

TEMPORAL CHANGES IN SULFATE, CHLORIDE, AND SODIUM  
CONCENTRATIONS IN FOUR EASTERN PENNSYLVANIA STREAMS

By James L. Barker

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FACTORS FOR CONVERTING FOOT-POUND UNITS TO METRIC  
(INTERNATIONAL SYSTEM) UNITS

<u>Multiply foot-pound units</u>	<u>By</u>	<u>To obtain metric units</u>
ton (short)	0.9072	megagram (Mg)
cubic foot per second (ft <sup>3</sup> /s)	0.02832	cubic meter per second (m <sup>3</sup> /s)
million gallons per day (Mgal/d)	3,785	cubic meters per day (m <sup>3</sup> /d)
square mile (mi <sup>2</sup> )	2.590	square kilometers (km <sup>2</sup> )

TEMPORAL CHANGES IN SULFATE, CHLORIDE, AND SODIUM CONCENTRATIONS IN  
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ABSTRACT

In the absence of pollution, the common ions of sulfate, chloride, and sodium are found in natural waters in concentrations that are consistent with the geology of the watershed. The relation of these concentrations to streamflows is expected to remain fairly stable if the only forces at work are the natural processes of weathering or the dissolution of soils and rocks through which the water flows.

Because of the marked land use changes in eastern Pennsylvania during the past 60 years, it is important to know if pollution from land and atmospheric sources has altered the natural or historical relations between streamflow and concentrations of sulfate, chloride, and sodium. Possible changing relations between concentrations of ions and streamflow are demonstrated by a single multiple regression model to show a shift in the relation for data collected during a 2- to 5-year period from 1964 and earlier, and those collected during a similar period in the late 1970's. Plotting of predicted concentration values developed from the linear regression equation for the earliest data and the plotting of observed concentration values for the period of record allows a graphical analyses of the relation and, in some cases, the period of divergence.

Results of the trend analyses of chemical quality and streamflow data collected at Conestoga, Schuylkill, Juniata, and Susquehanna Rivers during the past 20 to 30 years indicate that sulfate has decreased significantly in three of the streams, chloride has increased two to threefold in all streams, and sodium is variable. Plots of observed and predicted values versus time indicate that most changes were gradual, but the rate of change accelerated in the late 1950's and early 1960's. These changes are probably related to such cultural changes as the decreased demand for coal, use of low-sulfur coal, conversion of heating systems to oil and gas, population shifts, a marked increase in the percentage of the population served by sewage systems, and increased use of salt on roadways.

INTRODUCTION

Background

The past 60 years have been a period of marked industrial and cultural development for eastern Pennsylvania as it has been elsewhere in the northeast. Although some basins, particularly those within the anthracite region, have shown a downward trend in population over the past 40 years, others that are near important commercial and industrial centers have shown an upward trend (table 1).

Table 1.--Population trends in the study sub-basins of the Susquehanna and Delaware Rivers  
 [Population in thousands. Source: Pennsylvania Statistical Abstracts 1980 by Pennsylvania Dept. of Commerce]

Schuylkill River at Berne, Pennsylvania				
<u>1940</u>	<u>1950</u>	<u>1960</u>	<u>1970</u>	<u>1978</u>
228.3	200.6	173.0	160.1	157.1
Conestoga River at Lancaster, Pennsylvania				
<u>1940</u>	<u>1950</u>	<u>1960</u>	<u>1970</u>	<u>1978</u>
151.2	171.0	217.3	262.4	294.2
Juniata River at Newport, Pennsylvania				
<u>1940</u>	<u>1950</u>	<u>1960</u>	<u>1970</u>	<u>1978</u>
240.4	280.1	279.3	278.9	280.9
Susquehanna River at Danville, Pennsylvania				
<u>1940</u>	<u>1950</u>	<u>1960</u>	<u>1970</u>	<u>1978</u>
930.3	839.1	776.4	782.7	790.6

Table 2 compares 1964 and 1978 land use in the study basins. It is the apparent shift from agriculture to suburban development and other non-agricultural uses that is most significant. This development and shifting population, accompanied by changes in land use, have had an effect on the quality of water within the basins.

The environmental impacts of serious pollution are well documented, with acid mine drainage perhaps the most widely recognized. However, there is another kind of environmental change taking place that is not so obvious. This more subtle form of pollution from land and atmospheric sources has, in some cases, altered the natural or historical relation between streamflow and dissolved chemical constituents. That is, the concentrations of dissolved constituents, at a given streamflow, are not the same today as they were 20 or 30 years ago.

Since 1966, when the Secretary of the Interior appointed a National Technical Advisory Committee to develop water-quality criteria for specified uses, there have been a number of acts and public laws designed to protect and restore our waterways. Although the full effects of these protective measures may not yet be realized, the technological advances in air- and water-pollution control may have halted further deterioration.

Table 2.--Land use in 1964 and 1978 in the study sub-basins of the Susquehanna and Delaware Rivers

Subbasins		Percentage of Total Area			
		Agricultural	Forest	Urban	Other <sup>1/</sup>
Conestoga River at Lancaster	1964	59	28	6	7
	1978	45	28	8	19
Schuylkill River at Berne	1964	34	52	6	8
	1978	30	53	7	10
Juniata River at Newport	1964	26	66	4	4
	1978	15	66	5	14
Susquehanna River at Danville	1964	39	47	4	10
	1978	22	47	5	26

<sup>1/</sup> Other land includes nonagricultural land outside urban areas of more than 2,500 population, and agricultural land not used as cropland, pasture, or forest land.

Under natural conditions, the concentrations of dissolved constituents are altered by the relative proportions of ground water and surface water. The ground-water portion is fairly steady, whereas surface runoff varies with rainfall and seasons. During base low flow, when most of the flow is ground water, the concentrations of solutes are high. During runoff, the contributions to surface water, and concentrations of solutes are generally diluted. This inverse relation may be reversed if the surface runoff is severely polluted.

In the absence of pollution, the common ions of sulfate, chloride, and sodium are found in natural waters in concentrations that are consistent with the geology of the watershed. The relation of these concentrations to stream-flow is expected to remain fairly stable if the only forces at work are the natural processes of weathering or the dissolution of soils and rocks through which the water flows. Because of this relation, these three constituents were used to determine long-term trends in four drainage basins in Pennsylvania.

Sulfur is widely distributed in igneous and sedimentary rocks in the form of metallic sulfides and sulfates. Contact with aerated water oxidizes sulfide to sulfate which in turn can be transported in the water. A full discussion of the circulation of sulfate in natural water is contained in Hem (1970, p. 164-168).

The chloride ion is present in the various rock types in lower concentrations than any of the other major constituents of natural freshwater. Chloride ions do not significantly enter into oxidation or reduction reactions, form no important solute complexes with other ions, do not form salts of low solubility, are not significantly adsorbed on mineral surfaces, and play few vital biochemical roles (Hem, 1970).

The sodium ion is the principal cation in water from igneous terrane. When brought into solution, sodium tends to remain in that state and is not active in precipitation reactions. Sodium is retained in the uncombined state by adsorbing to mineral surfaces, especially minerals with high cation-exchange capacities such as clays (Hem, 1970).

The apparent trends of concentration observed in some streams is by no means universal, and may be a regional phenomena. A study by Harned (1980) of the Neuse River in North Carolina indicates the mean annual sulfate concentration increased from 7 to 11 (mg/L) milligrams per liter since 1955. He attributed the increase to air pollution from the combustion of coal and oil. A similar study of precipitation and surface water in New York by Peters and others (1981) concluded there was a decidedly downward trend in sulfate concentration in atmospheric precipitation that was reflected in six of the nine surface waters studied.

### Purpose and Scope

This report describes the findings of statistical analyses of long-term and seasonal trends in sulfate, chloride, and sodium concentrations in four streams in eastern Pennsylvania. The purpose is to determine if there has been a change in relations between concentrations of sulfate, chloride, and sodium, at a given streamflow over time. Observed trends in the relation between ionic concentration and streamflow are related, where possible, to cultural activities such as coal mining, population changes, domestic and industrial waste disposal, and the use of salt on roadways in each basin. The data presented represent only four drainage basins, but they are believed to be representative of many drainages in Pennsylvania that have undergone similar cultural changes within the past 20 years or more.

### Methods

The stream sites selected for temporal-change analyses were those sites where the U.S. Geological Survey has continuously collected streamflow and chemical data for at least 20 years. A data search for the State produced a list of widespread stream-gaging stations that have acceptable amounts of historical and current data for discharge and sulfate, chloride, and sodium ion concentrations.

Four representative gages were selected from this list; three are in the Susquehanna River basin and one is in the Delaware River basin (fig. 1). These gages are on drainage basins that range in size from 324 mi<sup>2</sup> to 11,220 mi<sup>2</sup>. Stream quality at two of them is affected by acid mine drainage.

Temporal changes in sulfate, chloride, and sodium concentrations with respect to water discharge at selected sites in the Susquehanna and Delaware River basins are demonstrated by regression analysis to show a shift in the relation for data collected during a 2- to 5-year period from 1964 and earlier (type 1), and those collected during a similar period in the late 1970's (type 2).

The premise that there has been a change in relation between ionic concentration and streamflow over time, was tested by comparing the straight-



line regression equation for the type 1 and type 2 data. A computer designed statistical "package", specifically the Statistical Analyses System (SAS, 1979), was used to reduce and analyze the data.

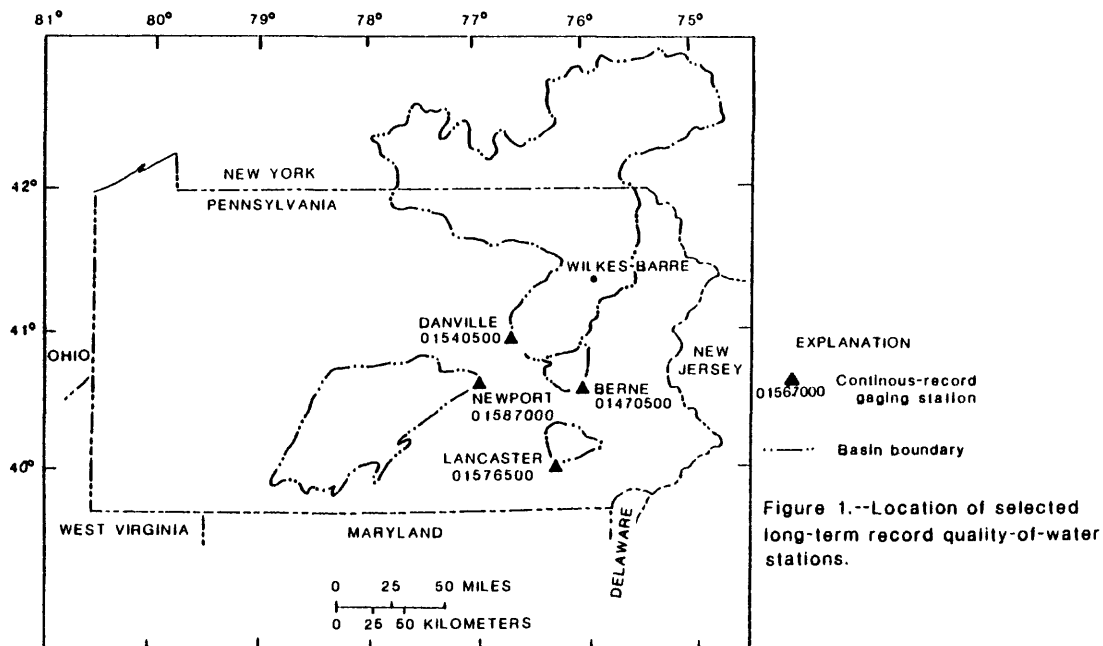


Figure 1.--Location of selected long-term record quality-of-water stations.

A single multiple regression model is fit to the data in the form:

$$\log C = a + b \log Q + c D$$

The dummy variable (D) then takes on the values of zero and one; the value zero for the type 1 data and one for the type 2 data. The resulting coefficient c is then tested using the t-test to see if it is significantly different from zero. If it is, there has been a shift in the relationship and that the intercept of the regression has shifted by the amount c.

In those cases where a significant change in the ion-streamflow relation has been documented, an attempt was made to correlate the change with one or more environmental impacts due to cultural activities. The plotting of predicted concentration values for sulfate, chloride, and sodium developed from the linear regression equation for the earliest (type 1) data and the plotting of measured concentration values for the period of record allows a graphical analysis of the change in relation between concentration and streamflow.

A problem encountered with this type of analysis is that the predicted concentrations are only as good as the equation derived from the earliest (type 1) data, and in some cases the correlation is very poor. Therefore, divergence from the initially observed relation between concentration and streamflow is difficult, if not impossible to ascertain. Also, as would be expected, any divergence from predicted values is generally subtle and progressive in nature, thereby making its inception difficult to establish chronologically.

Nevertheless, this type of analysis allows the period of change in the relation to be delineated satisfactorily. It is considerably more difficult to pinpoint the cause of the observed change, because it may be the product of many variables. The investigator has, without field investigations, drawn some general conclusions, based upon logic rather than statistics, on the origins of observed changes in stream quality.

#### TRENDS IN SULFATE, CHLORIDE, AND SODIUM CONCENTRATIONS

The effects of man's cultural activities on the concentrations of the common ions of sulfate, chloride, and sodium are illustrated by statistical analysis of water-quality and streamflow data collected in the past 20 to 30 years. Results of the trend analyses indicate that dissolved sulfate generally has decreased, dissolved chloride has increased two to threefold, and dissolved sodium is variable. These trend analyses indicate the late 1950's and early 1960's encompass a period when significant changes in ionic concentrations took place. The observed changes are postulated to result from changes in land use in the basins.

Although there is no supporting evidence, the observed changes are believed to be of no consequence to the environment because the ion concentrations are well within the ranges of natural waters that contain a diverse biota (McKee and Wolf, 1963).

The logarithmic plots of ionic concentrations and streamflow for the two time periods, the linear-regression coefficients (table 3) used to predict ionic concentrations for observed streamflows, examples of time plots of predicted and measured values, a summary of statistical analysis, and an explanation of the results are presented for the four basins examined.

#### Conestoga River at Lancaster

Station 01576500, Conestoga River at Lancaster, has a drainage area of 324 mi<sup>2</sup> and is a part of the Susquehanna River basin. This station is upstream from the city of Lancaster. The basin contains several sewage-treatment plants and is extensively farmed. There is no coal mining in the basin, but the region is experiencing rapid cultural development to accommodate a rising population. The time periods used for analysis were water years 1960-64 for type 1 period and 1970-76 for type 2 period.

Significant differences were found between the regressions for type 1 and type 2 data as shown in table 4. The data indicate trends toward increasing concentrations of ions for a given streamflow. In figures 2-4, the ionic concentrations for the two periods, denoted by circles and triangles, are plotted against streamflow.

Because of the poor correlations between ionic concentration and streamflow at this site, as indicated by the small values of  $r$  (table 3), plots of predicted values from type 1 regressions gave no information as to when the relation began to diverge. The poor correlation is believed due to changes in the streamflow ionic concentration relations prior to 1960. A plot of average monthly streamflow and dissolved chloride concentrations for both periods

(fig. 5) shows a consistent higher concentration of dissolved chloride during all months of the 1970-76 period regardless of streamflow. The peak in chloride during January for the 1970-76 data is believed the result of the application of roadway salt (NaCl).

Noted change in the dissolved sodium-streamflow relation in the Conestoga River is believed the result of significant increases in population, concurrent construction of municipal sewage-treatment plants, and increased use of roadway salts. From 1964 to 1976, the population of the basin increased by about 35,000 and the number of customers served by sewage-treatment plants nearly doubled, increasing from 97,000 to 181,000 (James D. Miller, Pennsylvania Department of Environmental Resources, written commun., 1981). The use of roadway salt has averaged more than 2,000 tons annually in the basin since 1970 (L. G. O'Brien, Pennsylvania Department of Transportation, written commun., 1981). Salt usage prior to 1970 is unknown, as records were not retained. However, according to the Pennsylvania Department of Transportation, salt usage prior to 1960 was considerably less than in recent years (George Pavolich, Pennsylvania Department of Transportation, oral commun., 1981).

Table 3.--Linear-regression model parameters and correlation coefficients for the logarithms of streamflow to sulfate, chloride, and sodium concentrations for the stations and water years indicated

Site		log a <sup>1/</sup>	b <sup>1/</sup>	correlation coefficient (r)
Conestoga River at Lancaster (1960-64)				
	x <sup>2/</sup>			
	y <sup>3/</sup>			
streamflow	sulfate	1.658	-0.074	0.19
	chloride	1.352	- .151	.79
	sodium	1.249	- .171	.41
Schuylkill River at Berne (1950-52)				
	x <sup>2/</sup>			
	y <sup>3/</sup>			
streamflow	sulfate	3.643	- .442	.81
	chloride	1.358	- .259	.86
	sodium	—	—	—
Juniata River at Newport (1944-48)				
	x <sup>2/</sup>			
	y <sup>3/</sup>			
streamflow	sulfate	2.832	- .363	.73
	chloride	2.408	- .484	.74
	sodium	2.896	- .553	.77
Susquehanna River at Danville (1946-47)				
	x <sup>2/</sup>			
	y <sup>3/</sup>			
streamflow	sulfate	3.894	- .516	.91
	chloride	2.103	- .361	.91
	sodium	2.235	- .372	.87

1/ from  $y = ax^b$   
 $\log y = \log a + b \log x$   
2/ cubic feet per second  
3/ milligrams per liter

Table 4.--Results of statistical analysis for Conestoga River at Lancaster

---

Sulfate, dissolved

$$\text{Log SO}_4 = 1.658 - 0.074 \text{ Log Q} + 0.082 \text{ D}$$

$$\text{D} = 0 \quad \text{Log SO}_4 = 1.658 - 0.074 \text{ Log Q}$$

$$\text{D} = 1 \quad \text{Log SO}_4 = 1.740 - 0.074 \text{ Log Q}$$

Probability level = 0.001      c value = 0.082

---

Chloride, dissolved

$$\text{Log Cl} = 1.352 - 0.151 \text{ Log Q} + 0.312 \text{ D}$$

$$\text{D} = 0 \quad \text{Log Cl} = 1.352 - 0.151 \text{ Log Q}$$

$$\text{D} = 1 \quad \text{Log Cl} = 1.665 - 0.151 \text{ Log Q}$$

Probability level = 0.001      c value = 0.312

---

Sodium, dissolved

$$\text{Log Na} = 1.249 - 0.171 \text{ Log Q} + 0.177 \text{ D}$$

$$\text{If D} = 0 \quad \text{Log Na} = 1.249 - 0.171 \text{ Log Q}$$

$$\text{If D} = 1 \quad \text{Log Na} = 1.426 - 0.171 \text{ Log Q}$$

Probability level = 0.001      c value = 0.177

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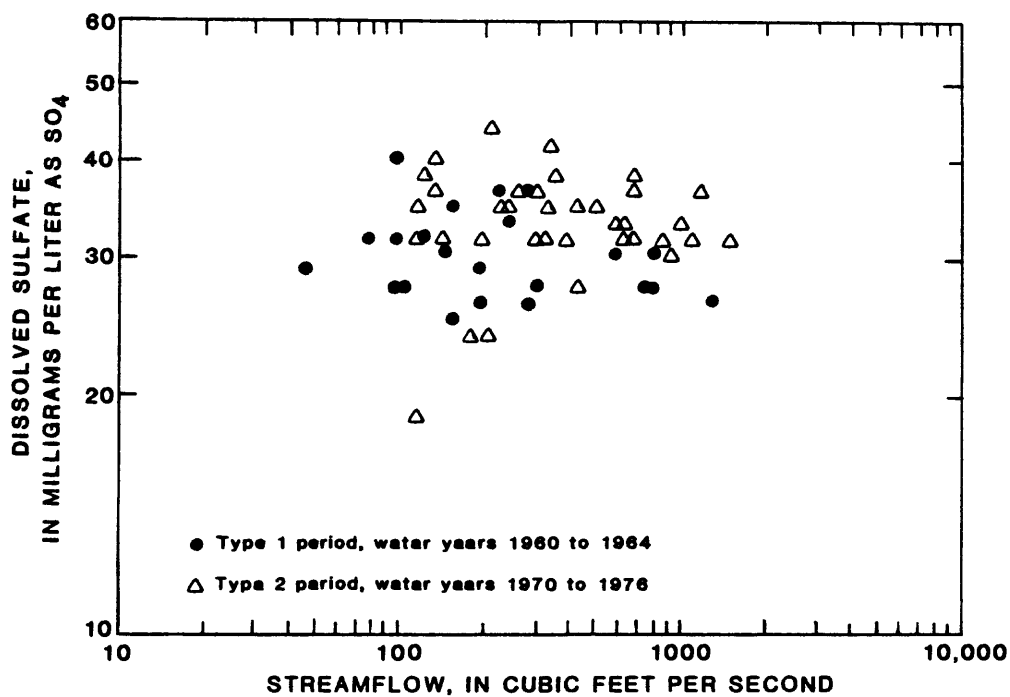


Figure 2.--Relationship between streamflow and concentration of sulfate, Conestoga River at Lancaster.

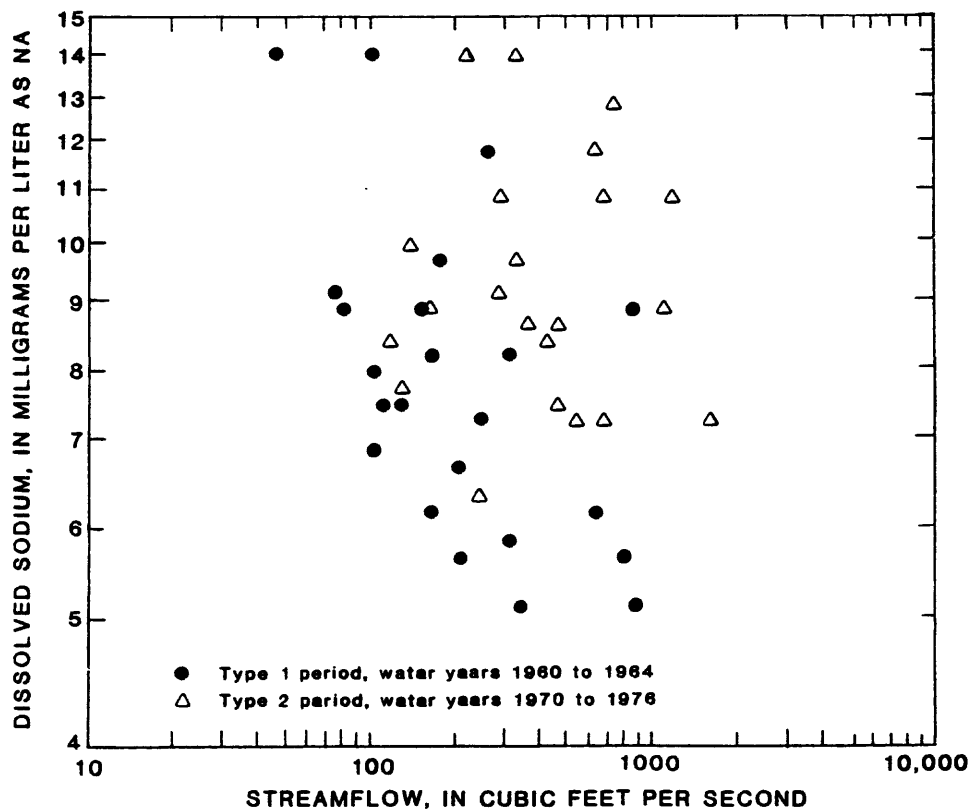


Figure 3.--Relationship between streamflow and concentration of sodium, Conestoga River at Lancaster.

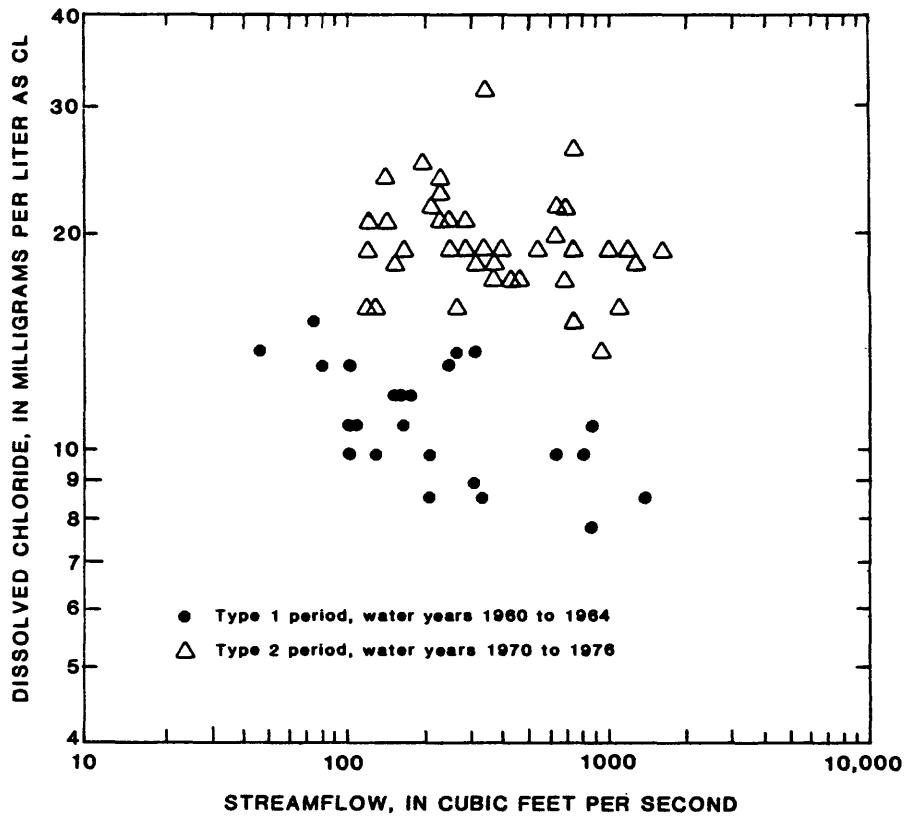


Figure 4.--Relationship between streamflow and concentration of chloride, Conestoga River at Lancaster.

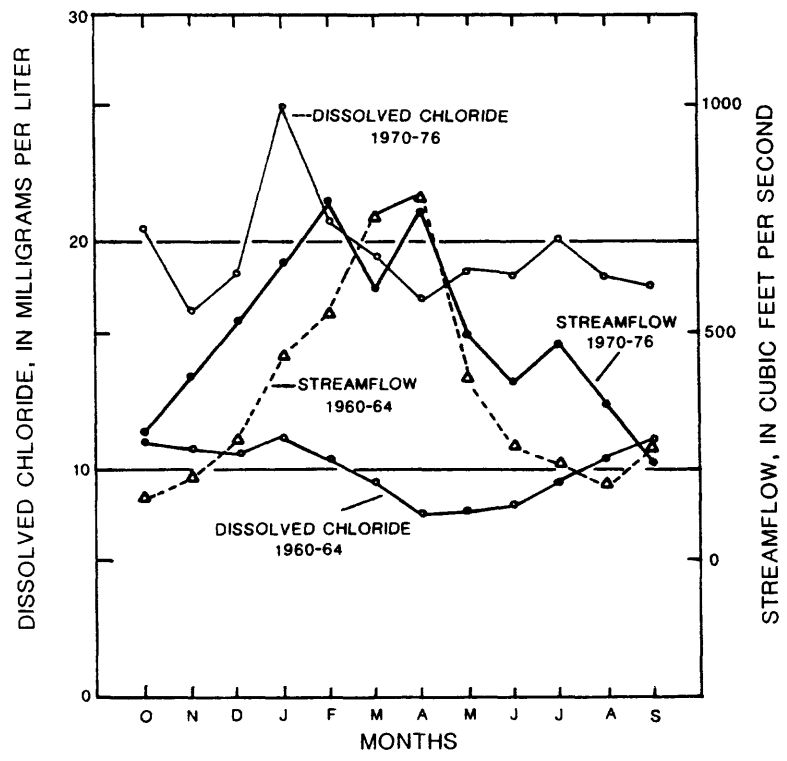


Figure 5.--Average monthly streamflow and dissolved chloride concentrations in the Conestoga River at Lancaster.

### Schuylkill River at Berne

Station 01470500, Schuylkill River at Berne, has a drainage area of 355 mi<sup>2</sup> and is a sub-basin of the Delaware River basin. The quality of streamflow at this station is influenced by several sewage-treatment plants. The site is at the lower terminus of an extensively mined basin. Population in the basin has decreased since mining peaked in the 1940's. The time periods used for analysis are water years 1950-52 for type 1 period, and 1974-78 for type 2 period.

Significant differences were found between the ion-streamflow relations between type 1 and type 2 data for sulfate and chloride, as shown in table 5.

In figures 6 and 7, the ionic concentrations for the two periods, denoted by circles and triangles, are plotted against stream discharges. Type 2 sodium data were insufficient for comparison with type 1 data. Sulfate values at a given streamflow for type 2 data are significantly lower than for type 1, but chloride values for type 2 are significantly higher.

A chronological plot of predicted sulfate values taken from the type 1 regression equation and observed values (fig. 8) indicates that the relation between sulfate and discharge changed after about 1958, with the observed or measured value generally less than that predicted by the equation. This change in relation coincides with a reduction in pumpage from the large coal mines in the basin (table 6), as well as with conversion of home heating units from sulfur-bearing coal to oil and natural gas (Altshuller, 1980).

A similar plot of predicted chloride values from the type 1 regression and observed values (fig. 9) indicates that concentrations increased as early as 1961. Increased chloride concentrations in the early 1960's can be attributed to increases in industrial pollutants and more communities being sewered. Although the population decreased between 1952 and 1978, as shown in table 1, the number of sewage-treatment plants increased from none to eleven, and the number of customers served increased to more than 70 thousand. The use of roadway salt has averaged more than 10,000 tons since 1970, (L. G. O'Brien, Pennsylvania Department of Transportation, written commun., 1981).

Table 5.--Results of statistical analysis for Schuylkill River at Berne

---

Sulfate, dissolved

Log SO<sub>4</sub> = 3.643 - 0.442 Log Q - 0.256 D

D = 0      Log SO<sub>4</sub> = 3.643 - 0.442 Log Q

D = 1      Log SO<sub>4</sub> = 3.201 - 0.442 Log Q

Probability level = 0.001      c value = -0.256

---

Chloride, dissolved

Log Cl = 1.358 - 0.259 Log Q + 0.449 D

D = 0      Log Cl = 1.358 - 0.259 Log Q

D = 1      Log Cl = 1.807 - 0.259 Log Q

Probability level = 0.001      c value = 0.449

---

Table 6.--Annual pumpage from the large coal mines in the Schuylkill River basin<sup>1/</sup>

Year	Annual pumpage (Mgal/d)
1944	38.5
1945	53.4
1946	44.7
1947	44.7
1948	40.8
1949	32.6
1950	38.0
1951	39.4
1952	50.5
1953	35.4
1954	26.1
1955	33.0
1956	29.8
1957	24.2
1958	17.4
1959	19.2
1960	13.3
1961	14.0
1962	15.8
1963	14.7
1964	14.5
1965	15.8

<sup>1/</sup>Based on data from U.S. Bureau of Mines, Pennsylvania Department of Mines and Mineral Industries, and various coal companies.



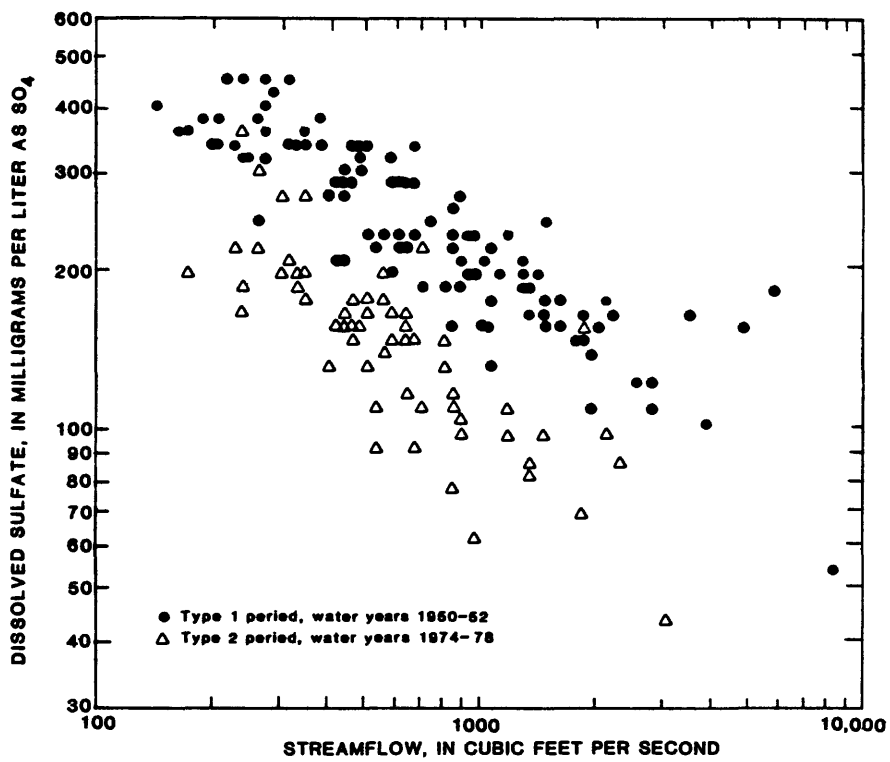


Figure 6.—Relationship between streamflow and concentration of sulfate, Schuylkill River at Berne.

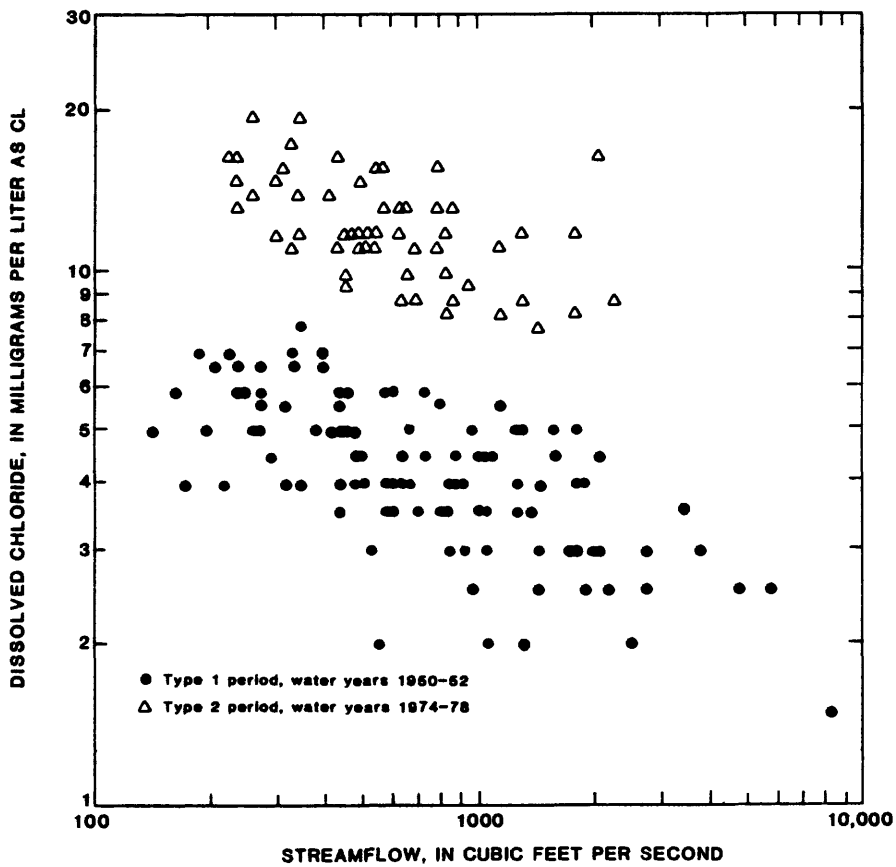


Figure 7.—Relationship between streamflow and concentration of chloride, Schuylkill River at Berne.

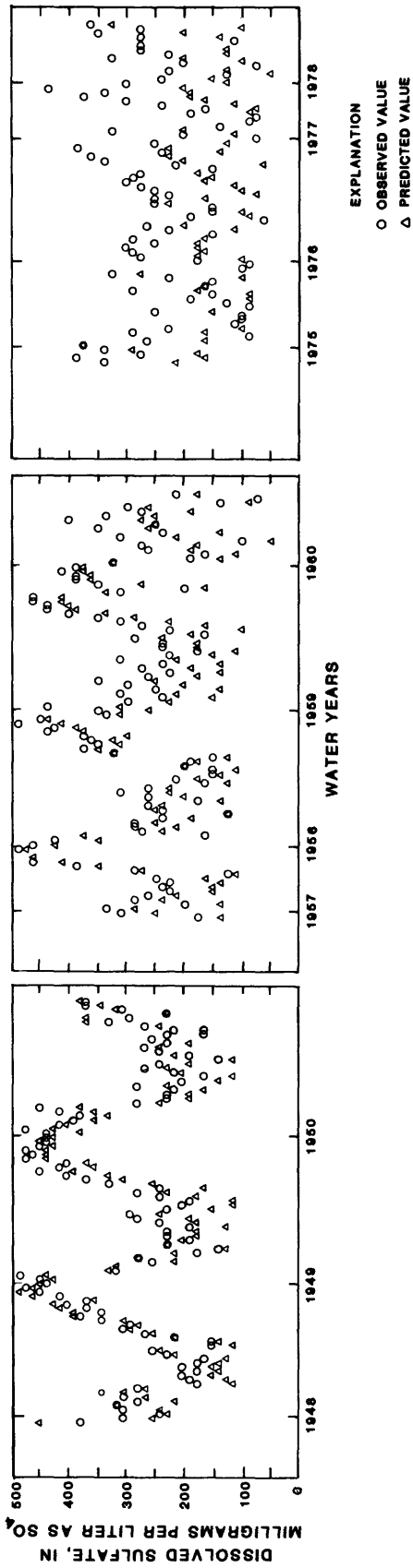


Figure 8.--Sulfate concentrations predicted by type 1 regression equation versus observed values, Schuylkill River at Berne.

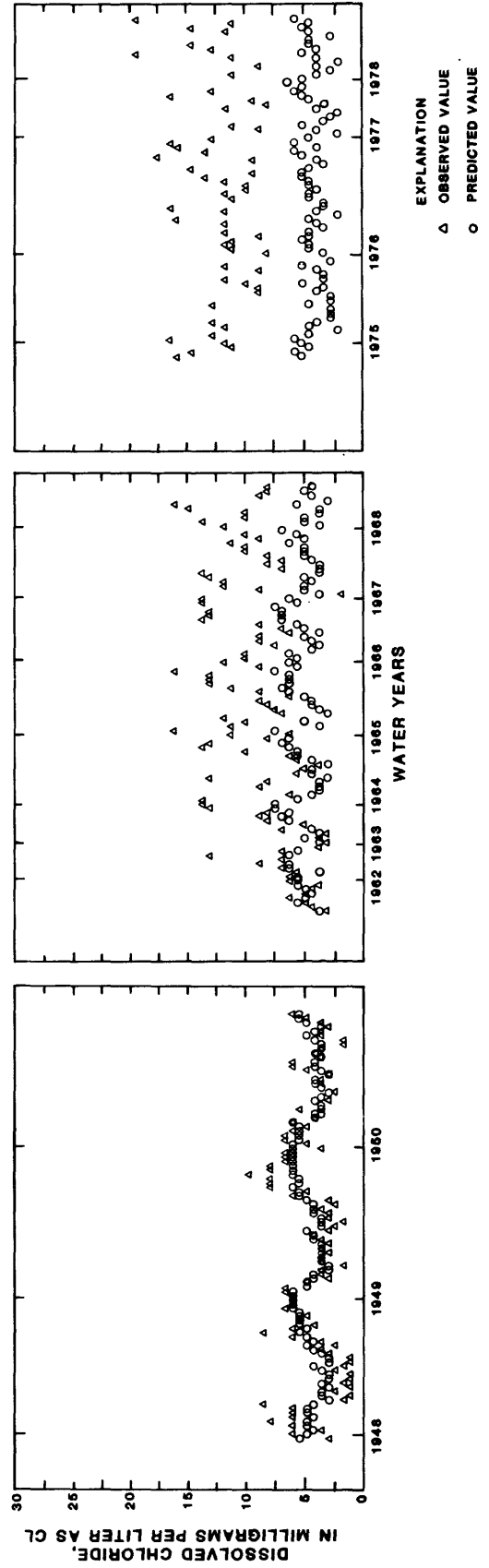


Figure 9.--Chloride concentrations predicted by the type 1 regression equation versus observed values, Schuylkill River at Berne.

### Juniata River at Newport

Station 01567000, Juniata River at Newport, has a drainage area of 3,354 mi<sup>2</sup> and is a sub-basin of the Susquehanna River basin. This large drainage basin has a stable population (table 1). The largest population center is Altoona. There are numerous rural communities and agriculture is the major industry. Although there is some mine drainage in the upper basin, it is not detectable at Newport. The time periods used for analysis are water years 1944-48 for type 1 period, and 1970-78 for type 2 period.

Significant differences were found between the types 1 and 2 regressions for chloride and sulfate. Sulfate values, for a given streamflow, for type 2 are significantly lower, but type 2 chloride is significantly higher (table 7) (figs. 10-12) than type 1 concentrations. Sodium values for type 1 and type 2 data showed no shift in the relation. In this case, the variability of the residuals for this relation was examined but no significant difference was found.

A plot of predicted sulfate concentrations from the linear-regression equation (table 3) against observed concentrations for this ion suggests a subtle decreasing trend that began about 1961. However, chloride concentrations began to increase after about 1958. The above plots are not shown because they are similar to those in figures 8 and 9.

The noted reduction in sulfate is due, at least in part, to a gradual reduction in the use of coal brought about by the conversion of heating systems to oil and gas and the use of low-sulfur instead of high-sulfur coal. The trend toward higher chloride concentrations in the late 1950's is attributed to increased discharge of treated sewage and an increase in the use of roadway salt. Salt usage since 1970 has been running about 17,000 tons annually (L. G. O'Brien, Pennsylvania Department of Transportation, written commun., 1981).

Table 7.--Results of statistical analysis for Juniata River at Newport

Sulfate, dissolved

$$\begin{aligned} & \text{Log SO}_4 = 2.832 - 0.363 \text{ Log Q} - 0.063 D \\ D = 0 & \quad \text{Log SO}_4 = 2.832 - 0.363 \text{ Log Q} \\ D = 1 & \quad \text{Log SO}_4 = 2.769 - 0.363 \text{ Log Q} \end{aligned}$$

Probability level = 0.001

c value = -0.063

Chloride, dissolved

$$\begin{aligned} & \text{Log Cl} = 2.408 - 0.484 \text{ Log Q} + 0.328 D \\ D = 0 & \quad \text{Log Cl} = 2.408 - 0.484 \text{ Log Q} \\ D = 1 & \quad \text{Log Cl} = 2.736 - 0.484 \text{ Log Q} \end{aligned}$$

Probability level = 0.001

c value = 0.328

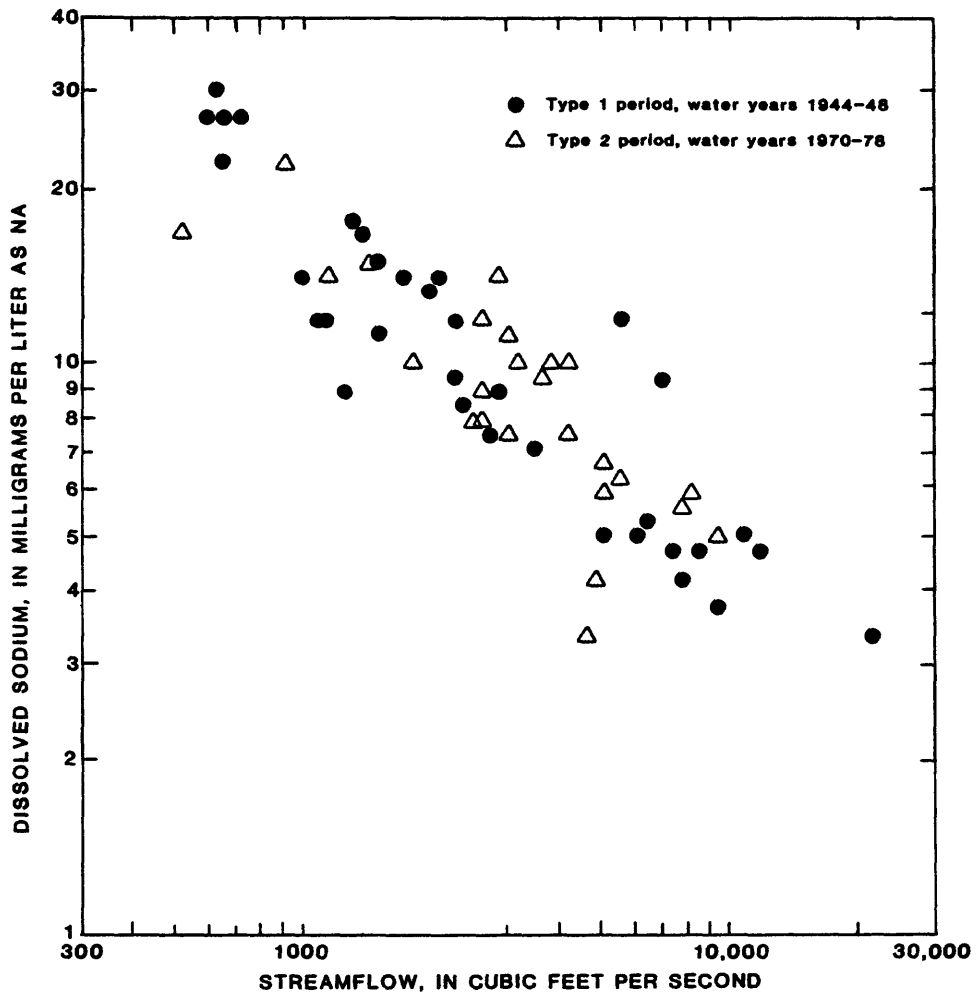


Figure 10.--Relationship between streamflow and concentration of sodium, Juniata River at Newport.

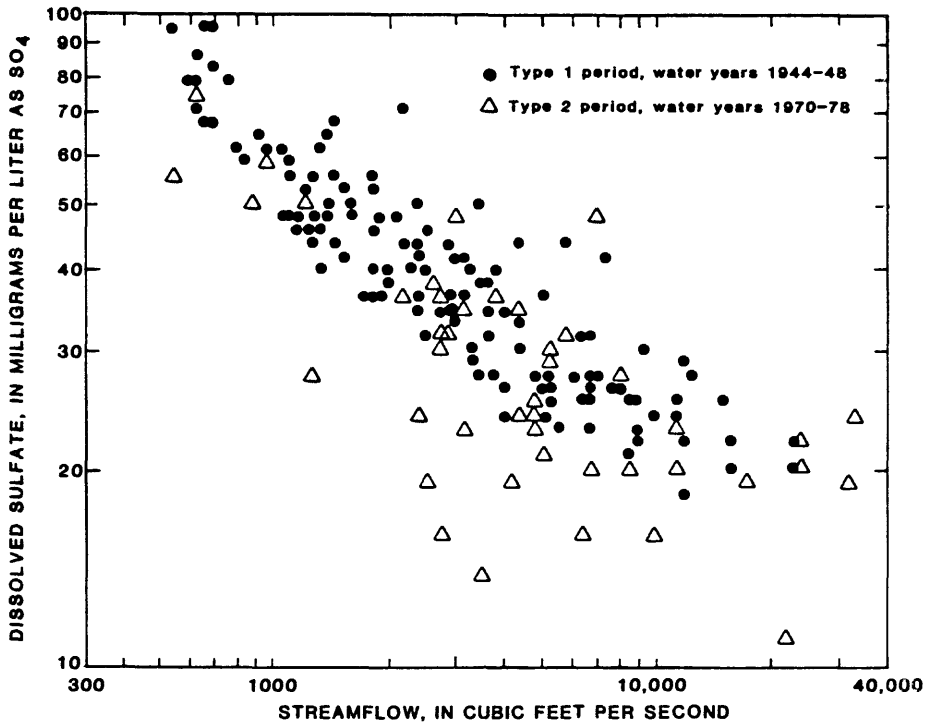


Figure 11.--Relationship between streamflow and concentration of sulfate, Juniata River at Newport.

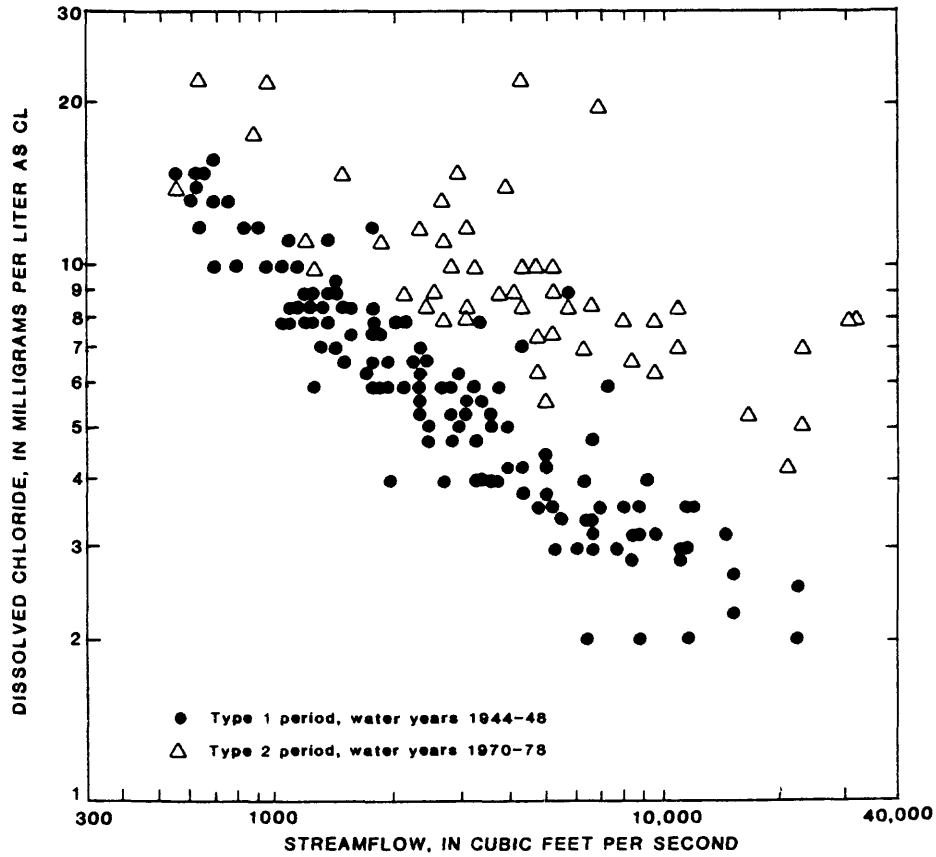


Figure 12.--Relationship between streamflow and concentration of chloride, Juniata River at Newport.

## Susquehanna River at Danville

Station 01540500, Susquehanna River at Danville, has a drainage area of 11,220 mi<sup>2</sup> and is a sub-basin of the Susquehanna River basin. This station represents a large drainage area that encompasses nearly all the anthracite fields in northeastern Pennsylvania, as well as the industrial and population centers of Wilkes-Barre and Scranton. Nearly one-half of the basin is forested (table 2). The time periods used for analysis are water years 1946-47 for type 1 period, and 1974-78 for type 2 period.

Significant differences were found among the regression lines for type 1 and type 2 data for sodium, chloride, and sulfate (table 8). Concentrations versus streamflows for these ions are plotted in figures 13-15 for type 1 and type 2 periods. The type 2 concentrations for sodium and chloride are significantly higher, but the type 2 concentrations for sulfate are significantly lower for a given streamflow than corresponding type 1 concentrations.

A chronological plot of observed concentrations versus those predicted from the type 1 linear-regression equation (table 3) for the period of record indicates that after the late 1950's sodium concentrations are generally higher than the equation predicted; chloride is higher after the mid-1950's; and, sulfate is lower after the mid-1950's. These trends (not shown), which are subtle, indicate a gradual change.

Documenting subtle trends is difficult, if not impossible; however, the noted changes in relation between streamflow and ionic concentrations coincide with similar changes in other basins where sewage plant construction, industrial development, increased use of roadway salt, and conversion of high sulfur-bearing coal heating units to oil and gas heating units are plausible explanations. The use of roadway salt has averaged more than 25,000 tons annually since 1970 (L. G. O'Brien, Pennsylvania Department of Transportation, written commun., 1981). Although the population in this basin has been declining (table 1), the number of sewage treatment plants increased from 5, prior to 1947, to 43 in 1978 (R. J. Donnelly, Pennsylvania Department of Environmental Resources, written commun., 1981).

Table 8.--Results of Statistical analysis for Susquehanna River at Danville

Sulfate, dissolved

$$\begin{aligned} & \text{Log SO}_4 = 3.894 - 0.156 \text{ Log Q} - 0.121 \text{ D} \\ \text{D} = 0 & \quad \text{Log SO}_4 = 3.894 - 0.156 \text{ Log Q} \\ \text{D} = 1 & \quad \text{Log SO}_4 = 3.772 - 0.156 \text{ Log Q} \end{aligned}$$

Probability level = 0.001

c value = -0.121

Chloride, dissolved

$$\begin{aligned} & \text{Log Cl} = 2.104 - 0.361 \text{ Log Q} + 0.399 \text{ D} \\ \text{D} = 0 & \quad \text{Log Cl} = 2.104 - 0.361 \text{ Log Q} \\ \text{D} = 1 & \quad \text{Log Cl} = 2.503 - 0.361 \text{ Log Q} \end{aligned}$$

Probability level = 0.001

c value = 0.399

Sodium, dissolved

$$\begin{aligned} & \text{Log Na} = 2.234 - 0.372 \text{ Log Q} + 0.189 \text{ D} \\ \text{D} = 0 & \quad \text{Log Na} = 2.234 - 0.372 \text{ Log Q} \\ \text{D} = 1 & \quad \text{Log Na} = 2.424 - 0.372 \text{ log Q} \end{aligned}$$

Probability level = 0.001

c value = 0.189

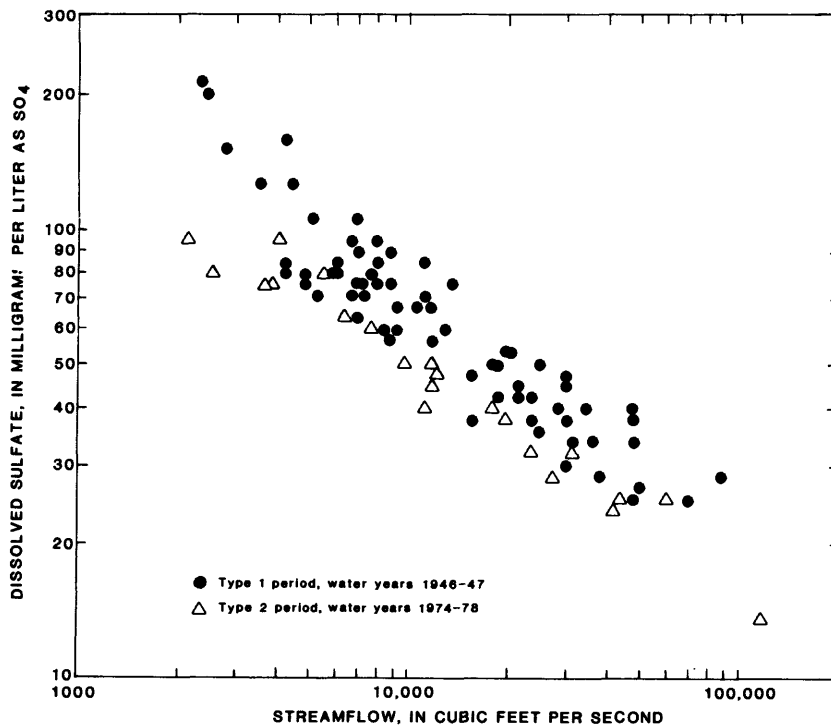


Figure 13.--Relationship between streamflow and concentration of sulfate, Susquehanna River at Danville.

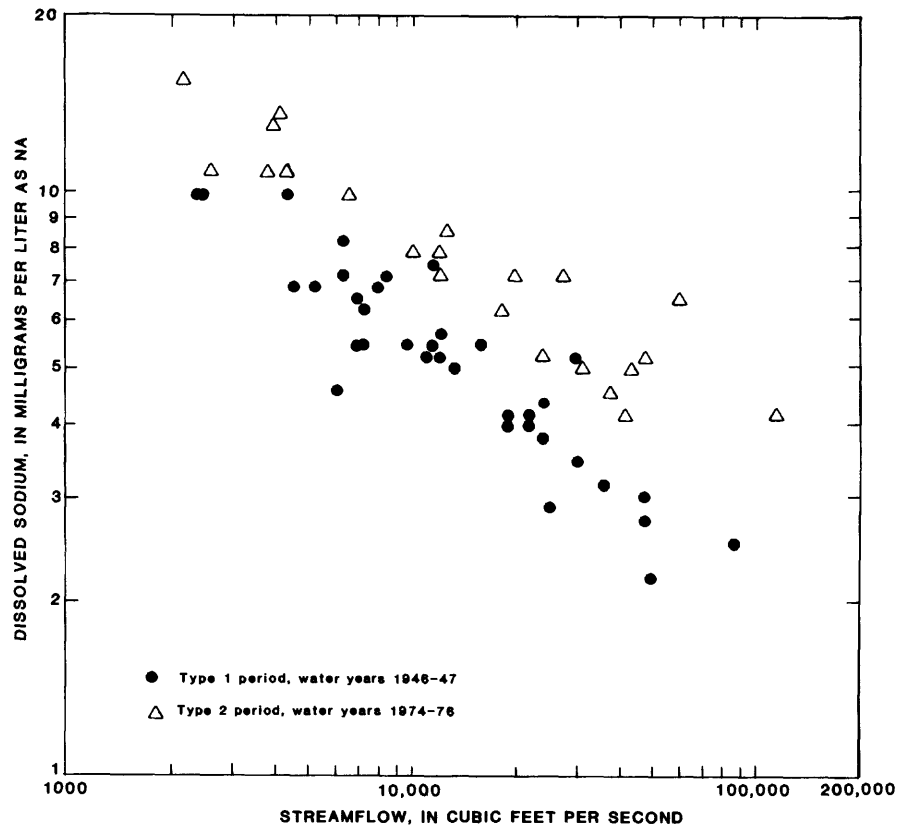


Figure 14.--Relationship between streamflow and concentration of sodium, Susquehanna River at Danville.

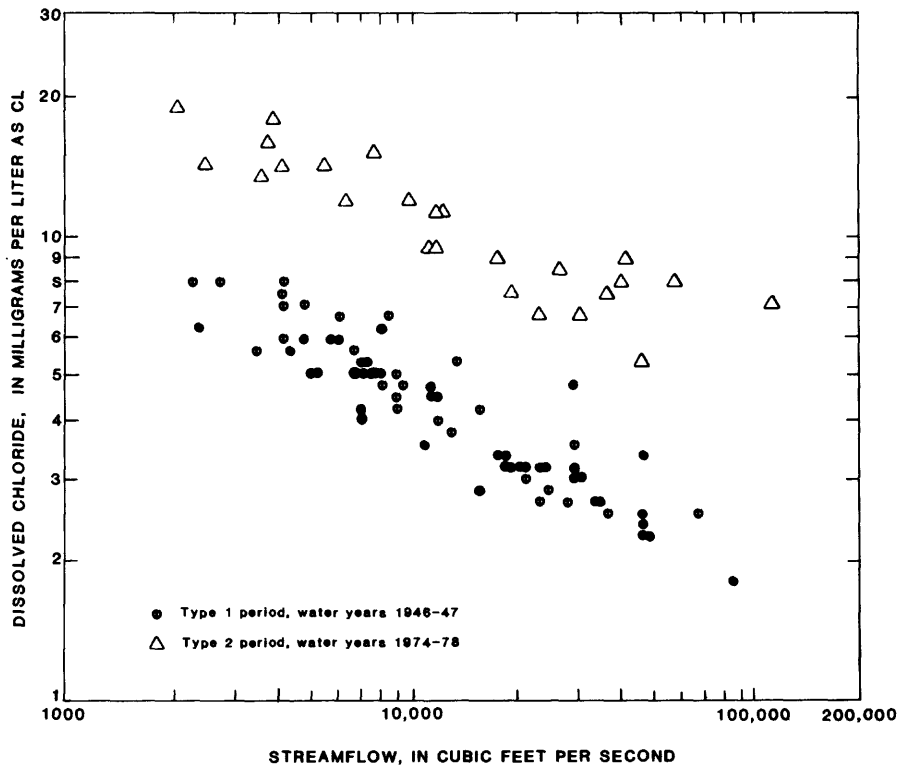


Figure 15.--Relationship between streamflow and concentration of chloride, Susquehanna River at Danville.



## SUMMARY

The purpose of this report was to demonstrate the changing relations between streamflow and concentrations of dominant ions and relate these changes to cultural activities in representative eastern Pennsylvania drainage basins. Analyses of chemical-quality and streamflow data collected during a period of approximately 20 to 30 years indicate that dissolved sulfate has generally decreased, dissolved sodium is variable, and dissolved chloride concentrations have increased two to threefold in all streams.

Long-term trend analyses consisting of plots of observed and predicted values versus time indicate that most changes were gradual, but the rate of change accelerated in the late 1950's and early 1960's. These changes are probably related to such cultural changes as the decreased demand for coal, use of low-sulfur coal, conversion of heating systems to oil and gas, population shifts, a marked increase in the percentage of the population served by sewage systems, and increased use of salt on roadways.

Although many of the observed changes in ion-streamflow relations are significant statistically, the impact on the environment is probably of little or no consequence because the ionic concentrations are well within the ranges of those found in natural waters that contain a diverse biota.

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