Evaluation of Estimated Total Nitrogen Concentrations for New Mexico Nutrient Thresholds

Introduction

The Surface Water Quality Bureau (SWQB) uses defensible data to assess water bodies against criteria designed to meet Clean Water Act and State Administrative Code (20.6.4 NMAC) requirements. These data are the primary source of information to satisfy statutory requirements of Section 303(d) and the reporting requirements of Sections 305(b) and 314 of the federal Water Pollution Control Act [33 U.S.C. 1251].

The majority of the SWQB water chemistry samples are submitted to the New Mexico Department of Health Scientific Laboratory Division (SLD). SLD provides numerous data streams from several units (Air & Heavy Metals Program, Radiochemistry Program, and the Water Chemistry Program). These data take the form of numerical reporting within the feasible reporting range bounded by low and high standard solutions, as adjusted by studies of the various method detection limits. Instrument data that fall below the value identified as the minimum level at which results can be confidently quantified (minimum reporting limit or "MRL") are censored with a "U" qualifier code and reported as being below (or less than) the MRL. The MRL is not the lowest concentration detectable through the various methods employed but represents the repeatable and defensible quantifiable data limit the lab determines to be appropriate given instrumentation, methods employed, sample matrix, analyst, and other variables that introduce inconstancy into the method. The lowest concentration that can be positively identified and distinguished from a method blank is known as the method detection limit or MDL. Instrument data reported between the MRL and MDL are typically acknowledged as estimated and identified with a "J" qualifier, indicating the analyte was positively identified in the sample but can not be quantified with confidence.

The SWQB collaborated with EPA and Tetra-Tech through the N-STEPS program to develop numeric nutrient thresholds in New Mexico, defined in the SWQB Comprehensive Assessment and Listing Methodology (CALM). The current MRL defined by SLD for EPA Methods 351.2 (Total Kjeldahl Nitrogen or TKN) and 353.2 (Nitrate+Nitrite) are 0.5 mg/L and 0.05 mg/L, respectively. The sum of the MRLs, 0.55 mg/L, is above the Total Nitrogen (TN) threshold for two of the three TN site classes, meaning that many of the reported results cannot be used unless J flagged data are accepted for assessment. The CALM states that data reported between the MRL and MDL (J flagged) can only be used for assessment when the data are part of a summed parameter (e.g., when summing congeners to determine total PCB concentration using EPA Method 1668 and its amendments). This analysis is intended to determine the feasibility of using summed J flagged Total Kjeldahl Nitrogen and Nitrate+Nitrite data to assess against applicable nutrient thresholds.

Comparison of Total Nitrogen calculated from sum of EPA Methods 351.2 and 353.2 (TKN and Nitrate+Nitrite) versus SM4500-NC (Total Persulfate Nitrogen)

Following the implementation of the 2016 revised numeric nutrient thresholds (NMED/SWQB 2016a), the SWQB recognized that the Total Nitrogen thresholds for two of the three site classes were below the MRL provided by SLD. An investigation of contract labs and alternate methods led the selection of Standard Method 4500-N-C (Total Persulfate Nitrogen or TPN) performed by the State of Montana

Laboratory Services Bureau (MTLSB). An investigation by the USGS (USGS 2003) concluded that the TPN method is more sensitive, accurate, and environmentally responsible than the traditional TKN method (351.2) yet the results from the two methods are comparable when accounting for the inherent nitrate interference in Method 351.2. During the 2016 through 2018 field seasons, SWQB collected over 900 concurrent TKN/nitrate+nitrite and TPN samples from streams, lakes and discharge effluent representing a variety of flow conditions, sources, and concentrations.

Comparing the two methods can be challenging due to differing reporting limits, additive versus reported results, and separate laboratories. However, the results from the two methods plotted in **Figure 1** fit closely to the ideal 1:1 ratio. Censored data and results reported below the MRL were removed to limit the sample frame to only results with confident quantification. The conclusion of a t-test indicates the difference between the TN and TPN sample populations is not significant with a $p < .05$. Differences due to nitrate interference in the TKN analysis and the exclusion of either TKN or nitrate+nitrite below MRL values from the TN calculation did not have a significant effect on result correlation. Also noteworthy, the correlation between the two methods improves above ~1.0 mg/L.

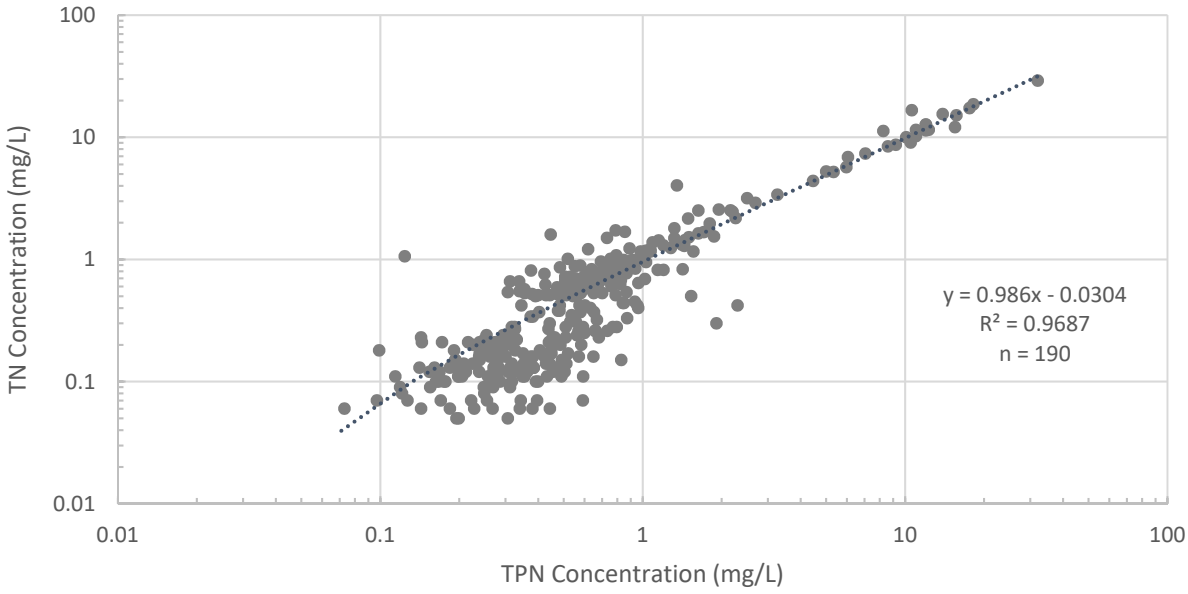

Figure 1. TPN (SM4500-N-C) versus TN (EPA 351.2+EPA 353.2) Concentration in mg/L

In 2017, SWQB and SLD entered into a memorandum of agreement (NMED/SWQB 2017) that requests SLD report TKN and nitrate+nitrite instrument values below the MRL in addition to its regular reporting. As a result, raw instrument data are available from the 2017-2018 field season. These "estimated" data were compared to the TPN results from MTLSB to examine the relationship between the two methods at levels below the SLD MRL and to determine at what concentration estimated data may be used with confidence. To complete the comparison, SLD TN and MTLSB TPN data reported at less than the MDL were removed. The inclusion of "estimated" SLD data significantly increases the sample frame from 190 to 405.

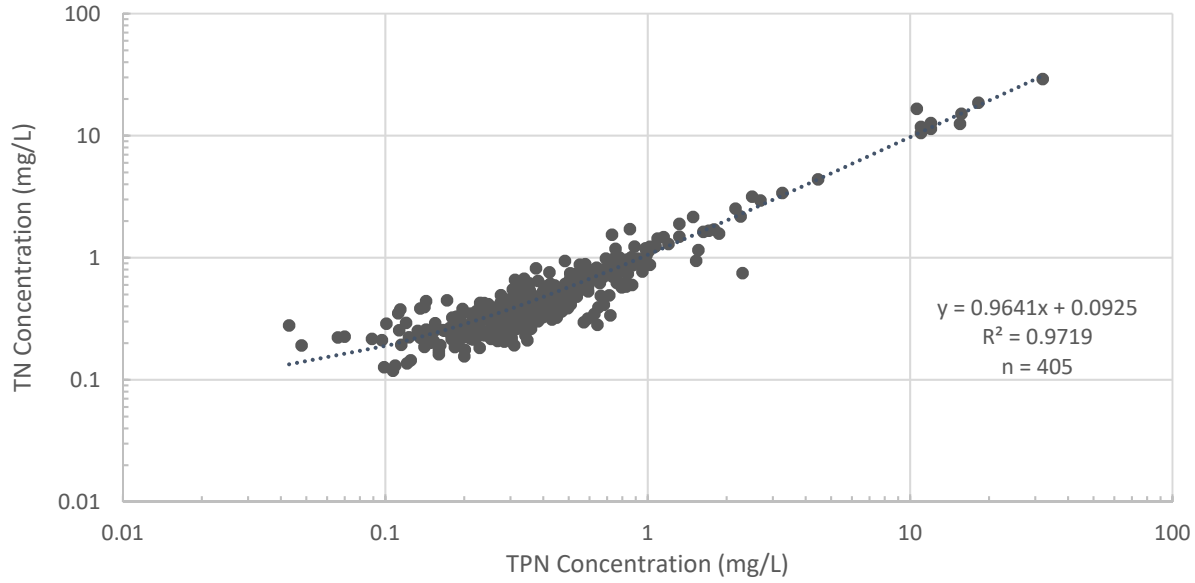

Figure 2. 2017-2018 TPN (SM4500-N-C) versus TN (EPA 351.2+EPA 353.2) Concentration in mg/L including estimated TN results

The resulting regression (near 1:1 with r^2 of 0.9719), **Figure 2**, is very similar to the relationship observed using results only above the MRL; however, the y-intercept is now positive. This change may be interpreted as resulting from inclusion of previously censored estimated values for either TKN or nitrate+nitrite. The result of this analysis is consistent with published studies that indicate that TN and TPN methods produce comparable values (Bronk, et. al. 2000, USGS 2003).

The SWQB Data Validation and Verification SOP (NMED/SWQB 2016b) specifies that duplicate and replicate samples must be within +/- 20% if greater than 4 times the MRL. This percentage can be used as a guideline, recognizing that the samples used for this analysis do not technically meet the definition of duplicates as they are different analysis methods from separate labs. A plot of the relative percent difference (RPD) between TN and TPN versus ranked order of TPN values (**Figure 3**) shows that the RPD decreases rapidly as TPN concentration increases until approximately 0.2 mg/L and then flattens as concentration continues to increase.

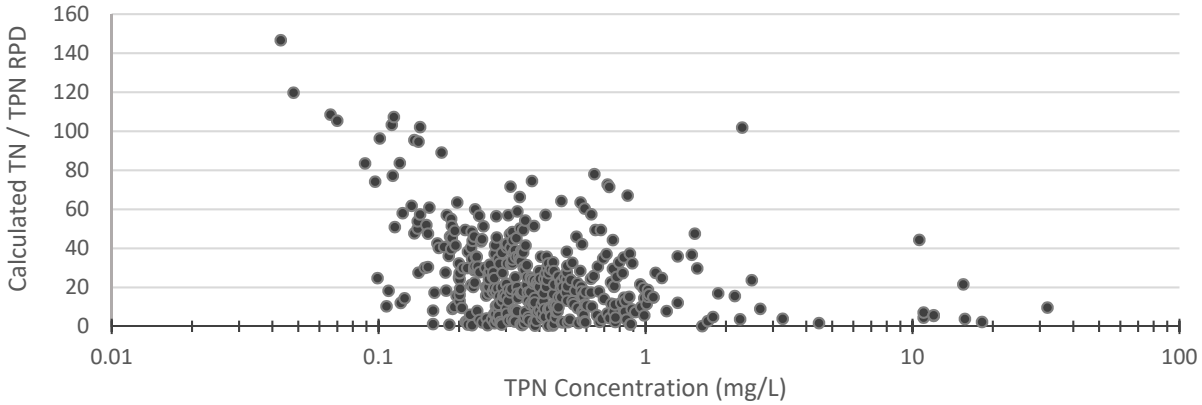

Figure 3. Plot of Increasing TPN Concentration versus RPD between Calculated TN and TPN

To determine the location and significance of this apparent change, a change point analysis was conducted on RPD sorted by ranked TPN concentration. The result of the analysis indicates a greater than 99.9% probability that agreeance between the calculated TN and TPN methods significantly improves at a concentration of approximately 0.25 mg/L (**Figure 4**). A T-Test of Independent Means for RPD populations above and below a TPN concentration of 0.25 mg/L concludes that the difference between the populations is significant at a greater than 99% confidence limit with a Hedge's-g calculated effect size of 1.01. Box plot A graphs the 25th percentile, median, and 75th percentile of RPD values for TPN results less than 0.25 mg/L. Box plot B graphs the 25th percentile, median, and 75th percentile of RPD values for TPN results greater than 0.25 mg/L. The median RPD value for TPN values greater than 0.25 mg/L is 17.4%

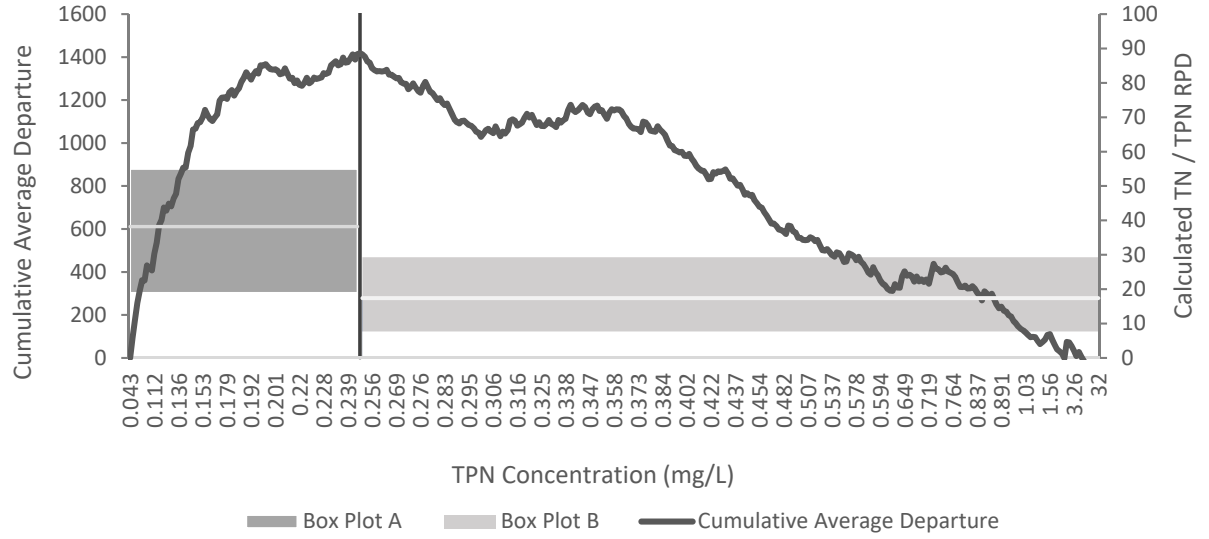

Figure 4. Plot of Change Point Analysis: Significant Improvement in Method RPD at 0.25 mg/L

Conclusion

While direct comparison of differing analytical methods from separate labs can be challenging, this analysis indicates that SLD calculated TN results and MTLSB TPN results share a close to 1:1 relationship. Previous studies have found that the TPN method (SM4500-N-C) is more sensitive and accurate than the traditional TKN method (351.2). Using TPN data as a benchmark, a change point analysis on relative percent with calculated TN indicates that above approximately 0.25 mg/L, agreeance between the methods improves significantly. Based on this analysis, use of estimated data (J flagged) below the current SLD additive TN MRL of 0.55 mg/L to a concentration of 0.25 mg/L is acceptable and can provide valuable quantitative information that would otherwise be absent. These results also indicate that SLD may be able to lower the current MRL for TKN method EPA 351.2 below its current value of 0.5 mg/L and still maintain confidence in the quantification.

References

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