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ESTIMATING NUTRIENT AND SEDIMENT THRESHOLD CRITERIA FOR BIOLOGICAL IMPAIRMENT IN PENNSYLVANIA WATERSHEDS[1]

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ABSTRACT: This study employs a simple nonlinear statistical approach to establish nitrogen, phosphorus, and sediment concentration and unit area load thresholds to aid in the evaluation of aquatic biological health of watersheds within the state of Pennsylvania. Flow, nitrogen and phosphorus species, sediment, basin area, land cover, and biological assessment data were assembled for 29 Pennsylvania watersheds. For each watershed, rating curves depicting flow versus load relationships were developed using the U.S. Environmental Protection Agency's (USEPA's) storage and retrieval database (STORET) flow and concentration data, then applied to daily flow data obtained from U.S. Geological Survey (USGS) daily flow gauging stations to estimate daily load between 1989 and 1999. The load estimates and concentration data were then sorted into six sets of data: mean annual unit area nitrogen, phosphorus, and sediment loads; and average nitrogen, phosphorus, and sediment concentrations. Results of Mann-Whitney tests conducted on each of the six datasets indicate that there is a statistically significant difference between the concentrations and unit area loads of nitrogen, phosphorus, and sediment in impaired and unimpaired watersheds. Concentration thresholds, calculated as the midpoint between the impaired and unimpaired watersheds' 95 percent confidence interval for the median, were estimated to be 2.01 mg/L, 0.07 mg/L, and 197.27 mg/L for nitrogen, phosphorus, and sediment, respectively. Annual unit area load thresholds were estimated to be equal to 8.64 kg/ha, 0.30 kg/ha, and 785.29 kg/ha, respectively, for nitrogen, phosphorus, and sediment species.
(KEY TERMS: nonpoint source pollution; total maximum daily load (TMDL); nutrient criteria; sediment criteria; watershed hydrology.)

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INTRODUCTION

Under Section 303(d) of the Clean Water Act, states are required to conduct Total Maximum Daily Load (TMDL) assessments for all water bodies that are currently not attaining the water quality standards for their designated use. This provision of the Clean Water Act has recently received attention due to a series of citizens' lawsuits, which required state environmental regulatory agencies and the U.S. Environmental Protection Agency (USEPA) to list impaired water bodies and annually demonstrate progress toward completion of TMDLs.

Within this context, the Pennsylvania Department of Environmental Protection (PADEP) has been making progress in the evaluation of water bodies in the state using standard biological survey techniques (PADEP, 2002). As of February 2002, of the approximately 134,000 river kilometers in the state, 52 percent are currently attaining their water use designation, 10 percent are deemed "nonattaining," and the remaining 38 percent are listed as "unassessed." Water bodies have been placed on the state's 303d list for a variety of reasons including acid rain, acid mine drainage, pesticides, streambank erosion and associated flow problems, sewage overflow, construction, habitat modification, and industrial and municipal point source pollution. However, nutrient pollution and sedimentation/siltation are listed as the primary cause of impairment for approximately 50 percent of the impaired water bodies in the state. Nonpoint source nutrient pollution and sediment pollution are difficult to assess and have been further

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complicated by the lack of established criteria or threshold upon which watersheds can be evaluated in the TMDL process.

In Pennsylvania, a geographic information system (GIS) based modeling approach has been developed to support TMDL assessments in watersheds where nutrients and/or sediment have been determined to be the primary causes of biological impairment. This approach involves the use of AVGWLF, a modeling tool that facilitates the use of the Generalized Watershed Loading Function (GWLF) watershed model (Haith and Shoemaker, 1987) and customized statewide datasets and model parameterization routines within an ArcView GIS software interface (Evans *et al.,* 2002). The general approach in such assessments is to: (1) derive input data for GWLF for use in an "impaired" watershed; (2) simulate nutrient and sediment loads within the impaired watershed; (3) compare simulated loads within the impaired watershed against loads simulated for a nearby "reference" watershed that exhibits similar landscape, development, and agricultural patterns but that also has been deemed unimpaired; and (4) identify and evaluate pollution mitigation strategies that could be applied in the impaired watershed to achieve pollutant loads similar to those calculated for the reference watershed.

The primary bases of comparison between impaired and reference watersheds are the average annual nutrient and sediment loads estimated for each. The main objective of the reference watershed approach is to estimate the degree to which the current nutrient and/or sediment loads in the watershed containing the impaired stream segment(s) would need to be reduced in order to achieve a level equivalent to or slightly lower than the loading rate in the non-impaired reference watershed. The underlying assumption is that this load reduction would allow biological health to return to the impaired stream segments.

While the reference watershed concept has provided a straightforward method for completing nonpoint source TMDL assessments in Pennsylvania, several problems are associated with this approach. First, the calculated reduction of loads for the impaired watershed is somewhat arbitrary. The percent reduction in pollutant loading is determined by comparison to the reference watershed, which is selected by the person(s) conducting the investigation. Therefore, the recommended reductions in nonpoint source pollution are dependent upon the reference watershed that is selected. Secondly, the selection of the reference watershed is frequently very difficult and labor intensive. Since pollution load is often related to land use within the watershed, it can be difficult to find a reference watershed that is similar to the impaired watershed in terms of physical characteristics that is also attaining the water quality standards for its designated use.

This study is intended to fulfill several objectives. First, existing data and simple statistical measures are employed in an attempt to develop methods of estimating nutrient and sediment thresholds that can be easily adopted for use in other geographical regions. Additionally, the results of this study provide a set of chemical load and concentration criteria that may be used as one indicator of aquatic biological health, provide evidence in support of current TMDL assessments, raise concerns regarding previously proposed ecoregional nutrient criteria, and generally serve as a stimulus to further discussion.

METHODS

For the purposes of this study, historical water quality data were evaluated for a number of watersheds throughout Pennsylvania. Based upon the availability of biological assessment and nutrient and sediment concentration data, 29 watersheds were included in the study (see Figure 1). Watershed selection was based on the presence of a completed biological assessment; multiple years of nitrate, nitrite, and ammonia nitrogen; total phosphorus; filterable and nonfilterable residue water quality data from the USEPA STORET Legacy Web site (USEPA, 2002); and at least one year of mean daily flow data between 1989 and 1999 available from the USGS water resource Web site (USGS, 2002). Nutrient criteria studies conducted by the USEPA (2000a,b,c,d; 2001) have investigated this issue at far greater spatial extent. This study limits the spatial extent, and consequently the spatial variability, to the Pennsylvania state boundary. While this boundary is not environmental, an attempt was made to represent the variability of physical basin characteristics (geology, slope, land cover distribution, soil type, physiographic providence, etc.) found throughout Pennsylvania.

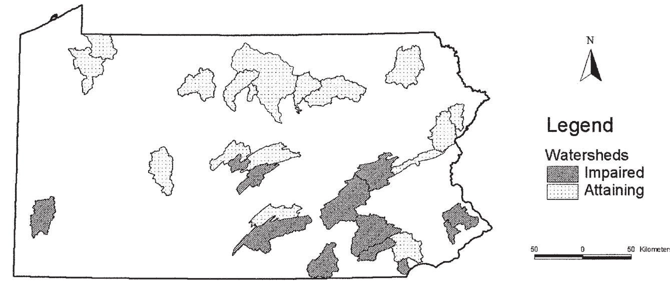

Figure 1. Map of the 29 Watersheds Included in the Data Analysis.

Once data from the watersheds meeting the above criteria were assembled, the watersheds were divided into subsets based upon the presence and cause of impairment. In Pennsylvania, stream impairment is assessed using biological techniques, which are commonly applied to detect ecosystem impairment. Biological data are ideally suited to detect ecosystem impairment but do not provide information on the causes of that impairment. Therefore, impairment is attributed to various causes based upon visual assessment of the watershed. Using a GIS, delineations of each basin were created and subsequently overlaid on a geographic version of the Pennsylvania 303d list developed by the PADEP that contained information on the assessment status and cause of impairment for all streams within the state. This overlay produced information on total, impaired, and unimpaired river mileage within each basin. These basins were then designated as impaired or unimpaired based upon the percentage of the total river mileage listed as impaired.

Basins with greater than 25 percent of the total river mileage determined to be impaired based on PADEP's stream assessment were designated as "impaired" for the purposes of this study. This method of assessing the impairment of a watershed introduces the potential of spatial mismatch between the point at which water chemistry data were collected and the stream segments designated as impaired through biological assessment. However, Pennsylvania water quality standards regulation assigns designated beneficial uses to waters. These waters are then assessed to determine if uses are being attained. Therefore, the listing of a water body as impaired is determined by both the biological assessment and its designated water use. Consequently, it is possible for adjacent stream segments to be assessed differently given similar chemical and biological characteristics. Since general differences between impaired and unimpaired watershed nutrient and sediment loads are of primary interest, the method employed here is thought to provide an accurate representation of watershed health.

Using the classification method described above, 17 of the 29 watersheds used in the analysis were listed as unimpaired. The remaining 12 watersheds were listed as impaired, with sedimentation listed as a cause in all, and 11 additionally listed for nitrogen and phosphorus impairments.

Nutrient and sediment concentration and daily flow rate data downloaded from the USEPA STORET Legacy Web site (USEPA, 2002) were used to develop rating curves for nitrogen, phosphorus, and sediment loads. While previous studies have expressed concerns over the use of rating curves in mixed land use watersheds (Preston *et al.,* 1989), R^2 values greater than 0.65 were calculated for all flow load relationships used in the study. The high statistical degree of fit between load and flow seen in all of the watersheds indicates that the rating curve approach is appropriate in this study. Total daily nitrogen, phosphorus, and sediment loads were determined using the following equations.

$$\text{TN Load} = ([NO_3^- \text{-N}] + [NO_2^- \text{-N}] + [NH_3\text{-N}]) * \text{Flow} * 2.4466 \quad (1)$$

$$\text{TP Load} = [TP] * \text{Flow} * 2.4466 \quad (2)$$

$$\text{Sediment Load} = ([NFR] + [FR]) * \text{Flow} * 2.4466 \quad (3)$$

where TN Load is total daily nitrogen load (kg N/day), $[NO_3^-\text{-N}]$ is nitrate-nitrogen concentration (mg N/L), $[NO_2^-\text{-N}]$ is nitrite-nitrogen concentration (mg N/L), $[NH_3\text{-N}]$ is ammonia-nitrogen concentration (mg N/L), TP Load is total daily phosphorus load (kg P/day), [TP] is total phosphorus concentration (mg P/L), Sediment Load is total daily sediment load (kg sediment/day), [NFR] is nonfilterable residue concentration (mg NFR/L), [FR] is filterable residue concentration (mg FR/L), Flow is average daily stream flow (cfs), and 2.4466 is the conversion from mg/L and cfs to kg /day.

Once daily nitrogen, phosphorus, and sediment loads were determined for all available samples, rating curves depicting the relationship between mean daily flow and daily load in each watershed were developed. To obtain the best fit for each constituent, exponential and linear relationships between daily flow and load were developed. The statistical relationship yielding the highest R^2 value in each case was then selected (see example in Figure 2).

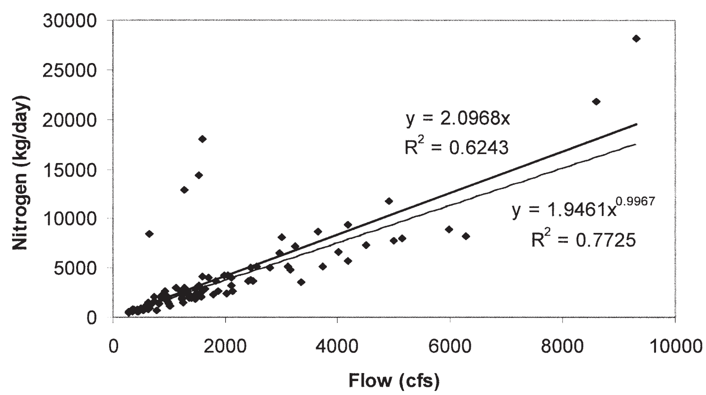

Figure 2. Rating Curve and Trendline Example.

The trendline equations derived from the rating curves were then used to estimate daily loads of nitrogen, phosphorus, and sediment from each of the watersheds using daily flow information downloaded from the USGS NWISWeb Web site (USGS, 2002). Flow data collected between 1989 and 1999 were used in the procedure. Of the 29 watersheds included in the study, 24 had a complete daily flow record, two had between 5 and 10 years of flow data, and three watersheds had one to five years of data. Watersheds with less than one complete year of flow data were not used in this study. Using the rating curves and daily flow records, daily loads of nitrogen, phosphorus, and sediment were calculated for each of the watersheds.

Mean annual loads and instream concentration estimates of nitrogen, phosphorus, and sediment were derived for each watershed. The mean annual loads of the three constituents were calculated by dividing the sum of the daily load estimates by the years of record as in Equation (4).

$$MAL = \sum(DL) / (CDL / 365 \text{ days/year}) \quad (4)$$

where MAL is the mean annual load (kg/year), DL is the daily load estimate, and CDL is the count of daily load estimates.

Mean annual unit area loads of nitrogen, phosphorus, and sediment were calculated by dividing the mean annual load (kg/year) by the watershed area in hectares (ha). Average stream nitrogen, phosphorus, and sediment concentration estimates were calculated by averaging the available nitrogen, phosphorus, and sediment concentration data for each watershed.

The mean unit area loads and instream concentrations for nitrogen, phosphorus, and sediment were then divided into the two groups described above (i.e., impaired and unimpaired watersheds). Using MINITAB® Statistical Software, Anderson-Darling normality tests were conducted on the six sets of results (mean nitrogen, phosphorus, and sediment concentration and unit area loads). Since the concentration and unit area load datasets were not normally distributed, nonparametric Mann-Whitney tests were used to determine whether differences between median values of nutrient and sediment concentrations and loads were statistically significant between the impaired and unimpaired watersheds. While linear statistical methods are generally preferred, the Mann-Whitney test has been used to investigate differences in ground water nitrogen concentration values (Hall, 1992), acid mine drainage (Hawkins, 1994), rainfall and runoff relationships (Rose, 1998), and other aspects of the hydrologic system. The results from the Mann-Whitney tests were then used to estimate nitrogen, phosphorus, and sediment concentration and unit area load thresholds, above which watersheds may be at risk of impairment due to the problems associated with excess nutrient and sediment inputs.

RESULTS AND DISCUSSION

Box plots depicting the 95 percent confidence intervals for the median of each of the six datasets are shown in Figures 3 through 8, and the results based on the statistical analyses are summarized in Table 1. Generally, box plots are applied to normally distributed data. However, MINITAB® calculates confidence

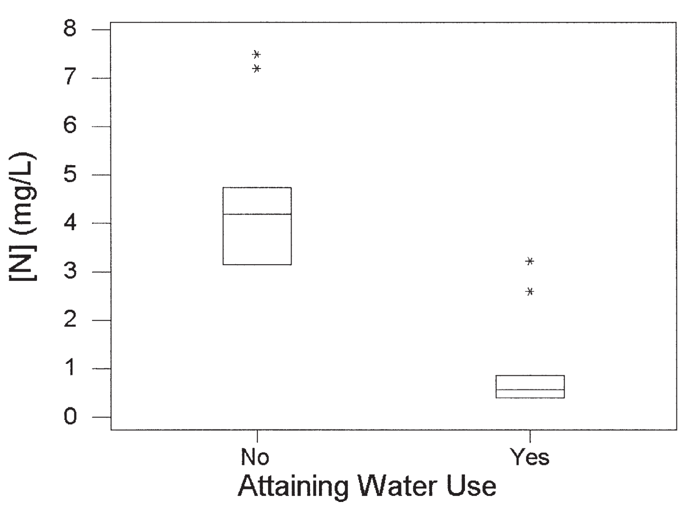

Figure 3. Statistical Box Plot of Median Nitrogen Concentration for Watersheds Listed as Attaining Their Water Use Designation and Watersheds Impaired by Nutrient Pollution.

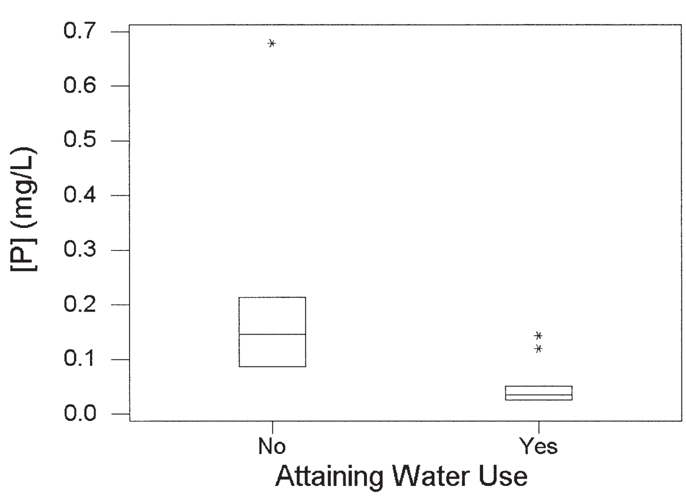

Figure 4. Statistical Box Plot of Median Phosphorus Concentration for Watersheds Listed as Attaining Their Water Use Designation and Watersheds Impaired by Nutrient Pollution.

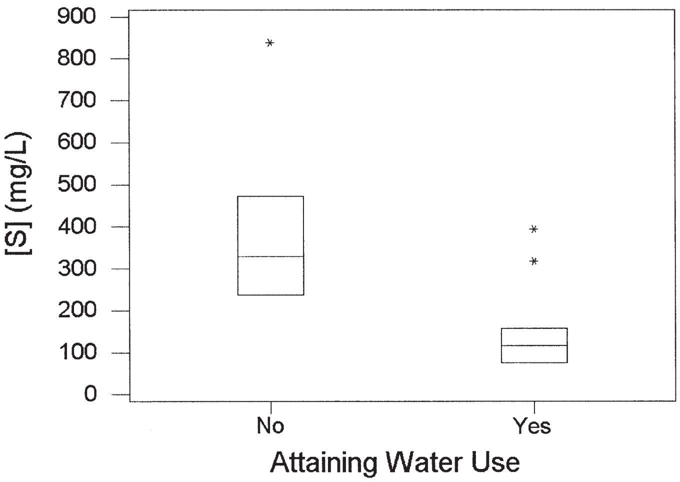

Figure 5. Statistical Box Plot of Median Sediment Concentration for Watersheds Listed as Attaining Their Water Use Designation and Watersheds Impaired by Sediment Pollution.

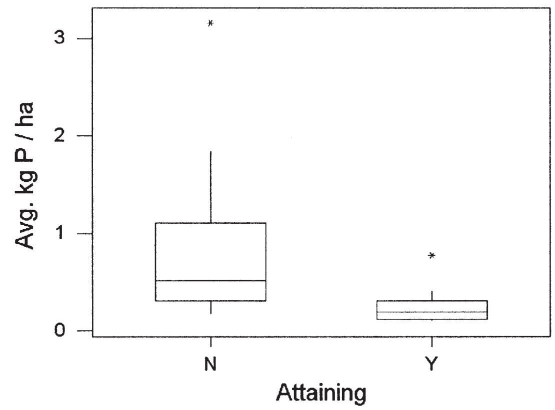

Figure 7. Statistical Box Plot of Median Phosphorus Load for Watersheds Listed as Attaining Their Water Use Designation and Watersheds Impaired by Nutrient Pollution.

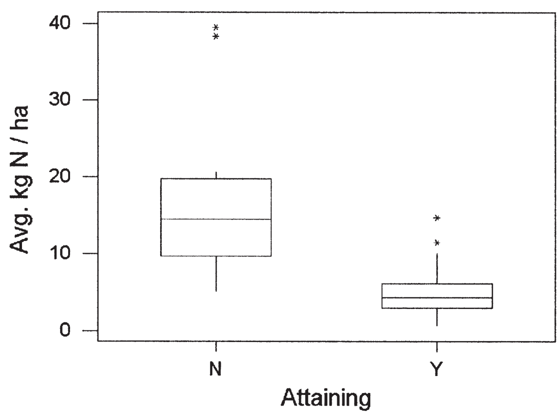

Figure 6. Statistical Box Plot of Median Nitrogen Load for Watersheds Listed as Attaining Their Water Use Designation and Watersheds Impaired by Nutrient Pollution.

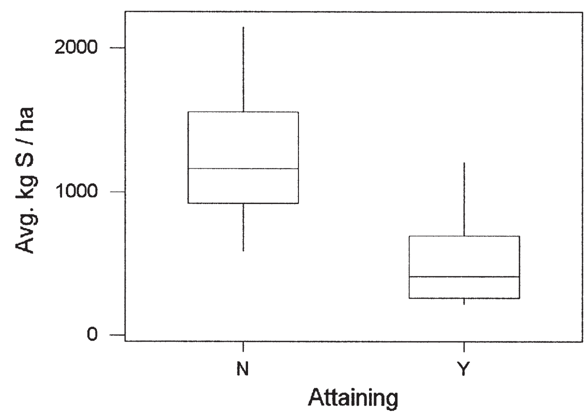

Figure 8. Statistical Box Plot of Median Sediment Load for Watersheds Listed as Attaining Their Water Use Designation and Watersheds Impaired by Sediment Pollution.

TABLE 1. Median and Upper and Lower Confidence Intervals for Average Nitrogen, Phosphorus, and Sediment Concentration and Unit Area Load Estimates.

		Attaining Watersheds			Nutrient/Sediment Impaired Watersheds		
Measurement	**Pollutant**	**Median of Data**	**Lower 95 Percent Confidence Interval Value**	**Upper 95 Percent Confidence Interval Value**	**Median of Data**	**Lower 95 percent Confidence Interval Value**	**Upper 95 Percent Confidence Interval Value**
Load (kg/ha/yr)	Nitrogen	4.32	3.11	5.90	14.77	11.38	22.20
	Phosphorus	0.19	0.12	0.29	0.49	0.31	1.17
	Sediment	408.94	262.29	646.78	1,164.54	923.80	1,557.10
Concentration (mg/L)	Nitrogen	0.56	0.40	0.86	4.19	3.15	4.75
	Phosphorus	0.03	0.03	0.05	0.15	0.09	0.21
	Sediment	115.06	75.02	157.25	329.53	237.30	472.77

intervals for the median based on interpolated order statistics and therefore is an appropriate illustration of results. Hettmansperger and Sheather (1986) describe the statistical method, which assumes that there is a unique median but makes no shape assumption. In Hettmansperger and Sheather's (1986) work, numerical calculations with a sample size of 10 show that the estimation method works reasonably well for asymmetric distributions. Thus, the confidence intervals produced using the 12 impaired and 17 unimpaired watersheds are adequate.

The results shown in Table 1 indicate that there is a statistically significant difference between the concentrations and unit area loads of nitrogen, phosphorus, and sediment in the impaired versus unimpaired watersheds. In all the cases tested, the median value derived for the impaired watersheds was significantly greater than the median value derived for the unimpaired watersheds at the 95 percent confidence interval level.

As the Mann-Whitney tests suggest, when the 95 percent confidence intervals were investigated, there was no overlap between the confidence intervals for impaired and unimpaired watersheds. Therefore, the nutrient criteria values illustrated in Table 2 were calculated as the midpoint between the impaired watershed's lower 95 percent confidence interval value and the unimpaired watershed's upper 95 percent confidence interval value. While these values are certainly not absolute, the statistical tests indicate that the intervals derived contain the true median concentration and load values from each group. Therefore it is not unreasonable to assume that in the watersheds used in this study, the threshold level between impaired and unimpaired systems should lie between the confidence interval endpoints.

TABLE 2. Estimated Nitrogen, Phosphorus, and Sediment Unit Area Load and Concentration Thresholds.

Constituent	Annual Load (kg/HA)	Concentration (mg/L)
Nitrogen	8.64	2.01
Phosphorus	0.30	0.07
Sediment	785.29	197.27

It is interesting to note that there is also a substantial difference between the average land cover characteristics in the impaired and unimpaired watersheds. Table 3 illustrates the mean percentages of developed, agricultural, and forested land comprising the impaired and unimpaired watersheds. The land cover statistics presented in this table support widely accepted relationships between land usage and nutrient and sediment pollution. Nutrient and sediment concentrations and loads are positively correlated with the magnitude of development and agricultural practices within the watershed. Forest land cover types typically export very low levels of pollution in comparison with disturbed areas and can exhibit buffering capacity in basins with mixed land cover. Given these relationships, it is not surprising that the watersheds categorized as impaired contain more developed and agricultural land and less forest land when compared to the unimpaired watersheds.

TABLE 3. Mean Land Cover Percentages for Impaired and Unimpaired Watersheds.

Watershed Designation	Developed Land (percent)	Agricultural Land (percent)	Forest Land (percent)
Impaired	10.9	46.6	40.5
Unimpared	1.4	18.1	78.0

While there is a clear statistical distinction between the nutrient and sediment median concentrations and loads in the impaired and unimpaired watersheds included in this study, pollution levels greater than the criteria may not constitute aquatic impairment for several reasons. For example, the watersheds used in this study are generally of uniform size. Headwater streams with similar nutrient and sediment concentrations may be evaluated as healthy ecosystems due to lower water temperatures, higher dissolved oxygen concentrations, faster travel times, or other factors. In addition to pollution considerations, countless studies have concluded that the biological health of an aquatic community is largely dependent upon suitable habitat characteristics (Ohio EPA, 1999; Fitzpatrick *et al.,* 2001; Johnson *et al.,* 2003; Jowett, 2003). While many habitat characteristics are correlated to aquatic nutrient and sediment concentrations, it is certainly possible for an aquatic community to be damaged due entirely to habitat modification. Therefore, conclusions based solely on the comparison of measured nutrient and sediment levels to the empirically derived criteria may prove misleading.

Using a different approach than described above, the USEPA developed ambient nutrient criteria recommendations for 14 ecoregions across the United States (USEPA, 2003). Portions of Regions VII (USEPA, 2000a), VIII (USEPA, 2001), IX (USEPA, 2000b), and XI (USEPA, 2000c) are found within the state of Pennsylvania. While no sediment concentration or load criteria were developed in these reports, the average nitrogen and phosphorus concentration values for the four regions are 0.48 and .022 mg/L, respectively. Ecoregions IX and XI account for most of Pennsylvania's land area. The average nitrogen and phosphorus concentration criteria values for these two regions are 0.5 and 0.023 mg/L, respectively. The average values for Ecoregions IX and XI are greater than the average of the four regions but still considerably less than the values derived in this report.

The estimates of the Pennsylvania nutrient criteria arrived at in this report may be more realistic than the criteria set forth by the USEPA in the aforementioned publications for several reasons. First, each of the ecoregions referred to in the USEPA reports cover vast areas of land, far greater than the geographic extent of Pennsylvania. Ecoregion XI, which runs northeast to southwest across the state of Pennsylvania, also encompasses portions of Ohio, West Virginia, Maryland, Virginia, Kentucky, North Carolina, Tennessee, Georgia, and Alabama. Significant variation in the characteristics of the climate and physical landscape can be found across such a large geographic extent. For example, stream temperature, flow, biological activity, and light availability have been shown to influence phosphorus utilization (Nalewajko and Lee, 1983; Meals *et al.,* 1999). Since nutrients need to be utilized for the problems associated with eutrophication to occur, consideration of the variability of stream temperature, flow, biological activity, light availability, and other factors may lead to more realistic estimates of nutrient threshold criteria. While this study does not explicitly address the impact that these and other factors have on nutrient uptake, limiting the scope of the investigation to the state of Pennsylvania reduces the variability of climate and landscape characteristics expressed in the various ecoregions and is believed to better reflect nutrient and sediment thresholds given more localized conditions in Pennsylvania.

Secondly, the nutrient data compiled for the unimpaired watersheds in this study suggest that the concentration criteria values recommended by the USEPA for the ecoregions of Pennsylvania may be too low. The streams in 17 of the watersheds used in this study were found to be unimpaired when surveyed using biological assessment procedures. Of these 17 unimpaired watersheds, only five of the watersheds meet the nitrogen concentration criteria proposed in the USEPA publications, and only four meet the phosphorus criteria. This comparison illustrates the discrepancy found between the proposed ecoregion nutrient criteria and the results obtained using the biological stream assessment procedures. A similar discrepancy was found by Pickett (1997) in a two-year field study of the Black River, a tributary of the Chehalis River in western Washington State. The two-year field study concluded that a protective criterion of 0.05 mg P/L be established to prevent eutrophic conditions in the watershed. This proposed criterion is considerably greater than the .01 mg P/L criterion proposed by the USEPA for Ecoregion II (USEPA, 2000d). Due to the intensive and localized nature of Pickett's (1997) investigation, the criteria developed for the Black River may be more realistic than the proposed Ecoregion II criteria. Similarly, the nutrient and sediment criteria derived using Pennsylvania nutrient concentration, flow, and biological assessment data may be more indicative of local ecosystem health than the criteria limits derived by the USEPA for each of the ecoregions that fall within the state.

CONCLUSION

The ability of a natural hydrologic system to assimilate pollutant loads is variable. Therefore, the threshold values derived using the procedure described above are not absolute. Factors including ground water chemistry, the volume of ground water input, aquatic biota, and many stream morphology characteristics can all affect the ability of an aquatic ecosystem to assimilate nutrient and sediment loads. Consequently, the threshold limits derived above should be used as one piece of evidence in determining potential impairment and not as an absolute measure of aquatic health. Furthermore, the results shown above were developed using data from watersheds representing a broad range of physical characteristics found in Pennsylvania. While the methods used to arrive at these results are sound and could be applied to other areas of interest, the values themselves are likely to be most representative of conditions in the northeastern United States.

Given the concerns stated above, the procedure discussed in this article yielded statistically significant differences between median values of nitrogen, phosphorus, and sediment instream concentrations and unit area loads in impaired and unimpaired Pennsylvania watersheds. Additionally, the differences in the median values between impaired and unimpaired watersheds were large enough that the 95 percent confidence intervals for the median values did not overlap. This allowed for the estimation of nitrogen, phosphorus, and sediment instream concentration and unit area load thresholds, above which watersheds of similar physical characteristics may be at risk of impairment due to the problems associated with excess nutrient and sediment inputs.

Using the current TMDL assessment approach discussed in the introduction, variation can be introduced into the analysis through the selection of the reference watershed. Additionally, as mentioned above, identifying a watershed that can be used as a reference can be a very time consuming procedure. While the criteria developed in this study should not be considered absolute, they may be helpful in the selection of a reference watershed, be used in cases where a suitable reference watershed has been difficult to find, and/or be used as evidence to support the recommended reduction of nonpoint source pollutants in impaired watersheds.

RECOMMENDATIONS FOR FUTURE WORK

The availability of both biological assessment and water chemistry data limited the scope of the work and, by extension, the applicability of the findings. Once biological assessment of the streams of Pennsylvania is complete, the procedure could be repeated using a larger number of watersheds. Applying the same methodology to a larger, more diverse selection of watersheds could yield useful information on the effect of watershed size on pollution concentrations associated with biological impairment. Alternatively, multivariate methods or a repeated measures design could be employed to assess the impact of both spatial variables (geology, land cover, topography, etc.) and temporal variables (precipitation, storm intensity, stream discharge, etc.) on instream nutrient and sediment concentrations. Pairing this information with aquatic biological assessment data could potentially lead to further insight.

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