# LEVELS OF PHOSPHORUS AND NITROGEN IN SHENANDOAH RIVER WATER[1]

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## ABSTRACT

In the period 1936-1941, smallmouth bass nests were counted in the Main Stem and South Fork of the Shenandoah River. Counts were made during the smallmouth bass spawning season when waters were clear, usually May 1-15. Due to eutrofication, the South Fork and Main Stem water now remains clear for only a few days. The enumeration and study of bass nests has been made more difficult due to the sudden development of blooms of algae. High levels of phosphorus and nitrogen in the South and North Forks and the Main Stem are believed to be the cause.

Total phosphate ranged from 0.33 to 4.80 parts per million in the South Fork and from 0.23 to 1.50 ppm. in the Main Stem. The highest seasonal averages occurred in the spring and fall. In the North Fork, total phosphate ranged from 0.14 to a maximum of 1.40 ppm., with the highest seasonal averages occurring in the spring and summer.

Orthophosphate ranged from 0.30 to 2.30 ppm. in the South Fork, and from 0.14 to 1.04 ppm. in the Main Stem. The North Fork ranged from 0.07 to 1.15. The highest averages occurred in the fall when the South Fork averaged 0.934 ppm. and the Main Stem 0.489 ppm. The highest average in the North Fork occurred in the Spring (0.453 ppm.).

Nitrate nitrogen levels were high in all sections of the river and based on past records is increasing steadily. In the South Fork, nitrate nitrogen as NO3 ranged from 1.18 to a maximum of 8.93 ppm. Spring and winter had the highest seasonal averages with 5.60 and 6.79; the Main Stem was from 0.82 to a maximum of 7.90 ppm. Spring and winter had the highest averages with 4.488 and 5.626 ppm., respectively. The North Fork had the highest nitrate nitrogen, with levels ranging from 1.087 to a maximum of 11.462 (an amount approaching safety limits for drinking water). Winter had the highest seasonal average, 7.584 ppm. In both the South and North Forks, the average, as well as winter and summer average nitrate and phosphate levels, decreased from their initial high levels in passage downstream.

Nitrite nitrogen levels and nitrogen/phosphorus ratios were also determined.

## INTRODUCTION

When the writer first began field studies of smallmouth bass in the Potomac River Basin in 1936, the Shenandoah River was either clear or in different stages of "muddiness" due to suspended silt, clay particles, etc. While counting bass nests during the period 1936-1941, (Surber, 1942) difficulties were rarely encountered in the observation of South Branch and Cacapon River nests due to turbid water. The Shenandoah River water was more likely to be muddy or in different degrees of turbidity due to rains or showers. Generally, the period May 1 to May 15, is the peak of the smallmouth bass spawning season in this area. During this period the river water is usually clear or clearing, with river levels stabilizing after high stages (following periods of heavy rainfall in April).

[1]A product of Virginia Dingell-Johnson Project F-14-S, Shenandoah River Survey.

When the project leader returned to the Shenandoah River Valley in 1964 to again count bass nests in the river, he encountered a new problem with respect to bass nest counting - that of "eutrofication". Plant nutrients, the most important of which are phosphorus and nitrogen had accumulated in the river water to such an extent that "blooms" of microscopic plants could develop over a two or three day period as a result of rapid multiplication of phytoplankton algae. When this occurred during the smallmouth bass spawning season, bass nests could no longer be counted in water two feet deep or more because the nests could not be seen.

The increased sources of nitrogen and phosphorus are a result of increased pollution in the valley due to wastes (domestic sewage) from increasing human populations, more intense farming of the land, runoff of fertilizers, chemical wastes (such as detergents used both in the home and in industrial processes), etc.

For the period April 1, 1929 to March 31, 1930, a report (Collins, W. D. *et. al.* 1930) on the Surface Waters of Virginia showed an average of 1.3 parts per million nitrate (as NO3) for the South Fork of the Shenandoah River near Luray. The range for the South Fork was 0.3 to 3.0 ppm. During this period the North Fork at Strasburg averaged 1.8 ppm. and the range was 0.62 to 3.3 ppm. NO3.

Kapustka (1957) gave the results of occasional nitrate nitrogen (NO3) determinations made in 1954 and 1955 at the old Riverside Bridge (South Fork) at Front Royal. Determinations ranging from 0.6 to a maximum of 4.5 ppm., with 60 per cent of the observations (10) under 3.0 ppm., and the average 2.2, were recorded. In the water year October, 1955 to September, 1956, the South Fork at Front Royal averaged 1.8 ppm. NO3, with 31 determinations ranging from 0.5 to 3.9 ppm. The highest values occurred during the winter months of January and February.

At the North Fork station located at Strasburg, during 1955 and 1956, 50 per cent of the observations (10) showed 3.0 parts per million or less NO3. The maximum was 5.5 and the minimum 0.4 ppm., the average 3.2 ppm.

The 1960 Report on "The Chemical Character of Surface Waters of Virginia" by the Division of Water Resources of The Commonwealth of Virginia, Department of Conservation and Economic Development, showed an average of 3.4 ppm. NO3 at Front Royal (6 determinations) with a maximum of 8.8 and a minimum of 0.2 ppm.

The North Fork at Strasburg averaged 4.9 ppm. with a maximum of 9.8 ppm. nitrate. An April 1959 sample at Mt. Jackson showed 14.0 ppm. present.

Large quantities of nitrate in natural waters indicate pollution originating from sewage or organic matter. In the North Fork Valley, runoff from many chicken and turkey farms are an important source.

Although a great deal of work has been done on the distribution and quantities of phosphorus in fish ponds and lakes, information on the quantities occurring in rivers is comparatively small. Keup (1968) made a thorough review of phosphorus in flowing waters.

The source of phosphorus in streams such as the Shenandoah River are land surface runoff, waste waters from cities, organic humus, and the leaching of phosphorus from bedrock. Limestone ledges are prevalent in the bed of the Shenandoah River and limestone contains 1.32 per cent phosphorus. Limestone outcrops occur throughout the valley floor.

Removal of phosphorus from surface waters can occur very rapidly as a result of plant growths, whether they are phytoplankton, epiphytic algae growing on the rocks in the stream bed, or coarse submersed plants. In limestone waters phosphorus is readily precipitated out, and sorption of phosphorus by particulate material plays an important role in the reduction of soluble concentrations.

The 1968 report of the National Technical Advisory Committee on Water Quality Criteria (1968) pointed out that an imbalanced organic enrichment, together with changes in temperature and salinity, bring about an almost complete change in the species composing an aquatic community.

The nitrogen-phosphorus ratio varies with the season, temperature and geological formation, ranging from 2:1 to 100:1. In the natural waters, the ratio is often very near 10:1 and this appears to be a good guideline. A N/P ratio of 5:1 is considered low.

According to the NTAC, allowable amounts of total phosphorus will vary, but in general it is believed that a desirable guideline is 100 ug/l (micrograms per liter) for rivers and 50 ug/l where streams enter lakes or reservoirs. In this report, results have been expressed in parts per million (1ppm=1 milligram per liter). A microgram is 1/millionth part of a gram. This is equal to 0.001 ppm or one part per billion.

Mackenthun (1965) cites results indicating that inorganic nitrogen at 0.3 mg/l and inorganic phosphorus at 0.01 mg/l, when present at the start of an active growing season, subsequently permitted algae blooms.

The objectives of this project have been to determine the levels of nitrogen and phosphorus occurring in the river and to determine if sudden blooms can be predicted. The river now supports blooms that may first appear in the South Fork and Main Stem around the first week in May and which may prevail throughout periods when the river was normally clear some 35 years ago. Eutrophication in the North Fork has resulted in plant growths just as profuse or more profuse, but in the form of filamentous, epiphytic algae and higher plants. Instead of phytoplankton forms, tremendous growths of *Hydrodictyon, Cladophera* and other filamentous species, and coarse weeds such as *Elodea* and *Heteranthera*, choke the water course (although the water remains clear).

## METHODS

The different forms of phosphorus and nitrogen were determined with a Hach Direct Reading Colorimeter, Model DR-EL field kit[1], battery powered.

Orthophosphate, metaphosphate and total phosphate were determined by the stannous methods described in the colorimeter kit manual. In the orthophosphate (simple or soluble phosphorus) determination 15 drops of ammonium molybdate were added to 25 ml. samples and a blank. "stanna Ver" powder pillows were then added after bringing the test temperature to 75 degrees F. The phosphorus was determined after the samples had stood 10 minutes by timer. "Total" phosphate (ortho plus meta) was determined by boiling (for 10 minutes) 25 ml. samples to which 18 drops or ammonium molybdate had been added. Distilled water was used following boiling to return samples to their original volume. "stanna Ver" powder pillows were then added and the "total" phosphorus determined with the aid of a colorimeter (after samples had set for 3 minutes). Organic phosphorus, which requires a special digestion procedure, was not determined.

Parts per million of metaphosphate was calculated by subtracting ppm. orthophosphate from total phosphate. Occasionally orthophosphate readings were higher than the "Total" Phosphate readings, and when the tests were repeated, more often than not, the same results were obtained.[2]

Nitrite nitrogen (in terms of the element) was determined by using 25 ml. samples and "Nitri Ver" powder pillows. Samples stood for 30 minutes before being placed in the light cell.

[1]Hach Chemical Co., Box 907, Ames, Iowa, 50010

[2]This problem has been overcome by recent changes in Hach procedures for the determination of both ortho and metaphosphate. Organic phosphate can also be determined by a simplified procedure.

Nitrate nitrogen as N was determined by the cadmium reduction method (usually on 5 ml. samples that had been diluted to 25 ml. with distilled water). The light cell reading was multiplied by a dilution factor of 5, and the result divided by 100 since the meter scale was calibrated for a sample dilution of 1:100.

The nitrate determinations include nitrite which is subtracted to obtain nitrate - N as N. Nitrate nitrogen (NO3) was calculated by multiplying the nitrate nitrogen as N by a factor of 4.4.

The nitrogen/phosphorus ratio was determined by dividing nitrate nitrogen (as N) by phosphorus as P. The latter was determined by dividing total phosphate by 3.

Location of sampling stations are given in Figure 1. South Fork stations are numbered 1-4, Main Stem stations 5-7, North Fork stations 1-5.

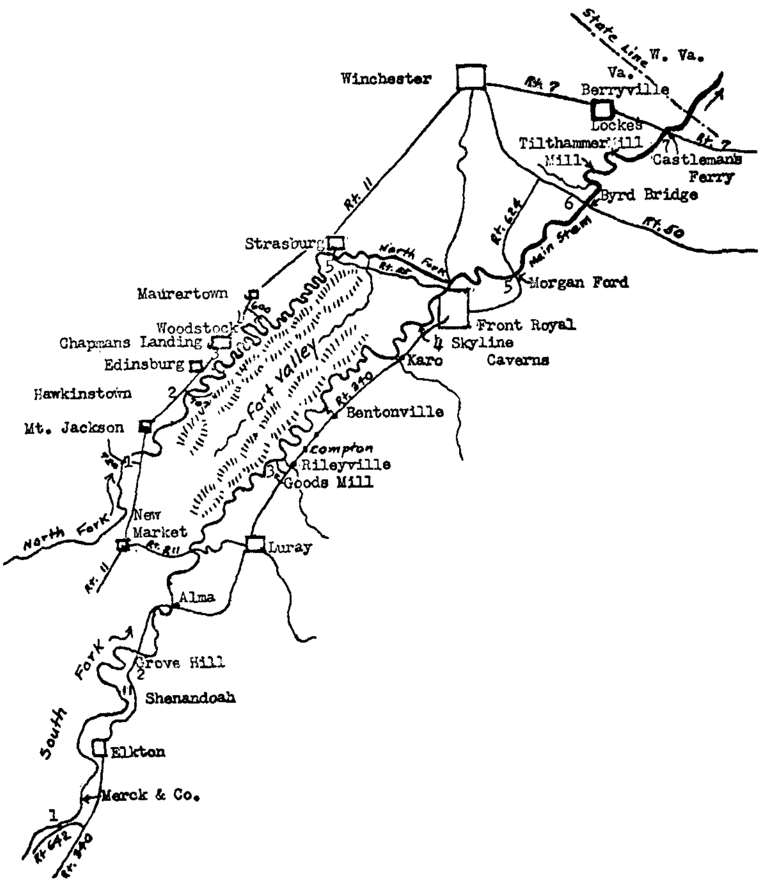


Figure 1. Map showing locations of Electrofishing and Water Sampling Stations on the Shenandoah River.

## RESULTS

Space permits giving only the general results of the phosphorus and nitrogen determinations. It was apparent that seasonal differences occured in nitrate-nitrogen content of the river water. For this reason, seasonal averages and ranges for each period of the year, spring, summer, fall and winter, for orthophosphate, total phosphate, nitrate nitrogen (as NO3), nitrite nitrogen (N), and Nitrogen/phosphorus ratios were calculated for the period of observations (November 20, 1969 to December 14, 1971). The results are given in Tables 1-3. There was a large gap in the spring, summer and fall data of 1970 due to illness of the project leader.

Orthophosphate ranged from 0.30 to 2.30 parts per million in the South Fork and 0.14 to 1.04 ppm. in the Main Stem. Both sections of the river had the highest averages in the fall season when the South Fork averaged 0.934 ppm. and the Main Stem 0.49 ppm. The North Fork orthophosphate ranged from 0.07 to 1.15 parts per million and seasonal averages were generally lower. The spring and fall averages were about the same (0.45 ppm).

In all sections of the river; South Fork, Main Stem, and North Fork; the winter period had the lowest average orthophosphate levels.

Total phosphate ranged from 0.33 to 4.80 ppm. in the South Fork and from 0.23 to 1.50 in the Main Stem. In both of these sections of the Shenandoah, the highest seasonal averages occurred in the spring and fall.

In the North Fork, total phosphate ranged from 0.14 to a maximum of 1.40 ppm., with the highest seasonal averages occurring in the spring and summer.

Nitrate nitrogen levels were high in all sections of the river and from past records appears to be increasing steadily. In the South Fork, nitrate nitrogen as NO3 ranged from 1.18 to a maximum 8.93 ppm. Spring and winter had the highest seasonal averages with 5.60 and 6.79 ppm., respectively. The range of nitrate nitrogen (as NO3) in the Main Stem was from 0.82 to a maximum of 7.90 ppm. Spring and winter again produced the highest averages with 4.49 and 5.63 ppm., respectively. The North Fork had the highest nitrate nitrogen, with levels ranging from 1.09 to a maximum of 11.46 ppm. Winter had the highest seasonal average, 7.58 ppm. nitrate nitrogen as NO3.

Nitrate nitrogen (as N) and total phosphate divided by 3 were used to calculate N/P ratios. The purpose was to examine the role of imbalanced ratios in creating unusual phytoplankton blooms or other vegetative growths. In the South Fork N/P ratios ranged from 0.38:1 to a maximum of 11.7:1. Seasonal averages were spring 4.3:1, summer 3.6:1, fall 3.5:1 and winter 6.8:1. In the Main Stem N/P ratios ranged from 0.9:1 to a maximum of 14.2:1. Seasonal averages for the Main Stem were spring 4.1:1, summer 3.2:1, fall 5.2:1 and winter 9.0:1. The North Fork had the highest N/P ratios, ranging from a minimum of 2.4:1 to a maximum 35.7:1. Winter conditions again maintained the highest average N/P ratio on the North Fork, with a ratio of 15.8:1. The North Fork's seasonal averages were: spring 7.3:1; summer 7.6:1; fall 11.5:1; winter 15.8:1.

Nitrite Nitrogen (as N) ranged from a minimum of 0.005 to a maximum of 0.075 ppm. Of the seasons, spring nitrite levels were the highest for the South Fork and Main Stem (with season averages twice as high as for other seasons).

The highest seasonal levels of phosphorus present in the Shenandoah River occurred in the spring and fall for the South Fork and Main Stem, while the spring and summer season levels were highest in the North Fork. Since P was determined by dividing total phosphate by 3, the levels of phosphorus follow the total phosphate trends. The minimum level of P determined was 0.04 ppm. below Strasburg on October 28, 1970 and maximum 1.60 at Grove Hill below Shenandoah and Elkton on the same date. The South Fork average for 48 determinations was 0.34 ppm. P., while the average for the Main Stem was 0.20 (36 determinations) and the North Fork 0.17 ppm. (50 determinations).

Table 1. Phosphorus and Nitrogen in the Shenandoah River. Seasonal Ranges and Averages.

| | **South Fork 1970-1971** Parts Per Million | | | |
|---|---|---|---|---|
| | Spring | Summer | Fall | Winter |
| Orthophosphate | 0.45 - 1.40 | 0.30 - 1.60 | 0.33 - 2.30 | 0.30 - 0.66 |
| Average | 0.892 | 0.788 | 0.934 | 0.415 |
| Total Phosphate | 0.42 - 2.20 | 0.38 - 1.80 | 0.42 - 4.80 | 0.33 - 0.68 |
| Average | 1.140 | 0.996 | 1.417 | 0.612 |
| Nitrite Nitrogen (N) | 0.013 - 0.093 | 0.006 - 0.070 | 0.006 - 0.048 | 0.012 - 0.045 |
| Average | 0.049 | 0.024 | 0.020 | 0.021 |
| Nitrate Nitrogen (NO3) | 3.577 - 8.523 | 1.184 - 8.932 | 2.649 - 6.327 | 4.444 - 6.939 |
| Average | 5.597 | 5.297 | 4.335 | 6.786 |
| Nitrogen/Phos. Ratio | 1.5 - 6.5 : 1 | 1.9 - 6.4 : 1 | 0.38 - 7.0 : 1 | 4.4 - 11.7 : 1 |
| Average | 4.3 : 1 | 3.6 : 1 | 3.5 : 1 | 6.8 : 1 |

Table 2. Phosphorus and Nitrogen in the Shenandoah River. Seasonal Ranges and Averages.

| | **Main Stem 1970-1971** Parts Per Million | | | |
|---|---|---|---|---|
| | Spring | Summer | Fall | Winter |
| Orthophosphate | 0.36 - 1.04 | 0.30 - 0.55 | 0.30 - 0.68 | 0.14 - 0.50 |
| Average | 0.473 | 0.358 | 0.489 | 0.339 |
| Total Phosphate | 0.55 - 1.50 | 0.30 - 0.80 | 0.30 - 1.10 | 0.23 - 0.90 |
| Average | 0.854 | 0.532 | 0.588 | 0.487 |
| Nitrite Nitrogen (N) | 0.016 - 0.098 | 0.010 - 0.030 | 0.005 - 0.025 | 0.001 - 0.015 |
| Average | 0.034 | 0.017 | 0.014 | 0.011 |
| Nitrate Nitrogen (NO3) | 2.640 - 6.930 | 0.823 - 4.752 | 2.253 - 4.580 | 4.567 - 7.898 |
| Average | 4.488 | 2.455 | 3.809 | 5.626 |
| Nitrogen/Phos. Ratio | 1.7 - 8.2 : 1 | 0.9 - 5.1 : 1 | 2.7 - 9.4 : 1 | 4.5 - 14.2 : 1 |
| Average | 4.1 : 1 | 3.2 : 1 | 5.2 : 1 | 9.0 : 1 |

Table 3. Phosphorus and Nitrogen in the Shenandoah River. Seasonal Ranges and Averages.

| | **North Fork 1970-1971** Parts Per Million | | | |
|---|---|---|---|---|
| | Spring | Summer | Fall | Winter |
| Orthophosphate | 0.20 - 0.80 | 0.24 - 0.80 | 0.07 - 1.15 | 0.13 - 0.35 |
| Average | 0.453 | 0.410 | 0.447 | 0.255 |
| Total Phosphate | 0.23 - 1.40 | 0.40 - 0.98 | 0.14 - 0.74 | 0.20 - 0.82 |
| Average | 0.650 | 0.646 | 0.363 | 0.375 |
| Nitrite Nitrogen (N) | 0.015 - 0.075 | 0.008 - 0.040 | 0.005 - 0.052 | 0.006 - 0.035 |
| Average | 0.033 | 0.018 | 0.020 | 0.016 |
| Nitrate Nitrogen (NO3) | 1.826 - 8.334 | 3.705 - 9.614 | 1.087 - 11.462 | 5.852 - 10.085 |
| Average | 5.478 | 7.423 | 5.621 | 7.584 |
| Nitrogen/Phos. Ratio | 2.4 - 15.9 : 1 | 6.5 - 9.5 : 1 | 3.2 - 35.7 : 1 | 5.5 - 27.4 : 1 |
| Average | 7.3 : 1 | 7.6 : 1 | 11.5 : 1 | 15.8 : 1 |

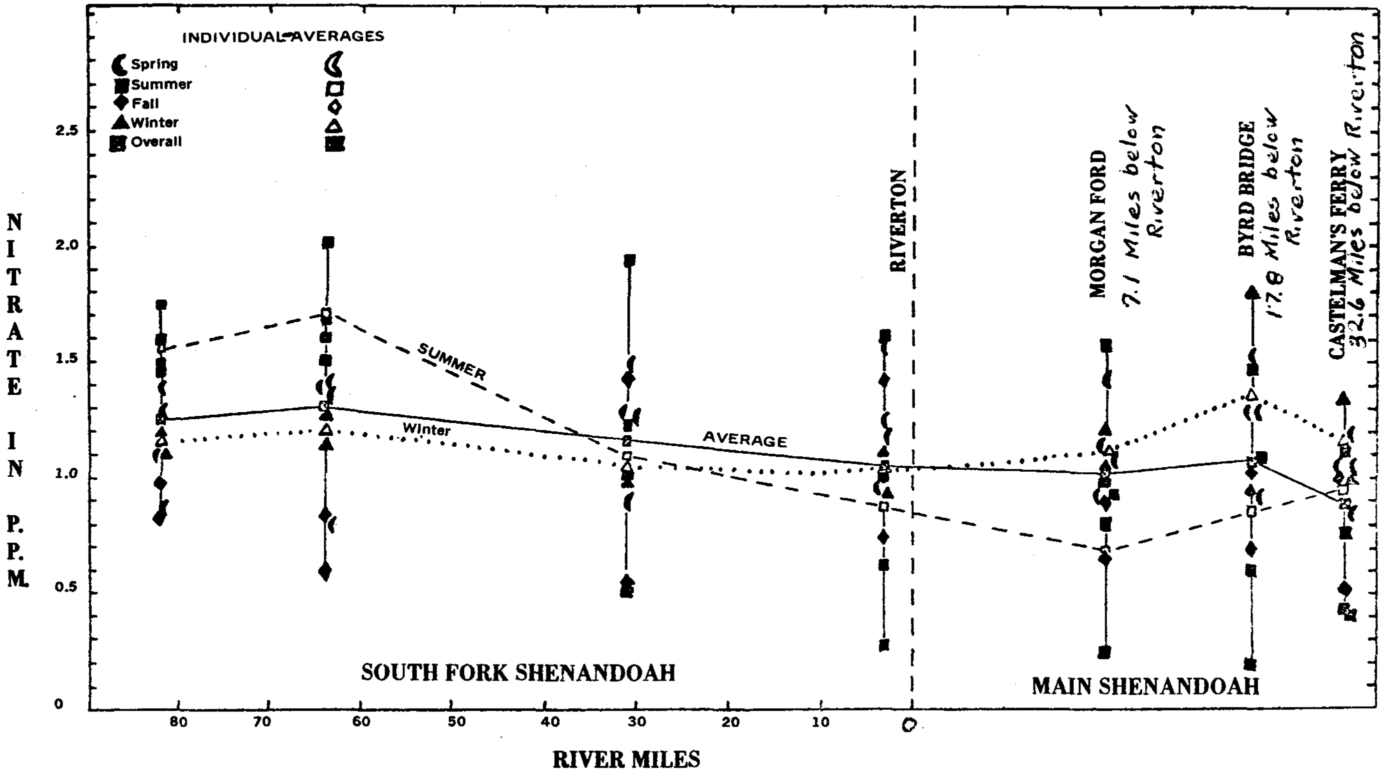


Figure 2. Nitrate Nitrogen (as NO3) in the Shenondoah River South Fork and Main Stem.

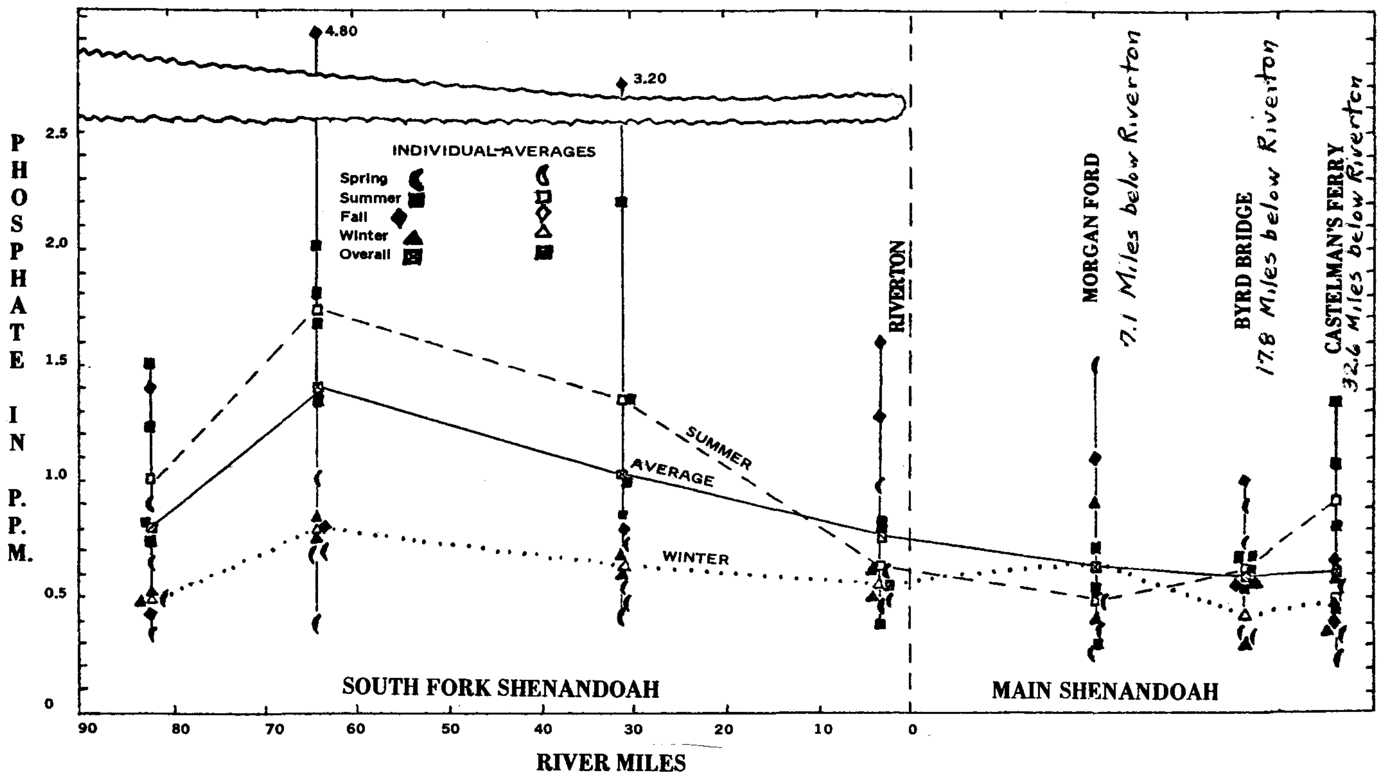


Figure 3. Total Phosphate (as PO4) in the Shenandoah River South Fork and Main Stem.

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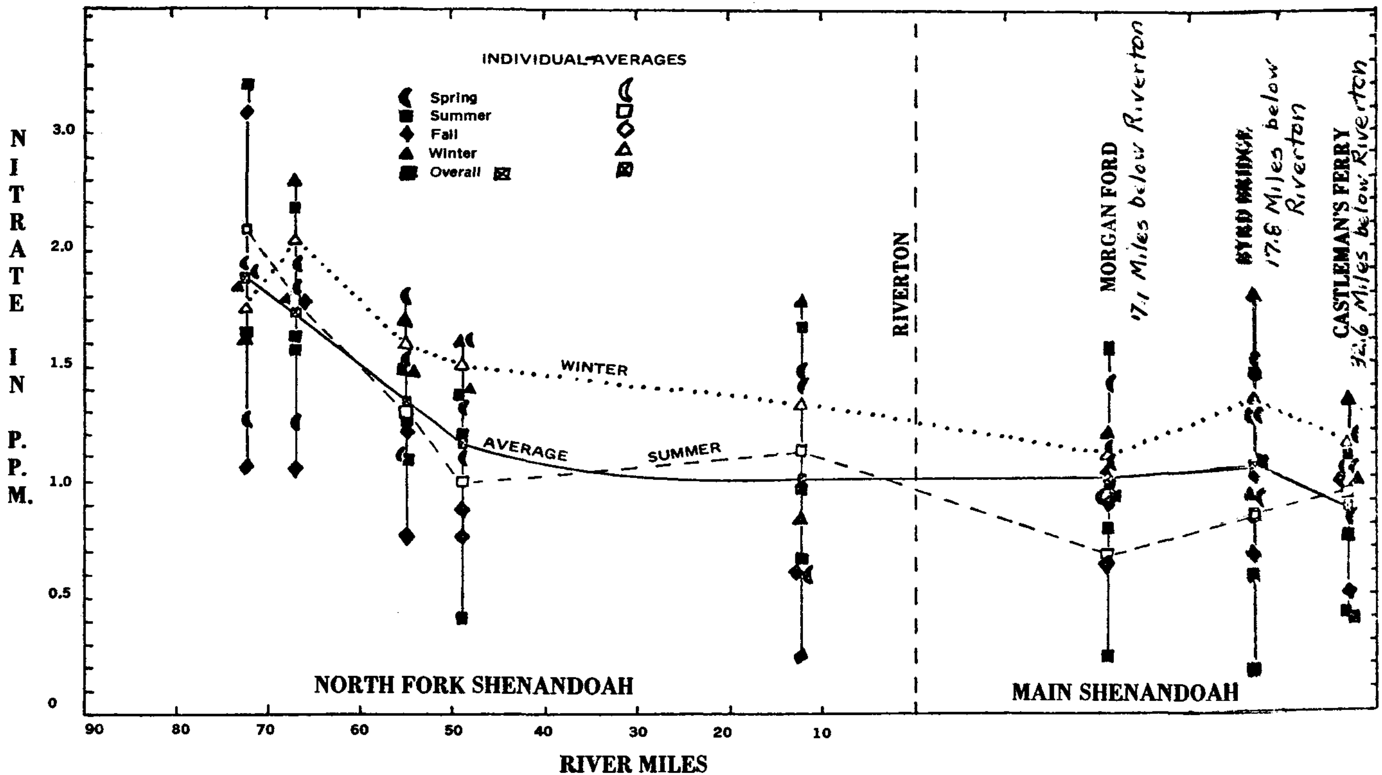


Figure 4. Nitrate Nitrogen (as NO3) in the North Fork.

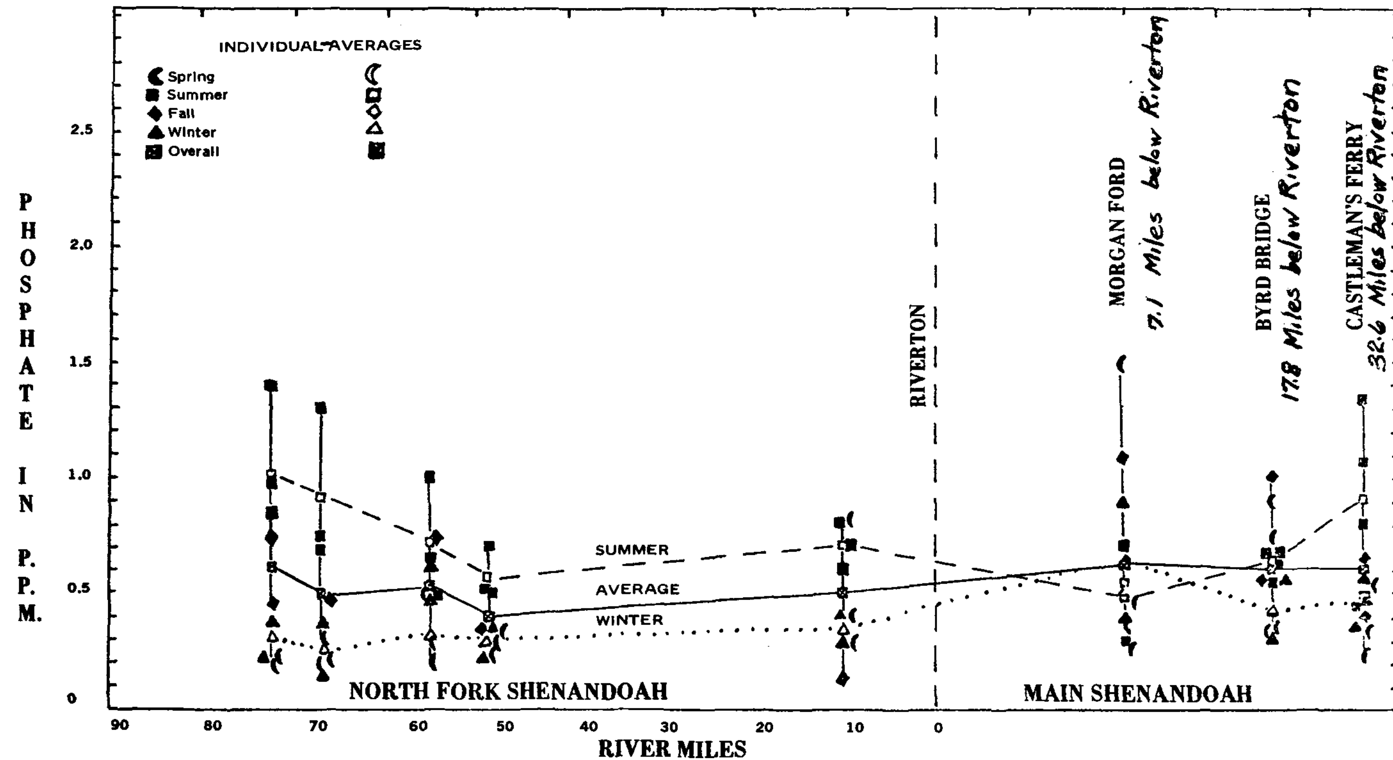


Figure 5. Total Phosphate (as PO4) in the North Fork of the Shenandoah River.

In both the South and North Forks, the average as well as summer and winter average nitrate and phosphate levels decreased (from high levels upstream in passage downstream as illustrated by the graphs in figures 2-5.[1]

## CONCLUSIONS

Assuming that a nitrogen/phosphorus ratio of more than 10:1 represents imbalanced conditions, the North Fork of the Shenandoah River has this condition of imbalance far more often than the South Fork and Main Stem.

An imbalanced condition with respect to N/P ratios occurred above the Merck Plant (11.6:1) on the South Fork on March 3, 1970, at Goods Mill (10.7:1) on the same date; at Grove Hill (11.7:1) and Castleman's Ferry (14.2:1) on March 6, 1970. In 84 determinations on samples of water from the South Fork and Main Stem, an imbalanced condition occurred only six times.

On the other hand, on 23 occasions between December 15, 1970 and June 1, 1971, imbalanced N/P ratios existed in the North Fork, yet this stream remains very clear throughout the year except immediately following rains.

Water blooms appear often in the South Fork and Main Stem due to heavy growths of Phytoplankton and high levels of phosphorus and nitrogen.

Judging from the results of this study, high levels of nitrogen and phosphorus compounds are characteristic of the Shenandoah River.

Average nitrate and phosphate levels decreased in passage downstream. The lowest seasonal average for orthophosphate in the South Fork was 0.42 ppm. and it occurred during the winter period. In the Main Stem, the lowest seasonal average for orthophosphate (0.34 ppm.) also occurred during the winter. This was also true of the North Fork where a winter season average of 0.26 ppm. occurred. Seasonal averages ranged from 0.42 to 0.93 ppm.

With regard to total phosphate, high levels occurred with seasonal averages ranging from 0.61 ppm. to 1.42 ppm. In terms of the element P, these averages are 0.21 to 0.47 ppm.

In the 1968 Report of the National Technical Advisory Committee on Water Quality Criteria, the Public Water Supply Subcommittee stated that "allowable amounts of total phosphorus will vary, but in general it is believed that a desirable guideline is 100 micrograms per liter for rivers. In parts per million this amount is equivalent to 0.1 ppm. as P. The results of this study show that from two to several times the desirable guideline is present in Shenandoah River water.

The NTAC report states that "Data collected by the Federal Water Pollution Control Administration (now Environmental Protection Agency), Division of Pollution Surveillance, indicate that total phosphorus concentrations exceeded 50 micrograms per liter (P) at 48 per cent of the stations sampled across the nation. Some potable surface water supplies now exceed 200 micrograms per liter (P) without experiencing notable problems due to aquatic growths. Fifty micrograms per liter of phosphorus (as P) would probably restrict noxious aquatic plant growths in flowing waters and in some standing waters. Some lakes, however, would experience algae nuisances at and below this level."

Fifty micrograms per liter was the lowest level of phosphate-P recorded in this study, therefore it is concluded that unusually high amounts of phosphorus are present.

Coarse weeds (water star-grass, Elodea, sago pond weed, and other Potamogetons) are far less abundant than when the writer visited the river in 1959. Since about 1960, water blooms have characterized the river water whenever the water cleared enough and came to the required temperature. Water blooms have not thus far occurred in the North Fork but large quantities

[1]The writer is indebted to Mr. Ray V. Corning for his interest in preparing these graphs plotted from the original data.

of filamentous algae and submersed weeds are usually present to quickly use the soluble phosphorus and nitrates present. In mid-summer these growths interfere with fishing.

Nitrogen compounds are present in the Shenandoah River in unusual quantities particularly in the North Fork.

Inorganic nitrogen determinations with only two exceptions exceeded the 0.3mg/l level suggested by Mackenthun (1965) which if present at the start of an active growing season subsequently permitted algae blooms.

Nitrate nitrogen as NO3 was calculated to enable comparisons with data in previous Virginia publications. Kapustka (1957) and a 1960 publication of the Virginia Division of Water Resources on the "Chemical Character of Surface Waters of Virginia." Kapustka (1957, p. 156) stated that according to the State Pollution Control Board of California (1952) large quantities of nitrate have been associated with infant methemoglobinemia (Cyanosis, or "blue babies") where the water containing large quantities of nitrate was used for preparing feeding formulas. Concentrations as low as 10 to 20 ppm. nitrate have been associated with the disease.

Concentrations as high as 10.0 ppm. nitrate nitrogen (NO3) did not occur in the South Fork and Main Stem, but comparisons with earlier Virginia nitrate determinations dating back to 1929-1930 show that nitrates are steadily increasing in these waters.

On the other hand, nitrates in the North Fork exceeded 10.0 ppm. on 3 occasions, and 8.0 ppm. on ten occasions. In other words, nitrates are reaching levels in the North Fork unsafe for drinking water supplies.

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