# VIRGINIA WATER RESOURCES RESEARCH CENTER

# A "Screening Approach" for Nutrient Criteria in Virginia

2016 Report of the Academic Advisory Committee for Virginia Department of Environmental Quality



# SPECIAL REPORT



## VIRGINIA POLYTECHNIC INSTITUTE AND STATE UNIVERSITY BLACKSBURG, VIRGINIA

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# A "SCREENING APPROACH" FOR NUTRIENT CRITERIA IN VIRGINIA

## 2016 Report of the Academic Advisory Committee for Virginia Department of Environmental Quality

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## I. Introduction

The Academic Advisory Committee (AAC) is providing assistance to the Virginia Department of Environmental Quality (VDEQ) in developing a scientifically sound and workable approach to water-quality criteria for Virginia.

This report provides information on development of nutrient criteria for wadeable freshwater rivers and streams. Activities conducted to complete two tasks from the AAC's fiscal year 2016 work plan are described in this report:

- <u>Revisit Observed-Effect Concentration (OEC) analysis (Section III in AAC 2012a)</u> working with advice from a VDEQ contact who is familiar with the agency's waterquality assessment process. Revisit after reconsidering two essential factors: (1) The implementation time frame, and (2) the probability of impairment used to define the OEC. Conduct the analysis for a period that would be compatible with VDEQ's assessment process, likely two years or longer.
- Explore development of No-Observed-Effect Concentrations (NOECs) on an ecoregional basis.

These tasks were conducted within a context established by the AAC's prior reports to VDEQ. Most notably, the July 2012 report of the AAC (2012a) describes a screening approach and its components (including OEC and NOEC) and explores methods for deriving OEC and NOEC values from VDEQ water-monitoring data. The December 2012 AAC (2012b) report describes the technical and policy context for the AAC's proposal that VDEQ adopt a screening approach to nutrient criteria in Virginia's wadeable freshwater rivers and streams. Both reports are available on VDEQ's "Nutrient Criteria Development" web page.<sup>1</sup> The two tasks described here follow analyses described previously by the AAC (2012a) and further explore those approaches.

Specialized acronyms and terms used in this report are stated in Table I-1.

<sup>&</sup>lt;sup>1</sup><u>http://www.deq.virginia.gov/Programs/Water/WaterQualityInformationTMDLs/WaterQualitySt</u> <u>andards/NutrientCriteriaDevelopment.aspx</u> (accessed June 3, 2016)

Acronym/Term	Meaning	Report section where defined
Hypothetical assessment (H-assessment)	An evaluation of VSCI data for a station/period by the AAC. Unlike an actual water-quality assessment conducted by VDEQ, an H-assessment can yield any one of three possible outcomes:	Section II
	H-impaired	
	H-indeterminate	
	H-not impaired	
NOEC	No-Observed-Effect Concentration	Section III (see also AAC 2012a and AAC 2012b)
OEC	Observed-Effect Concentration	Section II (see also AAC 2012a and AAC 2012b)
Station/Period	A single monitoring location during a six- year assessment period (2003-2008 or 2009-2014)	Section II
TPR value	Ten-percent-rule value: the concentration for a given station/period that would be a critical value for water-quality assessment if the 10 percent rule was being applied.	Section II

**Table I-1.** Specialized acronyms and terms used in the report, with meanings and report section where the term is defined.

#### **II. Development of Observed-Effect Concentrations**

Development of a screening approach for nutrient criteria requires development of OECs for in-stream nitrogen and phosphorous. The AAC's analyses have focused on total nitrogen (TN) and total phosphorous (TP) as in-stream nutrient concentration measures. *Observed-effect concentrations* (OECs) for TN and TP are concentrations above which nutrient impairment of the aquatic community can be reasonably expected. Under the nutrient criteria screening approach, monitoring sites with measured TN and/or TP concentrations greater than or equal to a corresponding OEC would be assessed as impaired.

The analyses reported in this section were conducted to investigate the potential to establish OECs through a conditional probability analysis applied to VDEQ monitoring data. As per AAC goals for the current year, we attempted to conduct the analysis in a manner that is consistent with VDEQ's water-quality assessment process.

#### Method

The method of analysis, derived from Paul and McDonald (2005), was applied to estimate potential OECs. The method of analysis is based on the assumption that the probability of a site being impaired for aquatic life (Stream Condition Index <60) increases with measured nutrient concentrations. Prior AAC reports have explored this expectation at the upper end of the nutrient-concentration range (AAC 2006, 2009, 2010, 2012a).

#### **Data Acquisition**

The water-quality monitoring data obtained from VDEQ included observations from Virginia streams in the Piedmont, Blue Ridge, Valley and Ridge, and Central Appalachians ecoregions. Observations from ecoregions other than the Piedmont were combined, as per US EPA Level II ecoregion designations, forming a "Mountains" ecoregion designation. The database obtained included measured values for TN and TP and values calculated by VDEQ for those parameters from measured components. The database obtained extended from the 1990s through early 2016.

Biological monitoring data were also obtained from VDEQ. These data included Virginia Stream Condition Index (VSCI) scores, habitat metrics, and ecoregion designations. The three western ecoregions were reclassified as "Mountains" as described above. "Northern Piedmont" observations were reclassified as "Piedmont." Observations from east of the Piedmont ecoregion were not used in the analysis.

#### Water-Quality Assessments (VDEQ) and Hypothetical Assessments (AAC)

Dr. Tish Robertson of VDEQ was consulted concerning the agency's water-quality assessment practices. Dr. Robertson explained that VDEQ conducts water-quality assessments every two years, and each assessment considers monitoring data for a six-year period. For conventional water-quality parameters with numerical criteria acting as acute stressors, the data from each monitoring location are compared to the criterion using the 10 percent rule (TPR). In accordance with this rule, a monitoring location will be assessed as impaired if >10% of observations, or two observations at minimum, exceed the criterion for the given parameter. At least 10 observations are required from any individual site before it can be assessed as "fully supporting" the water-quality standard.

Dr. Robertson explained that VSCI data are also used for water-quality assessments. If all VSCI observations from a given site are either <60 (indicating impairment) or >60 (indicating not impaired), the site is assessed in accord with those VSCI results. If multiple VSCI scores are available from a given site and are mixed in impairment status (i.e., one or more are <60, and one or more are >60), best professional judgement is applied in the assessment. Factors considered in that judgement include whether or not a majority of the VSCIs are either <60 or >60, and if a site's biological condition appears to be improving or deteriorating through time. In consultation with Dr. Robertson, we developed the following method for assigning *hypothetical assessments* (H-assessments) to water-monitoring locations with VSCI data:

- *H-not impaired* (site passes):
  - If the ratio of passing VSCI scores (VSCI>60) to total number of VSCI scores is > 65%, and the average VSCI > 60; or
  - If the ratio of passing VSCI scores to total number of VSCI scores is  $\geq$  50% but <65%, and the average VSCI is >65.
- *H-impaired* (site fails):
  - If the ratio of passing VSCI scores to total number of VSCI scores is <35%; or
  - If the ratio of passing VSCI scores to total number of VSCI scores is > 35% but  $\le 50\%$ , and the average VSCI <55.
- *H-indeterminate* (otherwise): All other sites not meeting the definitions above.

The "otherwise" classification was applied with the understanding that VDEQ does not have the option of using this assessment classification. However, this classification helps to avoid subjectivity in applying the hypothetical assessments for the purpose of this analysis.

### <u>Analysis</u>

We decided to conduct the analysis using two six-year time frames: 2009-2014 and 2003-2008. The 2009-2014 time frame was selected as a recent period that corresponds with a VDEQ assessment period (currently in process). We used 2003-2008 as a means of increasing the number of data elements that would be available for analysis. We did not use earlier data because many TP observations were recorded  $\leq 0.1 \text{ mg/L}$  up through the year 2000, rendering them incompatible for data-analysis purposes with more recent data that has been obtained with greater precision. Also, some pre-2003 habitat evaluation data appeared to be less compatible with current habitat data.

Water-quality and biological data for the two time periods selected were combined into a single database. The first step of analysis was to identify TPR values for TN and for TP for each monitoring station/period with  $\geq 10$  observations for that parameter. The *TPR values* are those concentrations that correspond with the 10 percent rule. In other words:

- If 10-19 observations are available, the  $2^{nd}$  highest value = TPR value
- If 20-29 observations are available, the  $3^{rd}$  highest value = TPR value
- If 30-39 observations are available, the 4<sup>th</sup>- highest value = TPR value
- And so forth.

The TPR values were determined by station/period. In other words, if a given monitoring station had  $\geq 10$  observations for a parameter (TN, TP) for both the 2003-2008 and 2009-2014 periods, two separate TPR values were calculated for that station, i.e., one for each station/period. Average TN and TP concentrations were also calculated for each station/period.

A hypothetical assessment was applied for each station/period. Then a conditional probability analysis was applied for both TN and TP by ecoregion, using all station/periods with sufficient data to calculate a TPR value.

Impairment probability curves were plotted for each ecoregion separately and for all data combined. As a means of estimating OECs at the 70%, 80%, and 90% probability-of-H-impairment level, LOWESS (locally-weighted scatterplot smoothing) curves were fit to the conditional probability plots. This operation was performed using the software program JMP (v. 11.0) using the "flexible split fit" option, which assigns a smoothing-spline fit lambda = 0.01 value, and which created spline fits with high  $R^2$  values. The spline fit plots were placed in a graphics program and manually interpolated (with graphics' software elements applied to maximize precision) to determine TN and TP concentrations associated with 70%, 80%, and 90% probabilities of H-impairment.

In addition to the median concentrations used in our prior analyses, we analyzed relationships of average and TPR concentrations to median concentrations for the Mountains and Piedmont ecoregions.

#### **Results and Discussion**

Hypothetical assessments were applied to 1,086 station/periods with VSCI data that could be linked to measured TN and/or TP concentrations. Of these, 37% were classified as H-impaired, 16% as H-indeterminate, and 47% as H-not impaired (Table II-1).

For both TN and TP, the Piedmont data yielded conditional probability plots closer to what was expected than did the Mountains data (Figures II-1 and II-2). It is possible that this result may have occurred because of greater site-condition differences among streams in the Mountains ecoregion. It is possible that greater variation among such characteristics for streams in the Mountains ecoregion caused greater variation of responses by the stream communities to elevated nutrient concentrations. It is also possible that streams in the Mountains ecoregion are not as responsive to nutrients, generally, compared to those in the Piedmont, perhaps because streams in the Mountains ecoregion are more shaded and generally have higher gradients. Streams with higher gradients and with greater shading can be expected to accommodate elevated nutrient concentrations with lower probabilities of impairment than streams with more open canopies and lower gradients. Regardless of the reason, the Mountains ecoregion failed to generate conditional probability plots of the expected forms.

Conditional probability plots were generated on two separate bases: (1) Probability of Himpairment, and (2) probability of H-impairment or H-indeterminate status. Both approaches produced conditional probability plots with similar forms for high-end probabilities in all cases except for TP in the Piedmont. Hence, most of the potential OEC values generated by the two approaches are either identical or very similar (Table II-2). Based on conversations with Dr. Robertson, we are confident that most or all of the H-impaired and H-Not-Impaired site/periods would have been assessed similarly by VDEQ in formal water-quality assessment, but we have no guidance about how the H-indeterminate site/periods would have been assessed. Potential OEC values for the Mountains ecoregion should be interpreted with an understanding of the data structures and interpolation methods that generated them (Figure II-3).

For TN in both ecoregions and for TP in the Mountains ecoregion, the basis for constructing the conditional probability curves had essentially no effect on the estimated OEC values (Table II-2). This effect occurred because no H-indeterminate station/periods occurred with TN TPR concentrations giving rise to conditional probabilities >70%. For TN in the Mountains ecoregion, the highest-probability H-indeterminate observation (64%) influenced the shape of the interpolated curves causing a slight difference in the two 90%-probability values. For TP in the Piedmont, derived OECs for 70% and 80% probabilities were influenced by choice of endpoint because a number of H-indeterminate station/periods were associated with conditional probabilities in the ~70% to ~85% conditional-probability range.

Data from the Piedmont ecoregion produced relationships that are consistent with the expectations that underlie the development of the conditional probability method, but results for the Mountains ecoregion did not. Although we have applied the methods described to generate potential/estimated OECs, we do not see the resulting values as suitable for potential application for several reasons, including the sparseness of supporting data. The failure of the data from the Mountains ecoregion to generate usable results was similar to the outcome of previous work by the AAC (2012a).

For both TN and TP, relationships of TPR concentrations to median values are shown in Figures II-4 through II-6. Those relationships enable rough comparisons of results for the analyses described here, which used TPR concentrations, to those conducted previously by the AAC (2012a) using medians. Considering the TPR/median ratios that are evident from Figures II-4 and II-6, it appears that most results of these analyses for the 90%-probability level for the Piedmont ecoregion are roughly similar to those generated in 2012 (AAC 2012a). Informal analyses with these data using site/period average TN and TP concentrations for the Piedmont ecoregion generated 90%-probability potential OECs that were nearly identical to those generated previously by the AAC (2012a) (data not shown).

Considering the variability of TPR/median ratios (Figures II-4 through II-6), we conducted an exploratory and supplemental analysis of potential influences on those ratios. We found no obvious relationships (Figures II-7 and II-8), suggesting that random factors associated with streamflows, seasonality, and other influences on point-in-time TN and TP concentrations influence those relationships.

Given that the TPR is typically applied as an indicator of near-maximum concentrations for conventional toxicants, with the purpose of limiting concentrations to less-than-toxic levels; and given that nutrients do not act as toxicants, these results cause us to question if the TPR is the best possible method for assessing nutrient concentrations for potential in-stream nutrient impairments. One would expect that the average or median concentration experienced during a given season would, perhaps, be a better indicator of in-stream algae levels and influences on dissolved oxygen. It is possible that scientific literature could be consulted to investigate the validity of this expectation, but as of this writing we have not done so.

#### Conclusions

We applied the conditional probability method to select potential OECs using an analysis framework similar to that applied by VDEQ in water-quality assessments. Although we generated potential OECs for the Mountains ecoregion, the nature of the underlying data would make them difficult to defend. The Piedmont ecoregion data behaved in a manner that was closer to expectations and which enable defensible interpretations of resulting OEC estimates, but the OEC values generated are very high relative to nutrient concentrations in most of the study region's streams. Hence, their application as a component of a screening approach would enable few definitive water-quality assessments. The analyses described here were conducted using procedures intended to replicate water-quality assessments conducted by VDEQ and produced results that are consistent with those generated previously by the AAC (2012a).

As a means of going forward, we recommend consideration of alternative approaches for developing OECs. For example, VDEQ has conducted a stressor analysis for use in benthic TMDLs (total maximum daily loads; VDEQ 2016). The VDEQ analysis identifies concentrations of TN ( $\geq 2$  mg/L), TP ( $\geq 0.1$  mg/L), and other stressors that indicate "high risk to aquatic life." As of this writing, that report remains in draft form. It is possible that the report, when completed, may provide an alternative approach for identifying OECs.

	H-Im	paired	H-Indetern	H-Indeterminate		H-Not Impaired	
	n	Mean	n	Mean	n	Mean	
		VSCI		VSCI		VSCI	
Mountains	149	46.6	64	60.0	282	71.5	
Piedmont	258	44.3	107	59.7	226	69.0	

Table II-1. Results of hypothetical assessments applied to station/periods.

**Table II-2.** Potential OEC values generated by the methods described in this report and compared to earlier AAC (2012a) results.

Ecoregion	Probability	H-	H-impairment +	AAC	AAC
		Impairment	H-Indeterminate	(2012a),	(2012a),
		-		12-month	6-month
		TN (mg	√L), TPR	TN (mg/L)	), median
Mountains	70%	5.0	5.0		
	80%	5.4	5.4		
	90%	6.0	5.9	n/a	3.2
Piedmont	70%	1.6	1.6		
	80%	1.9	1.9		
	90%	3.1	3.1	1.8	1.9
		TP (mg	/L) TPR	TP (mg/L)	median
Mountains	70%	0.70	0.70	(	,
	80%	0.80	0.80		
	90%	0.90	0.90	n/a	0.26
Piedmont	70%	0.21	0.04		
	80%	0.33	0.19		
	90%	0.46	0.45	0.15	0.22



**Figure II-1.** Conditional probability for TN in the Mountains (above) and Piedmont (below) ecoregions.



**Figure II-2.** Conditional probability for TP in the Mountains (above) and Piedmont (below) ecoregions.



**Figure II-3.** Example of LOWESS spline fits used to interpolate the estimated OEC values of Table II-2. These examples, for the Mountains ecoregion, were selected to demonstrate the poor fit when applying this method.



**Figure II-4.** Linear-function relationships of TPR values for TN and TP vs. corresponding medians, by ecoregion.

	2=Mountai			
'N TPR/Media	n Ratio	TP T	PR/Median	Ratio
5-			1	
		4	-	
4.5		1	L8-	
4-		1	L6-	
-		1	L4-	
3.5-		1	-	
2		-	1	
5		1	L0-	
2.5			8-	•
	-		6-	
2				Y
15			4	
1.5			2	
1			0-	
Quantiles		Qu	antiles	
100.0% maximur	n 4.75926	100	.0% maximum	20
99.5%	4.71101	99.5	5%	19.6617
97.5%	2.55218	97.5	5%	6.5
90.0% 75.0% quartil	2.0125	90.0	)% quartile	4
50.0% media	n 146253	50.0	)% qualitie )% mediar	2.5
25.0% quartil	e 1.29543	25.0	)% quartile	1.5
10.0%	1.19688	10.0	)%	1
2.5%	1.09586	2.5%	%	1
0.5%	1.06491	0.5%	%	1
0.0% minimur	n 1.0648	0.0%	% minimum	1
		Sui	mmary Stat	istics
Summary Sta	tistics			
Summary Sta Mean	tistics 1.5567253	Mea	an	2.3584918
Summary Sta Mean Std Dev	tistics 1.5567253 0.4067141	Mea Std	an Dev	2.3584918 1.808258
Summary Sta Mean Std Dev Std Err Mean	1.5567253 0.4067141 0.0284757	Mea Std Std	an Dev Err Mean	2.3584918 1.808258 0.1259873
Summary Sta Mean Std Dev Std Err Mean Upper 95% Mea Lower 95% Mean	tistics 1.5567253 0.4067141 0.0284757 1.6128713 1.5005792	Mea Std Std Upp	an Dev Err Mean Der 95% Mea	2.3584918 1.808258 0.1259873 2.6068889 2.1100948

**Figure II-5.** Relationship of TPR concentrations, which were used for our primary analysis, to median concentrations for TN and TP in the Mountains ecoregion. Each datapoint represents all measured values for a single monitoring station during a 6-year assessment period (station/period). Only data from station/periods with  $\geq 10$  observations were used.

N TPR/I	Median	Ratio		TP TPR	/Median	Ratio
				r		
7-			•	14		
6-				12-		
-				10-		
57			•	- 8-1		
4			•	6		
3-	_		2	4		
2			Ţ			
1			Ÿ	0-		
Quanti	es			Quant	tiles	
100.0% r	naximum	7.1875		100.0%	maximum	14
99.5%		7.12951		99.5%		13.83
97.5%		2.88783		97.5%		7.738
90.0%		2.20146		90.0%		4
75.0%	quartile	1.7764		75.0%	quartile	2.5
50.0%	mediar	1.48454		50.0%	mediar	1.75
25.0%	quartile	1.31579		25.0%	quartile	1.5
10.0%		1.20115		10.0%		1.25
2.5%		1.12805		2.5%		1
0.5%		1.08155		0.5%		1
0.0%	minimum	1.08108	1	0.0%	minimum	1
Summa	ary Stat	istics		Summ	nary Stat	istics
Mean		1.6486454		Mean		2.3183216
Std Dev		0.6109645		Std Dev	1	1.7376451
Std Err M	lean	0.0428813		Std Err	Mean	0.1182318
Upper 95	% Mea	1.7331978		Upper 9	95% Mea	2.5513635
Lower 95	% Mean	1.564093		Lower 9	5% Mean	2.0852798
NI		203		N		216

**Figure II-6.** Relationship of TPR concentrations, which were used for our primary analysis, to median concentrations for TN and TP in the Piedmont ecoregion. Each datapoint represents all measured values for a single monitoring station during a 6-year assessment period (station/period). Only data from station/periods with  $\geq 10$  observations were used.



**Figure II-7.** Relationships of TPR/Median ratios to median concentrations (left) and number of observations, labeled as "counts" (right) for TN (above) and TP (below). Each datapoint represents all measured values for a single monitoring station during a 6-year assessment period (station/period).



**Figure II-8.** Relationships of TPR/Average ratios to average concentrations (left) and observation counts (right) for TN (above) and TP (below). Each datapoint represents all measured values for a single monitoring station during a 6-year assessment period (station/period).

#### III. Development of No-Observed-Effect Concentrations -

### **Probabilistic Monitoring Data**

Here, we report activities conducted by the AAC to continue advising VDEQ's development of nutrient criteria for freshwater rivers and streams. This report section describes activities conducted to explore NOEC development on an ecoregional basis.

As the term is used in this report, *no-observed-effect concentrations* (NOECs) are nutrient concentrations expressed as TN and TP concentrations below which freshwater streams have a low probability of being impaired by nutrients. If VDEQ were to adopt nutrient criteria that incorporate a screening approach, as recommended by the AAC (2012a and 2012b), freshwater streams with TN and TP concentrations below the NOECs would be assessed as "not impaired by nutrients."

Our analysis is based on that described by the AAC's July 2012 report to VDEQ (AAC 2012a). We extend that analysis as a means of estimating candidate NOECs for TN and TP on an ecoregional basis.

#### Goal

Estimate candidate NOECs for the Mountains and Piedmont ecoregions by extending the analysis described previously by the AAC (2012a).

#### Method

#### Review of Method Applied Previously by the AAC

The method used by the AAC in 2012 is based on the premise that a nutrient-criteria reference dataset can be extracted from VDEQ probabilistic monitoring data, which can then be used as a basis for defining NOECs for TN and TP. The nutrient-criteria reference dataset would be comprised of data from water-monitoring observations where influence by non-nutrient stressors appears as minimal and, hence, relationships of VSCI scores to TN and TP concentrations can be analyzed to extract NOECs. The nutrient-criteria reference dataset was developed by applying a reference filter that has been used by VDEQ for EPA-approved studies (VDEQ 2006; reproduced here as Table III-1). For our analysis, we did not apply the TN and TP filters; the results of this activity were described as nutrient-criteria reference candidates. VDEQ biologists were then asked to apply their best professional judgement to identify sites that were not appropriate for use as nutrient-criteria references. Because time and other limitations prevent VDEQ biologists from evaluating all candidate sites, those candidates with VSCI scores < 60were identified, and VDEQ biologists were asked to apply their best professional judgement to those sites. Any candidates judged by the biologists as unworthy of reference status (see Table II-3 in AAC 2012a) were then deleted from the site list to produce a nutrient-criteria reference dataset.

Once the nutrient-criteria reference dataset was defined, we attempted to extract NOECs from TN vs. VSCI and TP vs. VSCI by drawing regression lines. We anticipated that such regressions would have downward slopes (i.e., negative responses by VSCI scores to increasing TN concentrations and to increasing TP concentrations). We also expected that TN values and TP values defined by the intersection of the respective regression line with VSCI = 60 might serve as NOECs. However, application of that method by the AAC (2012a) found such intersections occurred at TN and TP concentrations outside the range of observed values for the

nutrient-criteria reference dataset and, hence, were not suitable for use in defining NOECs. Therefore, the 90<sup>th</sup> percentiles of the nutrient-criteria reference TN and TP values were selected as candidate NOECs.

#### Method Applied in 2016

We obtained an updated probabilistic monitoring database from VDEQ. Since the prior analysis was based on data from 2009 and earlier, we applied a similar analysis to all observations from 2010 and later to identify additional nutrient-criteria reference data records (i.e., probabilistic monitoring locations with associated VSCI, TN, and TP values) using an identical selection process. We then added the new reference sites to those generated previously by the AAC (2012a) to create an expanded nutrient-criteria reference dataset.

We analyzed the new dataset using the methods described in AAC (2012a) to extract candidate NOECs – but with one major difference: In 2016, we derived candidate NOECs for each ecoregion. In contrast, because of a limited number of observations, the earlier AAC (2012a) analysis derived candidate NOECs for a region comprised of the Mountains and Piedmont ecoregions combined. Other differences between the two analyses are described in the results section below.

We report 90<sup>th</sup> percentiles of the reference distributions as potential NOECs. Considering EPA documentation describing possible approaches for developing nutrient criteria (see Chapter 7 in US EPA 2000), we have also reported 75th percentiles of the reference distributions.

#### Results

The new probabilistic monitoring database included 114 observations within the Mountains and Piedmont ecoregions during the 2010-2012 collection periods. The probabilistic monitoring observations reported by VDEQ from 2010-2012 were average values calculated from two complete sampling observations (fall and spring) for biology, water quality, and habitat. Thus, the new data included a single record for each sampling site that had been calculated as an average of the fall and spring samples. In contrast, the pre-2010 dataset included only a single observation, either fall or spring, whichever was associated with water-quality data. Thus, the combined dataset used for the 2016 analysis included single observations for some sites (collected pre-2010) and average observations for other sites (collected during 2010-2012).

Application of the VDEQ reference filter to the 2010-2012 probabilistic monitoring observations identified 26 additional NOEC-reference candidates. Inspection of those data revealed one site that was ill-suited for reference status (5AKIT002.65; VSCI = 35, TN = 1.99 mg/L; TP = 0.19 mg/L). This site was removed from the list of candidate sites, leaving 25 additional nutrient-criteria reference sites (Figure III-1).

Data records for these 25 additional nutrient-criteria reference sites were added to the AAC 2012 nutrient-criteria reference database (61 sites as per AAC 2012a), resulting in 86 total nutrient-criteria reference sites for the two ecoregions combined (Figure III-2, Appendix A). In light of current goals, the 86 nutrient-criteria references were disaggregated into Mountains and Piedmont ecoregion subsets.

As in 2012, attempts to define NOECs by modeling responses of VSCI scores to TN and TP concentrations were not successful. Only one of the resulting relationships was statistically

significant, but it produced model TN and TP estimates corresponding with a VSCI = 60 intersect at concentrations higher than any occurring within the reference dataset (Figures III-3a and III-3b).

Therefore, we applied the 90<sup>th</sup>-percentile method for identifying NOEC candidates, as in the previous work by the AAC (2012a) but for the Mountains and Piedmont ecoregions separately. Also in contrast to the earlier AAC (2012a) procedure, we removed VSCI<60 observations prior to this operation. The 90<sup>th</sup> percentile values derived from the TN and TP distributions for the nutrient-criteria reference data when VSCI > 60 (Figures III-4a and III-4b) are listed in Table III-2 as candidate NOEC values. The 75<sup>th</sup> percentile values, alternative candidate NOEC values, are listed in Table III-3.

#### **Discussion and Summary**

We see the approach described in this report as a valid and defensible means of estimating candidate NOEC values that would be subject to further investigation. However, the analysis reported here is based on a limited number of data records. Furthermore, each data record is supported by only one (2001-2009 data) or two (2010-2012 data) monitoring observations.

The probabilistic monitoring dataset was selected originally for the NOEC analysis because each data record included additional information that was seen as being of potential value. The prior study (AAC 2012a) attempted to make use of additional probabilistic monitoring data by applying more rigorous reference filters (see Table II-2 in AAC 2012a) and by exploring relationships of nutrient concentrations with benthic algal metrics (see Figure II-4 in AAC 2012a). The probabilistic monitoring database was selected for use in 2012 because it contains measurements that enabled such analyses. However, results of those analyses were not useful in NOEC development. Therefore, the current analysis makes use of data measurements that were available for a much larger segment of the VDEQ water-monitoring observation record. Hence, a similar analysis could be applied using pairings of general biological and water-monitoring data when both occur within similar time frames at specific monitoring locations.

Parameter	Reference Filter
% Urban	< 5%
Total Nitrogen (TN) <sup>†</sup>	< 1.5 mg/L
Total Phosphorus (TP) <sup>†</sup>	< 0.05 mg/L
Specific Conductance	$< 250 \ \mu \text{S/cm}$
Dissolved Oxygen	> 6 mg/L
рН	> 6 and < 9
Channel Alteration	> 11
Embeddedness (Mountains Ecoregions only)	> 11
Epifaunal Substrate/Cover	> 11
Riparian Vegetative Zone	> 11
Total Habitat Score	> 140

**Table III-1.** Reference filters applied by the Virginia Department of Environmental Quality (2006).

<sup>†</sup>TN and TP screens were not applied in the current analysis.

Table III-2. Candidate NOEC	values produced by the analy	ysis described in this report using
90th percentiles of TN and TP	distributions of Figure III-4. <sup>1</sup>	

Ecoregion	TN (mg/L)	TP (mg/L)
Mountains	0.59	0.029
Piedmont	0.62	0.054

<sup>†</sup>Numbers of observations in reference distributions: 53 for Mountains, 25 for Piedmont (see Figure III-4).

Table III-3. Alternativ	e candidate NOEC values	s produced by the	analysis described in this
report using 75th perce	ntiles of TN and TP distr	ibutions of Figure	III-4. <sup>†</sup>

Toport using 75th	percentities of fit and fi	
Ecoregion	TN (mg/L)	TP (mg/L)
Mountains	0.39	0.020
Piedmont	0.54	0.045

<sup>†</sup>Numbers of observations in reference distributions: 53 for Mountains, 25 for Piedmont (see Figure III-4).



**Figure III-1.** VSCI, TN, and TP distributions for nutrient-criteria reference data extracted from 2010, 2011, and 2012 probabilistic monitoring database.



**Figure III-2.** VSCI, TN, and TP distributions for nutrient-criteria reference data created by combining the AAC (2012a) references with those represented by Figure III-1.



**Figure III-3a.** Regressions of TN and TP concentrations (mg/L) against VSCI scores for the Mountains ecoregion. The TN regression (left) is statistically significant (p<0.05) as shown, but the TP regression (right) is not. More rigorous statistical approaches would employ data transformations so as produce regressions that satisfy statistical assumptions, such as normalized residuals. Explorations of such approaches failed to yield VSCI = 60 intercepts within the range of nutrient-criteria reference TN and TP values.



**Figure III-3b.** Regressions of TN and TP concentrations (mg/L) against VSCI scores for the Piedmont ecoregion. Neither regression is statistically significant (p<0.05) as shown. Note that one of the data records is missing a TN value.



**Figure III-4a.** Nutrient-criteria reference distributions of VSCI, TN, and TP for the Mountains ecoregion after two VSCI<60 data records were removed.



**Figure III-4b.** Nutrient-criteria reference distributions of VSCI, TN, and TP for the Piedmont ecoregion after six VSCI<60 data records were removed.

### IV. Development of No-Observed-Effect Concentrations –

## **Full Database**

The OEC analysis (Section II) developed a database comprised of TN, TP, and VSCI data from VDEQ water-monitoring sites in the Mountains and Piedmont ecoregions for two six-year water-quality assessment periods (2003-2008 and 2009-2014). The NOEC probabilistic monitoring analysis (Section III) identified what we refer to as "reference sites" within the probabilistic monitoring dataset, and attempted to derive NOECs from those data by analyzing the relationships between VSCI scores and nutrient concentrations. In Section III, we concluded that it would be possible to apply similar analyses using the complete water-monitoring database. In this section, we apply the analyses described in Section III to the water-monitoring database described in Section II for the purpose of further exploring the development of NOECs.

#### Methods

The database used for this analysis consisted of joined VSCI (with habitat) and water-quality data described in Section II of this report.

We defined reference station/periods using procedures similar but not identical to those described in Section III of this report. Because GIS data were not available for the majority of monitoring stations, the reference filter based on the percent of urban land was not applied. When multiple observations were available for a given station/period, the dissolved oxygen, pH, and specific conductance reference filters were applied to minimum and/or maximum recorded values as appropriate; i.e., if a single observation for these parameters violated the reference filter, that station/period was defined as "non-reference." The habitat filters were applied with less stringency. For station/periods with five or more habitat evaluations,  $\geq 80\%$  of all observations were required to comply with each filter. For station/periods with fewer than five habitat evaluations, 100% compliance was required. Unlike the procedure described in Section III, we did not request best professional judgement by regional biologists as a means of aiding reference designations. Therefore, we made reference designations simply on the basis of the water-monitoring and habitat-evaluation data.

We attempted to develop potential NOECs using procedures similar to those described in Section III: We defined reference sites by ecoregion, evaluated the relationships between VSCI scores and nutrient concentrations for these sites, and defined NOECs as the 90<sup>th</sup> percentiles of reference sites receiving the H-not impaired classification. For this latter operation, we used results of the H-assessments described in Section II. The term "H-not impaired" indicates station/periods not classified as H-impaired and not classified as H-indeterminate using the methods described in Section II.

For some analyses, we used both median concentrations and TPR concentrations for TN and TP as derived in Section II. We conducted the median analyses for both the entire dataset and for the subset with  $\geq 10$  observations. We focused on the station/periods with  $\geq 10$  observations because TPR concentrations were derived only for station/periods with  $\geq 10$  observations and because VDEQ assessments include sites with  $\geq 10$  observations during an actual assessment.

Because we have not analyzed VDEQ's water-monitoring dataset using these techniques previously, we compared certain categories of observations statistically. Statistical comparisons of mean water-quality values were performed using non-parametric Wilcoxon procedures, and mean VSCI comparisons were performed using standard ANOVA (analysis of variance).

#### Results

A total of 495 station/periods in the Mountains ecoregion were found to have data suitable for use in the analyses, and 591 station/periods were found similarly in the Piedmont (Table IV-1). A small number of station/periods had only TN or TP water-quality data. Less than half of total station/periods had  $\geq$ 10 observations. Less than a third of all Mountains station/periods and less than a fourth of all Piedmont station/periods were classified as reference. The subsets with  $\geq$ 10 observations had an even smaller fraction of reference classifications. The reference vs. nonreference classification was successful, as the station/periods classified as reference had lower TN and TP concentrations and higher mean VSCI scores than those that failed to satisfy the reference filters (Table IV-1).

Attempts to identify potential NOECs by defining nutrient concentration vs. VSCI relationships within reference subsets of available data were not successful. Although several of the data segments yielded linear regressions that were nominally statistically significant, were downward sloping, and intersected VSCI=60 within the range of available data (TN medians for all data in both ecoregions, and TN medians for the  $\geq 10$  observations subset in the Piedmont), these regressions were performed with datasets that exhibited skewed distributions, and the regressions failed to yield residuals with normal distributions. Application of log-transformations as required to produce residuals with normal-appearing distributions produced regressions that either failed to intersect VSCI=60 or produced intersections beyond the range of measured data (regressions not shown).

Hence, 90<sup>th</sup> percentile values for TN and TP medians and TPR concentrations for H-not impaired station/periods were calculated (Table IV-2) and were examined as candidate NOECs. The 75<sup>th</sup> percentiles are also reported for the H-not impaired station/periods (Table IV-3). Selected distributions are displayed as Figures IV-1 through IV-4. In addition, median distributions for all data are reported in Appendix B, and median distributions for  $\geq$ 10-observation data segments are reported in Appendix C. Distributions of TPR values for TN and TP are provided in Appendix D.

#### **Discussion and Summary**

All of the data used to calculate the 90<sup>th</sup>-percentile values of Table IV-2 are from H-notimpaired station/periods, meaning that station/periods receiving hypothetical assessments as "Himpaired" or "H-indeterminate" were excluded from these analyses. In all cases, the 90<sup>th</sup>percentiles of TN and TP data calculated for the entire H-not-impaired segment of the dataset were higher than the corresponding values calculated for reference sites only, and in some cases, they were much higher. Reasons why these results occurred are not clear. However, the mean VSCI scores for the reference station/periods are significantly higher than are those from the non-reference station/periods, both overall (Table IV-1) and at the subset of station/periods that were used to calculate the 90<sup>th</sup>-percentile nutrient concentrations (potential NOECs; Table IV-4).

The candidate-NOEC values based on the 90th-percentiles of the reference sites yielded by this exercise are of similar magnitudes to those yielded by the probabilistic monitoring NOEC analysis. This analysis is more robust than that based on the probabilistic monitoring data because of the larger numbers of observations. Although the subsets of data with  $\geq 10$ 

observations are generally small, the resulting 90<sup>th</sup>-percentile values of these medians are similar to those calculated using all data, which had much larger numbers of observations. The 90<sup>th</sup>-percentile TPR values are higher than the corresponding values calculated for the medians. Possible reasons for this trend are provided in Section II (e.g., random factors such as differences in streamflows, seasonality, etc.). We do not consider the 90<sup>th</sup>-percentile TPR to be especially robust, given the small numbers of stations/periods at reference sites and the variability of TPR relationships to median and average concentration values (Figures II-4 through II-8). As with prior analyses, we are also reporting 75<sup>th</sup> percentiles (Table IV-3).

The subset of reference sites classified as H-not impaired is comprised of high-quality monitoring sites. In addition to satisfying most of the VDEQ reference filter criteria (Table III-1), most are characterized by site-mean VSCI scores well above 60 (Figure IV-5).

Ecoregion	Measure	Obs	A	11	Refe	rence	Non-Re	ference -	
			n	Mean	n	Mean	n	Mean	
Total Nitrogen (mg/L)									
Mountains	Median	all	493	0.82	133	0.34*	360	1.00	
Mountains	Median	≥10	204	0.94	35	0.27*	169	1.08	
Mountains	TPR	≥10	204	1.36	35	0.42*	169	1.56	
Piedmont	Median	all	586	0.85	128	0.45*	458	0.96	
Piedmont	Median	≥10	203	1.05	23	0.42*	180	1.14	
Piedmont	TPR	≥10	203	1.84	23	0.70*	180	1.98	
			Total Phosphorous (mg/L)						
Mountains	Median	all	490	0.032	132	0.018*	358	0.037	
Mountains	Median	≥10	206	0.034	34	0.017*	172	0.038	
Mountains	TPR	≥10	206	0.081	34	0.031*	172	0.091	
Piedmont	Median	all	585	0.047	129	0.035*	456	0.050	
Piedmont	Median	≥10	216	0.047	23	$0.032^{\dagger}$	193	0.049	
Piedmont	TPR	≥10	216	0.122	23	$0.065^{\dagger}$	193	0.129	
					VSCI (Station	/Period m	eans)		
Mountains	Mean	all	495	62.5	133	71.2*	362	59.3	
Mountains	Mean	≥10	208	60.4	35	70.9*	173	58.3	
Piedmont	Mean	all	591	56.5	131	65.0*	460	54.1	
Piedmont	Mean	>10	215	55.9	23	67.3*	192	54.5	

**Table IV-1.** Mean values of median and TPR nutrient concentrations (TN, TP) and station/period mean VSCI scores for all station/periods, and reference vs. non-reference comparisons, for the Mountains and Piedmont ecoregions.

\* designates reference-site mean values that are significantly different from non-reference site mean values a p<0.05; and <sup>†</sup> designates 0.05 < p<0.10 differences.

			All H-Ne	All H-Not Impaired		ot Impaired	
Ecoregion	Measure	Obs	n	90 <sup>th</sup> %tile	n	90 <sup>th</sup> %tile	
				Total N	N (mg/L)		
Mountains	Median	All	280	1.38	111	0.49	
Mountains	Median	$\geq 10$	101	1.69	30	0.39	
Mountains	TPR	$\geq 10$	101	2.48	30	0.66	
Piedmont	Median	All	224	0.92	87	0.73	
Piedmont	Median	$\geq 10$	72	1.04	19	0.69	
Piedmont	TPR	$\geq 10$	72	1.67	19	0.88	
				Total P (mg/L)			
Mountains	Median	All	277	0.04	110	0.035	
Mountains	Median	$\geq 10$	103	0.56	29	0.03	
Mountains	TPR	≥10	103	0.13	29	0.06	
Piedmont	Median	All	222	0.060	87	0.05	
Piedmont	Median	$\geq 10$	76	0.06	19	0.055	
Piedmont	TPR	≥10	76	0.16	19	0.12	

**Table IV-2.** 90<sup>th</sup> percentile TN and TP concentrations for all station/periods and reference sites that were H-assessed as "not impaired."<sup> $\dagger$ </sup>

<sup>†</sup>Values are rounded to 2 significant figures, unless third digit is a "5".

			All H-Not Impai	red Ref H-N	ot Impaired	
Ecoregion	Measure	Obs	n 75 <sup>th</sup> %	tile n	75 <sup>th</sup> %tile	
			Te	otal N (mg/L)		
Mountains	Median	All	280 0	.73 111	0.375	
Mountains	Median	≥10	101 0	.89 30	0.35	
Mountains	TPR	≥10	101 1	.22 30	0.54	
Piedmont	Median	All	224 0	.63 87	0.485	
Piedmont	Median	≥10	72 0	.77 19	0.445	
Piedmont	TPR	≥10	72 1	.10 19	0.69	
			T	Total P (mg/L)		
Mountains	Median	All	277 0.0	110	0.02	
Mountains	Median	≥10	103 0	.03 29	0.02	
Mountains	TPR	≥10	103 0	.06 29	0.04	
Piedmont	Median	All	222 0	.04 87	0.04	
Piedmont	Median	≥10	76 0	.04 19	0.04	
Piedmont	TPR	≥10	76 0	.08 19	0.09	

**Table IV-3.** 75<sup>th</sup> percentile TN and TP concentrations for all station/periods and reference sites that were H-assessed as "not impaired."<sup>†</sup>

<sup>†</sup>Values are rounded to 2 significant figures, unless third digit is a "5".

Table IV-4. Mean VSCI scores calcu	ulated from	H-not-impaired	station/period	1 means 1	for
reference and non-reference station/p	eriods.				

Ecoregion	Reference	Non-Reference
Mountains	74.4*	69.6
Piedmont	70.3*	68.1

\* designates reference means that are significantly different from non-reference means, p<0.001.



**Figure IV-1.** Distributions of all TN median concentrations (mg/L) for H-not impaired station/periods in the Mountains ecoregion.



**Figure IV-2.** Distributions of all TP median concentrations (mg/L) for H-not impaired station/periods in the Mountains ecoregion.



**Figure IV-3.** Distributions of all TN median concentrations (mg/L) for H-not impaired station/periods in the Piedmont ecoregion.



**Figure IV-4.** Distributions of all TP median concentrations (mg/L) for H-not impaired station/periods in the Piedmont ecoregion.



**Figure IV-5.** Station/period mean VSCI scores for the three H-assessment classes by ecoregion and with the H-not-impaired class disaggregated by reference status. The boxes represent the  $25^{\text{th}}$ ,  $50^{\text{th}}$ , and  $75^{\text{th}}$  percentiles. The horizontal lines for each box plot represent the mean value. The dashed horizontal lines represent the VSCI = 60 impairment threshold that is applied to individual VSCI measurements.

### Conclusions

The application of conditional probability analysis with the intention of estimating potential OECs did not yield useful results, but the efforts to estimate NOECs from reference datasets was more successful.

We interpret the potential NOECs generated from the full dataset to be more robust than those developed from the probabilistic monitoring dataset for two reasons: (1) The full dataset includes a larger number of aggregated observations (station/periods) than does the probabilistic monitoring dataset; and (2) most of the full dataset's aggregated observations are based on a larger number of water-quality measurements than are those in the probabilistic monitoring dataset, which is populated by TN and TP values derived from only one or two water-quality measurements. Despite those differences, the two data analyses yielded potential NOECs of similar magnitudes.

Based on the results of these analyses and on AAC activities in prior years, we suggest that VDEQ evaluate the following series of actions as a possible way forward in developing a nutrient-criteria framework for wadeable freshwater rivers and streams that incorporates a screening approach:

- 1. Investigate alternative approaches to OEC development. For example, the analysis described in VDEQ (2016), once published in final form, is one such approach that may merit such consideration.
- 2. Consider adopting NOECs that are based on the full dataset's reference distributions.

We see NOEC values based on either the 90<sup>th</sup> or the 75<sup>th</sup> percentile of reference distributions to be scientifically defensible. The decision concerning which percentile to select is a policy decision, not a scientific decision. Either choice or an intermediate percentile would carry some risk of incorrect assessments.

Because of the nature of the TN and TP distributions in Virginia's waters, there is considerable spread between the 75<sup>th</sup> and 90<sup>th</sup> percentiles (i.e., comparison of values in Tables IV-2 vs. IV-3). An advantage of selecting the 90<sup>th</sup> percentile would be the increased feasibility that VDEQ would be able to implement nutrient criteria as a screening approach, even with the increased demand for biological assessments that would result. VDEQ implementation would be more likely if NOECs were defined based on the 90<sup>th</sup> percentile because the increased biological-assessment demand would be less with NOECs based on 90<sup>th</sup> percentiles, relative to criteria with NOECs based on 75<sup>th</sup> percentiles.

We would expect far fewer incorrect assessments to result from nutrient criteria implemented with a screening approach compared to those that would result from application of conventional single-threshold criteria. The presumed reduced risk of incorrect assessment occurs because benthic macroinvertebrate monitoring would be conducted in stream reaches with inconclusive nutrient assessments and with inconclusive visual assessments, if such were to be applied (AAC 2012a). Thus, the benthic macroinvertebrate assessment would become the basis for assessment for most stream reaches in which an assessment based solely on nutrient concentrations would have the greatest risk of being incorrect.

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StationID	Year	Lat	Long	Season	Eco	VSCI	TN (mg/L)	TP (mg/L)
2-BNF003.52	2001	37.71877	-79.20181	Fall	Mtns	83.21	0.15	0.04
2-COO002.35	2001	37.51947	-78.52337	Fall	Pdmt	68.42	0.25	0.01
2-CWP023.28	2001	37.93828	-79.72109	Fall	Mtns	75.32	0.15	0.01
2-CWP053.78	2001	38.09981	-79.64977	Fall	Mtns	82.56	0.15	0.01
2-JOB001.02	2001	37.50300	-80.11505	Fall	Mtns	71.96	0.15	0.01
2-OGL005.53	2001	37.83987	-80.12246	Fall	Mtns	74.79	0.27	0.01
2-SMR004.80	2001	37.93492	-79.08797	Fall	Mtns	77.91	0.15	0.01
2-SUA001.55	2001	37.32956	-78.67655	Fall	Pdmt	68.60	0.55	0.05
4ASRV012.19	2001	36.64801	-79.55161	Fall	Pdmt	67.10	0.15	0.02
9-WFC010.66	2001	37.27888	-80.92542	Fall	Mtns	68.99	0.31	0.01
1BCDR010.21	2002	39.06128	-78.34596	Spring	Mtns	64.17	0.27	0.01
1BNFS102.55	2002	38.70317	-78.92056	Spring	Mtns	60.61	0.8	0.01
4ABEE001.20	2002	36.54342	-78.63229	Spring	Pdmt	41.06	0.46	0.04
6CSFH084.73	2002	36.69161	-81.77183	Spring	Mtns	60.50	0.62	0.04
2-XSB000.88	2003	37.72587	-79.56125	Spring	Mtns	67.87	0.4	0.03
4AHRN007.65	2003	36.66096	-80.01521	Spring	Pdmt	68.00	0.35	0.02
9-WLK026.82	2003	37.19857	-80.80576	Spring	Mtns	65.38	0.65	0.02
9-XDP000.65	2003	36.66652	-81.13315	Spring	Mtns	71.51	0.48	0.02
1AXJS001.20	2004	39.32431	-78.26570	Spring	Mtns	66.12	0.37	0.01
1BCDR027.54	2004	39.02172	-78.45979	Spring	Mtns	74.12	0.54	0.01
2-DCK003.94	2004	37.46334	-80.34827	Spring	Mtns	76.35	0.16	0.02
2-MIW003.45	2004	37.99656	-79.71186	Spring	Mtns	84.13	0.1	0.01
2-STV000.48	2004	37.62049	-80.18680	Spring	Mtns	79.80	0.1	0.01
2-WIC004.64	2004	37.47777	-78.88221	Spring	Pdmt	63.58	0.42	0.02
6BLSR004.78	2004	36.87209	-82.47342	Spring	Mtns	77.55	0.18	0.01
8-POR015.70	2004	38.20326	-77.63980	Spring	Pdmt	65.67	0.3	0.03
9-SFK002.81	2004	36.98483	-81.18752	Spring	Mtns	68.12	0.14	0.01
2-APP037.08	2005	37.28548	-77.72863	Spring	Pdmt	70.72	0.41	0.05
2-CSR003.94	2005	37.72799	-80.10520	Spring	Mtns	81.57	0.2	0.02
2-CWP006.87	2005	37.80957	-79.73910	Spring	Mtns	77.25	0.14	0.01
3-RPP150.20	2005	38.58206	-77.87496	Spring	Pdmt	79.57	0.64	0.03
4ACOX007.73	2005	36.72017	-78.25190	Spring	Pdmt	53.00		0.06
4AFSF004.02	2005	37.22043	-78.98518	Spring	Pdmt	62.44	0.18	0.02
8-NAR025.28	2005	37.94938	-77.61710	Spring	Pdmt	72.05	0.46	0.02
9-CPL009.78	2005	36.83265	-81.05106	Spring	Mtns	69.56	0.97	0.01
9-LFK005.39	2005	37.24309	-81.17130	Spring	Mtns	59.08	0.15	0.01
1AXLB001.49	2006	38.44479	-77.49889	Spring	Pdmt	68.25	0.46	0.03
2AXQS001.07	2006	37.71675	-79.77361	Spring	Mtns	83.32	0.1	0.01
2-BCC001.90	2006	38.04966	-79.90579	Spring	Mtns	73.41	0.42	0.01
4ACLB001.90	2006	36.58867	-78.91039	Spring	Pdmt	49.85	0.42	0.03
4AXNB000.60	2006	37.32821	-80.14344	Spring	Mtns	74.42	0.14	0.02
9-CPL012.73	2006	36.83618	-81.08703	Spring	Mtns	79.28	0.5	0.02

# Appendix A: Nutrient-criteria Reference Dataset Developed in Section III

1BNTH046.56	2007	38.33238	-79.23751	Spring	Mtns	69.60	0.2	0.01
2-BVC003.09	2007	37.73594	-78.72230	Spring	Pdmt	73.12	0.34	0.02
4ACEC000.82	2007	36.99435	-79.53321	Spring	Pdmt	64.55	0.12	0.01
6CLAL001.79	2007	36.64236	-81.80495	Spring	Mtns	67.70	0.38	0.01
9-XEO000.57	2007	36.75187	-80.54190	Spring	Mtns	71.54	0.3	0.02
2-CWP042.31	2008	38.01378	-79.63621	Spring	Mtns	55.89	0.22	0.02
2-SWS000.90	2008	37.71363	-79.89366	Spring	Mtns	77.03	0.1	0.01
5ABTR000.76	2008	37.08638	-77.67635	Spring	Pdmt	66.54	0.6	0.06
8-POR024.64	2008	38.22926	-77.73251	Spring	Pdmt	65.82	0.23	0.04
8-SAR058.13	2008	37.87805	-77.90921	Spring	Pdmt	77.77	0.55	0.05
9-DPW002.31	2008	36.91659	-80.63063	Spring	Mtns	81.29	0.1	0.01
2DAPP015.51	2009	37.22422	-77.46174	Spring	Pdmt	59.02	0.54	0.04
2-HKY001.26	2009	37.92418	-80.03744	Spring	Mtns	87.92	0.3	0.01
2-TYE028.94	2009	37.79979	-79.00654	Spring	Pdmt	53.77	0.16	0.02
3-XGR000.95	2009	38.39059	-78.46591	Spring	Mtns	88.22	0.24	0.06
5ALTL001.38	2009	36.59803	-77.74101	Spring	Pdmt	57.50	0.19	0.02
6CLIB001.06	2009	36.95873	-81.47481	Spring	Mtns	78.19	0.2	0.02
8-RIG003.01	2009	38.21874	-77.94060	Spring	Pdmt	63.02	0.59	0.05
9-KNS002.44	2009	36.77292	-81.25101	Spring	Mtns	80.52	0.12	0.01
1BBRY005.09	2010	38.44218	-79.10192	S+F Avg	Mtns	71.24	0.27	0.006
2BXAC000.38	2010	37.58897	-78.75307	S+F Avg	Pdmt	62.37	0.095	0.015
2-CRG074.32	2010	37.33535	-80.32894	S+F Avg	Mtns	69.06	0.08	0.015
2-JKS076.16	2010	38.18453	-79.73117	S+F Avg	Mtns	67.54	0.285	0.02
2-PMC000.59	2010	37.78018	-79.96359	S+F Avg	Mtns	76.61	0.11	0.01
4ACEC001.24	2010	36.98819	-79.55127	S+F Avg	Pdmt	77.87	0.115	0.02
4AXNA001.18	2010	37.16825	-79.76720	S+F Avg	Pdmt	61.80	0.645	0.09
6CSFH082.78	2010	36.67808	-81.79000	S+F Avg	Mtns	78.71	0.69	0.015
6CSFH099.18	2010	36.77460	-81.60880	S+F Avg	Mtns	81.91	0.47	0.01
9-SFK003.38	2010	36.99069	-81.19332	S+F Avg	Mtns	70.11	0.13	0.01
9-SNC008.04	2010	37.41741	-80.60808	S+F Avg	Mtns	77.66	0.095	0.01
1BBGR004.08	2011	38.29140	-78.69940	S+F Avg	Mtns	75.01	0.13	0.01
2-CRG047.95	2011	37.51120	-80.08760	S+F Avg	Mtns	70.59	0.275	0.01
2-DCK003.94b	2011	37.46347	-80.34805	S+F Avg	Mtns	71.42	0.15	0.01
2-DDY000.75b	2011	38.17732	-79.37611	S+F Avg	Mtns	81.44	0.095	0.01
2-RED003.65b	2011	37.50908	-79.38327	S+F Avg	Pdmt	66.28	0.535	0.025
6CLAL000.19	2011	36.64940	-81.82940	S+F Avg	Mtns	70.83	0.395	0.015
9-ECM001.01	2011	36.71690	-81.27070	S+F Avg	Mtns	71.22	0.425	0.03
9-WLK033.29	2011	37.16270	-80.85490	S+F Avg	Mtns	60.86	0.355	0.015
1aXMJ000.42	2012	38.63750	-77.50550	S+F Avg	Pdmt	75.92	0.105	0.02
2BLIR007.16	2012	37.76450	-79.16440	S+F Avg	Mtns	82.06	0.22	0.02
2BXRK001.64	2012	37.81140	-78.72990	S+F Avg	Pdmt	73.34	0.28	0.01
4ASRE063.69	2012	36.84360	-80.16170	S+F Avg	Pdmt	79.74	0.11	0.01
4AXOE001.26	2012	36.64800	-80.38120	S+F Avg	Mtns	79.62	0.38	0.025
4AXOF001.26	2012	36.80200	-79.70090	S+F Avg	Pdmt	74.15	0.08	0.01

## Appendix B: Distributions of Median Values for All Station-periods Analyzed





## Appendix C: Distributions of TN and TP Median Values (≥10 Observations Only)



Appendix D: Distributions of TPR Values for TN and TP