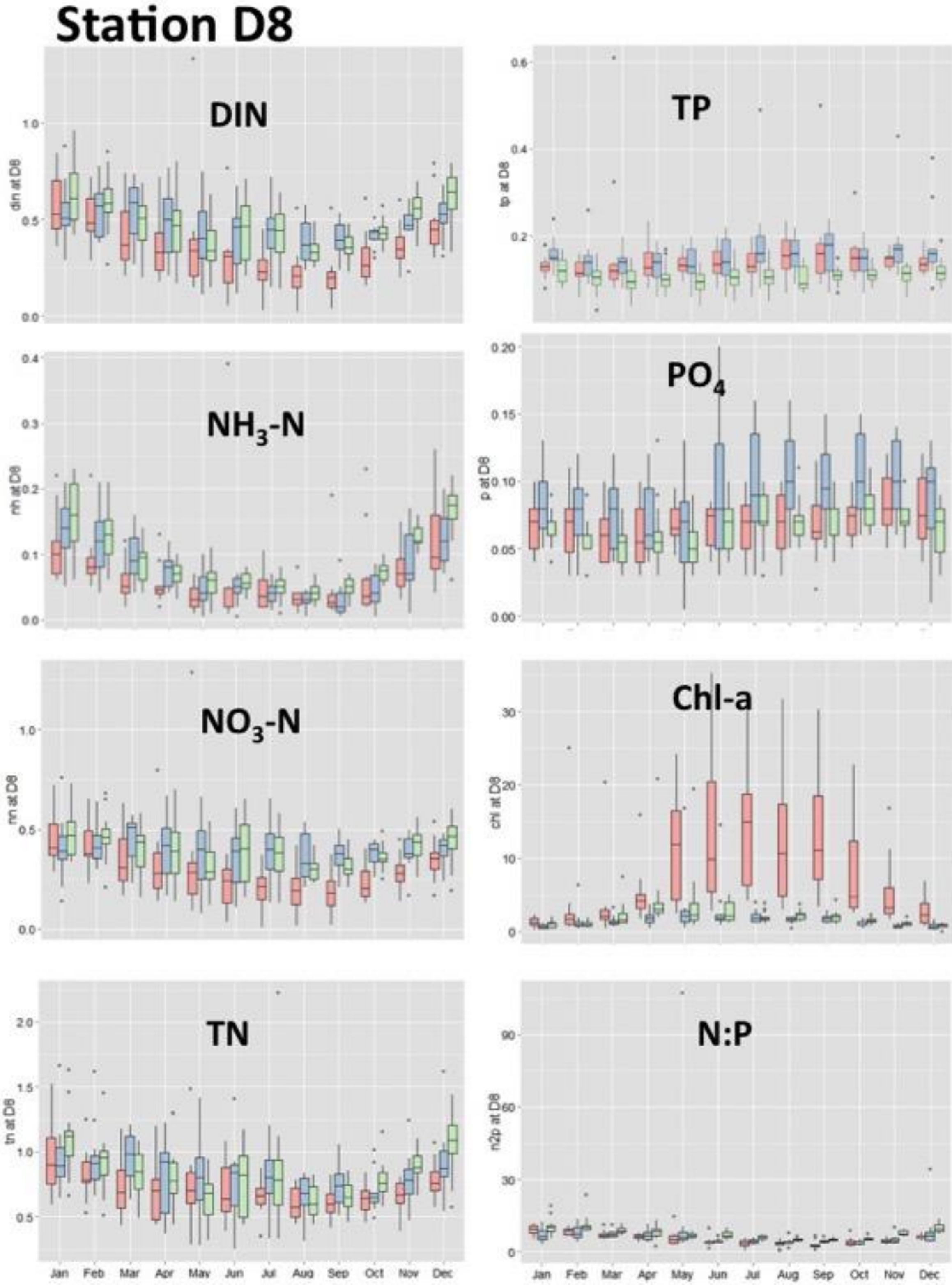


Figure 2.19 Seasonal and temporal variation in DIN, NH3-N, NO3-N, TN, TP, PO4, chl-a, and nitrogen:phosphorus (N:P) at Station D8 (Suisun Bay off Middle Point).

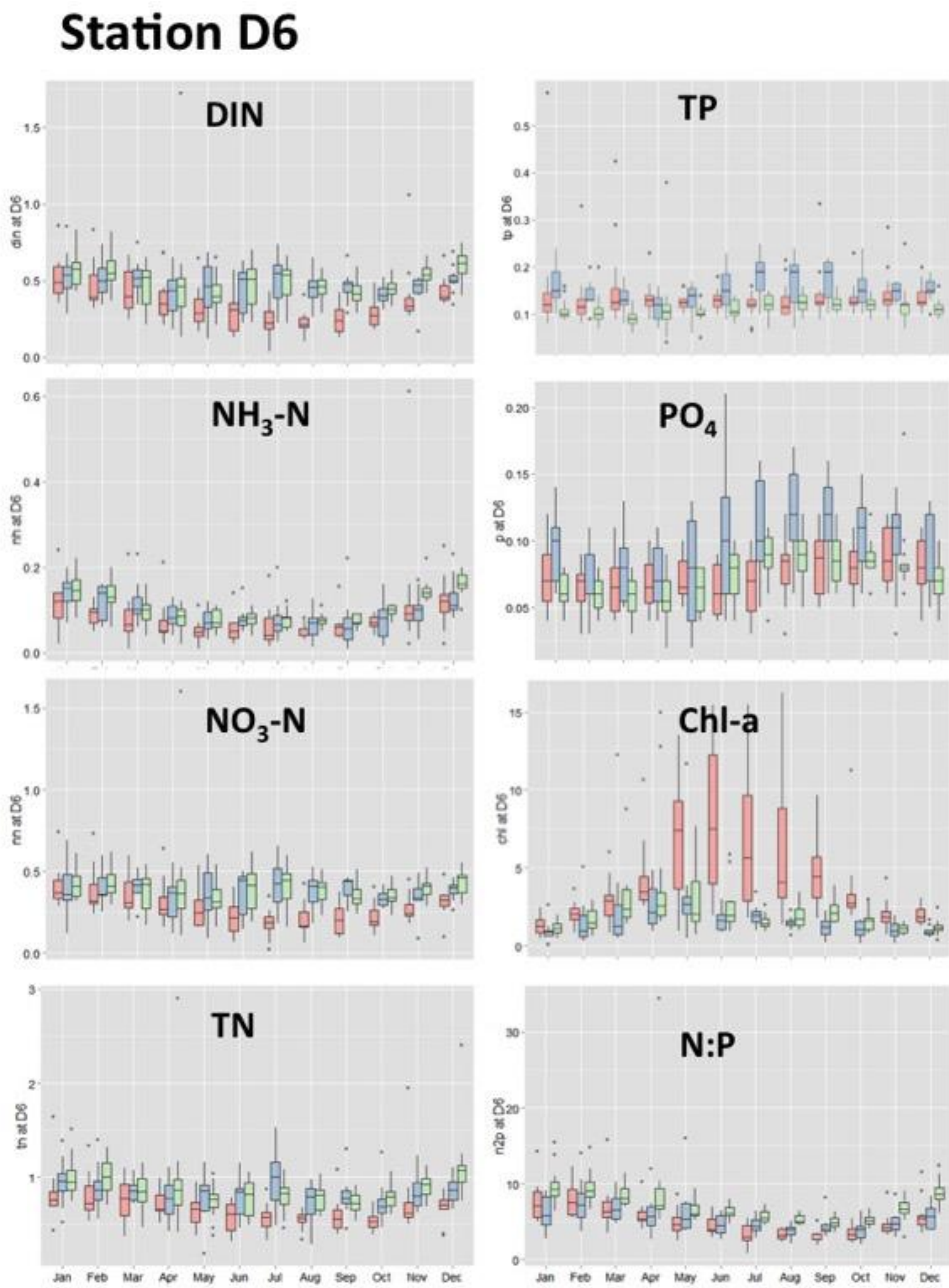


Figure 2.20 Seasonal and temporal variation in DIN, NH3-N, NO3-N, TN, TP, PO4, chl-a, and nitrogen:phosphorus (N:P) at Station D6 (Suisun Bay near Martinez).

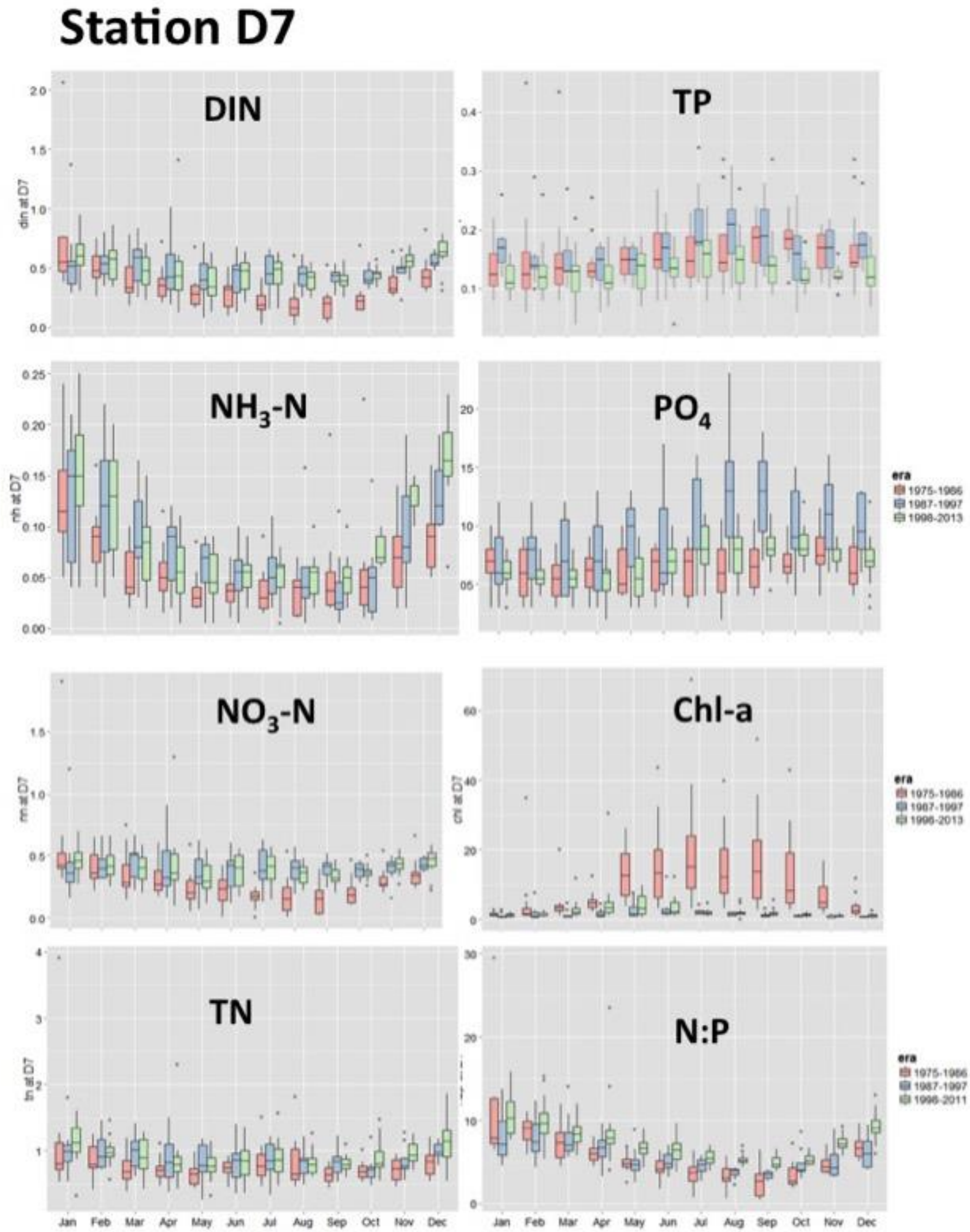


Figure 2.21 Seasonal and temporal variation in DIN, NH3-N, NO3-N, TN, TP, PO4, chl-a, and nitrogen:phosphorus (N:P) at Station D7 (Grizzly Bay).

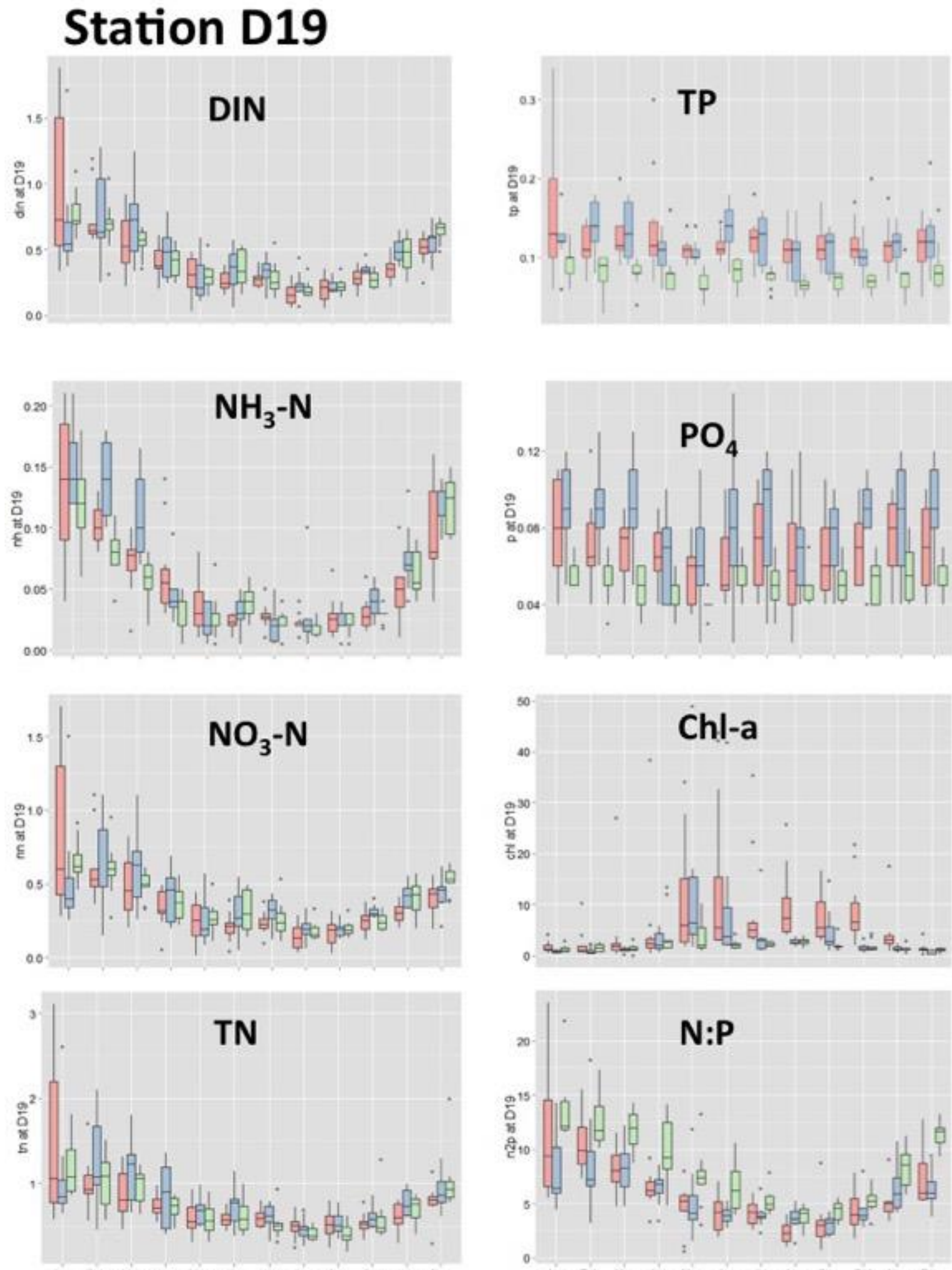


Figure 2.22 Seasonal and temporal variation in DIN, NH3-N, NO3-N, TN, TP, PO4, chl-a, and nitrogen:phosphorus (N:P) at Station D19 (Frank's Tract).

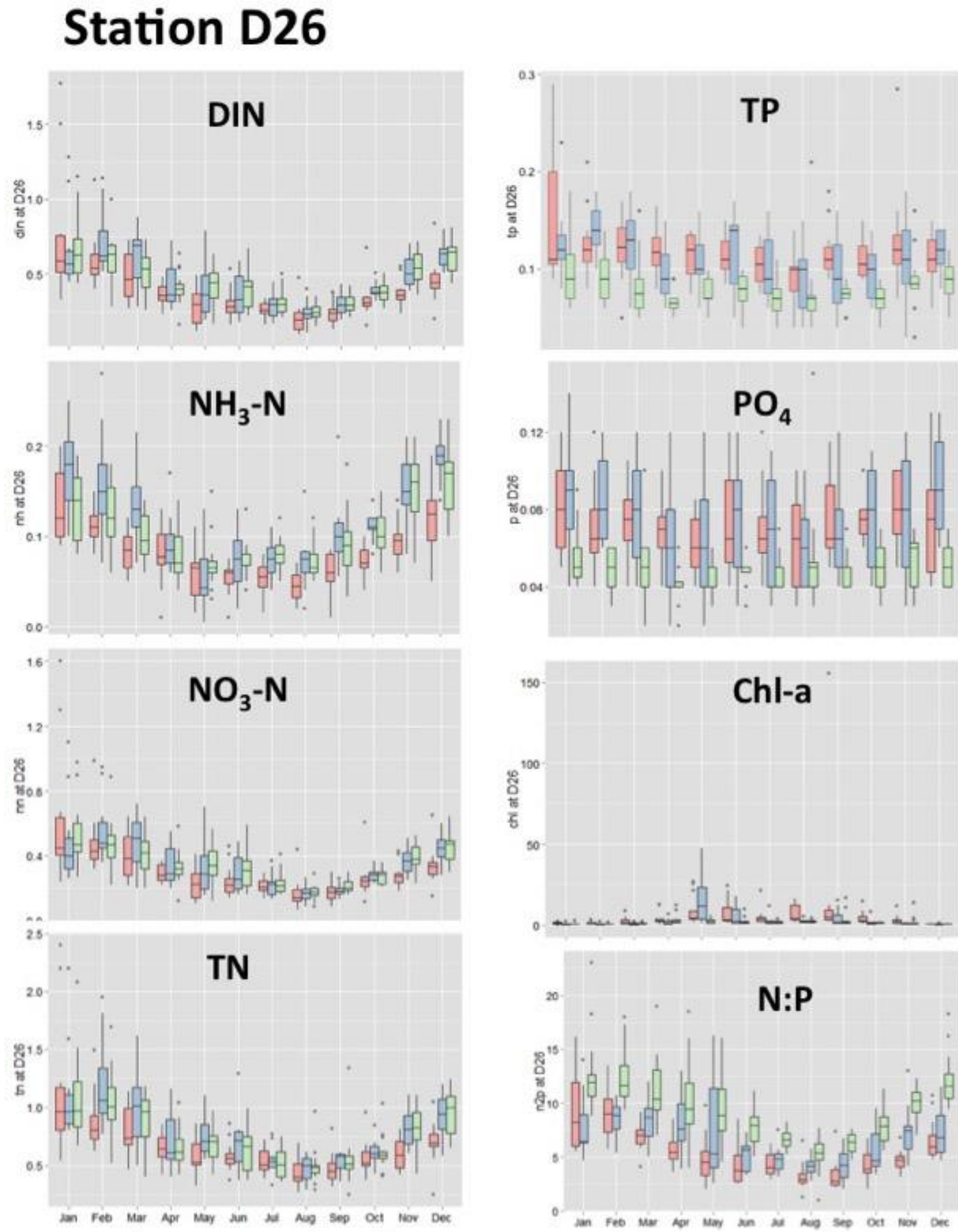


Figure 2.23 Seasonal and temporal variation in DIN, NH3-N, NO3-N, TN, TP, PO4, chl-a, and nitrogen:phosphorus (N:P) at Station D26 (San Joaquin River at Potato Point).

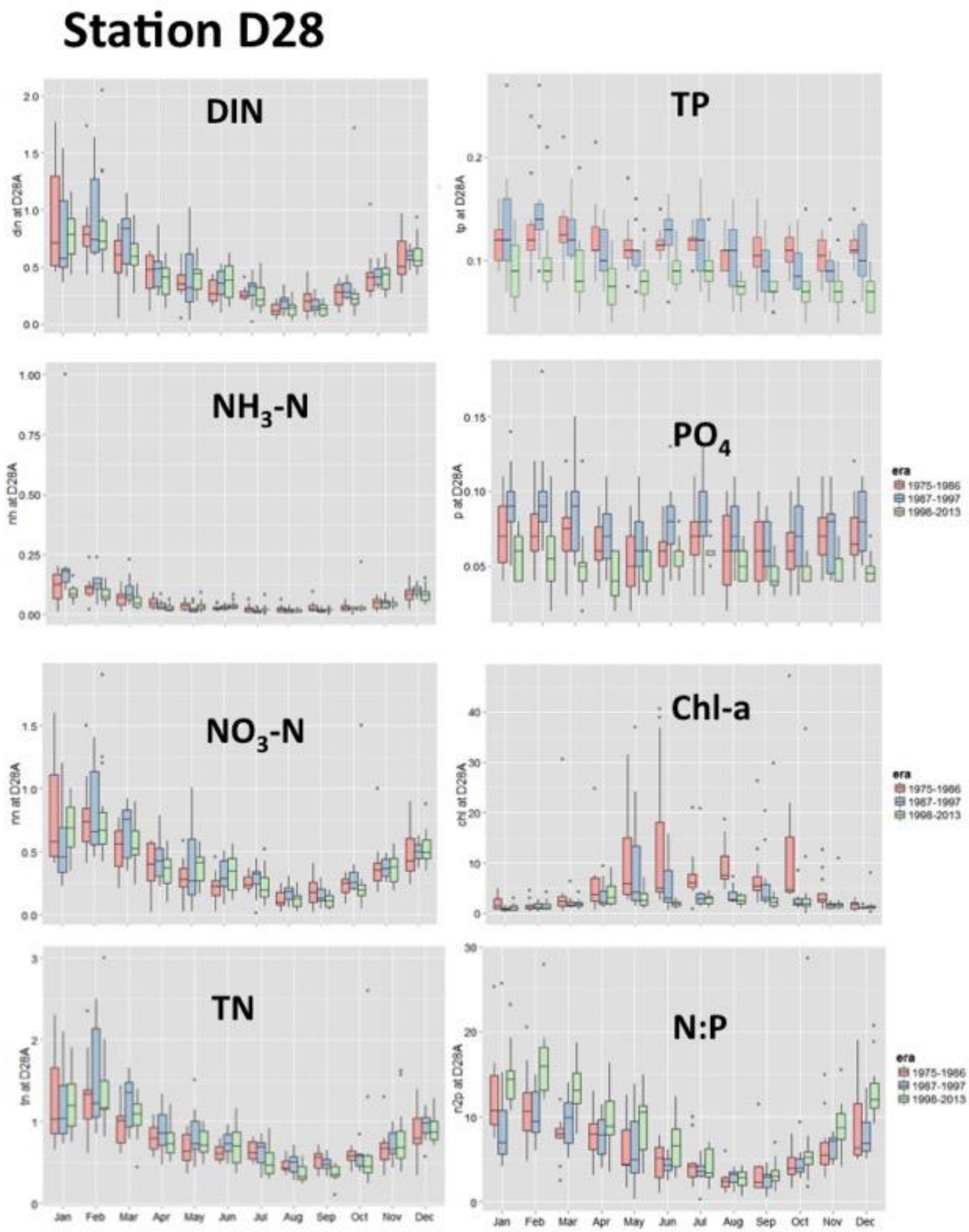


Figure 2.24 Seasonal and temporal variation in DIN, NH3-N, NO3-N, TN, TP, PO4, chl-a, and nitrogen:phosphorus (N:P) at Station D28 (Old River).

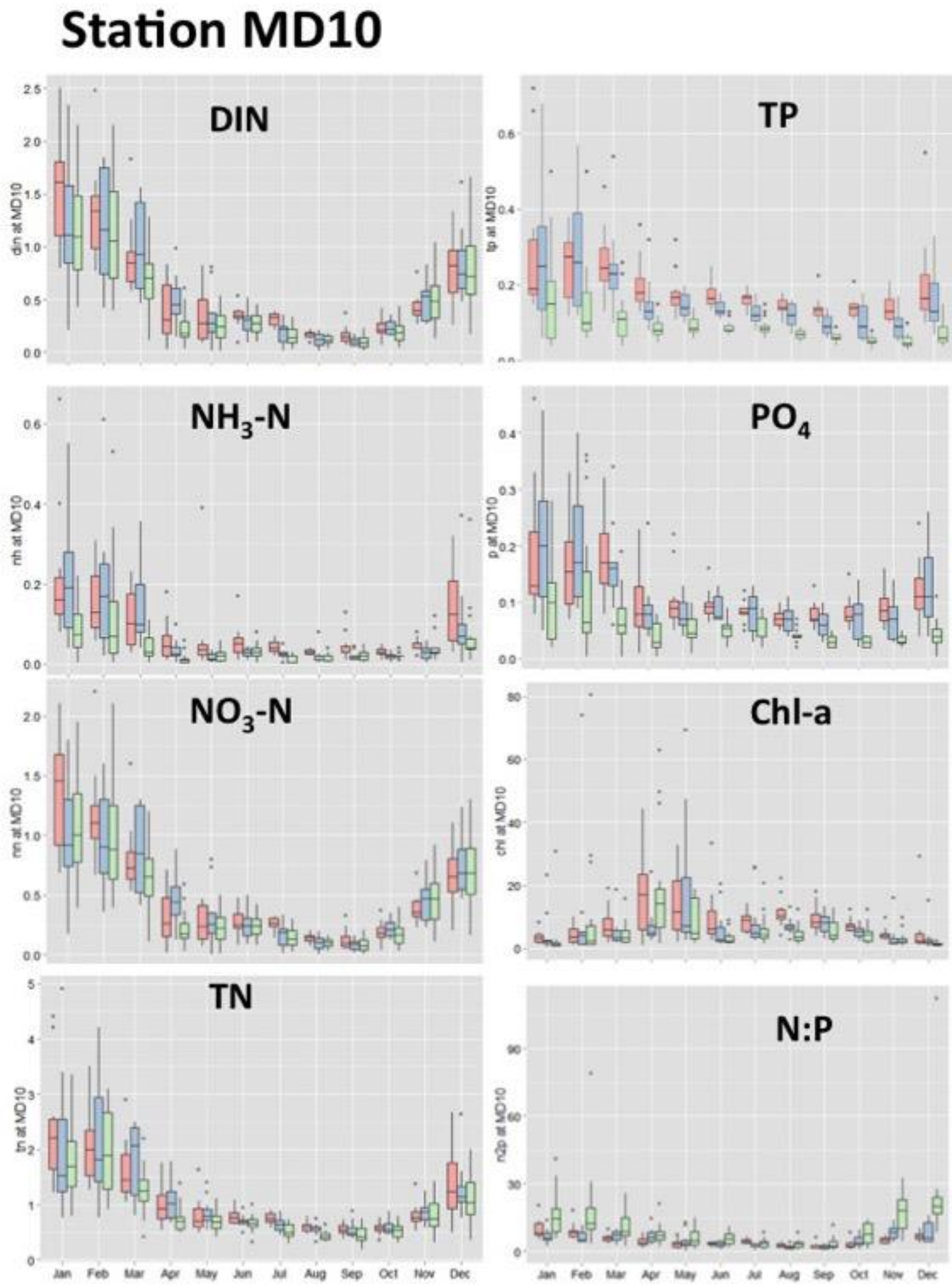


Figure 2.25 Seasonal and temporal variation in DIN, NH3-N, NO3-N, TN, TP, PO4, chl-a, and nitrogen:phosphorus (N:P) at Station MD10 (Disappointment Slough).

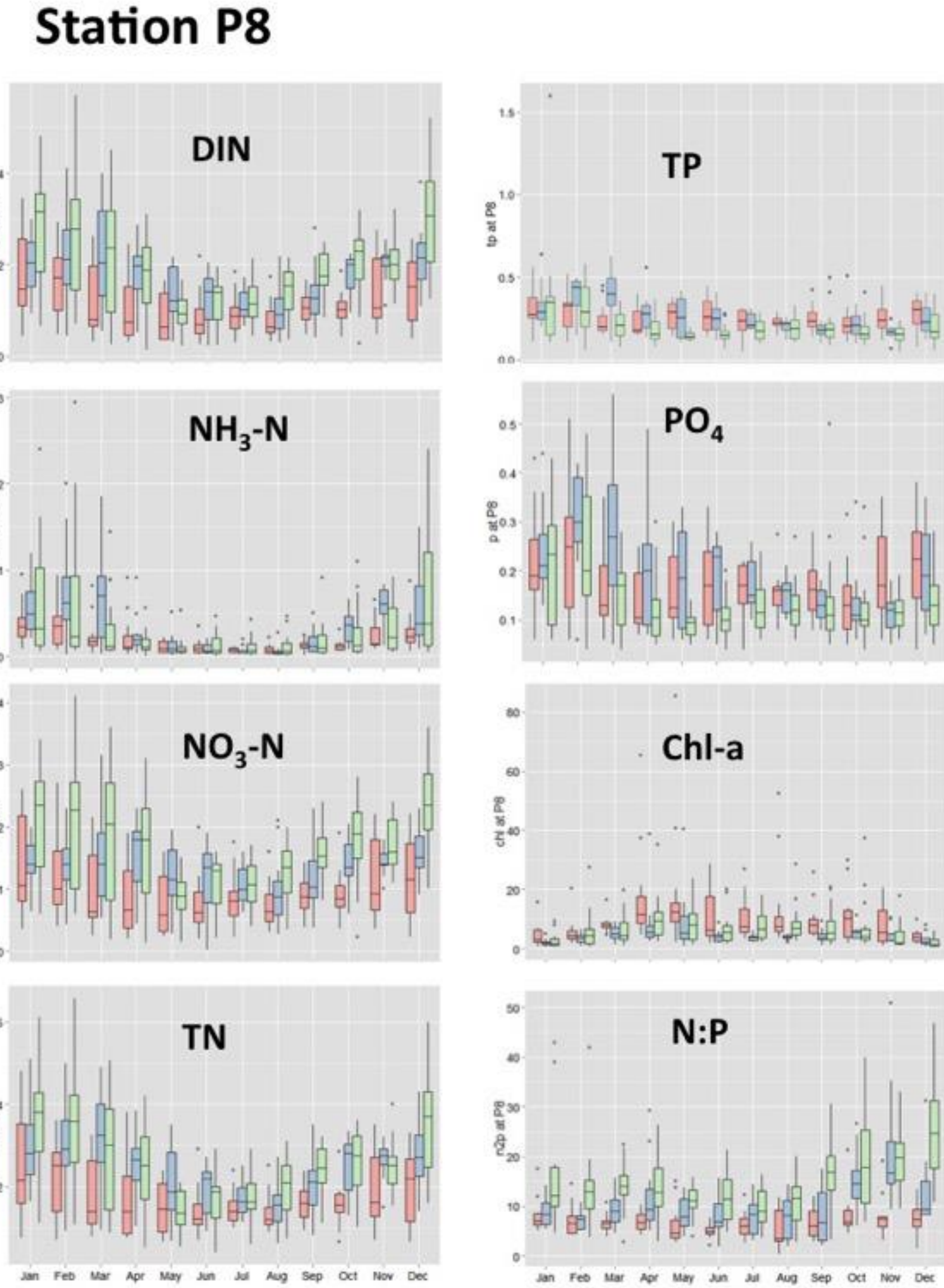


Figure 2.26 Seasonal and temporal variation in DIN, NH3-N, NO3-N, TN, TP, PO4, chl-a, and nitrogen:phosphorus (N:P) at Station P8 (San Joaquin River at Buckley Cove).

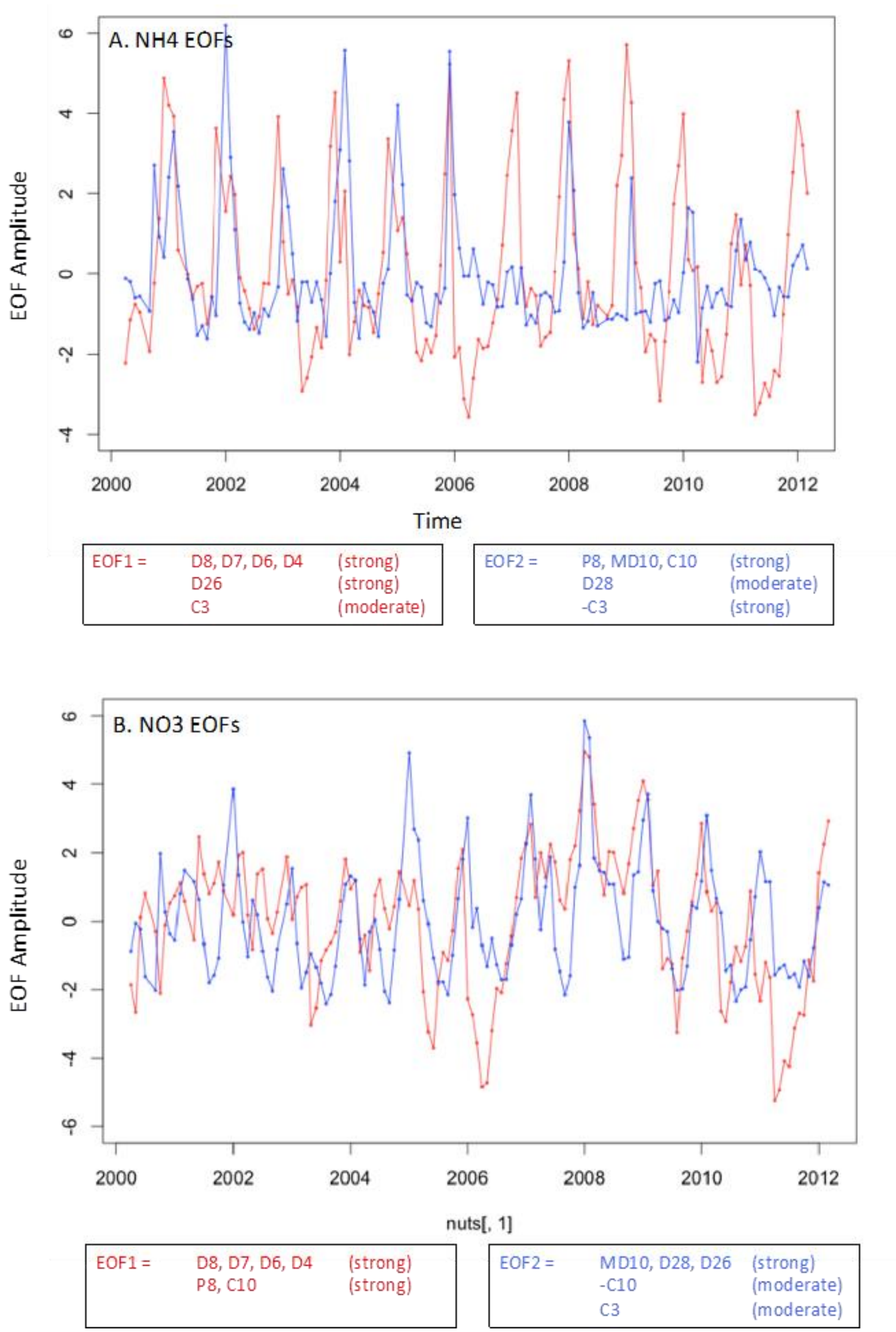


Figure 2.27 Results of empirical orthogonal function (EOF) analysis, by N species, for A. NH4 and B. NO3, for the period 2000-2011.

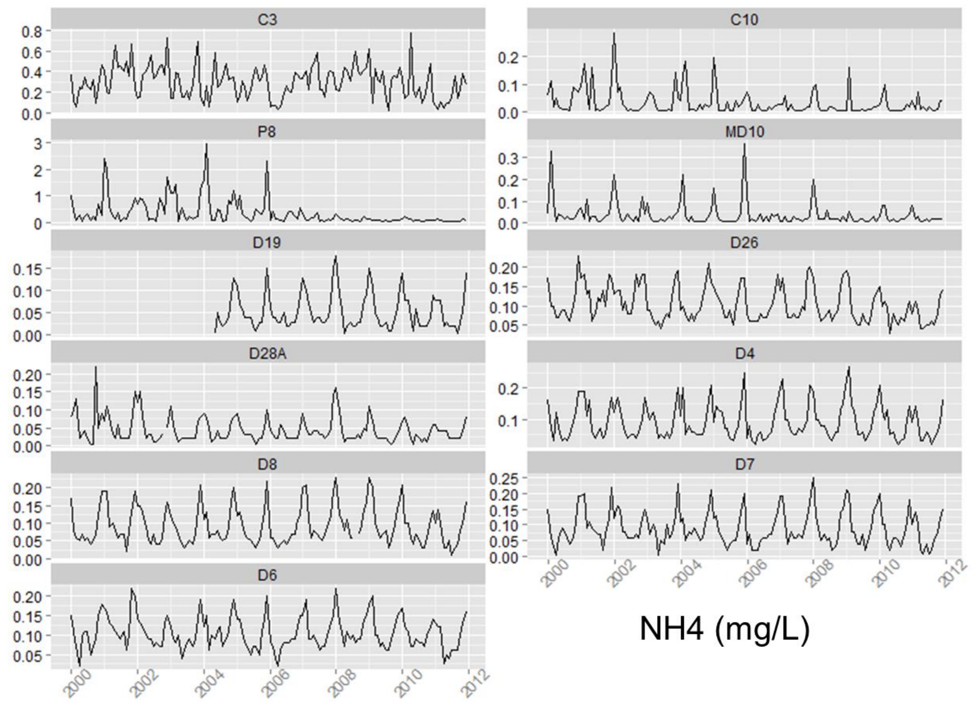


Figure 2.28 Time-series of NH4 (mg N/L) at select DWR-IEP water quality monitoring stations, 2000-2011. Note varying y-axis scales

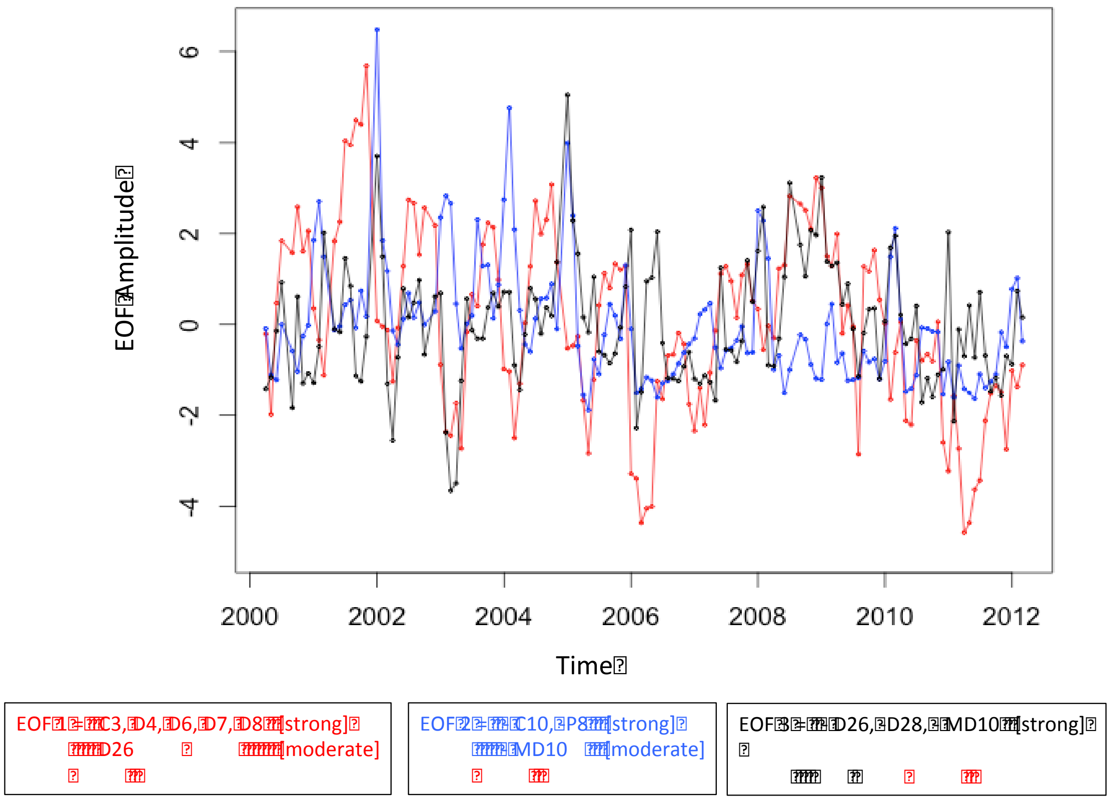


Figure 2.29 Results of EOF analysis for o-PO4, for the period 2000-2011.

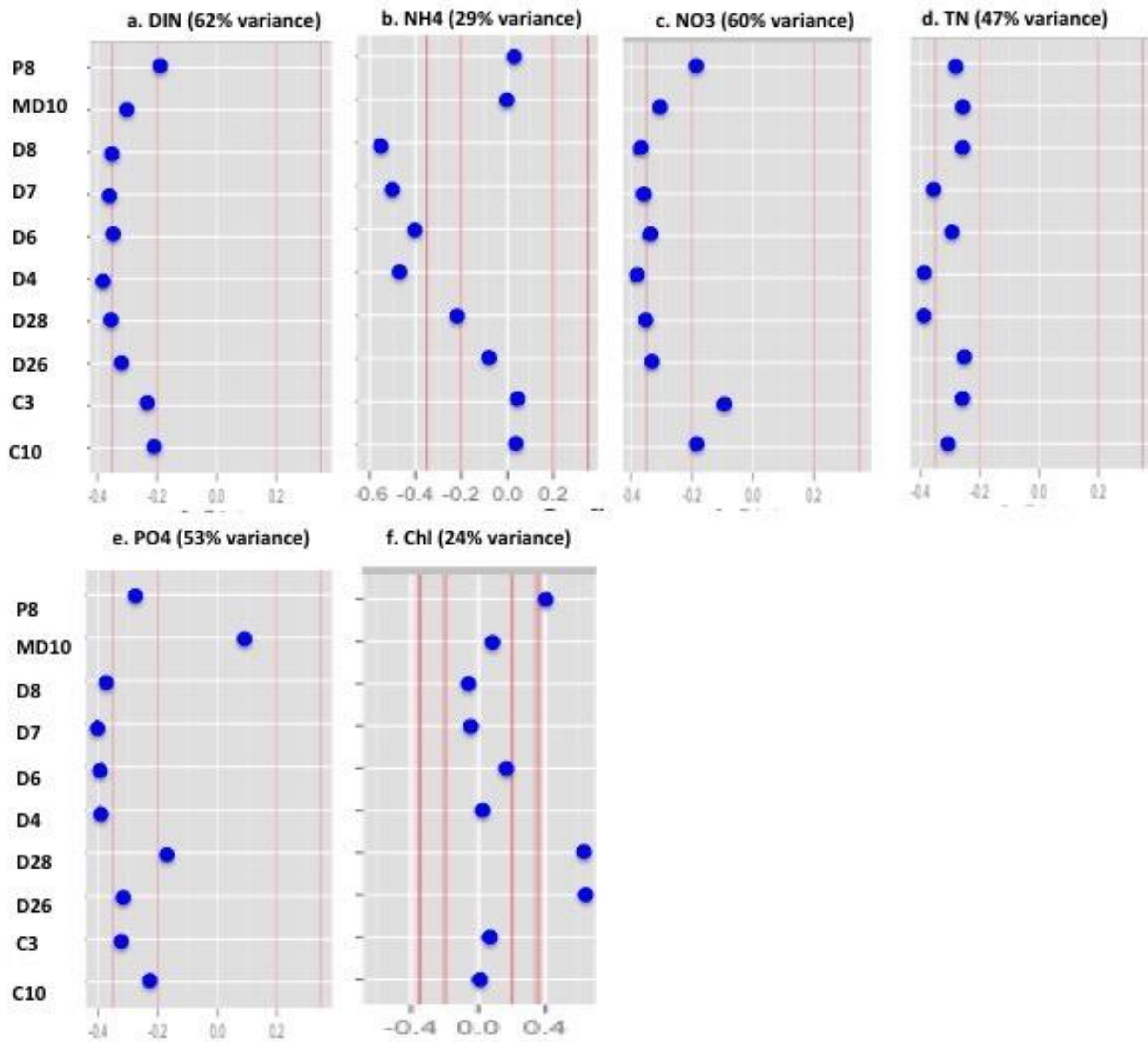


Figure 2.30 First modes of variability (EOF mode 1) for parameters (a) DIN, (b) NH4, (c) NO3, (d) TN, (e) PO4, and (c) chl-a. The amount of variance explained by EOF mode 1 for each parameter is indicated in parentheses. The x axis is a dimensionless coefficient. The coefficient is a measure for how much variance is explained by this mode of variability: higher coefficients suggest (either positive or negative) indicate greater explanatory power. Similar coefficients for a given parameter suggest a similar influence of this mode of variability across stations. For example, Figures a and d suggests that the influence of EOF1 is similar across all stations for DIN and TN.

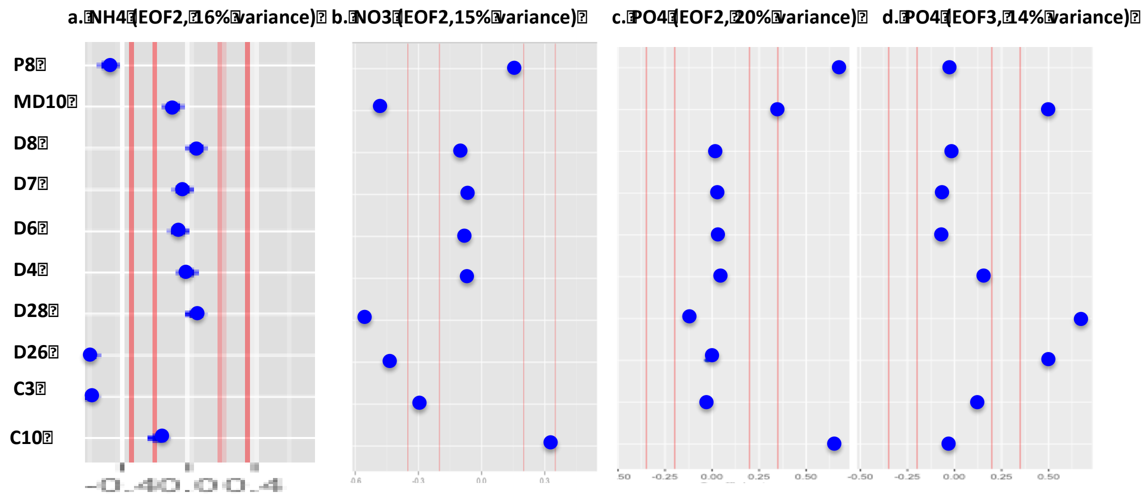


Figure 2.31 Spatial patterns of the second EOF modes for (a) NH4, (b) NO3, (c) o-PO4, and for the third EOF mode for o-PO4 (d).

Appendix 2-I Detailed results from Seasonal Kendall Tests.

1975-2013

Row Labels	chl	din	don	n2p	nh	nh2nn	nn	tp	phe	tn
C3	0.4	**1.7**	0.0	**2.8**	**2.1**	**1.0**	**0.7**	**-1.6**	-0.3	**1.2**
D4	**-2.0**	**1.0**	**-0.4**	**1.7**	**2.1**	**1.2**	**0.8**	**-0.9**	**-4.4**	0.2
D8	**-2.5**	**1.0**	0.0	**1.6**	**1.6**	0.4	**1.0**	**-0.4**	**-4.3**	**0.5**
D7	**-3.5**	**1.1**	0.0	**1.5**	**1.4**	0.0	**1.1**	-0.2	**-4.3**	**0.5**
D6	**-1.6**	**1.2**	**0.4**	**1.6**	**1.3**	-0.1	**1.2**	-0.4	**-3.5**	**1.0**
D19	**-2.1**	0.5	-0.4	**1.4**	0.1	-0.4	**0.6**	**-1.0**	**-3.0**	0.1
D28A	**-2.3**	-0.1	0.0	**1.2**	-0.5	-0.5	0.0	**-1.1**	**-3.3**	-0.2
MD10	**-1.9**	**-0.9**	-0.1	**1.7**	**-2.4**	**-1.5**	**-0.7**	**-2.4**	**-3.5**	**-0.7**
D26	**-1.5**	**0.7**	0.0	**2.1**	**0.8**	0.0	**0.7**	**-1.4**	**-2.7**	**0.5**
P8	**-1.7**	**1.4**	-0.4	**2.7**	-0.3	**-1.6**	**1.8**	**-1.2**	**-3.2**	**0.9**
C10	-0.3	0.2	0.0	**1.1**	**-5.7**	**-6.5**	0.5	**-0.9**	**-1.8**	-0.1

1987-2013

Row Labels	chl	din	don	n2p	nh	nh2nn	nn	tp	phe	tn
C3	**2.2**	**0.8**	-0.1	**2.4**	**0.7**	-0.7	**1.0**	**-2.3**	0.0	0.4
D4	0.4	0.4	**-0.8**	**1.8**	**1.3**	**1.2**	0.2	**-2.1**	**-2.7**	-0.2
D8	0.4	0.4	0.0	**1.7**	**1.1**	0.7	0.2	**-1.7**	**-3.2**	0.2
D7	**1.2**	0.3	-0.1	**1.6**	0.5	0.2	0.1	**-1.7**	**-2.1**	0.2
D6	1.0	**0.5**	0.0	**1.7**	0.6	0.0	0.4	**-1.6**	**-2.9**	0.3
D19	-0.2	-0.1	-0.5	**1.7**	-1.0	-1.1	-0.1	**-2.0**	**-2.1**	-0.4
D28A	**-1.7**	-0.8	-0.1	1.1	**-1.0**	-0.5	-0.8	**-1.9**	**-3.0**	**-0.8**
MD10	**-2.5**	**-1.3**	-0.2	1.8	**-1.5**	-0.8	**-1.3**	**-3.6**	**-5.4**	**-1.2**
D26	0.0	0.2	-0.5	**1.9**	-0.6	**-0.9**	0.5	**-2.2**	**-2.7**	0.0
P8	-1.1	0.1	**-1.5**	**2.0**	**-3.7**	**-4.3**	1.0	**-1.9**	**-3.5**	-0.4
C10	0.7	**-1.4**	-0.2	0.8	**-8.2**	**-4.3**	**-1.2**	**-2.2**	**-2.2**	**-1.4**

1998-2013

Row Labels	chl	din	don	n2p	nh	nh2nn	nn	tp	phe	tn
C3	0.6	-0.5	0.0	0.7	**-0.9**	**-2.8**	1.2	-0.9	**2.6**	-0.5
D4	0.9	-0.9	-0.7	0.3	**-1.7**	-0.5	-0.7	-1.2	-1.7	-1.0
D8	0.3	-0.5	0.1	0.7	-1.0	-0.5	-0.3	**-1.4**	**-3.8**	-0.7
D7	0.6	-0.4	-0.7	1.0	**-1.3**	-0.5	-0.2	**-1.3**	-2.2	-0.6
D6	0.9	0.1	-0.5	1.2	-0.6	-0.3	0.4	-0.8	**-2.3**	-0.2
D19	3.5	-3.5	-0.7	-2.5	-2.8	1.0	-3.5	-0.9	0.9	-2.3
D28A	**-3.7**	**-2.2**	-0.1	**-1.9**	**-1.7**	1.4	-2.4	0.0	-1.3	**-1.6**
MD10	**-2.8**	**-2.9**	0.3	**-5.4**	-2.2	1.5	**-2.8**	**3.2**	-1.8	**-1.6**
D26	-0.3	-0.9	-1.0	-0.7	**-2.3**	**-1.8**	-0.5	-0.3	**-1.7**	-0.4
P8	**-8.0**	**-2.2**	-1.1	-1.7	**-12.1**	**-11.1**	-0.7	-0.1	**-9.5**	**-2.1**
C10	1.7	**-3.3**	0.1	-0.9	-4.0	0.6	**-3.1**	**-2.9**	1.5	**-2.7**

Trends in %/yr.

Appendix 2-II. Detailed results for trend correlation among variables across stations from Kendall's tau-test.

Blue = significant positive correlation. Red = significant negative correlation

	1975-2013		1987-2013		1998-2013	
	Kendall τ	p-value	Kendall τ	p-value	Kendall τ	p-value
DIN vs NH	**0.455**	**0.052**	**0.709**	**0.002**	**0.673**	**0.004**
DIN vs NN	**0.782**	**0.001**	**0.600**	**0.010**	**0.782**	**0.001**
DIN vs TN	**0.917**	**0.000**	**0.818**	**0.000**	**0.673**	**0.004**
DIN vs. PO4	0.236	0.312	0.220	0.349	-0.200	0.392
DIN vs Chl	0.091	0.697	**0.564**	**0.016**	0.018	0.938
PO4 vs Chl	-0.382	0.102	0.110	0.639	**-0.455**	**0.052**
NH4 vs NN	0.309	0.186	0.309	0.186	0.600	0.010
Chl vs Phe	0.564	0.016	0.527	0.024	0.345	0.139
TN vs. DON	0.330	0.160	0.309	0.186	-0.055	0.815
NH vs Chl	-0.091	0.697	0.345	0.139	-0.055	0.815
NN vs Chl	-0.127	0.586	0.309	0.186	0.127	0.586