# Technical Review of Information Related to Development of Revised Nutrient Criteria for Colorado Lakes

Prepared for:

Colorado Wastewater Utility Council

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**Summary**

The Water Quality Control Division (WQCD) established a technical advisory committee (TAC) in 2019 to support revision of nutrient criteria for Colorado lakes, and Tetra Tech was contracted by the US Environmental Protection Agency (EPA) to provide technical support for the WQCD and the TAC. The N-STEPS Colorado Lakes Final Technical Report proposes revised criteria for total phosphorus (TP) and total nitrogen (TN) for Colorado lakes, to be considered by the Water Quality Control Commission at the November 2022 Rulemaking Hearing. The purpose of this report is to provide 1) background information about nutrients and algal growth in lakes, 2) a technical review of the Tetra Tech report, and 3) recommendations for development and implementation of nutrient criteria for Colorado lakes.

Suspended algae (phytoplankton) are an important source of nutrition for higher trophic levels, but high biomass of phytoplankton can contribute to water-quality problems that interfere with beneficial uses. Temperature, water-residence time, and light all affect the growth of algae in lakes, but measures to control algal growth often have been focused on control of TP, TN, or both. Generally, control of TP is the most effective and economical means to control algal biomass in lakes.

CDPHE provided Tetra Tech with water-quality data for almost 200 Colorado lakes. The data set, which reflects sampling and field measurements by local, state, tribal, and federal organizations, includes information about chlorophyll a (an indicator of algal biomass), TP, TN, and other water-quality variables. The data set was partitioned according to Aquatic Life Use (Warm, Cold), and the proposed criteria (Table A) were determined from relationships between seasonal-average values for chlorophyll a, TP, and TN.

Table A. Criteria for chlorophyll a, total phosphorus, and total nitrogen.

| | Criteria, µg/L | | |
|---|---|---|---|
| Aquatic life use | Chlorophyll a=* | Total phosphorus** | Total nitrogen** |
| Cold lakes | 8 | 20*** | 330 |
| Warm lakes | 20 | 36 | 600 |

* adopted 2012; 5 µg/L for direct-use water supplies ** proposed
*** Observed to expected ratio for Secchi transparency as covariate

Review of the data set identified various types of errors, including errors that could bias the results of analyses leading to the proposed criteria for TP and TN. Decisions about data handling (e.g., minimum sample requirements for seasonal-mean values) also impaired the analyses leading to the proposed criteria. Because criteria for TP and TN were developed separately, attainment of standards for both TP and TN would be redundant (i.e., control of chlorophyll a could be achieved through control of either TP or TN).

Errors in the data set and decisions about data handling (e.g., minimum sample size) should be addressed before the criteria for TP and TN are finalized. If such concerns cannot be addressed before the November Rulemaking Hearing, postponement of the hearing may be appropriate. Also, important questions about implementation of criteria for TP and TN should be resolved before the criteria are implemented.

## Introduction

Following the March 2012 Rulemaking Hearing, the Water Quality Control Commission (WQCC) adopted interim numeric standards for chlorophyll a, total phosphorus (TP), and total nitrogen (TN). The interim values were adopted for Colorado lakes (including reservoirs) larger than 25 acres, with the expectation that standards for smaller lakes would be developed later. The US Environmental Protection Agency (EPA) approved the interim standards that were adopted in 2012. However, in a July 2016 letter to the WQCC, the EPA indicated that that the interim standards for TP and TN might not be sufficiently protective for all Colorado lakes. Algal growth in lakes is affected by site-specific factors other than nutrients, and the EPA raised concerns that the Water Quality Control Division (WQCD) did not consider the role that such factors can play in limiting algal growth. In its 2016 letter, the EPA listed non-algal turbidity and TN:TP ratios as site-specific factors that could be considered as a means to adjust the numeric values for nutrients. The EPA also noted that the responses of algal growth to nutrients differ between cold and warm lakes. The EPA concluded that the WQCD did not provide adequate justification for the 2012 interim nutrient standards. Also, the EPA made recommendations for revisions that were intended to ensure that nutrient standards adopted by the WQCC would be protective of all Colorado lakes.

The WQCD established a technical advisory committee (TAC) in 2019 to support revision of nutrient criteria for Colorado lakes, and Tetra Tech was contracted by the EPA to provide technical support for the WQCD and the TAC. A draft report on Tetra Tech's work related to revision of the 2012 nutrient criteria was completed on April 29, 2022. The final version of the report (N-STEPS Colorado Lakes Final Technical Report) was completed on July 20, 2022. The Tetra Tech Final Technical Report describes the process through which proposed criteria for TP and TN were developed. The chlorophyll-a values that are being used as targets for development of revised nutrient criteria have remained unchanged and are the same values that were adopted in 2012 (i.e., 5 μg/L for direct-use water supplies, 8 μg/L for other cold lakes, and 20 μg/L for other warm lakes).

A new rulemaking hearing of the WQCC is scheduled for November 2022, and the WQCD Proponent's Prehearing Statement (PPHS) was released on August 4, 2022. In the PPHS, the WQCD proposes revisions to the interim nutrient criteria for Colorado lakes. The final version of the Tetra Tech report, which is the basis for the proposed revisions, is included as Exhibit O of the PPHS. The purpose of this report is to provide 1) background information about nutrients and algal growth in lakes, 2) a technical review of the final Tetra Tech report, and 3) recommendations for development and implementation of nutrient criteria for Colorado lakes. Ultimately, the purpose of this report is to support the Colorado Wastewater Utility Council (CWWUC) in decisions about its participation in the November 2022 Rulemaking Hearing.

**Background information about nutrients and algal growth in lakes**

Suspended algae (phytoplankton) are an important source of nutrition for higher trophic levels, and fish production in lakes is correlated with biomass and production of phytoplankton (e.g., Downing and Plante 1993). However, high biomass of phytoplankton (often measured as chlorophyll a) can contribute to water-quality problems that interfere with beneficial uses. Loss of oxygen from bottom water is common in highly productive lakes, and some groups of phytoplankton produce harmful toxins (Carmichael 1992, O'Neil et al. 2012). Also, phytoplankton growth can cause taste and odor problems and can contribute to the formation of harmful disinfection byproducts in municipal water supplies (e.g., Watson et al. 2008, Khan et al. 2021).

Growth of phytoplankton requires carbon, nitrogen, phosphorus, and other elements that form the building blocks of algal biomass. Alfred Redfield recognized that marine plankton communities have relatively constant N:P ratios (Redfield 1934), although N:P ratios of phytoplankton cells vary somewhat from the nominal Redfield ratio of 16:1 (molar ratio; Smith 1982, Falkowski 2000). As algal cells grow, dissolved, bio-available forms of P and N are incorporated into biomass. Algal growth can continue as long as dissolved, bio-available forms of P and N are present and other factors do not limit growth. Ultimately, the maximum biomass of algae in a lake is limited by the total amounts of P and N that are available for assimilation, but biomass may not reach the potential maximum set by nutrient requirements if other factors limit growth.

In lakes where availability of P or N limits growth, phytoplankton biomass (chlorophyll a) may be strongly correlated with the concentration of the limiting nutrient (e.g., Dillon and Rigler 1974). In addition to P and N, many other factors can limit the growth of algae in lakes. For example, growth can be limited by the supply of any required element (e.g., silica for diatoms). Light availability also can limit algal growth, and the upper bounds on algal biomass in nutrient-rich lakes are determined by light availability (Krause-Jensen and Sand-Jensen 1998). In addition to self-shading by algal cells, non-algal particles and humic substances reduce light available to support phytoplankton growth. Temperature controls rates of biological processes, and even where nutrients are abundant, growth rates of algae are suppressed at low temperatures. Water temperature also affects vertical mixing, which affects the light environment of phytoplankton, nutrient availability, and the seasonal succession of phytoplankton communities (e.g., shifts in dominance from diatoms to cyanobacteria). Response of algal growth to nutrients can be suppressed in lakes with short residence time (e.g., Dillon 1975), and residence time is an important factor controlling phytoplankton growth in many Colorado lakes. Finally, depth and other morphometric features of lakes can affect phytoplankton growth (Sakamoto 1966, Fee 1979; Figure 1).

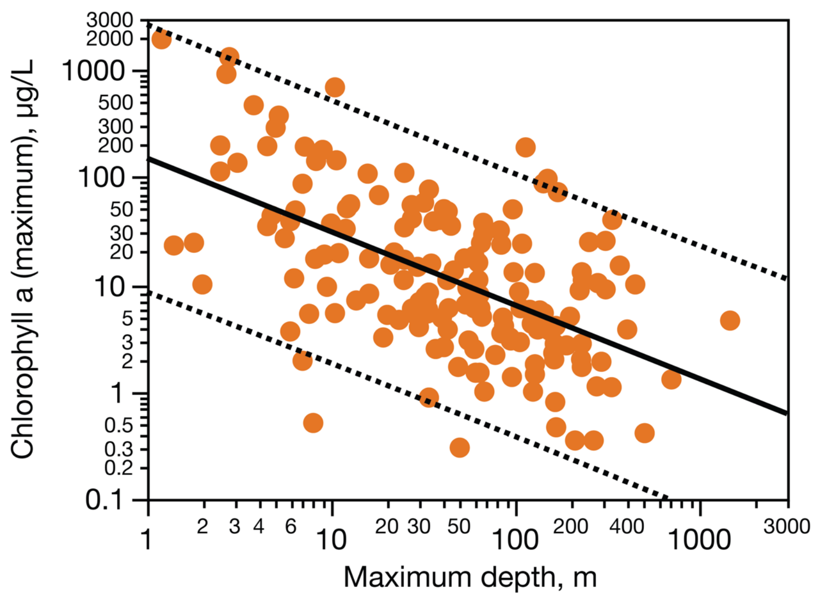


Figure 1. Relationship between maximum phytoplankton biomass, as chlorophyll a, and lake depth. Data are from the World Lake Database of the International Lake Environment Committee Foundation (ILEC) and J. McCutchan (unpublished data).

For lakes generally, temperature, water-residence time, and light availability all play important roles in the control of algal growth. For individual lakes, however, it may not be feasible to control such factors in order to control algal growth. Therefore, measures to control phytoplankton growth often have been focused on control of TP or TN, or both. Diversion of sewage from Lake Washington demonstrated the potential for phosphorus control as a means to control phytoplankton growth in lakes (Edmondson 1970), and reduction of P loading is accompanied by reduction of algal biomass in most lakes (e.g., Smith and Shapiro 1981). Generally, control of P has been the most effective and economical means to control phytoplankton growth in lakes (e.g., Fee 1979, Smith 1982).

Although control of phosphorus has been effective in controlling algae, many efforts to control algal biomass have involved dual control (i.e., control of both N and P). Phytoplankton growth responds positively to additions of N + P in many lakes, and algal growth in downstream ecosystems may be limited by N (e.g., Paerl et al. 2016). For many point sources of nutrients, the molar N:P ratio is less than the 16:1 Redfield ratio. Thus, the N:P ratio tends to be lower in eutrophic (nutrient-rich) lakes than in oligotrophic (nutrient-poor) lakes (Figure 2). Where the N:P ratio is low, including many nutrient-rich lakes, addition of nitrogen may stimulate algal growth. Modest reduction of P in lakes with low N:P ratios may not be accompanied by reductions in algal biomass, especially if P is high prior to initiation of phosphorus control (e.g., Cherry Creek Reservoir; Lewis et al. 2008). However, emphasis on N reduction as a means to control algae may be unwarranted in nutrient-rich lakes with low N:P ratios because some groups of cyanobacteria can compensate for N reduction through biological N fixation, and cyanobacterial dominance is common in lakes where algal biomass is high and N:P ratios are low (Smith 1983, Downing et al. 2001). Thus, it is important to consider N control as a supplement to P control, but P control is generally the most effective and economical means to control algal biomass in lakes.

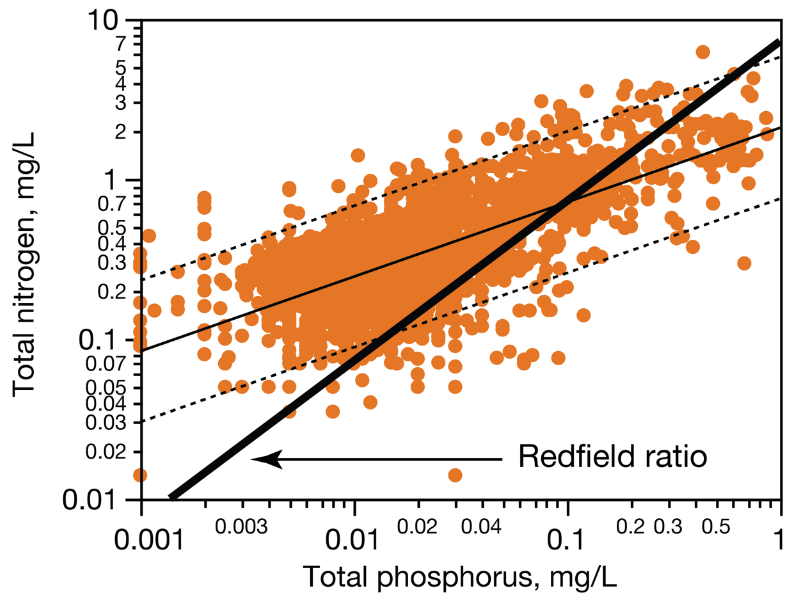


Figure 2. Relationship between total nitrogen (TN) and total phosphorus (TP) for Colorado lakes. The bold line indicates the nominal Redfield ratio of 16:1 (molar ratio; mass ratio = 7.2:1), which is typical of phytoplankton biomass.

**Description of the Final Technical Report and Data for Notice**

The Tetra Tech N-STEPS Colorado Lakes Final Technical Report (Exhibit O of the WQCD PPHS, dated July 20, 2022) proposes revised criteria for TP and TN in lakes larger than 25 acres, to be considered by the WQCC at the November 2022 Rulemaking Hearing. The Tetra Tech report describes the data that were assembled by CDPHE for development of the revised criteria, the process of preparing the data for analysis, decisions about classification of lakes, and the methods of data analysis leading to the revised criteria.

*Assembly and processing of the data set* – CDPHE provided Tetra Tech with water-quality data for almost 200 Colorado lakes. The data set, which reflects sampling and field measurements by local, state, tribal, and federal organizations, includes information about chlorophyll a, phosphorus fractions, nitrogen fractions, and other water-quality variables. Because the data were collected by many different organizations, the data set was processed to provide consistency across files. The data set (Finalized data) was made available to the public in November 2021, and a revised data set (Data for Notice) was made available on July 28, 2022. The revised data set includes 22 files in csv format (comma-separated values) that contain results for individual samples and field measurements. The revised data set also includes a file with means of replicate values for a given station and depth (SiteDate.csv), a file with seasonal-average values for the primary station on each lake (LakeYear.csv), and other supporting documents.

Data submitted by individual organizations were standardized to achieve consistency of units, variable names, and lake names. Results for lakes less than 20 acres and results of laboratory blanks and other quality-analysis (QA) samples were excluded from analyses. Results of replicate analyses for the same station and depth on a given date were averaged. Generally, concentrations reported as zero or below detection were set to half the detection limit. Analyses were restricted to data collected since 1990 and to results for a single station on each lake (typically the most downstream station). The csv files include sampling results for June – October, but only results for July – September were considered in development of the proposed criteria. The minimum sample size for calculation of seasonal-mean values was one sampling date from the July – September growing season.

In addition to seasonal-average values for measured variables, two sets of derived values were calculated at the suggestion of the EPA. For each sampling event, the TN:TP ratio was calculated as an indicator of nutrient limitation. Expected Secchi transparency ($Z_{Secchi}$) was predicted from chlorophyll a, according to the relationship derived by Carlson (1977), as follows (Equation 1):

$$\ln(Z_{Secchi}, \text{m}) = 2.04 - 0.68 \ln(\text{chlorophyll a}, \mu\text{g/L}) \qquad \text{Equation 1}$$

The ratio of observed to expected Secchi transparency (Secchi O/E) was used as an indicator of non-algal light attenuation.

*Classification of lakes* – The EPA encouraged the WQCD to consider the effects of lake class on the relationships between nutrient concentration and chlorophyll a. Relationships between nutrient concentrations and chlorophyll a were analyzed to identify significant effects of covariates. Aquatic Life Use (Warm, Cold), ecoregion (Plains, Rockies, Xeric), and lake type (natural lake, reservoir) were considered as categorical variables, and lake area, elevation, Secchi O/E, and TN:TP ratio were considered as continuous variables.

*Development of proposed criteria* – A four-step process was used to derive the proposed criteria for TP and TN. The interim chlorophyll values have an allowable exceedance frequency of one in five years and were adjusted from 80$^{th}$ percentiles to median values using relationships developed from results for well-sampled lakes; separate relationships were used for Aquatic Life Cold and Aquatic Life Warm lakes. Quantile regression then was used to derive targets for seasonal-average values of TP and TN. The 0.75 quantile was chosen to represent relationships between nutrients and chlorophyll a, to ensure protection of a larger proportion of lakes than would be protected by use of a lower quantile. The resulting seasonal-mean concentrations of TP and TN then were converted to 80$^{th}$ percentile values from the relationships between mean and 80$^{th}$ percentile for well-sampled lakes. The proposed criteria are shown in Table 1, along with the chlorophyll criteria that were adopted in 2012.

Table 1. Criteria for chlorophyll a, total phosphorus, and total nitrogen.

| | Criteria, µg/L | | |
|---|---|---|---|
| Aquatic life use | Chlorophyll a=* | Total phosphorus** | Total nitrogen** |
| Cold lakes | 8 | 20*** | 330 |
| Warm lakes | 20 | 36 | 600 |

* adopted 2012; 5 µg/L for direct-use water supplies ** proposed

*** Observed to expected ratio for Secchi transparency as covariate

**Comments on the Final Technical Report and Data for Notice**

The data set (Finalized data) associated with Tetra Tech's Draft Technical Report included various types of errors (e.g., typographical errors, incorrectly identified lakes and stations, inconsistent treatment of values below detection, incorrect designations for Aquatic Life Use). Some of the errors identified in the Finalized data were corrected before release of the revised data set (Data for Notice). However, some errors remain in the revised data set and are not trivial; these remaining affect results of analyses leading to the proposed nutrient criteria. The purpose of this section of the review is to describe the types of errors that remain in the revised data set and explain the consequences of these errors. Important assumptions and steps in development of the proposed criteria also are reviewed here.

*Site inventory* – The revised data set (Data for Notice) includes an inventory of sampling locations (Site Inventory.csv). The list of lakes in the site inventory does not match the list of lakes in the lake-year file (LakeYear.csv) or in the site-date file (SiteDate.csv). Some lakes listed in the sampling-location inventory are not listed in either the site-date file or the lake-year file, as expected. However, twelve lakes that were sampled as part of the National Lakes Assessment (NLA) are listed in the lake-year file and the site-date file, but not in the site inventory. The site-date file indicates that some of the NLA lakes were sampled by multiple organizations, but the twelve NLA lakes are listed separately from other lakes in the lake-year file. Names of some lakes are misspelled, and some names are spelled more than one way (e.g., Williams Creek and Willams Creek). Misspellings of lake names and double-listing of some NLA lakes resulted in some lakes being listed twice in the lake-year file.

*Anomalous and missing values* – The 22 csv files that were assembled by the WQCD contain some anomalous values for chlorophyll a, total N, and total P. For example, TP data for Chatfield Reservoir are shown in Figure 3. The highest of these values are anomalous and almost certainly represent typographical errors or gross analytical errors. The net effect of such errors on the proposed criteria is unknown, but retention of such errors in the data set would affect the relationships between nutrients and chlorophyll a, on which the criteria for TP and TN will be based.

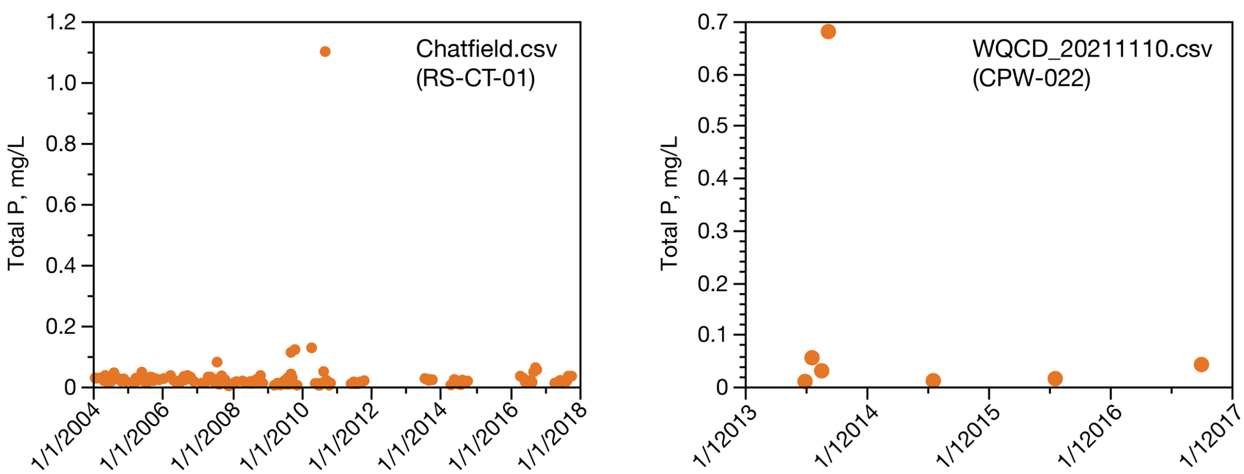


Figure 3. Results of total phosphorus analyses for Chatfield Reservoir. The highest values are anomalous and almost certainly represent typographical or analytical errors.

Chlorophyll data for Green Mountain Reservoir (1991 – 2019) are reported in the ResultValue column of the csv file from the Summit Water Quality Committee (SWQC), but not in the FinalResultValue column. Consequently, chlorophyll data for Green Mountain

Reservoir were omitted from the site-date file and the lake-year file. For some other lakes with long sampling records (e.g., Milton Seaman Reservoir, Boyd Lake), only a subset of available data are included in the revised data set. These long records, which include results for multiple sampling events within the July – September season, are particularly valuable for development of nutrient criteria.

*Detection limits* – The Tetra Tech report states that non-detects and values below the minimum detection limit (method detection limit or method detection level; MDL) were set to half the MDL, or if no MDL was reported, values below detection were set to half the reported value. Detection limits were defined differently by different organizations, and the type of detection limit was not specified for approximately half of the values in the data set (Table 2). In some cases, values less than detection were set to half the practical quantitation limit (PQL) or lower reporting limit (LRL), rather than half the MDL. Also, in the csv file from the WQCD, many values below the LRL were set to one fifth the LRL.

Table 2. Types of detection limits reported in the 22 csv files of the revised data set.

| | Number of values | | | | | | |
|---|---|---|---|---|---|---|---|
| Detection-limit type | Chlorophyll a | Inorganic N (nitrate, nitrite) | Kjeldahl N | Nitrate-N | Nitrite-N | Total N | Total P |
| Lower reporting limit (LRL)* | 455 | 1385 | 981 | 396 | 592 | 889 | 2116 |
| Historical lower reporting limit | 8 | 271 | 96 | 810 | 686 | 502 | 122 |
| Method detection level (MDL)** | 1555 | 918 | 992 | 236 | 183 | 238 | 1338 |
| Long term method detection level | 0 | 75 | 12 | 0 | 92 | 105 | 106 |
| Elevated detection limit | 0 | 2 | 0 | 0 | 0 | 0 | 0 |
| Estimated detection level | 0 | 31 | 0 | 0 | 117 | 0 | 0 |
| Not specified | 2391 | 630 | 782 | 2484 | 1400 | 1977 | 2560 |

* same as lower quantitation limit, practical quantitation limit, laboratory reporting level
** same as method detection level

Detection limits varied widely within and among variables (Figure 4). Reported detection limits typically are less than 1 µg/L for chlorophyll a and less than 0.1 mg/L for nitrate-N. For most analyses, detection limits for Kjeldahl N and TN were less than about 0.5 mg/L, and detection limits for TP typically were less than 0.01 mg/L. Reported detection limits for TP are near 10 mg/L in only a few cases, but many results for TN had detection limits above 0.5 mg/L and above the proposed criteria for TN. Some of the results used in the Tetra Tech analyses are based on methods that met the analytical requirements dictated by Regulation 85. Because the numeric limits associated with Regulation 85 are much higher than the values that are being proposed here, monitoring results that were collected to evaluate compliance with Regulation 85 may not be suitable for development of nutrient criteria associated with Regulation 31.

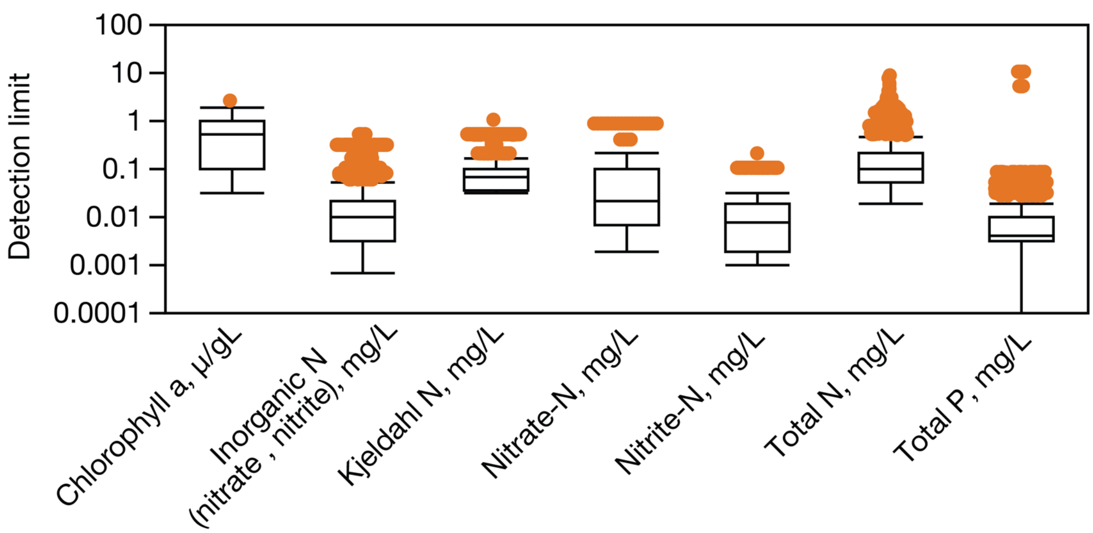


Figure 3. Range of detection limits (DetectionLimit1_Value) for selected variables. Units are µg/L for chlorophyll and mg/L for other variables. Boxes show medians, 25th percentiles, and 75th percentiles; whiskers show ranges, except values more than 1.5 times the interquartile range are shown as outliers (orange symbols).

*USGS TN data* – Tetra Tech observed anomalies with the TN data reported by USGS and concluded that calculated TN values (TKN + nitrate-N + nitrite-N) generally should be excluded from data analyses. Reported TN data were used preferentially, and calculated TN values were used in data analyses only if TN data were not reported. The decision to exclude calculated TN values from data analyses was based partly on reports of positive bias of TKN results for samples with high nitrate concentration (Rus et al. 2012). Because TKN values grossly exceed TN (e.g., TKN = 2 x TN) only for samples with low nitrate concentration (Figure 5), the anomalies observed by Tetra Tech were not caused by high concentrations of nitrate.

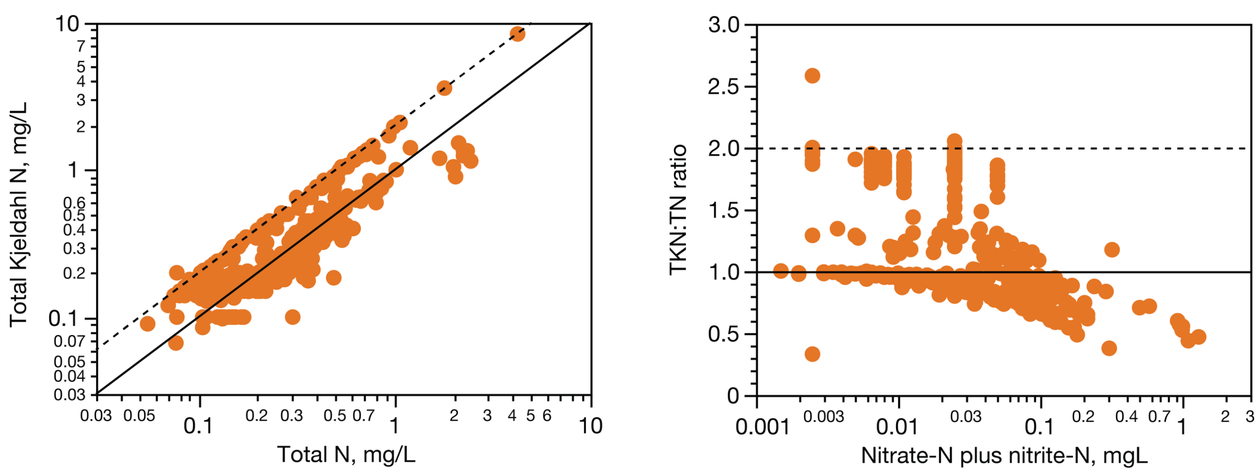


Figure 5. Nitrogen data reported by the USGS. The left panel shows the relationship between total Kjeldahl N (TKN) and total N (TN); the right panel shows the relationship between the TKN:TN ratio and the sum of nitrate-N and nitrite-N.

TN data reported by the USGS were analyzed by the AKP01 method (Nutrients, unfiltered water, acidified, alkaline-persulfate digestion, continuous flow colorimetry) or the ALGOR method (Computation by NWIS algorithm). ALGOR TN values were reported by USGS with a less-than symbol (<) preceding each numeric value; these results were assumed to be below detection and were divided by two. Furthermore, the type of method detection limit (DetectionLimit1_Type) for the ALGOR method is listed as "Historical Lower Reporting Limit", and the ALGOR detection limits are consistently higher than the AKP01 TN values (Figure 6). The ALGOR TN values are not measured values, and dividing these values by 2 would be inappropriate. Instead, measurements by the AKP01 method or calculated values (i.e., the sum of TKN, nitrate-N, and nitrite-N) should be used for TN. Retention of ALGOR values that were divided by 2 would bias the analyses leading to development of TN criteria.

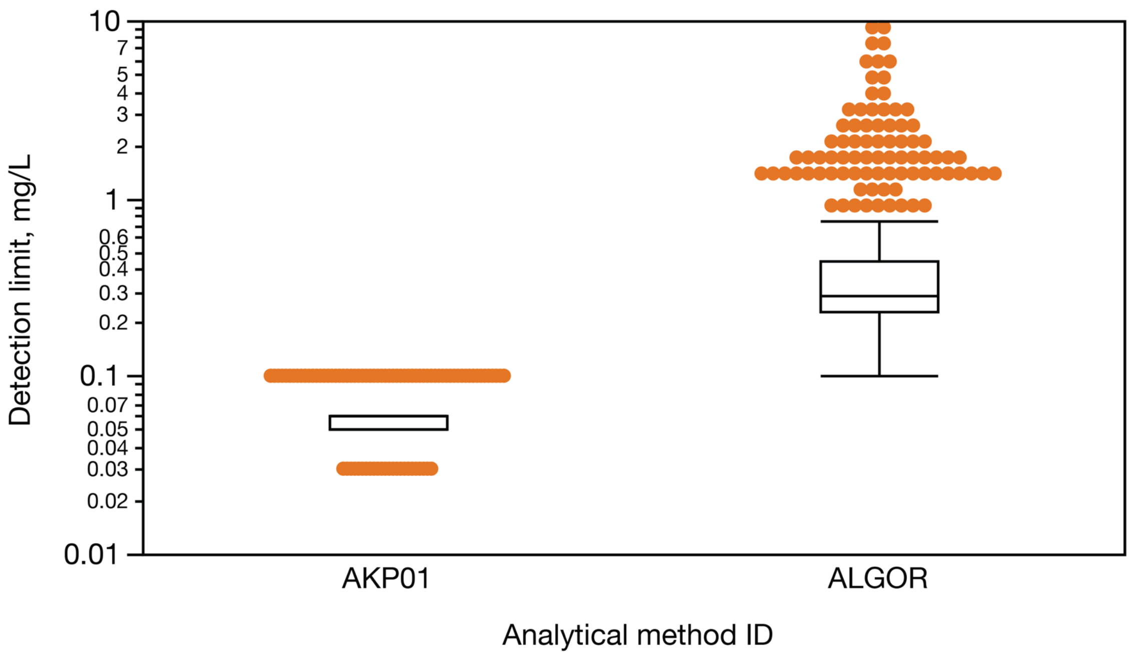


Figure 6. Range of detection limits (DetectionLimit1_Value) for total-N analyses reported by USGS (USGS.csv). Boxes show medians, 25th percentiles, and 75th percentiles; whiskers show ranges, except values more than 1.5 times the interquartile range are shown as outliers (orange symbols).

*Data for bottom samples* – Water-quality data provided by CDPHE to Tetra Tech include results of sampling and field measurements across multiple depths. According to the Final Technical Report, proposed criteria were developed from results for surface samples (e.g., top, surface, upper 1 m of the water column, photic zone), and data for other depths were excluded from analyses. However, data for some bottom samples were carried forward in calculations of seasonal-average values that were used for development of the proposed criteria. Mislabeling bottom data as surface data was particularly common for USGS data. In the csv file for USGS data, ActivityTopDepth is entered as "Photic" for all rows. Comparison of results in the csv file with results accessed directly from the National Water Information System (NWIS) confirmed that many of the rows in the csv file for USGS data represent bottom samples. Chlorophyll, temperature, and dissolved oxygen can differ greatly between surface water and bottom water. Concentrations of nutrients also can differ between surface water and bottom water for various reasons (e.g., nutrient release from sediments during periods of stratification). Because the csv file for USGS data reflects sampling from more than 40 lakes, failure to exclude results of bottom samples from analyses could cause biases in the proposed criteria for TP and TN.

*Minimum sample size* – Tetra Tech and the WQCD determined that a single sampling event within the July – September season would be adequate for calculation of seasonal-mean values that were used for development of the proposed criteria. If seasonal variation is low, the result for a single sampling event may provide a reasonable estimate of the seasonal-mean value. If seasonal variation is high, however, the result from a single sampling event would not provide a reliable estimate of the seasonal mean. Figures 7 – 9 show ranges (July – September) of chlorophyll a, TP, and TN for Dillon Reservoir, Cherry Creek Reservoir, and Barr Lake, respectively. For each of the three lakes, concentrations are highly variable for some years. Therefore, selection of a single value at random would not provide a reliable estimate of the seasonal mean for a given year.

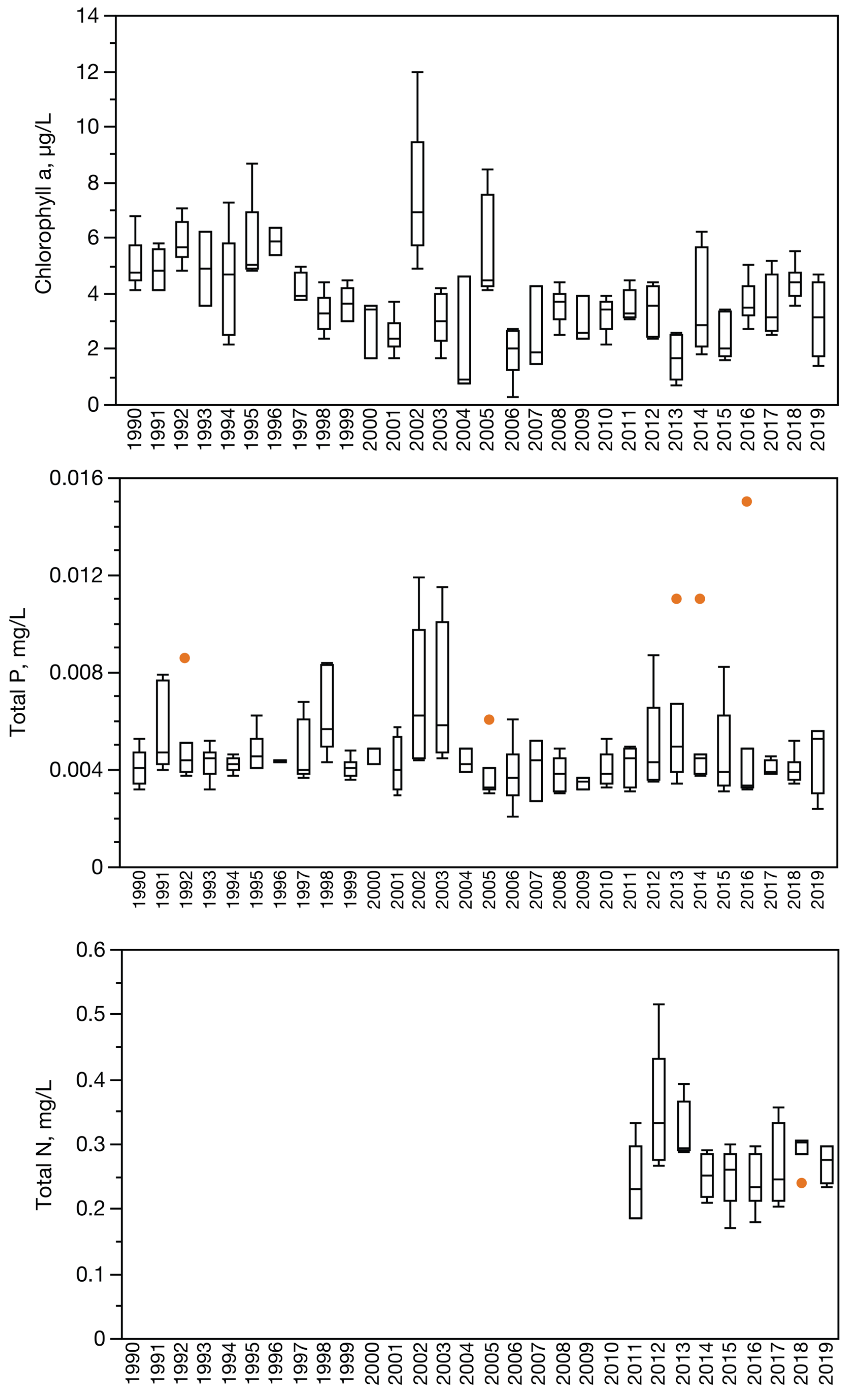


Figure 7. Seasonal (July – September) ranges of chlorophyll a, TP, and TN for Dillon Reservoir. Boxes show medians, 25th percentiles, and 75th percentiles; whiskers show ranges, except values more than 1.5 times the interquartile range are shown as outliers (orange symbols).

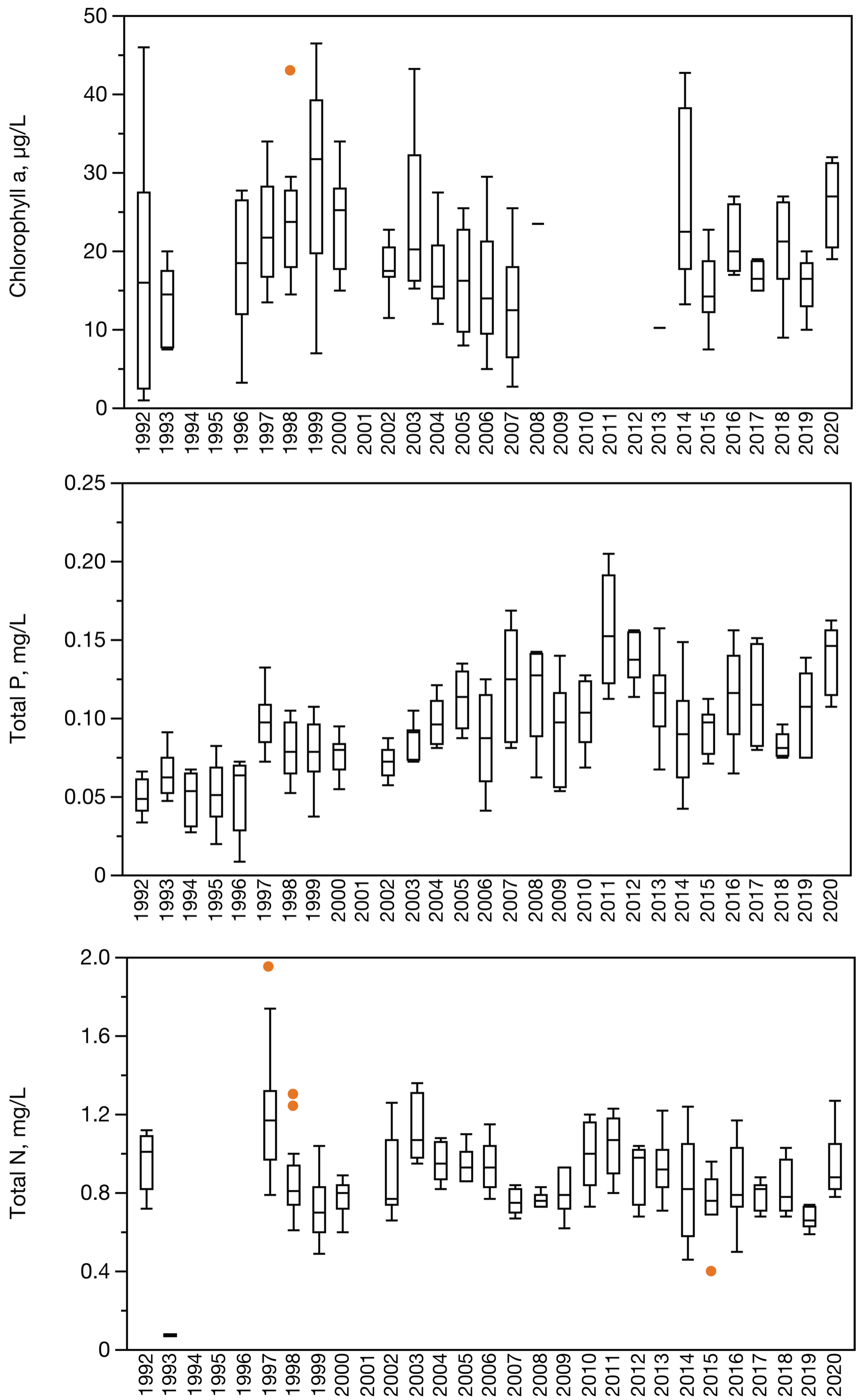


Figure 8. Seasonal (July – September) ranges of chlorophyll a, TP, and TN for Cherry Creek Reservoir. Boxes show medians, 25th percentiles, and 75th percentiles; whiskers show ranges, except values more than 1.5 times the interquartile range are shown as outliers (orange symbols).

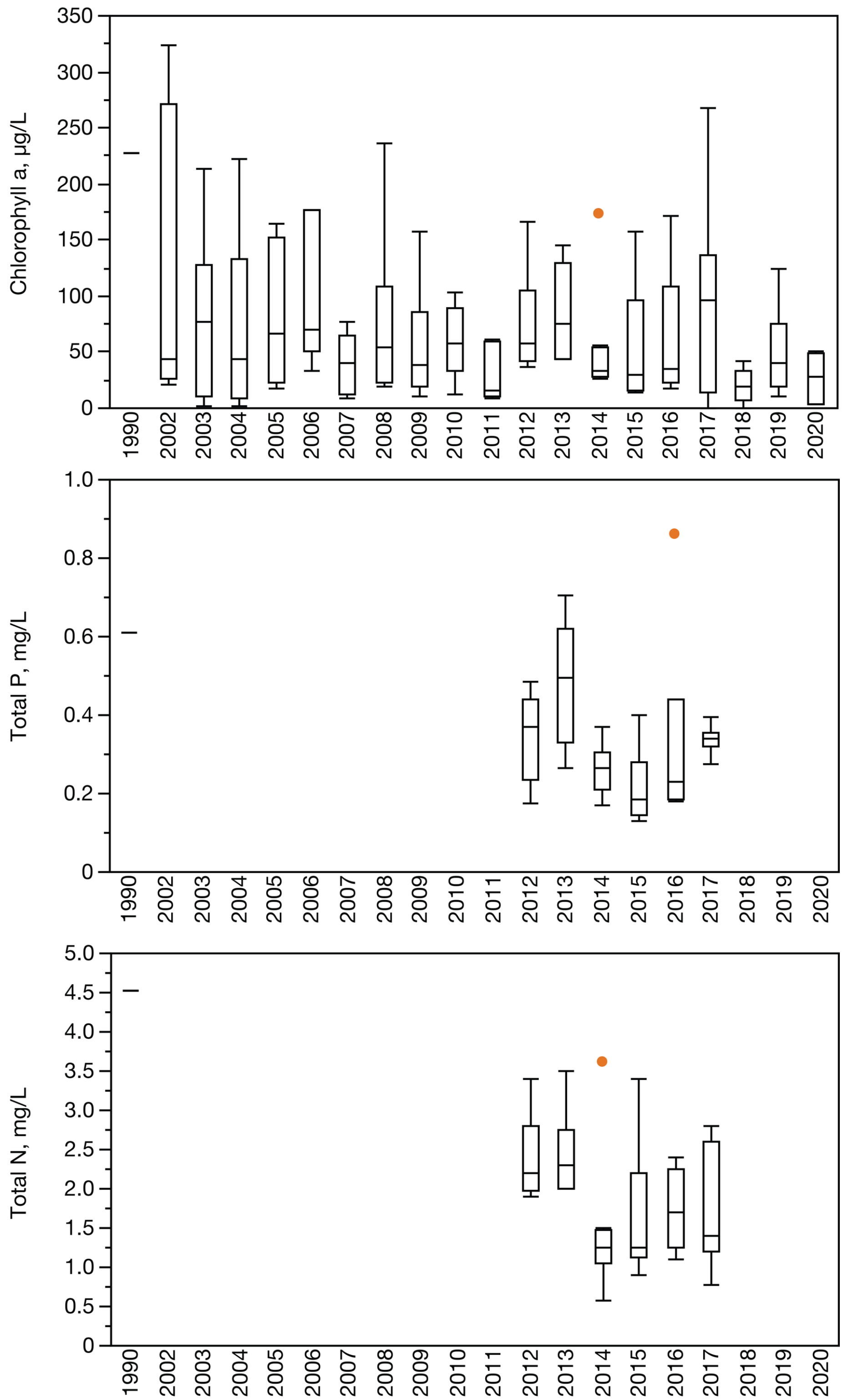


Figure 9. Seasonal (July – September) ranges of chlorophyll a, TP, and TN for Barr Lake. Boxes show medians, 25th percentiles, and 75th percentiles; whiskers show ranges, except values more than 1.5 times the interquartile range are shown as outliers (orange symbols).

For measurements of chlorophyll a, TP, or TN over the July – September season, the standard deviation (SD) increases with the seasonal mean (Figure 10). These relationships between standard deviation and seasonal mean (Equations 2 – 4) are similar to the relationship shown by the WQCD in its 2012 Prehearing Statement (Exhibit H of the WQCD PPHS for the November 2022 Rulemaking Hearing). These relationships also provide a basis for predicting the range of variation for individual measurements over the July – September season. Figure 11 shows predictions for chlorophyll a at three seasonal-mean values. Especially for high mean concentrations, the predicted range of values for individual measurements is quite broad. Thus, especially for mesotrophic (intermediate level of nutrient enrichment) and eutrophic lakes in Colorado, seasonal-mean values cannot be estimated reliably from results for a single sampling event. Even for oligotrophic lakes such as Dillon Reservoir, reliable estimates of seasonal-mean values would require results from multiple sampling events.

SD, Chl. a = Exp(-1.09 + 1.17*ln(Seasonal-mean, chl. a)); $r^2 = 0.85$ Equation 2

SD, TP = Exp(-1.12 + 1.03*Ln(Seasonal-mean, TP)); $r^2 = 0.69$ Equation 3

SD, TN = EXP(-1.53 + 1.12*Ln(Seasonal-mean, TN)); $r^2 = 0.51$ Equation 4

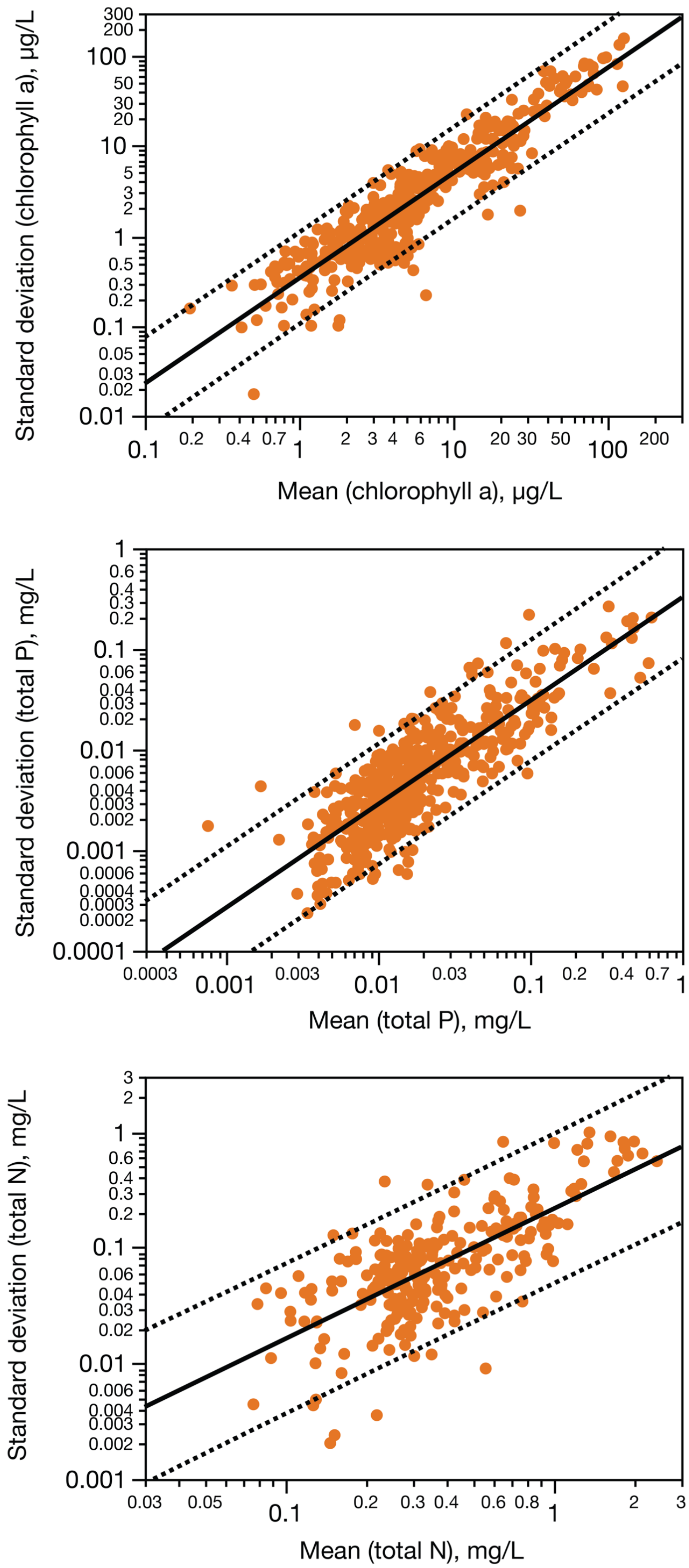


Figure 10. Relationships between standard deviation and seasonal mean for chlorophyll a, TN, and TP, for Colorado lakes that were sampled 3 or more times within the July – September season.

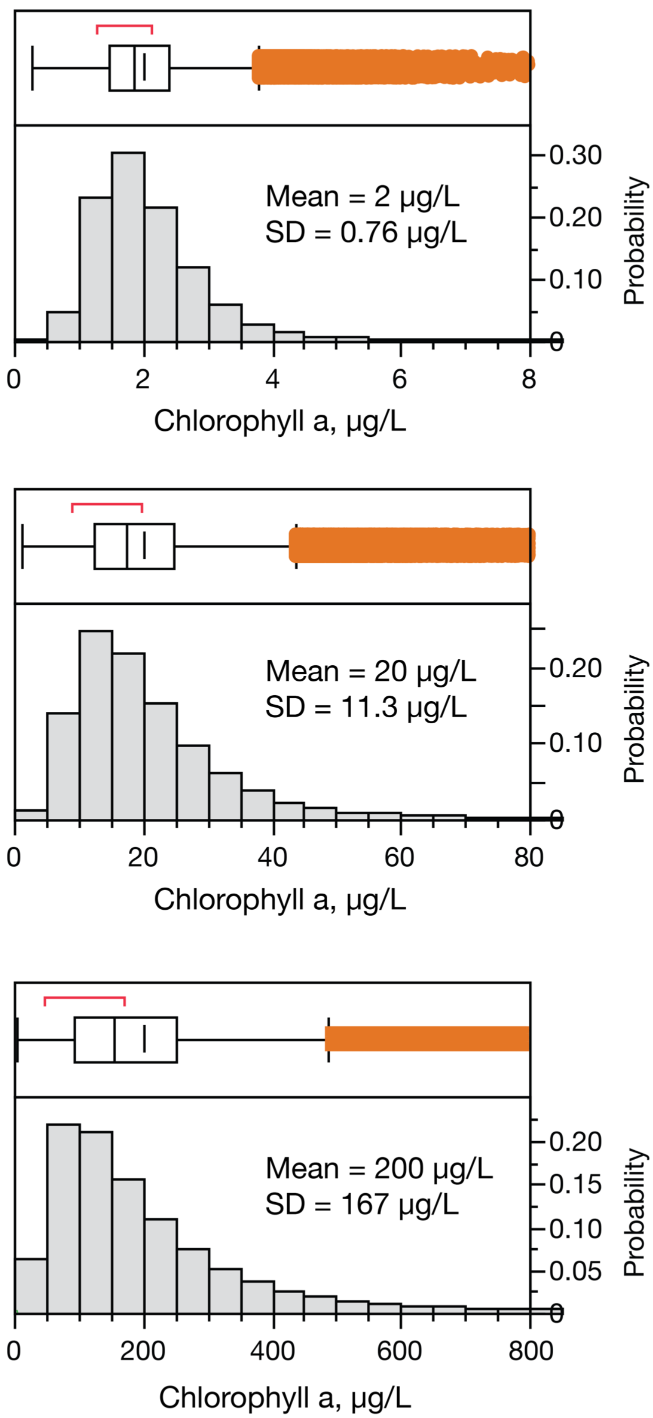


Figure 11. Predicted range of individual values for chlorophyll a, at seasonal-mean concentrations of 2, 20, and 200 µg/L. Concentrations were selected randomly from log-normal distributions with standard deviations predicted by Equation 2.

*Use of paired data* – For each lake, seasonal-mean values were calculated separately for chlorophyll a, TP, and TN. Paired measurements (i.e., chlorophyll a, TP, TN all collected on the same date) were not required. Failure to use only paired measurements could mask relationships between chlorophyll a and nutrients, and this problem is compounded for lakes that were sampled infrequently. For example, a single TP measurement from late July (i.e., near the warmest time of the year) may not have any meaningful relationship to a single chlorophyll measurement from late September.

*Lake classification* – At the recommendation of the EPA, Tetra Tech evaluated nutrient-chlorophyll relationships for different classes of lakes. Aquatic Life Use (Warm, Cold), ecoregion (Plains, Rockies, Xeric), and lake type (natural lake, reservoir) were considered as categorical variables, and lake area, elevation, Secchi O/E, and TN:TP ratio were considered as continuous variables. Tetra Tech showed results of statistical analyses for the split between Aquatic Life Use Warm and Aquatic Life Use Cold lakes, but similar information was not shown for partitioning of the data set based on other classifications. Furthermore, the decision to classify lakes on the basis of Aquatic Life Use was made before the data set was finalized.

Aquatic Life Use is related to water temperature, but there is substantial overlap in July – September temperatures between Aquatic Life Cold and Aquatic Life Warm lakes (Figure 12). Thus, Aquatic Life Use may not be the best classification for partitioning the nutrient-chlorophyll relationships. Temperature was not considered as a variable for partitioning the data set and possibly would provide for better predictions of chlorophyll a than Aquatic Life Use. Lake depth and water-residence time also were excluded from the list considered by Tetra Tech. Each of these variables can limit algal growth in lakes, and the Tetra Tech

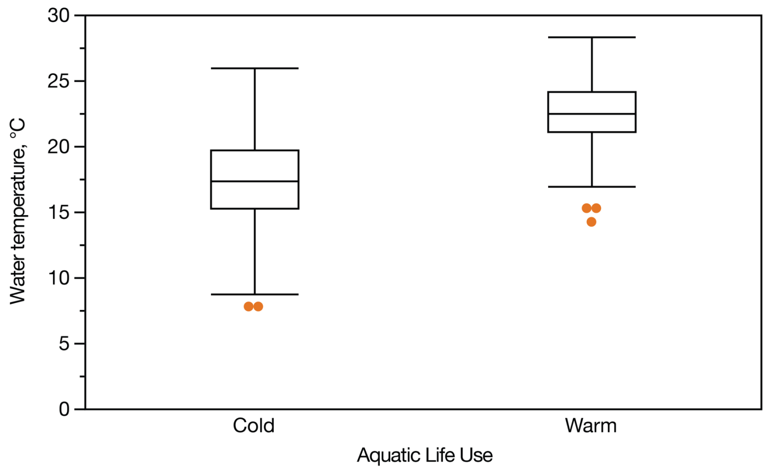


Figure 12. Water temperatures (July – September) for Cold and Warm lakes. Boxes show medians, 25th percentiles, and 75th percentiles; whiskers show ranges, except values more than 1.5 times the interquartile range are shown as outliers (orange symbols).

report does not provide enough information to evaluate whether Aquatic Life Use is the most appropriate basis for partitioning relationships between nutrient concentrations and chlorophyll. Decisions about classification are important for development of nutrient criteria because relationships between chlorophyll a and any single variable (TP, TN, temperature, depth, water-residence time, etc.) have poor predictive power.

*Criteria development* – Interim table-value standards for chlorophyll a were adopted in 2012 for protection of beneficial uses, including Aquatic Life and Domestic Water Supply uses. Corresponding criteria are being developed for TP and TN, to prevent harmful growth of algae that could jeopardize beneficial uses. The proposed criteria for phosphorus were developed from empirical relationships between TP and chlorophyll a, and Secchi O/E (the ratio of observed to expected Secchi transparency) was considered as a covariate for Aquatic-Life Cold lakes. Separately, the proposed nitrogen criteria were developed from empirical relationships between TN and chlorophyll a. Thus, the proposed criteria for TP do not depend on information about TN, and vice versa.

The purpose of criteria for TP and TN is fundamentally different from the purpose of criteria for other regulated constituents. With TP and TN, the purpose of the criteria is not to protect beneficial uses directly, but rather to guard against harmful growth of algae (chlorophyll a), which threatens beneficial uses. As long as beneficial uses are protected (i.e., through control of algal biomass, nitrate, etc.), the primary concern with high concentrations of TP and TN is the potential for transport of nutrients to downstream ecosystems. If attainment of criteria for TP is sufficient for attainment of the chlorophyll standards, and therefore sufficient for protection of the relevant beneficial uses in a lake, concurrent attainment of the proposed criteria for TN would be redundant. Similarly, if attainment of criteria for TN is sufficient for attainment of the chlorophyll standards, attainment of both TN and TP criteria would be redundant. Algal growth requires both phosphorus and nitrogen, and control of algal growth can be achieved not only through dual control but also through control of either TP or TN.

Although dual control of nutrients may be appropriate in many cases, the status of P control should be considered in decisions about N control. Dominance by cyanobacteria, including groups that produce toxins, is common in lakes with high nutrient concentrations and low TN:TP ratios. Thus, for eutrophic lakes, reduction of N without P reduction could maintain conditions that are favorable for dominance by N-fixing cyanobacteria. Also, TP and TN differ with regard to treatment technologies. Even the most efficient biological-treatment processes do not reduce TN concentrations to the range of background concentrations for many natural systems, and biological N removal is energy intensive

(McCarty 2018). Treatment by reverse osmosis (RO) can reduce nitrogen in wastewater to very low levels but is costly, and disposal of RO brine is problematic. In contrast, phosphorus concentrations can be reduced to very low levels with existing treatment processes (e.g., facilities upstream of Dillon Reservoir).

**Recommendations for development and implementation of nutrient criteria**

The WQCD PPHS for the November 2022 Rulemaking Hearing proposes revised criteria for TP and TN for Colorado lakes. The proposed criteria are based on work described by Tetra Tech in Exhibit O of the PPHS (N-STEPS Colorado Lakes Final Technical Report). The Final Technical Report is based on analyses of the revised data set (Data for Notice), which reflects correction of some of the errors that existed in the earlier data set. However, review of the revised data set identified a range of errors that could affect the results of the Tetra Tech analyses and the numeric values for the proposed criteria. Handling of USGS TN data and averaging results for surface samples and bottom samples could meaningfully affect results of analyses that are the basis for the proposed criteria, and decisions about minimum sample size and lake classifications could affect the strength of relationships between chlorophyll a and nutrient concentrations. Each of these issues should be addressed before the criteria for TP and TN are finalized. Also, important matters related to lake assessments and implementation of standards should be addressed.

*Revised data set and supporting files* – The site inventory should be revised to reflect the complete list of lakes. The data set should be screened again to identify anomalous values, and the screening process should be carried out on a site-by-site basis. Because the range of concentrations across lakes is large, identification of statistical outliers for the entire data set may be inadequate for identification of erroneous values. The chlorophyll data for Green Mountain Reservoir should be included in the final analyses, and other missing data for lakes with long sampling records (e.g., data for Milton Seaman Reservoir) should be added to the data set if possible. Many of these long sampling records reflect high-frequency sampling (e.g., biweekly) and would be particularly valuable for development of nutrient criteria.

*Detection limits* – Detection limits should be handled consistently throughout the analyses. Also, results for samples with high detection limits relative to the proposed numeric values for TP and TN should be excluded from analyses. If results are below detection, inclusion of results for methods with high detection limits could weaken the apparent relationships between chlorophyll a and nutrients.

*USGS TN values* – Tetra Tech identified anomalies with the USGS TN data but incorrectly identified the cause of the anomalies. TN values based on the ALGOR method (computation by NWIS algorithm) do not represent actual measurements and should not have been used in development of criteria for TN. Instead, the calculated TN values (i.e., TKN + nitrate-N + nitrite-N) should be used in place of the ALGOR values. Use of ALGOR TN values that were divided by 2 would cause a negative bias in the numeric values for the TN criteria.

*Bottom samples* – For the USGS data and for data from some other organizations, bottom data were combined with surface data in calculations of seasonal-mean values. The data set should be carefully reviewed, and bottom data should be excluded from analyses.

*Minimum sample size* – Historically, the WQCD has preferred at least three sampling events per year for lake assessments. In the Tetra Tech analyses, however, the minimum sample size for calculation of seasonal-mean values was only one sampling event. Even for oligotrophic lakes in Colorado, seasonal-mean values cannot be reliably determined from a single sampling event. For development of criteria for TP and TN, seasonal-mean values for chlorophyll a, TP, and TN should be calculated from at least three values. Particularly for eutrophic lakes, more than three values may be required for reliable estimates of seasonal-mean values.

*Lake classification* – The classification analyses were conducted prior to release of the revised data set, and the data set still contains errors that should be addressed. After the data set has been revised to correct such errors, the classification analyses should be repeated. Also, other factors that affect algal growth in lakes (e.g., lake depth, water-residence time) should be considered in the classification analyses. Finally, Tetra Tech should provide more information about the results of the classification analyses, in order to document the rationale for decisions about classification of lakes.

*Criteria development* –Some of the errors in the revised data set are minor and are unlikely to have any significant effect on the final numeric values for TP and TN. However, failure to correct some types of errors (e.g., handling of USGS TN data, averaging results for top and bottom samples, failure to exclude some results with high detection limits) could significantly affect the numeric values. Errors related to the USGS TN values and averages that include results for bottom samples are particularly important because they probably have resulted in biases in the proposed criteria.

Most of the seasonal-mean values used to derive the proposed criteria were based on only one or two measurements within the July – September season. Even if analytical precision for individual measurements is excellent, seasonal means cannot be reliably estimated from only one or two values (Figures 7 – 11). For the most productive lakes, more than three samples may be required for reliable determination of seasonal means.

Low-quality data, including erroneous TN data and seasonal means based on small sample size, weaken the apparent relationships between chlorophyll a and nutrients. The desire of the WQCD to include results for many lakes is understandable, but only the most reliable results and seasonal means should be used in derivation of nutrient criteria for Colorado lakes. After revisions to correct errors and omissions in the data set and after finalization of the classification analyses, Tetra Tech should repeat the four-step process through which the proposed criteria were developed. If this work cannot be accomplished before the November 2022 Rulemaking hearing, the WQCD and the WQCC should consider postponement of the hearing.

*Implementation* – Some of the most important matters regarding the proposed criteria for TP and TN relate to implementation of the criteria. These matters include decisions about minimum sample size for lake assessments, equal treatment for TP and TN criteria, nutrient-use efficiency, and direct-use water supplies.

In the PPHS, the WQCD indicates its intention to change the sample-size requirement for lake assessments from a minimum of three samples per season to a single sample per season. Whether for the purpose of standards development or assessment of standards compliance, seasonal means cannot be reliably estimated from results for a single sample. If lake assessments are based on a single sample per year, even oligotrophic lakes with low seasonal-mean chlorophyll concentrations may be listed for impairment, and the probability of inaccurate assessments could be higher still for mesotrophic and eutrophic lakes. Sample-size requirements for lake assessments should be based on expectations about seasonal variation in regulated constituents (e.g., relationships for chlorophyll a, TP, and TN shown in Figure 10) and the required level of uncertainty for assessments. Decisions about listings for impairments are made for individual lakes, and evaluation of standards compliance for individual lakes should be based on adequate assessment methodologies.

Because algal cells require both phosphorus and nitrogen, control of algal growth in lakes can be achieved through control of either TP or TN. The proposed criteria for TP and TN were derived independently. Transport of nutrients to downstream ecosystems should be considered on a case-by-case basis, but attainment of the proposed criteria for either TP or TN in a given lake should be sufficient to meet the adopted targets for chlorophyll a. In a lake where algal biomass is adequately controlled through control of phosphorous, the need for nitrogen control may be lessened. Similarly, the need for phosphorus control would be reduced where algal growth is controlled through control of nitrogen. Generally, phosphorus control is the most reliable means of control for harmful algal growth; this has been demonstrated in Colorado (e.g., in Dillon Reservoir) and generally. Furthermore, it is often technologically infeasible to treat TN in municipal wastewater to the levels necessary to achieve the desired level of control for algal biomass in lakes (i.e., consistent with the adopted numeric values for chlorophyll a). Nutrient criteria could be implemented through a phased approach, where criteria for TP are implemented initially and implementation of criteria for TN is delayed. Alternatively, TN criteria could be implemented only on a site-specific basis, for lakes where desired outcomes with regard to chlorophyll a cannot be achieved through P control alone or in cases where control of N is required for control of algal growth in downstream segments.

Control of algal growth usually can be achieved through control of TP, or through control of TP and TN. In some lakes, however, factors other than nutrients limit the growth of phytoplankton, and concentrations of chlorophyll a remain well below the expectations based on TP and TN. Consideration of non-algal light attenuation (Secchi O/E) in the TP criteria for Aquatic Life Cold lakes acknowledges that chlorophyll a can remain low relative to expectations based on nutrient concentrations. However, no such considerations were made for warm lakes or for TN criteria. The 0.75 quantile regressions were used in determination of the criteria for TP and TN. In lakes where algal biomass is limited by nutrients, use of a high quantile in derivation of the criteria helps to ensure consistency between chlorophyll targets and nutrient criteria, so that lakes are unlikely to exceed the chlorophyll targets without exceedance of the criteria for TP and TN. However, use of a high quantile also increases the probability that the criteria for TP and TN will be exceeded in lakes where the chlorophyll targets are met. Because the purpose of criteria for TP and TN is prevention of harmful growth of algae, exceedance of TP or TN criteria, without exceedance of the chlorophyll criteria, should not necessarily result in listing for impairment.

The WQCC determined in 2012 that the 5 μg/L target for direct-use water supplies (DUWS) would be applied on a discretionary basis. In some cases, application of the 5 μg/L target might not be necessary to protect beneficial uses. In the PPHS, however, the WQCD is proposing that the 5 μg/L standard be applied to all lakes (of any size, including reservoirs) with DUWS. For any lake with DUWS , failure to meet the 5 μg/L standard would cause listing for impairment, and upstream dischargers could be subject to effluent limitations based on a Total Maximum Daily Load (TMDL) assessment. The proposal to implement the

5 μg/L target for all DUWS, without consideration of need, should be questioned. If the 5 μg/L chlorophyll standard is applied to all lakes with DUWS, any upstream discharger could be subject to limitations imposed by a Total Maximum Daily Load (TMDL) assessment, should the 5 μg/L standard be exceeded.

## Conclusions

The WQCD is proposing revised criteria for TP and TN for Colorado lakes, to be considered by the WQCC at the November 2022 Rulemaking Hearing. The proposed criteria are based on work described by Tetra Tech in Exhibit O of the WQCD PPHS (N-STEPS Colorado Lakes Final Technical Report). Because of errors in the data set used for development of the proposed criteria and inappropriate decisions about processing of the data, the proposed criteria for TP and TN are questionable. Decisions about sample-size requirements are a particular concern, in the context of standards development and also with regard to assessment of standards attainment. These matters need to be addressed before the criteria for TP and TN are finalized. Furthermore, important questions remain about implementation of criteria for TP and TN.

## References

Carmichael, W. W. 1992. Cyanobacteria secondary metabolites – the cyanotoxins. J. Appl. Bacteriology 72: 445 – 449.

Dillon, P. J. 1975. The phosphorus budget of Cameron Lake, Ontario: the importance of flushing rate to the degree of eutrophy of lakes. Limnol. Oceanogr. 20: 28 – 39.

Dillon, P. J., and F. H. Rigler. 1974. The phosphorus-chlorophyll relationship in lakes. Limnol. Oceanogr. 19: 767 – 773.

Downing, J. A., and C. Plante. 1003. Production of fish populations in lakes. Can. J. Fish. Aquat. Sci. 50: 110 – 120.

Downing, J. A., S. B. Watson, and E. McCauley. 2001. Predicting cyanobacteria dominance in lakes. Can. J. Fish. Aquat. Sci. 58: 1905 – 1908.

Edmondson, W. T. 1970. Phosphorus, nitrogen, and algae in Lake Washington after diversion of sewage. Science 169: 690 – 691.

Falkowski, P. G. 2000. Rationalizing elemental ratios in unicellular algae. J. Phycol. 36: 3 – 6.

Fee, E. J. 1979. A relation between lake morphometry and primary productivity and its use in interpreting whole-lake eutrophication experiments. Limnol. Oceanogr. 24: 401 – 416.

Khan, A. L.,. E. R. Sokol, D. M. McKnight, J. F. Saunders, A. K. Hohner, and R. S. Summers. 2021. Phytoplankton drivers of dissolved organic material production in Colorado reservoirs and the formation of disinfection by-products. Frontiers in Environmental Science 9: Article number 673627.

Krause-Jensen, D., and K. Sand-Jensen. 1998. Light attenuation and photosynthesis of aquatic plant communities. Limnol. Oceangr. 43: 396 – 407.

Lewis, W. M., Jr., J. F. Saunders III, and J. H. McCutchan, Jr. 2008. Application of a nutrient-saturation concept to the control of algal growth in lakes. Lake and Reservoir Management 24: 41 – 46.

McCarty, P. L. 2018. What is the best biological process for nitrogen removal: when and why? Environ. Sci. Technol. 52: 3835 – 3841.

Paerl, H. W., J. T. Scott, M. J. McCarthy, S. E. Newell, W. S. Gardner, K. E. Havens, D. K. Hoffman, S. W. Wilhelm, and W. A. Wurtsbaugh. 2016.

Watson, S. B., J. Ridal, and G. L. Boyer. 2008. Taste and odor and cyanobacterial toxins: impairment, prediction, and management in the Great Lakes. Can. J. Fish. Aquat. Sci. 6: 1779 – 1796.

O'Neil, J. M., T. W. Davis, M. A. Burford, and C. J. Gobler. 2012. The rise of harmful cyanobacteria blooms: the potential roles of eutrophication and climate change. Harmful Algae 14: 313 – 334.

Redfield, A. C. 1934. On the proportions of organic derivatives in sea water and their relation to the composition of plankton. *In* Daniel, R. J. (Ed.) James Johnstone Memorial Volume. University Press of Liverpool. pp. 177 – 192.

Rus, D. L., C. J. Patton, D. K. Mueller, and C. G. Crawford. 2012. Assessing total nitrogen in surface-water samples— Precision and bias of analytical and computational methods: U.S. Geological Survey Scientific Investigations Report 2012–5281, 38 p.

Sakamoto, M. 1966. Primary production by phytoplankton community in some Japanese lakes and its dependence on lake depth. Arch. Hydrobiol. 62: 1 – 28.

Smith, V. H. 1982. The nitrogen and phosphorus dependence of algal biomass in lakes: an empirical and theoretical analysis. Limnol. Oceanogr. 27: 1101 – 1112.

Smith, V. H. 1983. Low nitrogen to phosphorus ratios favor dominance by blue-green algae in lake phytoplankton. Science 221: 669 – 671.

Smith, V. H., and J. Shapiro. 1981. Chlorophyll - phosphorus relations in individual lakes. Their importance to lake restoration strategies. Environ. Sci. Tech. 15: 444 – 451.