

AREAL AND TEMPORAL VARIATIONS IN SURFACE-WATER QUALITY

IN THE UPPER POTOMAC RIVER BASIN

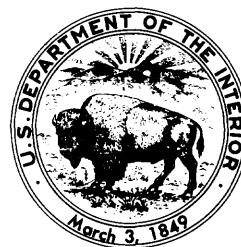
By Thomas J. Trombley

U.S. GEOLOGICAL SURVEY

Water-Resources Investigations Report 89-4139

Towson, Maryland

1992



U.S. DEPARTMENT OF THE INTERIOR

MANUEL LUJAN, JR., Secretary

U.S. GEOLOGICAL SURVEY

Dallas L. Peck, Director

For additional information
write to:

District Chief
U.S. Geological Survey
208 Carroll Building
8600 La Salle Road
Towson, Maryland 21204

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ABSTRACT

The Upper Potomac River basin, the second largest tributary to the Chesapeake Bay, drains an area of 11,570 square miles upstream from Chain Bridge at Washington, D.C., in the States of Maryland, Pennsylvania, Virginia, and West Virginia. Data stored on the U.S. Geological Survey's WATSTORE database system were used to evaluate the water quality at 25 surface-water stations in the Upper Potomac River basin for areal and temporal trends. Three of these stations--the Potomac River at Shepherdstown, West Virginia, the Potomac River at Chain Bridge at Washington, D.C., and the Shenandoah River at Millville, West Virginia--are part of the National Stream-Quality Assessment Network (NASQAN). Trends were determined using parametric and nonparametric statistical tests. Trends were evaluated to determine general causative factors and to suggest a sampling strategy that will enable future trend analysis.

Water quality in the basin is related to the physiography. The Appalachian Plateau streams have low pH and low concentrations of alkalinity, and elevated concentrations of sodium, chloride, sulfate, metals and dissolved solids. The Valley and Ridge streams have low concentrations of dissolved solids. The Great Valley streams have elevated concentrations of calcium, magnesium, and alkalinity, and the Piedmont streams have elevated concentrations of suspended sediment.

Temporal trends generally have been toward improved water quality. Alkalinity, pH and concentrations of dissolved oxygen have been increasing throughout the basin. Iron and manganese concentrations have decreased sharply in the Appalachian Plateau streams since the mid-1960's, but have increased slightly in other parts of the basin. An increase in the use of deicing salts may have increased chloride concentrations in streams throughout the basin.

Periodic sampling needs to be combined with flow-based sampling at tributary sites within each physiographic province and at sites along the mainstem Potomac River to better determine and monitor the development of areal and temporal water-quality trends within the basin.

INTRODUCTION

Background

The water quality of the Potomac River, the second largest tributary to Chesapeake Bay, is an important influence on water quality in the bay. The drainage area of the Upper Potomac River basin (fig. 1), upstream from Chain Bridge at Washington, D.C., is 11,570 mi² (square miles) in the States of Maryland, Pennsylvania, Virginia, and West Virginia. Water quality is monitored at a series of State and Federal surface-water stations located throughout the basin (pl. 1). Three of these monitoring stations--the Potomac River at Shepherdstown, W. Va. (5,936 mi²); the Potomac River at Chain Bridge, Washington, D.C. (11,570 mi²); and the Shenandoah River at Millville, W. Va. (3,040 mi²)--are part of the U.S. Geological Survey's National Stream-Quality Assessment Network (NASQAN).

The objective of the NASQAN program is to describe the areal and temporal variability of water quality in the Nation's streams. A potential problem is that stations with large drainage areas may not provide a consistent representation of water-quality conditions within their basins. The standard approach to defining that variability is to collect and analyze samples from a representative number of sites or stations in the streams. However, the data obtained at a given station represents only the quality of water leaving the drainage area upstream from the station, so that data from stations that drain large areas may not indicate or reflect variation of water quality within the basin. For example, if a large source of contamination is located near a monitoring station, the contaminants may mask an overall "good" quality water within the basin as well as minor fluctuations in that quality.

It is necessary to know the relation of water-quality data collected at these sites to data collected at other sites within the basin to assess the ability of the three NASQAN stations in the Upper Potomac River basin to adequately describe the areal and temporal variability of water quality in their respective basins. General causative factors such as land use/land cover, water use, and geology also must be assessed. To address these issues, a 2-year study of the surface-water quality of the Upper Potomac River basin was begun by the U.S. Geological Survey in 1985, with funding provided by the Water Resources Division, Office of Water Quality.

Purpose and Scope

The purpose of this report is to (1) describe areal and temporal variations in the surface-water quality in the Upper Potomac River basin; (2) relate water-quality variability to factors such as land use/land cover, water use, and geology; and (3) suggest a sampling strategy that will improve future trend analysis. Analytical methods of the study included parametric and nonparametric statistical tests of water-quality data stored in the Survey's WATSTORE (National Water Data Storage and Retrieval) data-base management system for 25 surface-water stations in the Upper Potomac River basin, including the three NASQAN stations.

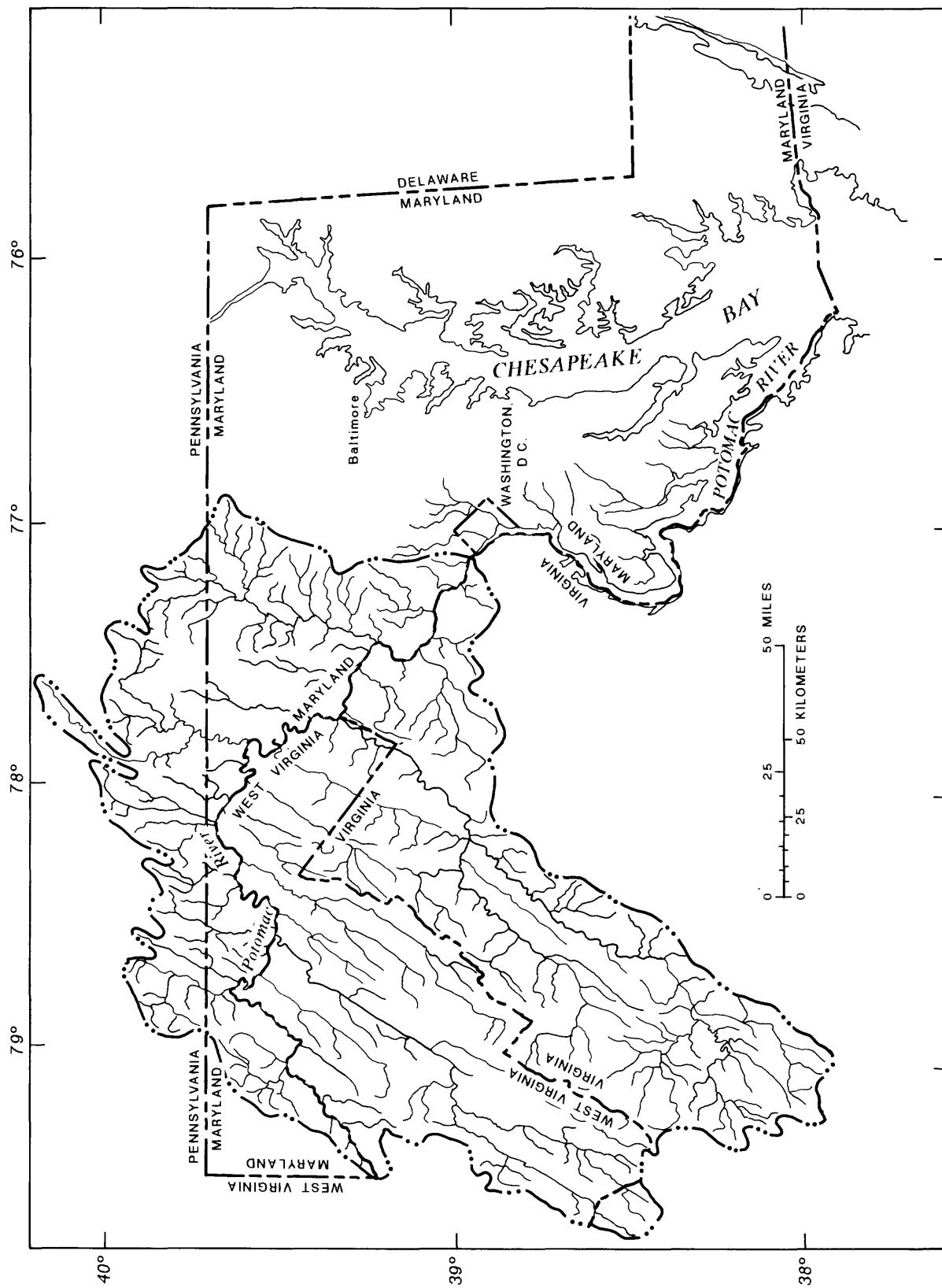


Figure 1.--Location of study area.

Physiography

The Upper Potomac River basin lies within five physiographic provinces (pl. 1)--the Appalachian Plateaus, Valley and Ridge, Great Valley (the eastern part of the Valley and Ridge), Blue Ridge, and Piedmont.

The Appalachian Plateau is a broad upland containing nearly horizontal beds of shale, sandstone, coal, and some limestone (Sinnott and Cushing, 1978, p. 114). Local relief is commonly 500 to 1,000 ft (feet) above sea level along the eastern edge of the province (Trainer and Watkins, 1975, p. 6) and can be as much as 2,000 ft above sea level. Although the relief from mountain top to valley bottom varies, the mountain tops are at nearly the same elevation, suggesting a former plateau (Vokes and Edwards, 1974, p. 71).

The Valley and Ridge province consists of northeasterly trending ridges of massive sandstone and quartzitic beds separated by valleys eroded into weaker shale and limestone beds (Vokes and Edwards, 1974, p. 69). The Great Valley--also called Hagerstown Valley in Maryland, Cumberland Valley in Pennsylvania, and the Shenandoah Valley in Virginia--is part of the Valley and Ridge province. The Great Valley is a broad lowland with a gently rolling floor composed of a thick sequence of Cambrian and lower Ordovician limestones and upper Ordovician shales in the western part (Vokes and Edwards, 1974, p. 69).

The Blue Ridge province, with an average width of less than 10 miles (Sinnott and Cushing, 1978, p. 19), consists of metamorphosed sediments and igneous rocks similar to the crystalline rocks of the Piedmont, but more resistant to erosion. It acts as a divide between the Great Valley and Piedmont provinces.

The Piedmont province has a broad, undulating surface with low hills and ridges and numerous deep and narrow stream valleys (Vokes and Edwards, 1974, p. 56). It is composed of weathered metamorphic, carbonate, and igneous rocks.

Land and Water Use

Cropland in the Appalachian Plateau province is limited due to its steep slopes. The area is primarily forested, with some coal mining (U.S. Department of Agriculture, 1963, p. 27). Rasin and others (1986, p. 41) state that the major water-quality problems in the area are due to acid drainage from coal mines and raw sewage in Georges Creek. One major contributor to water-quality improvement in the region is Bloomington Dam and Reservoir, which was completed in 1982 (Rasin and others, 1986, p. 19).

Forestry is important in the hillslope areas of the Valley and Ridge province (U.S. Department of Agriculture, 1963, p. 26). Farming competes with industrial growth in the broader flood-plain valleys.

Rasin and others (1986, p. 70-76) indicate that water quality throughout the Valley and Ridge province is generally considered good. Contamination problems in the past have been attributed to municipal sewage-treatment-plant

discharge and agricultural runoff. Connate water (pore water present during original deposition of the sediments) with elevated concentrations of chloride and sulfate near the surface in broad, synclinal valleys composed of shale and siltstone, is another potential source of water-quality problems (Hobba and others, 1972, p. 81, 89-91).

Agricultural runoff and domestic and industrial waste present potential water-quality problems in the Great Valley; however, the overall water quality in the region is considered good to excellent (Rasin and Brooks, 1982, p. 27-33). Steep forested slopes and thin soils make the Blue Ridge province generally unsuitable for agriculture (U.S. Department of Agriculture, 1963, p. 23-25). Stream-water quality in the Blue Ridge is generally good with low dissolved solids (Sinnott and Cushing, 1978, p. 19). Sediment from agricultural runoff, septic systems, and urban development near Frederick, Md., and Washington, D.C., have caused water-quality problems in the Piedmont (Rasin and Brooks, 1982, p. 40-46).

METHODS

Analyses of water quality and water-quality trends were conducted on historical USGS data for water years 1960-85 at 25 surface-water stations located within the Upper Potomac River basin (pl. 1). Table 1 lists the stations, drainage areas, and time periods for which water quality was analyzed for this report. Table 2 lists the constituents analyzed.

Water-quality data tend to have a skewed distribution; chemical concentrations vary seasonally and are typically serially correlated (Smith and others, 1982, p. 5). As a result, temporal trend analysis requires distribution-free tests that are not sensitive to skewness and seasonality. The Seasonal Kendall test described by Crawford and others (1983) was used to evaluate water-quality data for temporal trends. In the procedure, all possible pairs of data are compared. If a value later in time is higher, a plus is recorded; if a later value is lower, a minus is recorded. If there is a positive trend, the number of pluses will greatly exceed the number of minuses. If there is a negative trend, the number of minuses will greatly exceed the number of pluses (Crawford and others, 1983, p. 56). The magnitude or slope of the trend is estimated as the median of the slopes of the ordered pairs of data values compared in the Seasonal Kendall test.

Seasonal variation in the data was limited by using the median value for each of four equal annual seasons. The seasonal values were then compared to values from the same season in subsequent years (Crawford and others, 1983, p. 57).

The effects of variability in discharge may either mask trends or give a false impression of trends. Apparent trends may be due to changes in the streamflow rather than changes in overall water quality. Regressions were used to determine the relation between discharge and concentration. This relation was then used to compute flow-adjusted concentrations by subtracting computed concentration from the observed concentration. This technique, described by Smith and others (1982, p. 6-8), is generally referred to as residual analysis.

Table 1.--Water-quality stations

[mi² = square miles; NASQAN = National Stream-Quality Assessment Network]

Site no.	Station	Station name	Latitude (° ' ")	Longitude (° ' ")	Drainage area (mi ²)	Sample period (years)
1	01595800	North Branch Potomac River at Barnum, W. Va.	39 26 44	79 06 39	266	1967-80
2	01599000	Georges Creek at Franklin, Md.	39 29 38	79 02 42	72.4	1965-72, 1979-81
3	01600000	North Branch Potomac River at Pinto, Md.	39 33 59	78 50 25	596	1964, 1969-81
4	01603000	North Branch Potomac River at Cumberland, Md.	39 37 16	78 46 24	875	1960-69, 1963-83
5	01604500	Patterson Creek near Headsville, W. Va.	39 26 35	78 49 20	219	1960, 1969-85
6	01605500	South Branch Potomac River at Franklin, W. Va.	38 38 14	79 20 14	182	1976-83
7	01606500	South Branch Potomac River near Petersburg, W. Va.	38 59 34	79 10 26	642	1969-83
8	01607500	South Fork South Branch Potomac River at Brandywine, W. Va.	38 37 53	79 14 38	102	1969-85
9	01608000	South Fork South Branch Potomac River near Moorefield, W. Va.	39 00 44	78 57 23	283	1969-85
10	01608500	South Branch Potomac River near Springfield, W. Va.	39 26 49	78 39 16	1,471	1969-83
11	01610200	Lost River (Head of Cacapon River) at McCauley near Baker, W. Va.	39 03 18	78 43 31	155	1972-79
12	01611500	Cacapon River near Great Cacapon, W. Va.	39 34 43	78 18 34	677	1960-61 1969-83
13	01613000	Potomac River at Hancock, Md.	39 41 49	78 10 39	4,073	1961, 1965, 1969-72 1975-78, 1980
14	01614500	Conococheague Creek at Fairview, Md.	39 42 57	77 49 28	494	1961, 1964-83, 1985
15	01616500	Opequon Creek near Martinsburg, W. Va.	39 25 25	77 56 20	272	1960, 1969-83
16	01618000	Potomac River at Shepherdstown, W. Va. (NASQAN)	39 26 04	77 48 07	5,936	1979-85
17	01619500	Antietam Creek near Sharpsburg, Md.	39 27 01	77 43 52	281	1963-83, 1985
18	01631000	South Fork Shenandoah River at Front Royal, Va.	38 54 50	78 12 40	1,642	1967-85
19	01634000	North Fork Shenandoah River near Strasburg, Va.	38 58 36	78 20 11	768	1968-85
20	01636500	Shenandoah River at Millville, W. Va. (NASQAN)	39 16 55	77 47 22	3,040	1960-61, 1969-71, 1973-74, 1976-77, 1979-85
21	01638500	Potomac River at Point of Rocks, Md.	39 16 25	77 32 35	9,651	1961-83
22	01641810	Monocacy River near Walkersville, Md.	39 28 47	77 23 18	637	1974-79, 1982-83
23	01643020	Monocacy River at Reich's Ford Bridge near Frederick, Md.	39 23 16	77 22 40	817	1963-83
24	01645000	Seneca Creek at Dawsonville, Md.	39 07 41	77 20 13	101	1961, 1963-83
25	01646580	Potomac River at Chain Bridge at Washington D.C. (NASQAN)	39 55 46	77 07 02	11,570	1973-85

Table 2.--Water-quality constituents analyzed

[$\mu\text{S}/\text{cm}$ = microsiemens per centimeter at
25 degrees Celsius; mg/L = milligrams per liter;
 $\mu\text{g}/\text{L}$ = micrograms per liter]

<u>Constituent</u>	<u>Unit</u>
Specific conductance	$\mu\text{S}/\text{cm}$
pH	units
Alkalinity, total as CaCO_3	mg/L
Nitrite plus nitrate, dissolved as N	mg/L
Phosphorus, total as P	mg/L
Calcium, dissolved (Ca)	mg/L
Magnesium, dissolved (Mg)	mg/L
Sodium, dissolved (Na)	mg/L
Potassium, dissolved (K)	mg/L
Chloride, dissolved (Cl)	mg/L
Sulfate, dissolved (SO_4)	mg/L
Iron, total (Fe)	$\mu\text{g}/\text{L}$
Manganese, total (Mn)	$\mu\text{g}/\text{L}$
Dissolved solids, residue at 180 °C	mg/L
Suspended sediment	mg/L

The method used for examining sampling strategy as a function of discharge was suggested by German and Schiffer (German, E.R., U.S. Geological Survey, written commun., 1985). Sampling strategy was evaluated using histograms of the number of samples collected for a number of constituents plotted against 10-percent increments of flow duration. These histograms showed the sampling distribution over the range of discharge.

AREAL AND TEMPORAL VARIATIONS

Alkalinity and pH

Alkalinity is a measure of the acid-buffering capacity of water expressed as milligrams per liter (mg/L) of calcium carbonate. The U.S. Environmental Protection Agency (USEPA) has established a standard of 20 mg/L (U.S. Environmental Protection Agency, 1986b) as the minimum value necessary to support freshwater aquatic life properly. The acid-base equilibrium of the water is measured by the pH, which is related to the hydrogen-ion concentration. For domestic water supplies, a pH range of 5.0 to 9.0 is recommended (U.S. Environmental Protection Agency, 1986c). However, in order to maintain the viability of freshwater aquatic life, a range of 6.5 to 9.0 is recommended.

Figure 2 shows boxplots of alkalinities in the Upper Potomac River basin. With the exception of the coal-mining areas in the North Branch Potomac River basin, most of the observed alkalinities are higher than the 20 mg/L minimum recommended by the U.S. Environmental Protection Agency (1986b). The lowest observed values are in the North Branch Potomac River at Barnum, W. Va. (site 1), and in Georges Creek (site 2). Alkalinity increases downstream at Pinto, Md. (site 3), as a result of dilution of the acid-mine drainage by the Savage River (pl. 1), which does not drain a heavily mined area. Alkalinity also rises in the North Branch Potomac River at Cumberland, Md. (site 4), due to dilution from Wills Creek (pl. 1).

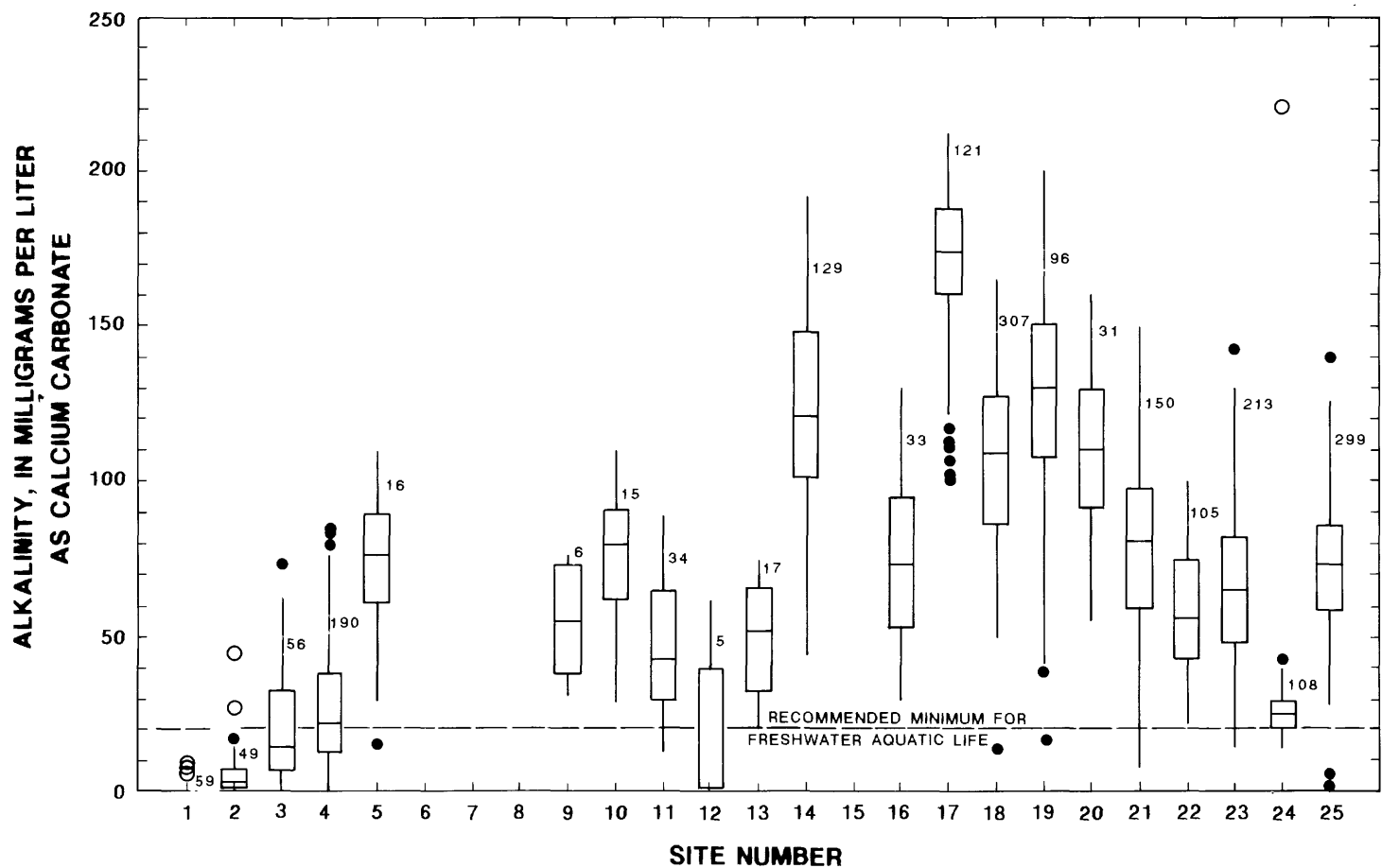
In the Valley and Ridge streams (sites 5-13), alkalinity is generally 50 to 100 mg/L. Dissolved limestone from the tributary valleys drained by Patterson Creek, the South Branch Potomac River, and others, help increase the alkalinity in the Potomac River at Hancock, Md. (site 13), to about 50 mg/L. Streams in the Great Valley (sites 14-20) have somewhat elevated alkalinity values because they drain an area that is primarily underlain by limestone. Conococheague Creek (site 14), with a median alkalinity of about 120 mg/L, helps raise the alkalinity in the Potomac River at Shepherdstown, W. Va. (site 16), to about 70 mg/L. Antietam Creek (site 17) and the Shenandoah River (site 20), with median alkalinities of about 170 and 110 mg/L, help bring the alkalinity in the Potomac River at Point of Rocks, Md. (site 21), to about 80 mg/L.

The Piedmont province, which includes the Monocacy River basin and Seneca Creek basin (pl. 1), contains less carbonate rock than the Great Valley. As a result, alkalinities are lower and the median value in the Potomac River at Chain Bridge (site 25) is reduced to about 70 mg/L.

The pH is related to the alkalinity of the water. Where alkalinities are low, as in the North Branch of the Potomac River, pH also tends to be low. Figure 3 shows boxplots of pH for the Upper Potomac River basin. Except for the North Branch Potomac River basin upstream from Cumberland, Md. (sites 1-4), the pH values are generally within the recommended range for freshwater aquatic life.

The North Branch Potomac River at Barnum, W. Va. (site 1), and Georges Creek (site 2) have low pH values, almost completely outside the range for freshwater aquatic life and lower than the recommended minimum of 5.0 for domestic water supply. The pH problems in the North Branch Potomac River basin are a direct result of acid-mine drainage from coal mines in the basin.

Temporal trends in alkalinity and pH are summarized in table 3. The column labeled Concentration lists the trends for the observed concentrations. The column labeled Flow-adjusted concentration lists the trends for concentrations adjusted for discharge. The Slope column is the slope of the trend in milligrams per liter per year for alkalinity and in pH units per year for pH. If the value of Slope is positive, observed values are increasing as time progresses; if the value is negative, observed values are decreasing as time progresses. The Slope column was left blank in cases where there were



EXPLANATION

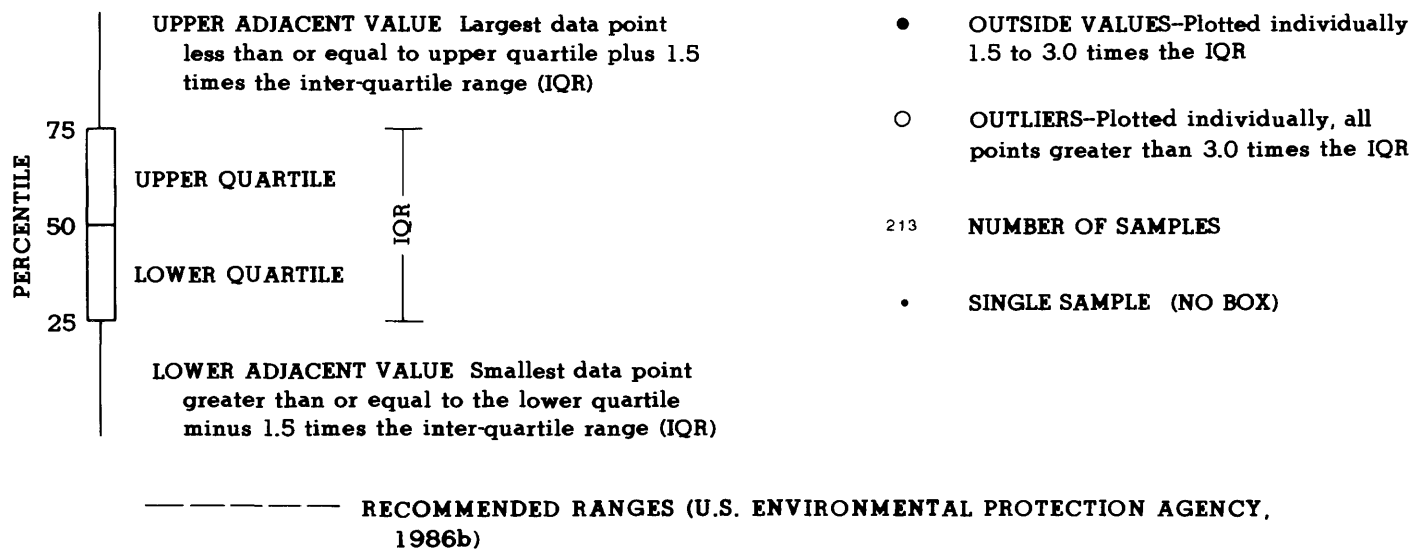
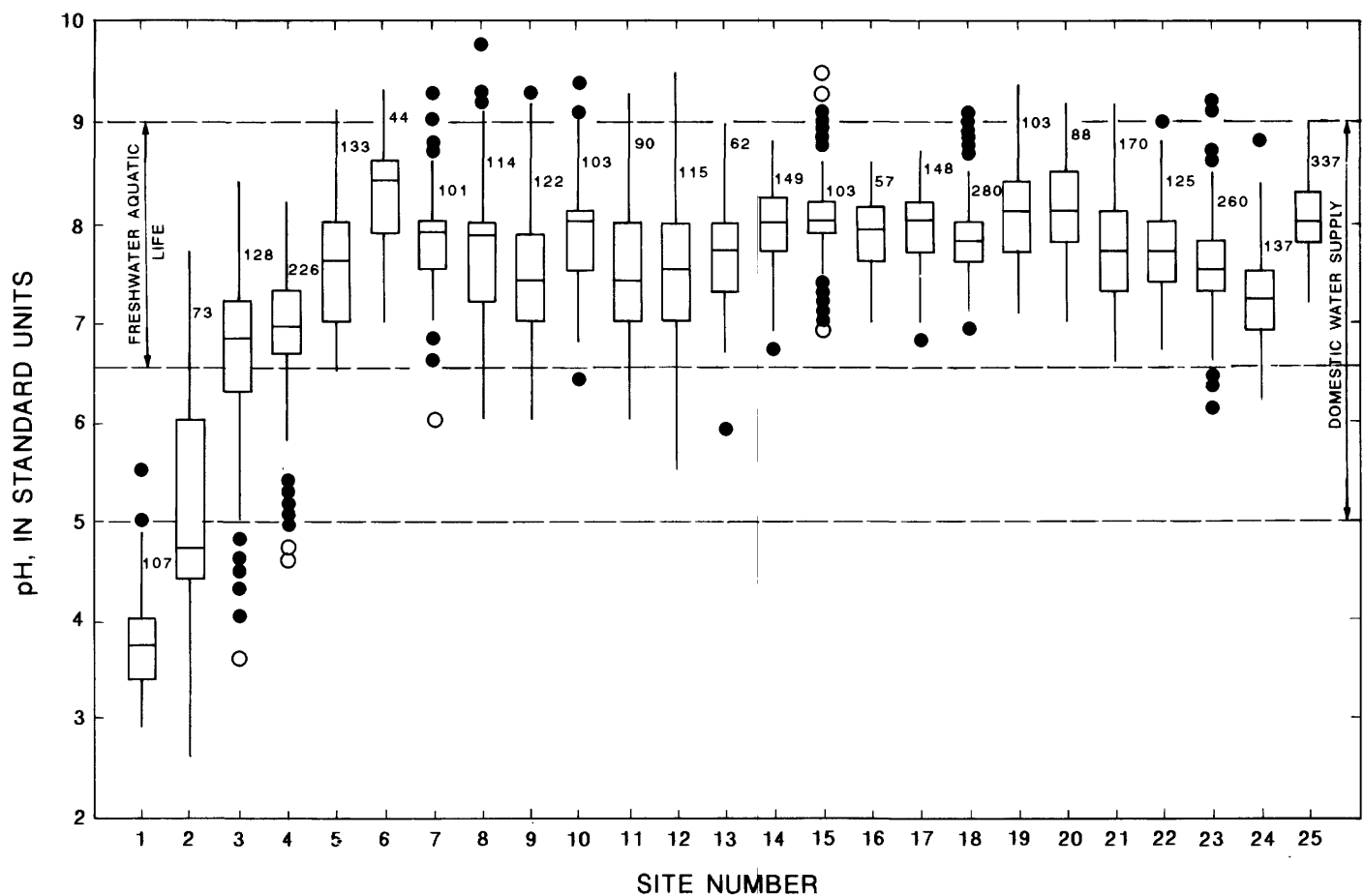


Figure 2.—Distribution of alkalinity concentration at surface-water sites.



EXPLANATION

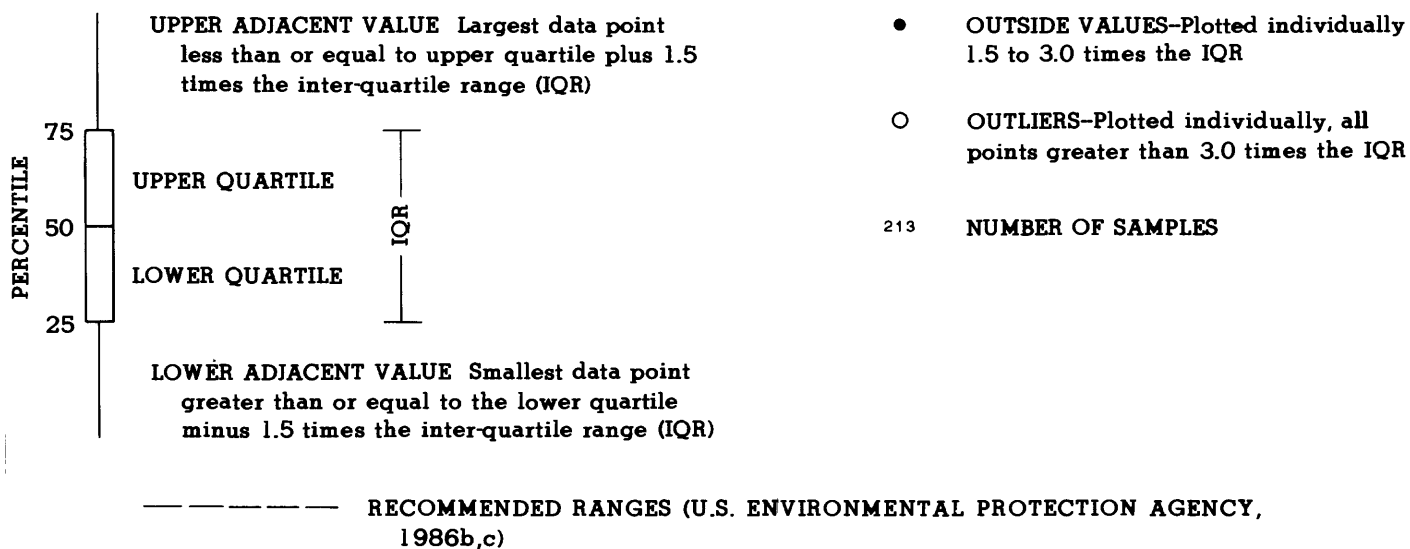


Figure 3.—Distribution of pH at surface-water sites.

Table 3.--Summary of Seasonal Kendall test results for temporal trends for alkalinity and pH

SLOPE: Slope of the trend, in milligrams per liter per year except where noted.
P: Probability that no trend exists.
NVALS: Number of values used to compute the trend
*: P exceeds cutoff value of 0.20.
#: Logarithmic slope, expressed as percent change per year.
blank: Insufficient data to compute trends.
+: Nonsignificant flow-concentration regression.
NASQAN: National Stream-Quality Assessment Network

Station name	Alkalinity				pH			
	Concentration		Flow-adjusted concentration		Units		Flow-adjusted units	
	Slope	P/NVALS	Slope	P/NVALS	Slope	P/NVALS	Slope	P/NVALS
1 North Branch Potomac River at Barnum, W. Va.	0.11	0.00/32	0.12	0.00/46	0.12	0.00/46	#2.94	0.00/46
2 Georges Creek at Franklin, Md.	.56	.00/22			.14	.00/28	.14	.00/28
3 North Branch Potomac River at Pinto, Md.	.93	.16/35	.71	.02/35	.09	.00/35	.06	.00/39
4 North Branch Potomac River at Cumberland, Md.	*		.88	.00/64	.03	.00/79	*	
5 Patterson Creek near Headsville, W. Va.	*				*			
6 South Branch Potomac River at Franklin, W. Va.					- .08	.03/26	- .04	.10/26
7 South Branch Potomac River near Petersburg, W. Va.					*			
8 South Fork South Branch Potomac River at Brandywine, W. Va.					.02	.05/62	+	
9 South Fork South Branch Potomac River near Moorefield, W. Va.	*				.03	.00/65	+	
10 South Branch Potomac River near Springfield, W. Va.	*				*			
11 Lost River at McCauley near Baker, W. Va.	*		*		.12	.01/32	.14	.02/32
12 Cacapon River near Great Cacapon, W. Va.	*				.02	.12/58	+	
13 Potomac River at Hancock, Md.	*				*		*	
14 Conococheague Creek at Fairview, Md.	*		# .90	.00/49	.03	.00/69	.03	.00/63
15 Opequon Creek near Martinsburg, W. Va.	*				.02	.02/54	+	
16 Potomac River at Shepherdstown, W. Va. (NASQAN)	1.27	.12/15	+		*			
17 Antietam Creek near Sharpsburg, Md.	.70	.03/58	1.80	.00/52	.02	.03/69	+	
18 South Fork Shenandoah River at Front Royal, Va.	*		*		.05	.00/54	.11	.01/27
19 North Fork Shenandoah River near Strasburg, Va.	*		*		.03	.00/54	*	
20 Shenandoah River at Millville, W. Va. (NASQAN)	2.29	.14/13	*		.02	.03/44	+	
21 Potomac River at Point of Rocks, Md.	*		1.24	.00/61	.06	.00/80	.06	.00/73
22 Monocacy River near Walkersville, Md.	*		*		.08	.03/24	.04	.17/24
23 Monocacy River at Reich's Ford Bridge near Frederick, Md.	.58	.12/65	1.06	.00/59	.04	.00/75	+	
24 Seneca Creek at Dawsonville, Md.	.33	.01/56	#2.33	.00/51	.05	.00/71	+	
25 Potomac River at Chain Bridge at Washington, D.C. (NASQAN)	*		*		- .02	.04/51	- .01	.18/51

insufficient data to compute a trend. In cases where a logarithmic regression was used to adjust concentration for discharge ("#" in the Slope column), the slope is in natural log units and is expressed as percent change per year. P is the probability that no trend exists. If this probability is greater than 0.20, no trend was assumed and "*" was entered into the Slope column. NVALS is the number of values used in the analysis. No significant relation between flow and concentration at a station is denoted by "+".

There appear to be positive alkalinity trends at 11 of the 25 stations in the Upper Potomac River basin. Note that all four of the stations in the North Branch Potomac River basin show rising alkalinity trends. Figure 4 shows boxplots of yearly alkalinities for Georges Creek (site 2). The slope of the trend is not readily apparent, but the overall rise in alkalinity is evident in the late 1970's and early 1980's. Also, there are positive alkalinity trends in Conococheague Creek (site 14), the Potomac River at Shepherdstown, W. Va. (site 16), Antietam Creek (site 17), the Shenandoah River (site 20), the Potomac River at Point of Rocks, Md. (site 21), the Monocacy River at Reich's Ford Bridge (site 23), and Seneca Creek (site 24). Interestingly, there appears to be no alkalinity trend in the Potomac River at Chain Bridge (site 25). This lack of consistency with the upstream stations may be because the Chain Bridge site has about 10 years less record.

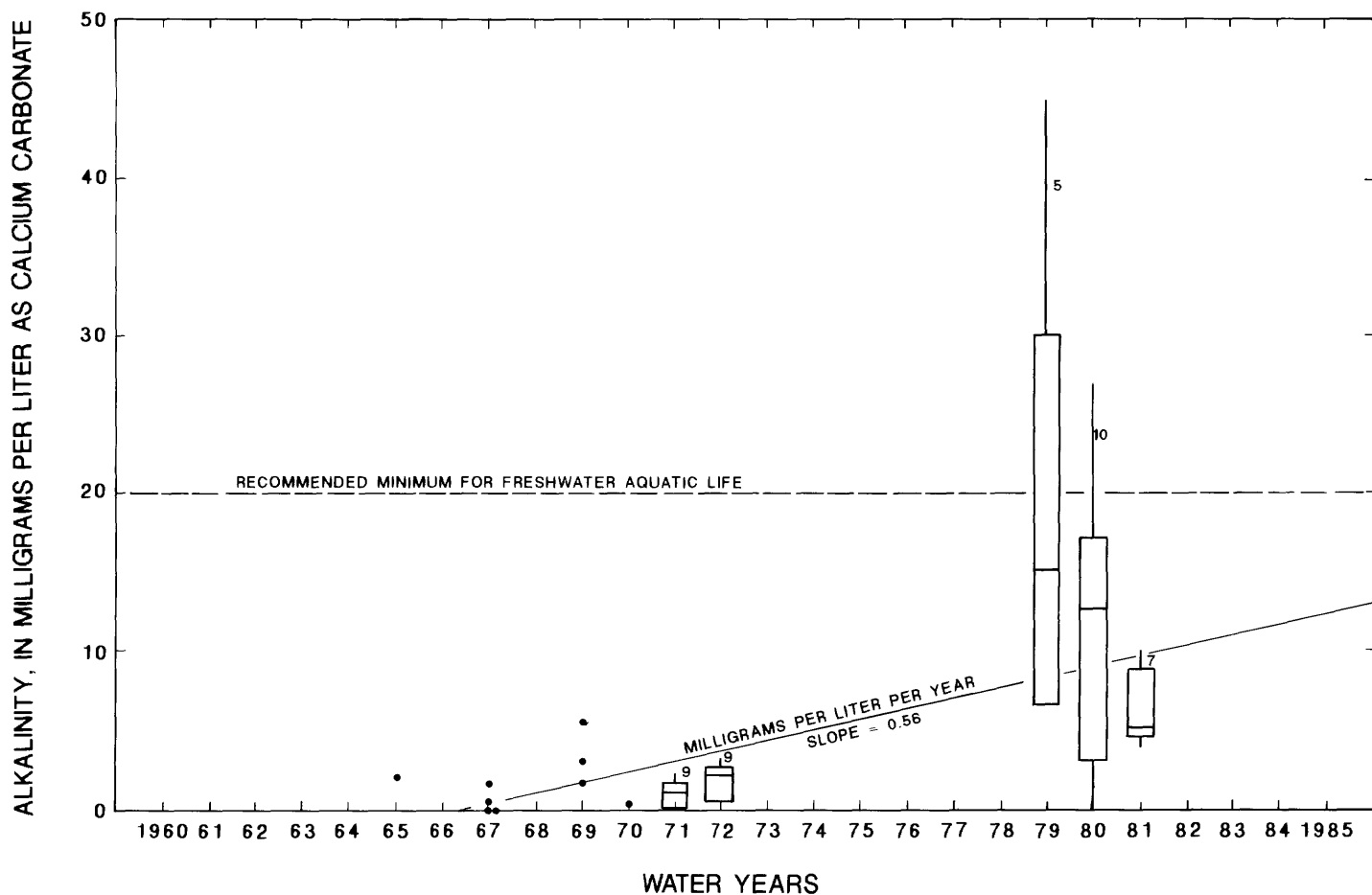
With two exceptions, where pH trends are present, they are positive throughout the upper basin. As with alkalinity, pH is increasing in the Appalachian Plateau streams (North Branch Potomac River). Figure 5 shows boxplots of the annual pH distribution in Georges Creek (site 2). Note that pH trends tend to follow the alkalinity trends. The positive trend slopes in the Appalachian Plateau may be attributable to increased treatment of acid-mine drainage.

Trends at the two stations with negative trend-slopes [South Branch Potomac River at Franklin, W. Va. (site 6), and the Potomac River at Chain Bridge (site 25)] are not very pronounced. They are, however, noticeable as illustrated in figure 6, which shows the annual distribution of pH at Chain Bridge (site 25) where the trend-slope is -0.02 pH units per year. At Chain Bridge, the range in pH decreases as well as the values.

Suspended Sediment

The Interstate Commission on the Potomac River Basin rates suspended-sediment concentrations as follows: less than 25 mg/L (natural log = 3.2) is considered "excellent"; 25 to 80 mg/L (natural log of 80 = 4.38) is considered "good"; 81 to 400 mg/L (natural log of 400 = 5.99) is considered "fair"; and greater than 400 mg/L is considered "poor" (Rasin and Brooks, 1982, p. 8).

Boxplots of the natural logarithms of suspended-sediment concentration (fig. 7) show the distribution at 10 of the 25 stations. The three stations located in the North Branch Potomac River basin (sites 2-4) fall primarily within the "good" to "excellent" range. Lost River at McCauley, W. Va. (site 11), has the widest range of values, from "excellent" to "poor". Most of the samples from Lost River, however, fall within the "good" to "excellent" range. The Cacapon River near Great Cacapon, W. Va. (site 12), which is downstream from the Lost River station, lies entirely within the "excellent" range. Two



EXPLANATION

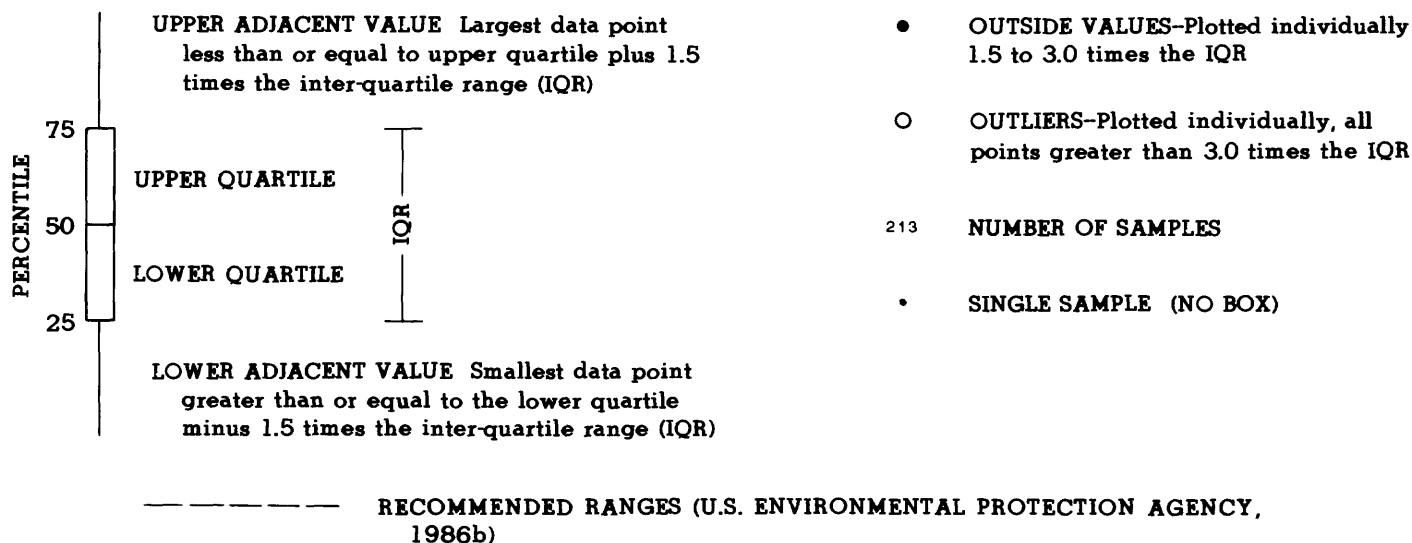
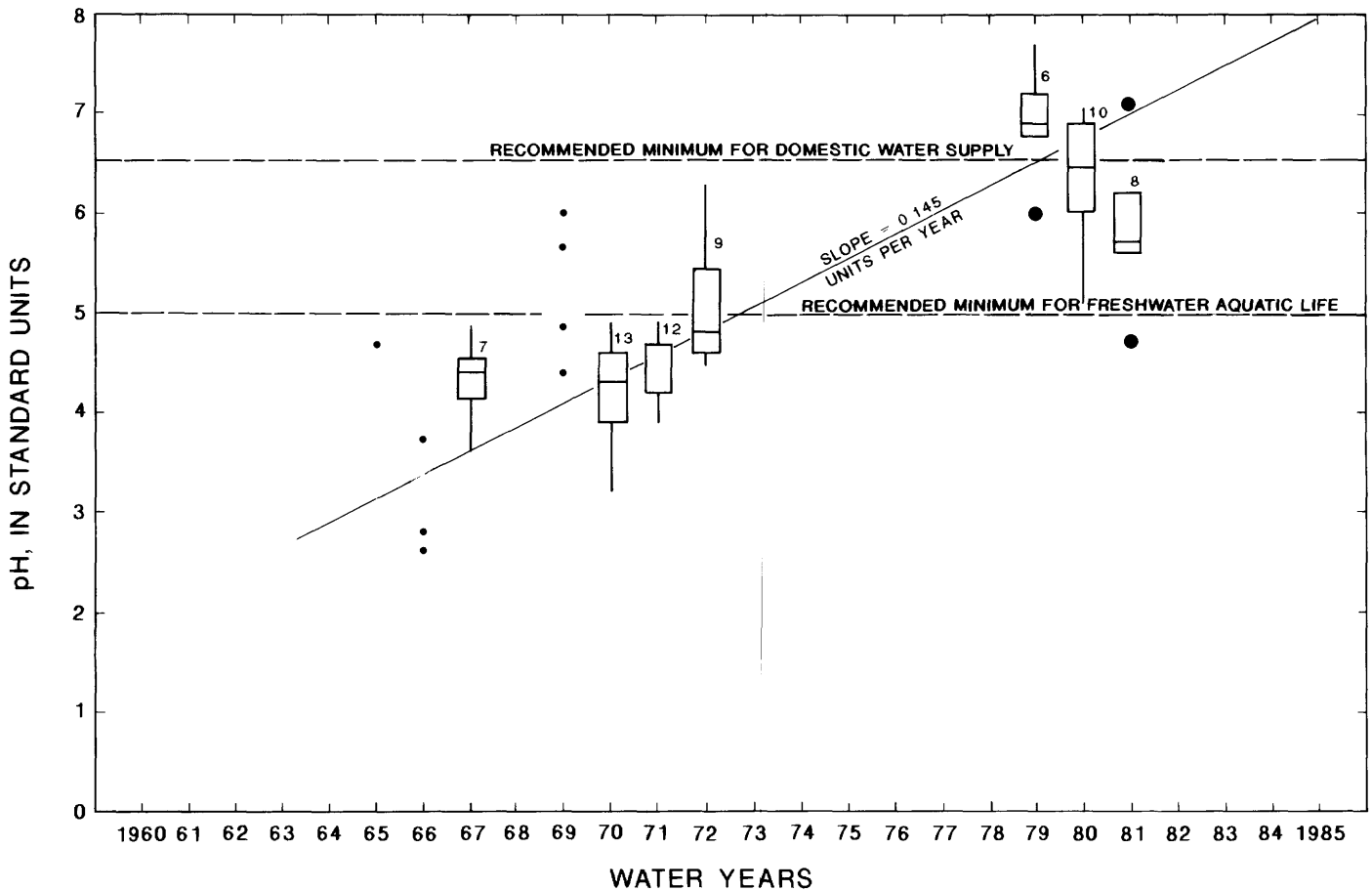


Figure 4.—Annual distribution of alkalinity in Georges Creek at Franklin, Md.



EXPLANATION

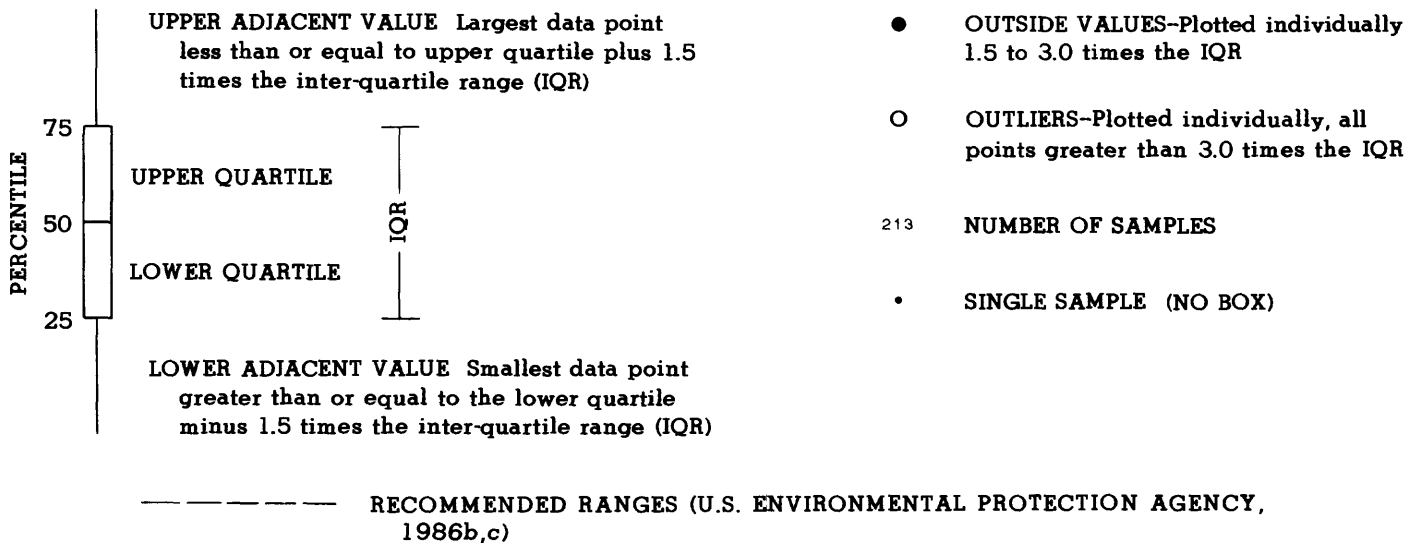
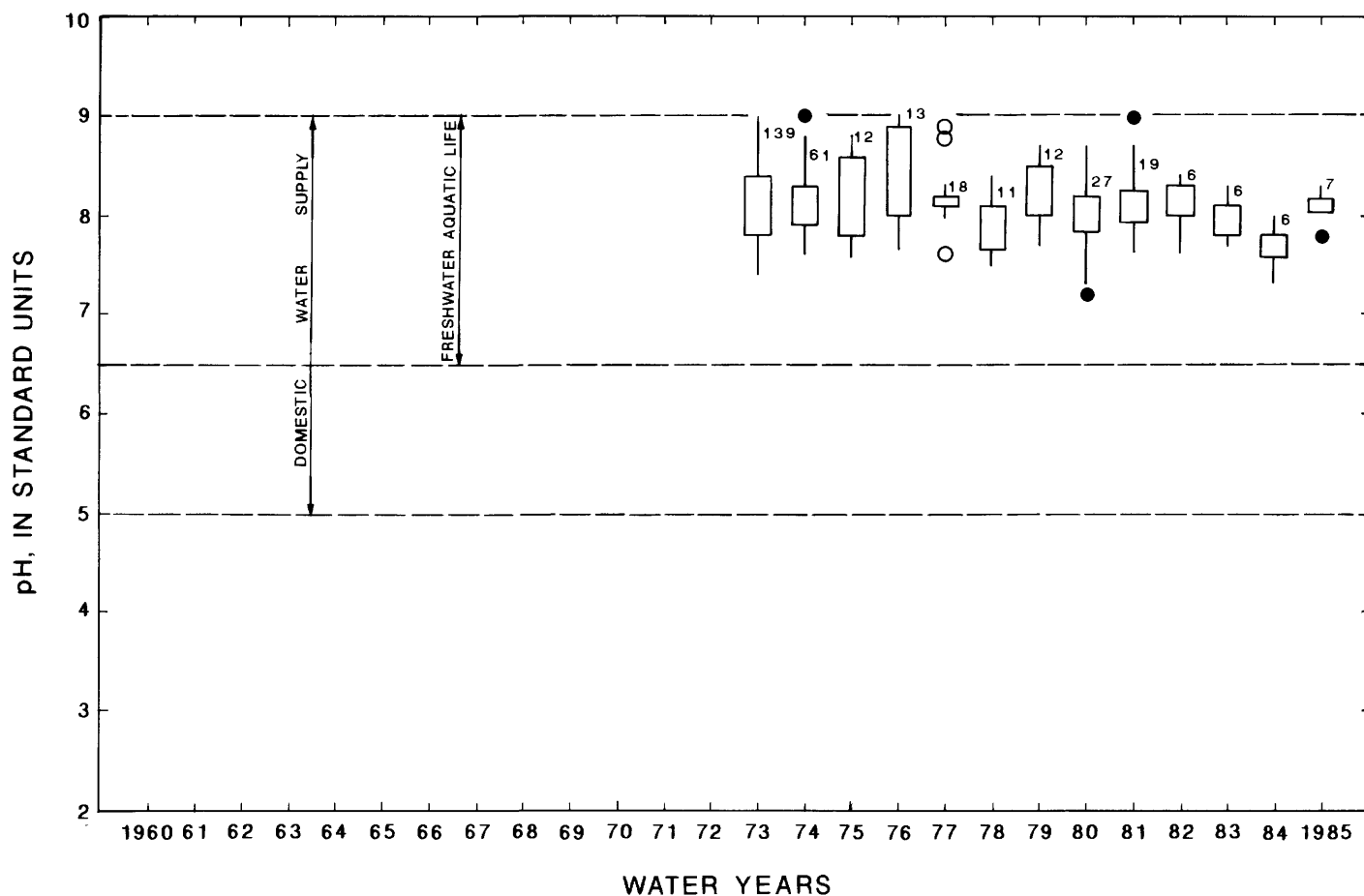


Figure 5.—Annual distribution of pH in Georges Creek at Franklin, Md.



EXPLANATION

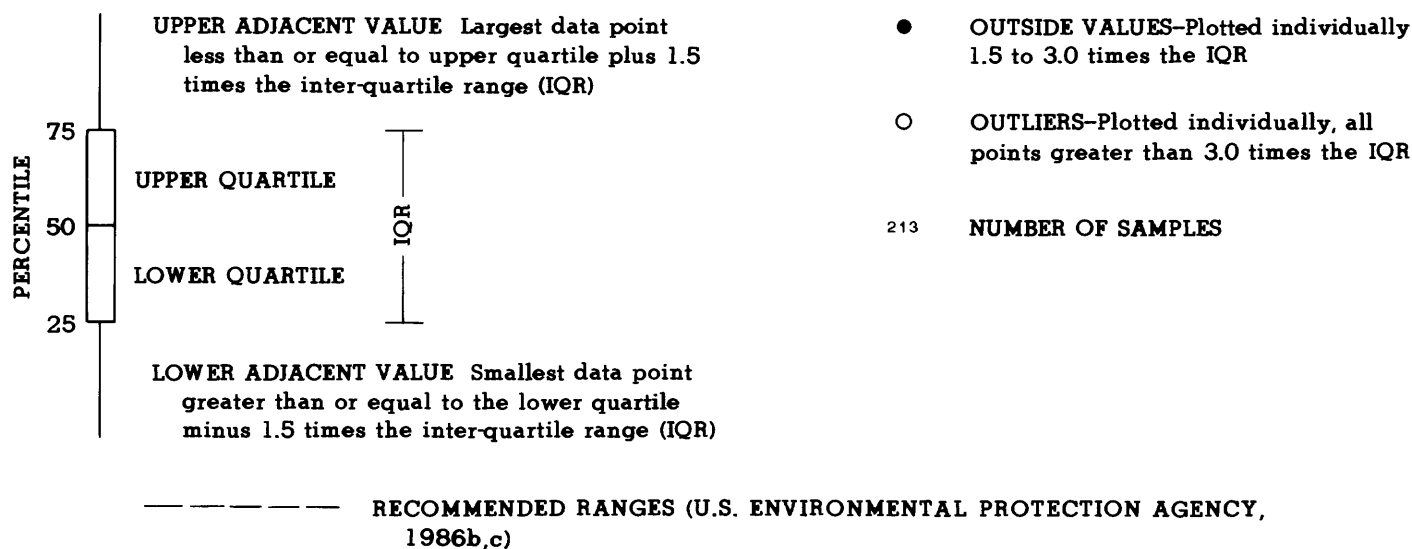
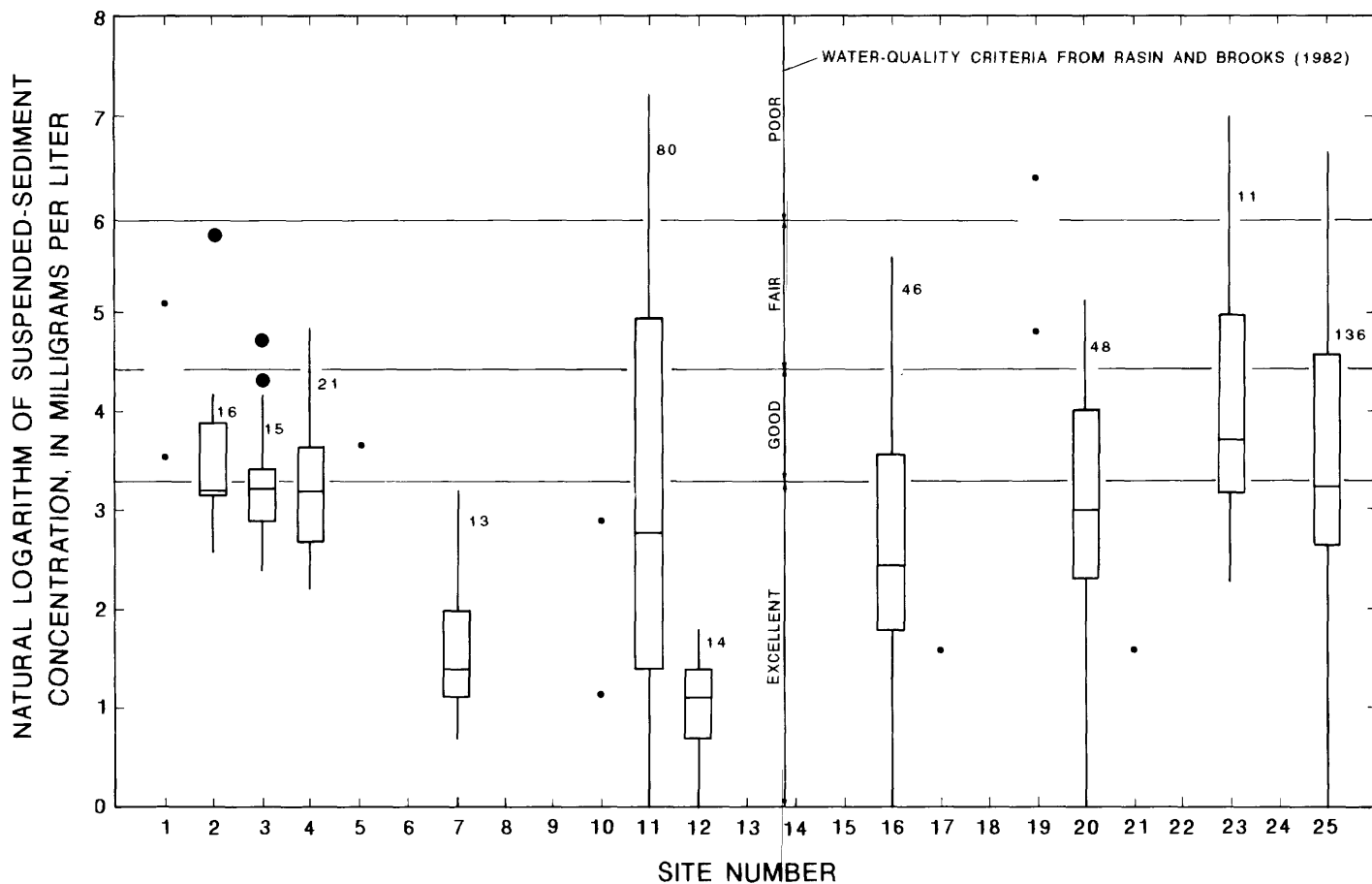


Figure 6.—Annual distribution of pH in the Potomac River at Chain Bridge at Washington, D.C.



EXPLANATION

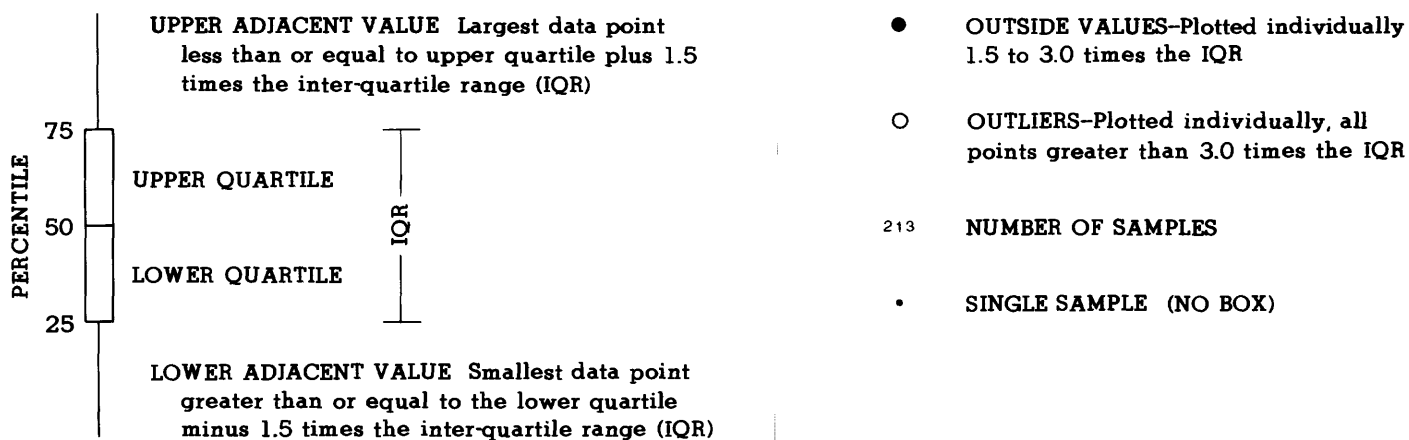


Figure 7.--Distribution of suspended-sediment concentration at surface-water sites.

NASQAN stations--the Potomac River at Shepherdstown, W. Va. (site 16), and the Shenandoah River at Millville, W. Va. (site 20)--generally have "good" to "excellent" suspended-sediment concentrations, with a few "fair" observations.

The Monocacy River (site 23) has the highest median suspended-sediment concentration of about 40 mg/L (natural log = 3.7). Even though the river has been identified as having problems with high suspended sediment due to agricultural runoff, Rasin and Brooks (1982, p. 43) rated most of the observed concentrations in the "good" range, with some "excellent", some "fair", and a few "poor". Finally, suspended-sediment concentrations at the NASQAN station on the Potomac River at Chain Bridge (site 25) lie mostly within the "good" to "excellent" range, with about half of the observations in the "excellent" range. There are some "fair" observations and a few "poor" observations.

Of the 10 stations with suspended-sediment observations, only 4 showed any significant trends (table 4). The North Branch Potomac River at Cumberland, Md. (site 4), the Lost River at McCauley, W. Va. (site 11), and the Shenandoah River NASQAN station at Millville, W. Va. (site 20), all showed negative trends in observed concentration. There were no observed trends in flow-adjusted concentration at the Cumberland or McCauley stations. No flow adjustment was made at the Millville station because there was no clear concentration-discharge relation. A negative trend of -3.44 percent per year was observed in the flow-adjusted concentrations for the Potomac River NASQAN station at Chain Bridge (site 25). The fact that the observed trends are all negative may indicate decreasing soil erosion due to improved farm-management practices. However, the loss of significant downward trends with flow adjustment at the Cumberland and McCauley stations suggests that change in streamflow may be an important cause of these trends.

Total Dissolved Solids and Specific Conductance

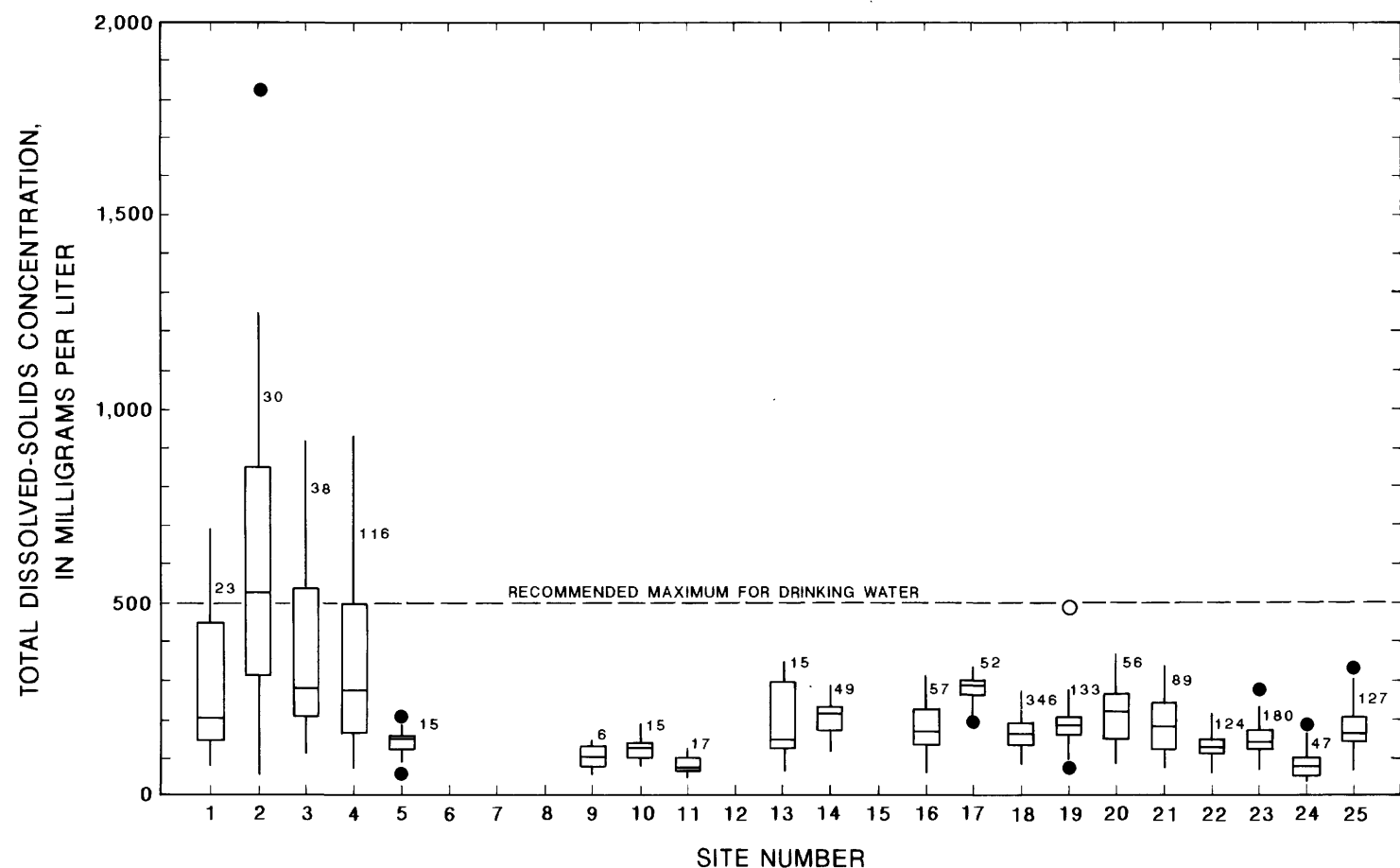
Analyses for total dissolved solids are available for 20 of the 25 stations. The U.S. Environmental Protection Agency (1986c) recommends a maximum total dissolved-solids concentration of 500 mg/L for drinking water when more suitable water supplies are unavailable. For freshwater fish, the recommended maximum is 15,000 mg/L. The boxplots in figure 8 show that none of the stations exceed the standard for freshwater fish. The four stations in the North Branch Potomac River basin (sites 1-4) are the only stations with values that exceed the recommended drinking water limit. The values at most of the other stations are generally between 100 and 300 mg/L, which is well below the recommended limit. The North Branch Potomac River basin stations stand out from the others with higher observed values and wider distributions, probably because of acid-mine drainage in the basin.

Specific conductance is an indicator of total dissolved-solids concentration that was measured at all 25 stations. The boxplots in figure 9, which show the specific-conductance distributions at the 25 stations, generally reflect the distributions for total dissolved solids. Note that the lowest specific conductances and total dissolved-solids concentrations are in the basins in the Valley and Ridge province--the South Branch Potomac River (sites 6-10), Cacapon River (sites 11-12), and Seneca Creek (site 24).

Table 4.--Summary of Seasonal Kendall test results for temporal trends for suspended sediment

SLOPE: Slope of the trend, in milligrams per liter per year except where noted.
 P: Probability that no trend exists.
 NVALS: Number of values used to compute the trend.
 *: P exceeds cutoff value of 0.20.
 #: Logarithmic slope, expressed as percent change per year.
 blank: Insufficient data to compute trends.
 +: Nonsignificant flow-concentration regression.
 NASQAN: National Stream-Quality Assessment Network

Station name	Suspended sediment			
	Concentration		Flow-adjusted concentration	
	Slope	P/NVALS	Slope	P/NVALS
1 North Branch Potomac River at Barnum, W. Va.	*			
2 Georges Creek at Franklin, Md.	*			
3 North Branch Potomac River at Pinto, Md.	*			
4 North Branch Potomac River at Cumberland, Md.	-13.40	0.06/12	*	
5 Patterson Creek near Headsville, W. Va.	*			
6 South Branch Potomac River at Franklin, W. Va.				
7 South Branch Potomac River near Petersburg, W. Va.	*			
8 South Fork South Branch Potomac River at Brandywine, W. Va.				
9 South Fork South Branch Potomac River near Moorefield, W. Va.				
10 South Branch Potomac River near Springfield, W. Va.	*			
11 Lost River at McCauley near Baker, W. Va.	-3.00	.17/17	*	
12 Cacapon River near Great Cacapon, W. Va.	*			
13 Potomac River at Hancock, Md.				
14 Conococheague Creek at Fairview, Md.	*			
15 Opequon Creek near Martinsburg, W. Va.				
16 Potomac River at Shepherdstown, W. Va. (NASQAN)	*			
17 Antietam Creek near Sharpsburg, Md.	*			
18 South Fork Shenandoah River at Front Royal, Va.	*		*	
19 North Fork Shenandoah River near Strasburg, Va.	*			
20 Shenandoah River at Millville, W. Va. (NASQAN)	-3.00	.05/24	+	
21 Potomac River at Point of Rocks, Md.	*			
22 Monocacy River near Walkersville, Md.				
23 Monocacy River at Reich's Ford Bridge near Frederick, Md.	*			
24 Seneca Creek at Dawsonville, Md.				
25 Potomac River at Chain Bridge at Washington, D.C. (NASQAN)	*		#-3.44	0.06/49



EXPLANATION

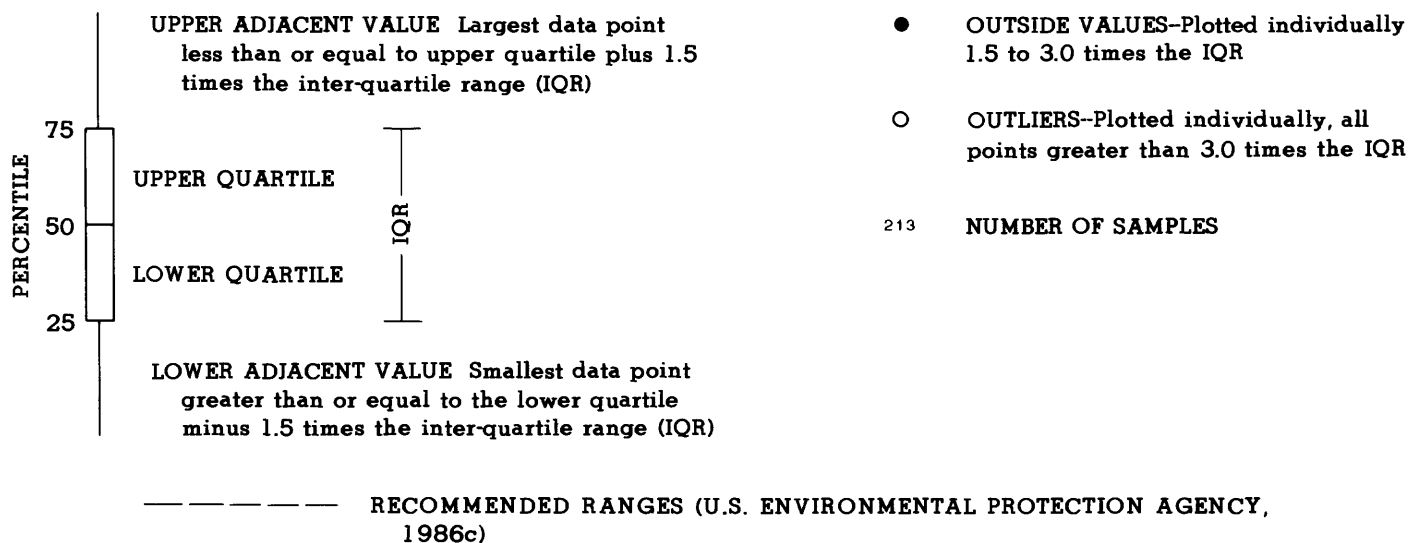
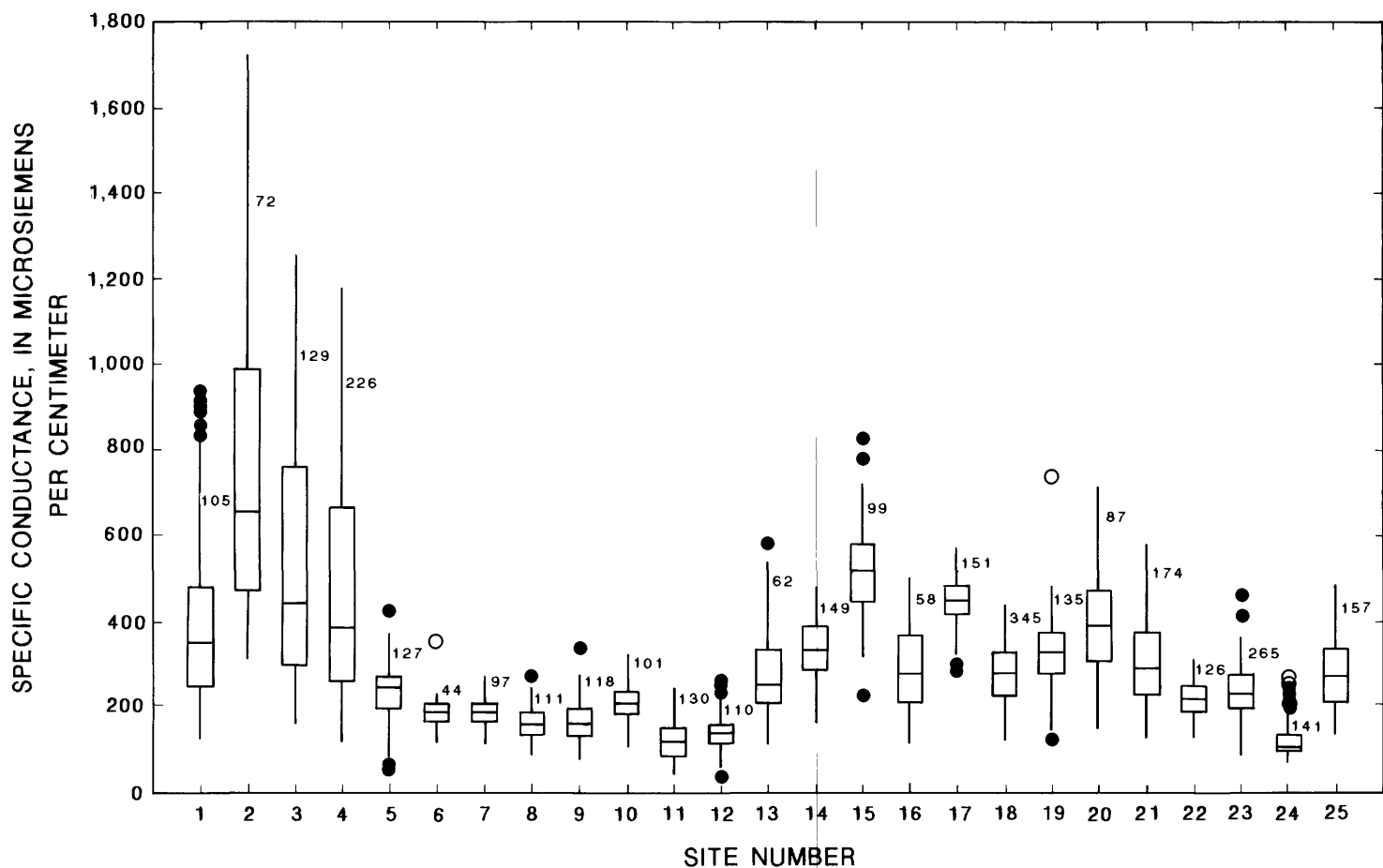
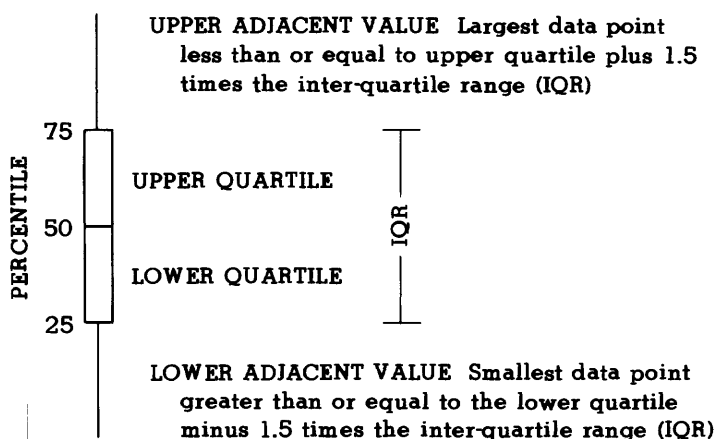


Figure 8.—Distribution of total dissolved-solids concentration at surface-water sites.



EXPLANATION



● OUTSIDE VALUES—Plotted individually 1.5 to 3.0 times the IQR

○ OUTLIERS—Plotted individually, all points greater than 3.0 times the IQR

213 NUMBER OF SAMPLES

Figure 9.—Distribution of specific conductance at surface-water sites.

Twelve stations show positive trends in observed specific conductance (table 5). Only four of these stations show positive trends in observed total dissolved solids. The North Fork Shenandoah River near Strasburg, Va. (site 19), shows a positive trend (no trend in flow-adjusted concentrations) in observed total dissolved solids and no trend in specific conductance. The North Branch Potomac River at Barnum W. Va. (site 1), with the greatest trend-slope in observed specific conductance, is the only station indicating a negative trend.

Specific conductance and total dissolved-solids measurements are sensitive to changes in discharge, and are more meaningful when adjusted for discharge. Eleven stations showed trends in the flow-adjusted specific-conductance values. Four stations showed trends that did not appear in the observed values, and five stations showed no trend after the specific-conductance values were adjusted for discharge. No flow adjustments were made to the specific-conductance values for Seneca Creek (site 24) because there was no clear concentration-discharge relation at that station.

Five stations showed rising trends in flow-adjusted total dissolved-solids concentrations. Two of these stations showed rising trends in both observed and flow-adjusted concentration. The Potomac River NASQAN station at Shepherdstown, W. Va. (site 16), has a rising trend in observed conductance and total dissolved solids and no trend in either flow-adjusted conductance or total dissolved solids. The Shenandoah River NASQAN station at Millville, W. Va. (site 20), has no trends indicated for conductance or total dissolved solids. The Potomac River NASQAN station at Chain Bridge (site 25) has rising trends in conductance and flow-adjusted conductance, but no trends in total dissolved solids. The reason for fewer trends in total dissolved solids than in specific conductance is probably because there are fewer dissolved-solids data available.

Seven stations showed no trends in either conductance or total dissolved solids. Only two stations had falling trends--the North Branch Potomac River at Barnum, W. Va. (site 1), and the Lost River at McCauley, W. Va. (site 11). The reason these two stations have falling trends while most of the other stations have rising trends is not readily apparent.

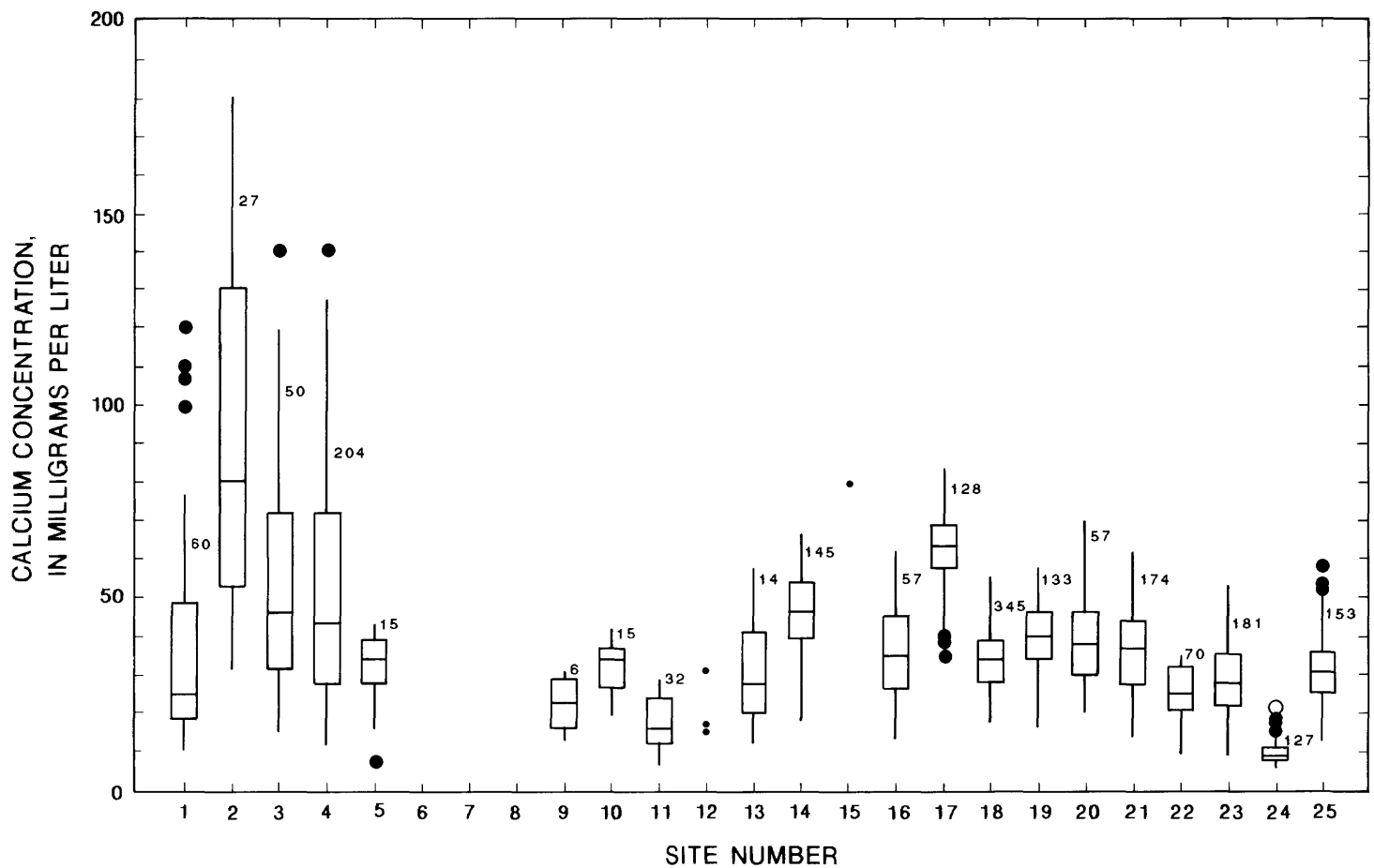
Major Ions

The primary source for dissolved calcium (fig. 10) and magnesium (fig. 11) in the Upper Potomac River basin is the dissolution of carbonate rocks. Acid-mine drainage causes increased dissolution in the North Branch Potomac River basin (sites 1-4). Calcium and magnesium levels are higher in streams draining the Great Valley (sites 14-20) because the valley is underlain almost entirely by carbonate rocks. The highest concentration and widest distribution occur in Georges Creek (site 2) in the North Branch Potomac River basin, which is more populated and more extensively mined than other areas in the basin (Rasin and Brooks, 1982, p. 21). The lowest concentrations with the narrowest distributions occur in the Valley and Ridge (sites 5-13) and Piedmont (sites 22-25) streams where there are a variety of rock types, including carbonates, that are not subjected to acid-mine drainage. The distribution of potassium concentrations (fig. 12) appears to be fairly constant throughout the basin, with values generally less than 4 mg/L.

Table 5.--Summary of Seasonal Kendall test results for temporal trends for
total dissolved solids and specific conductance

SLOPE: Slope of the trend, in milligrams per liter per year except where noted.
P: Probability that no trend exists.
NVALS: Number of values used to compute the trend
*: P exceeds cutoff value of 0.20.
#: Logarithmic slope, expressed as percent change per year.
blank: Insufficient data to compute trends.
+: Nonsignificant flow-concentration regression.
NASQAN: National Stream-Quality Assessment Network

Station name	Total dissolved solids				Specific conductance			
	Concentration		Flow-adjusted concentration		Conductance		Flow-adjusted conductance	
	Slope	P/NVALS	Slope	P/NVALS	Slope	P/NVALS	Slope	P/NVALS
1 North Branch Potomac River at Barnum, W. Va.	*		*		-11.4	0.00/47	- 7.81	0.00/47
2 Georges Creek at Franklin, Md.	*		*		*		*	
3 North Branch Potomac River at Pinto, Md.	*				*		10.95	.01/39
4 North Branch Potomac River at Cumberland, Md.	*		3.12	0.02/48	*		# .60	.03/72
5 Patterson Creek near Headsville, W. Va.	*				1.82	.14/65	# .50	.04/64
6 South Branch Potomac River at Franklin, W. Va.					6.00	.01/26	5.94	.01/26
7 South Branch Potomac River near Petersburg, W. Va.					*		*	
8 South Fork South Branch Potomac River at Brandywine, W. Va.					*		*	
9 South Fork South Branch Potomac River near Moorefield, W. Va.	*				1.50	.10/65	*	
10 South Branch Potomac River near Springfield, W. Va.	*				*		*	
11 Lost River at McCauley near Baker, W. Va.	*				*		- 3.14	.02/32
12 Cacapon River near Great Cacapon, W. Va.					2.26	.01/58	*	
13 Potomac River at Hancock, Md.	*				3.12	.14/27	*	
14 Conococheague Creek at Fairview, Md.	*		1.94	.01/15	1.20	.18/69	2.34	.00/63
15 Opequon Creek near Martinsburg, W. Va.					*		*	
16 Potomac River at Shepherdstown, W. Va. (NASQAN)	4.17	0.01/31	+		4.58	.11/31	*	
17 Antietam Creek near Sharpsburg, Md.	1.35	.01/42	2.19	.00/37	3.58	.00/71	4.15	.00/65
18 South Fork Shenandoah River at Front Royal, Va.	*		*		*		*	
19 North Fork Shenandoah River near Strasburg, Va.	1.33	.07/70	*		*		*	
20 Shenandoah River at Millville, W. Va. (NASQAN)	*		*		*		*	
21 Potomac River at Point of Rocks, Md.	*		1.48	.10/40	*		2.99	.00/74
22 Monocacy River near Walkersville, Md.	*		*		1.00	.17/24	*	
23 Monocacy River at Reich's Ford Bridge near Frederick, Md.	1.69	.00/60	2.01	.00/54	3.75	.00/75	# 1.82	.00/69
24 Seneca Creek at Dawsonville, Md.	4.50	.00/35	+		5.26	.00/72	+	
25 Potomac River at Chain Bridge at Washington, D.C. (NASQAN)	*		*		2.98	.12/51	# .70	.02/51



EXPLANATION

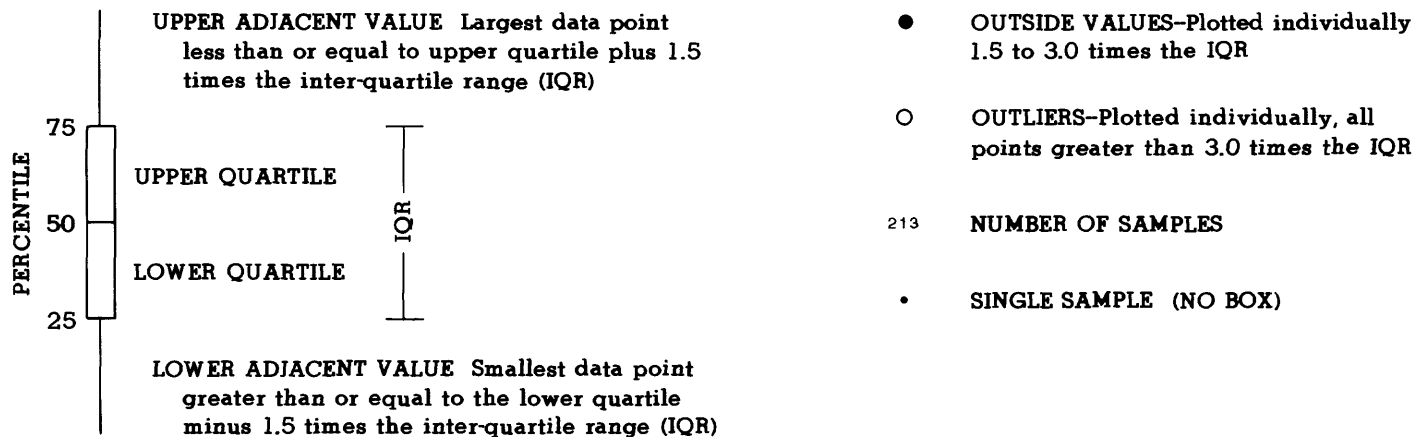
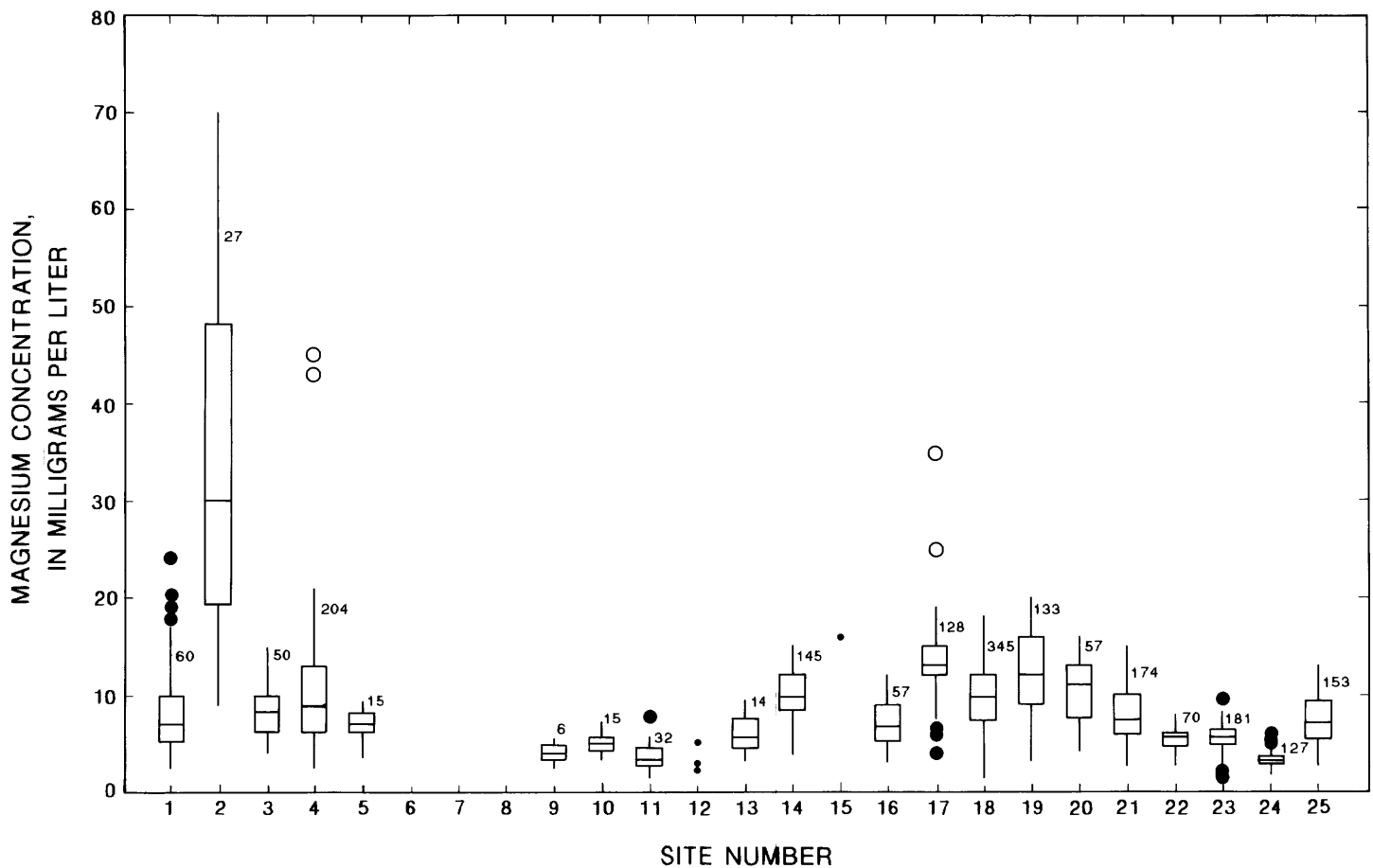


Figure 10.--Distribution of calcium concentration at surface-water sites.



EXPLANATION

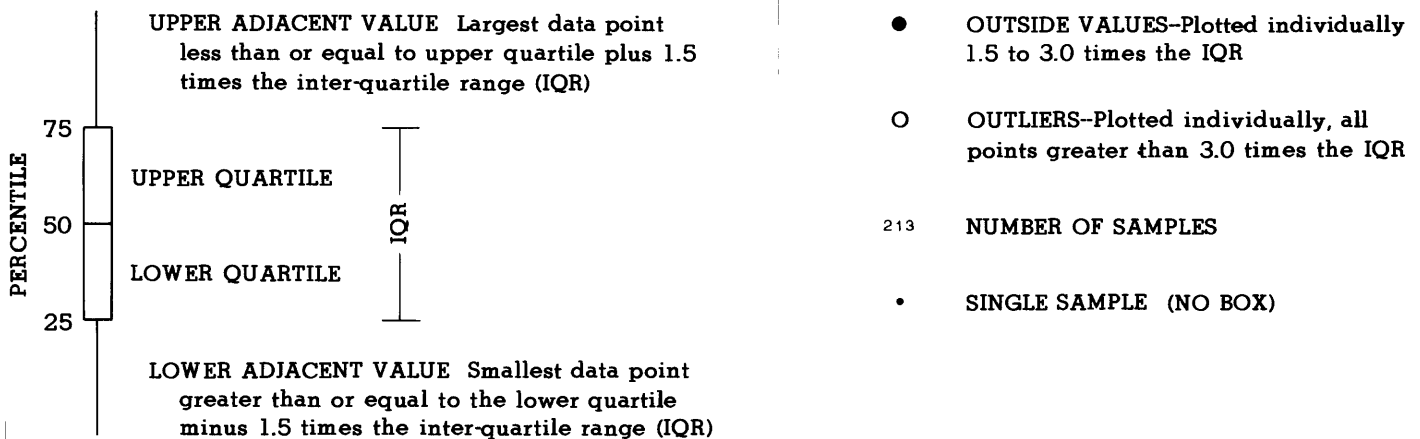
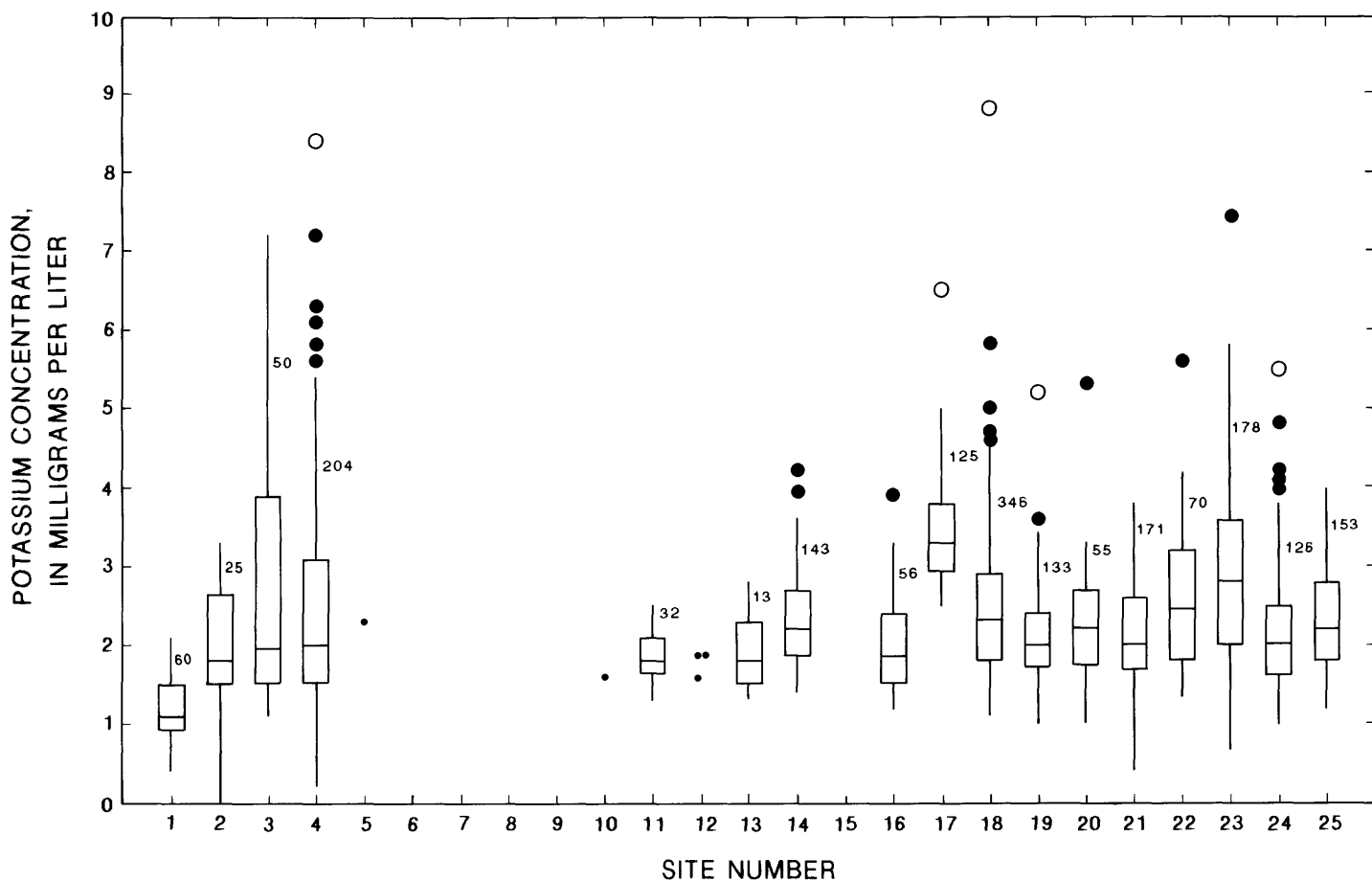
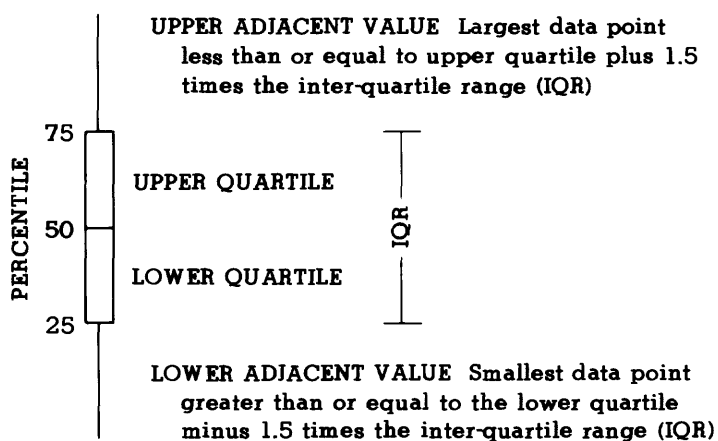


Figure 11.--Distribution of magnesium concentration at surface-water sites.



EXPLANATION



- **OUTSIDE VALUES**—Plotted individually 1.5 to 3.0 times the IQR
- **OUTLIERS**—Plotted individually, all points greater than 3.0 times the IQR
- 213 **NUMBER OF SAMPLES**
- **SINGLE SAMPLE (NO BOX)**

Figure 12.—Distribution of potassium concentration at surface-water sites.

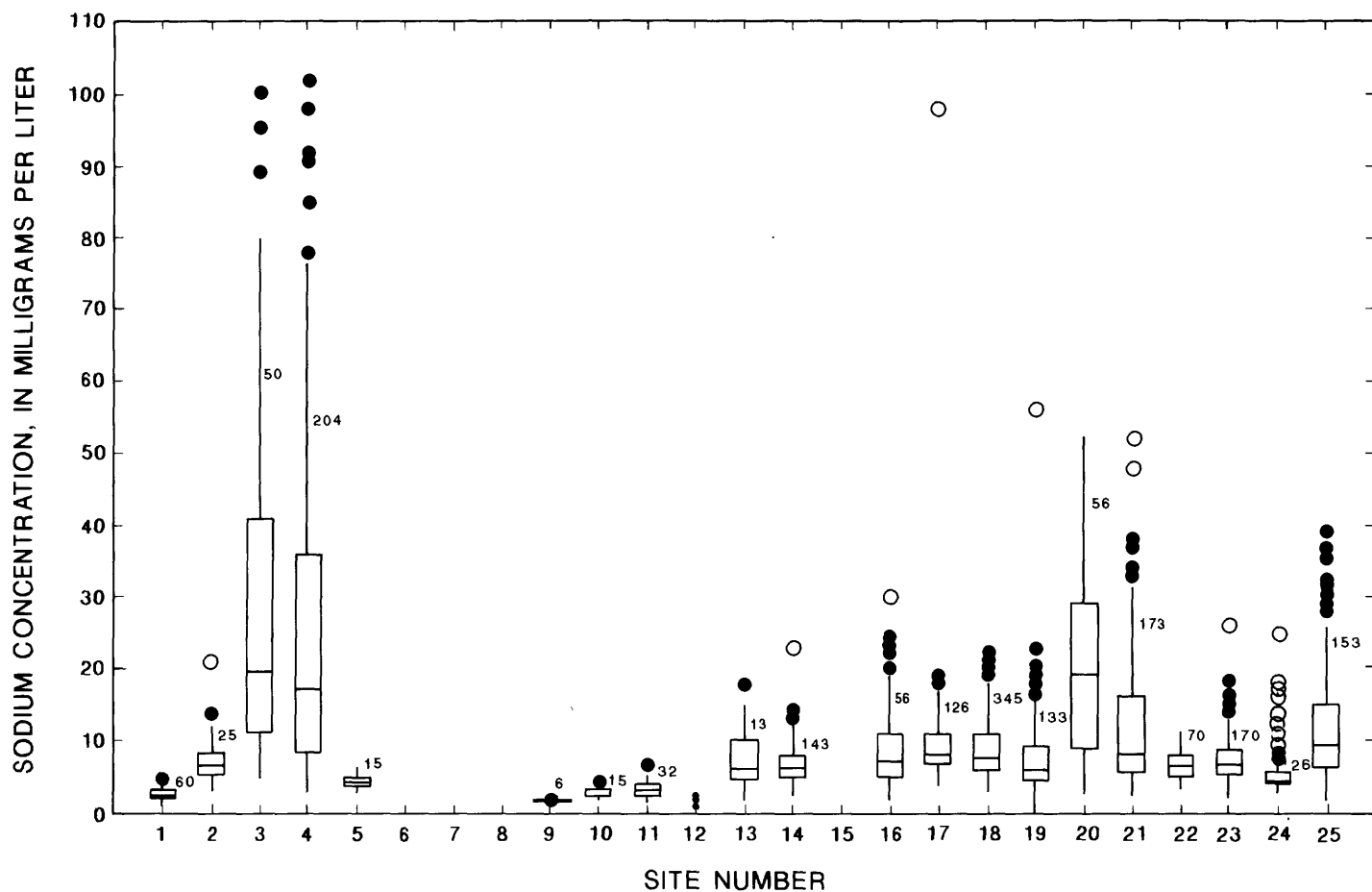
The draft health advisory drinking-water standard for sodium is 20 mg/L for people who are on very restricted diets (U.S. Environmental Protection Agency, 1986a). There are only three stations where sodium concentrations at the 75th percentile (fig. 13) exceed the 20-mg/L standard--the North Branch Potomac River at Pinto, Md. (site 3) and Cumberland, Md. (site 4), and the Shenandoah River at Millville, W. Va. (site 20). The primary source for sodium at these stations is probably road salt. The two Maryland stations are located in a mountainous area that receives more snow than other parts of the basin. As a result, a major east-west highway that cuts across the northern part of Maryland requires the application of more deicing salts than roads in other parts of the basin. High concentrations of sodium are not generally a problem at the other stations.

The USEPA (1986c) recommends a maximum chloride concentration of 250 mg/L in drinking water to prevent a salty taste. None of the 25 stations located in the Upper Potomac River basin had sample values exceeding this standard (fig. 14). As with sodium, the highest chloride concentrations and widest distributions were observed in the North Branch Potomac River at Pinto, Md. (site 3), and Cumberland, Md. (site 4).

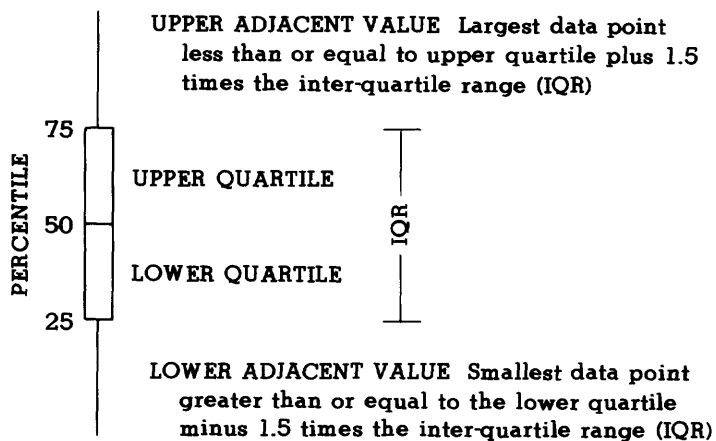
The USEPA (1986c) recommends a maximum sulfate concentration of 250 mg/L in drinking water because higher concentrations can have a laxative effect. The North Branch Potomac River basin is the only part of the Upper Potomac River basin (fig. 15) where sulfate levels exceed the recommended standard. Hobba and others (1972, p.81, 89-91) state that connate water with elevated concentrations of chloride and sulfate, lies near the surface in broad, synclinal valleys located in the Valley and Ridge and Great Valley provinces (sites 5-20). The stations located within this region have some of the lowest observed concentrations of both chloride and sulfate. Either connate water does not affect surface-water quality or, because the presence of connate water is localized in the valleys, basin sampling is not detecting its presence.

Table 6 summarizes the temporal trend results for the major ions. In the North Branch Potomac River basin, there is a rising trend in flow-adjusted calcium concentrations at Barnum, W. Va. (site 1), plus a rising trend in both calcium and magnesium concentrations at Pinto, Md. (site 3). There is a slight upward trend in sodium concentration at Barnum and Georges Creek (site 2), and a strong (3.05 percent per year) upward trend at Pinto. There is a small rising trend in potassium concentration at Barnum, W. Va., and Cumberland, Md. (site 4). Chloride concentration has a strong (4.5 percent per year) rising trend in Georges Creek and a slight rise at Pinto that may be traced to the rise in Georges Creek. Sulfate concentration is rising at Georges Creek and at Cumberland, Md.

It appears that the concentration of major ions in the North Branch Potomac River basin is increasing. The cause may be coal-mining operations and treatment of mine-discharge water. Because a rise in major-ions concentration is consistent throughout the basin, it is desirable to monitor the rise and determine its source and overall effect on the water quality in the basin.

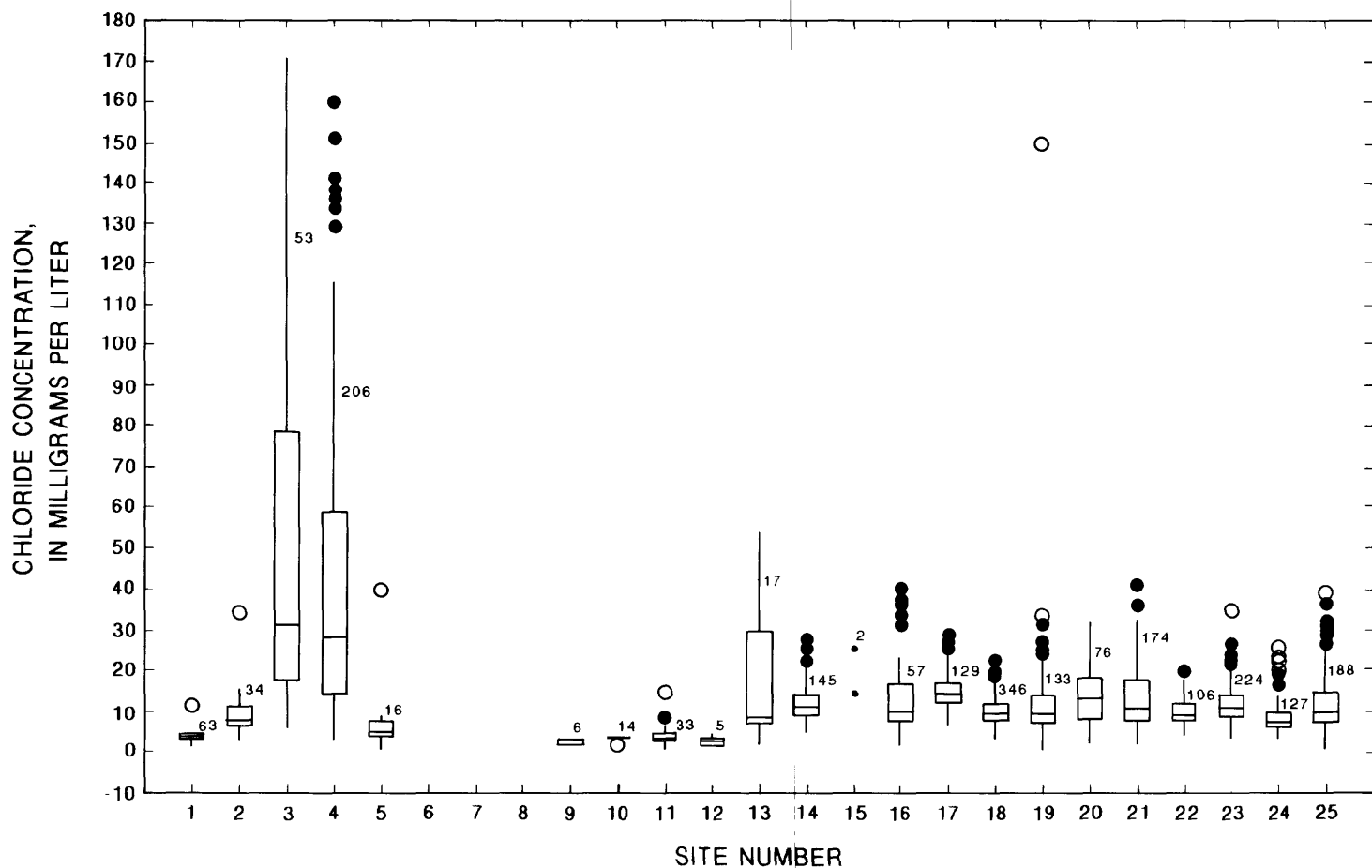


EXPLANATION



- OUTSIDE VALUES—Plotted individually 1.5 to 3.0 times the IQR
- OUTLIERS—Plotted individually, all points greater than 3.0 times the IQR
- 213 NUMBER OF SAMPLES
- SINGLE SAMPLE (NO BOX)

Figure 13.—Distribution of sodium concentration at surface-water sites.



EXPLANATION

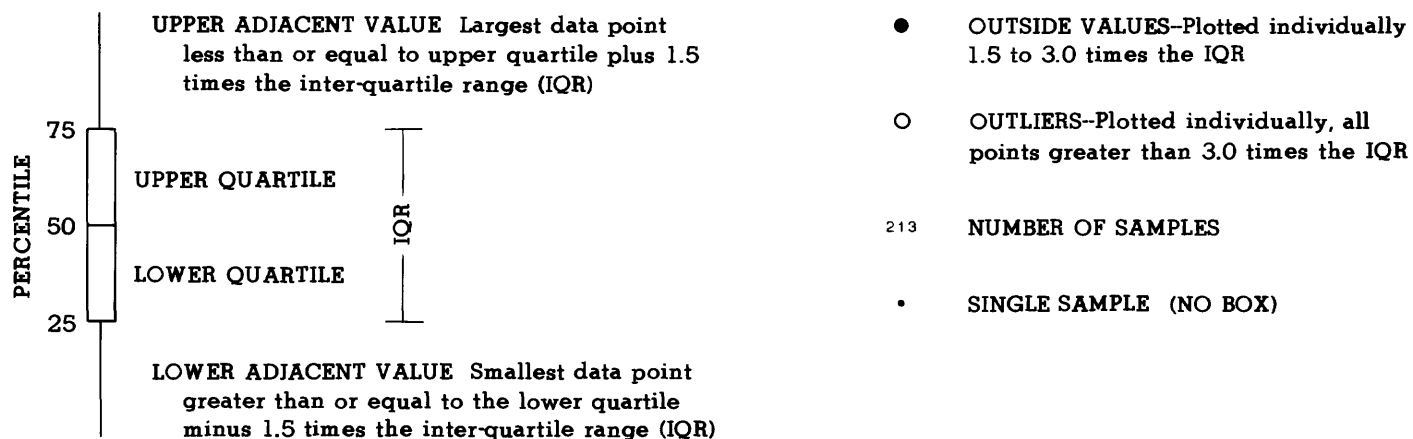
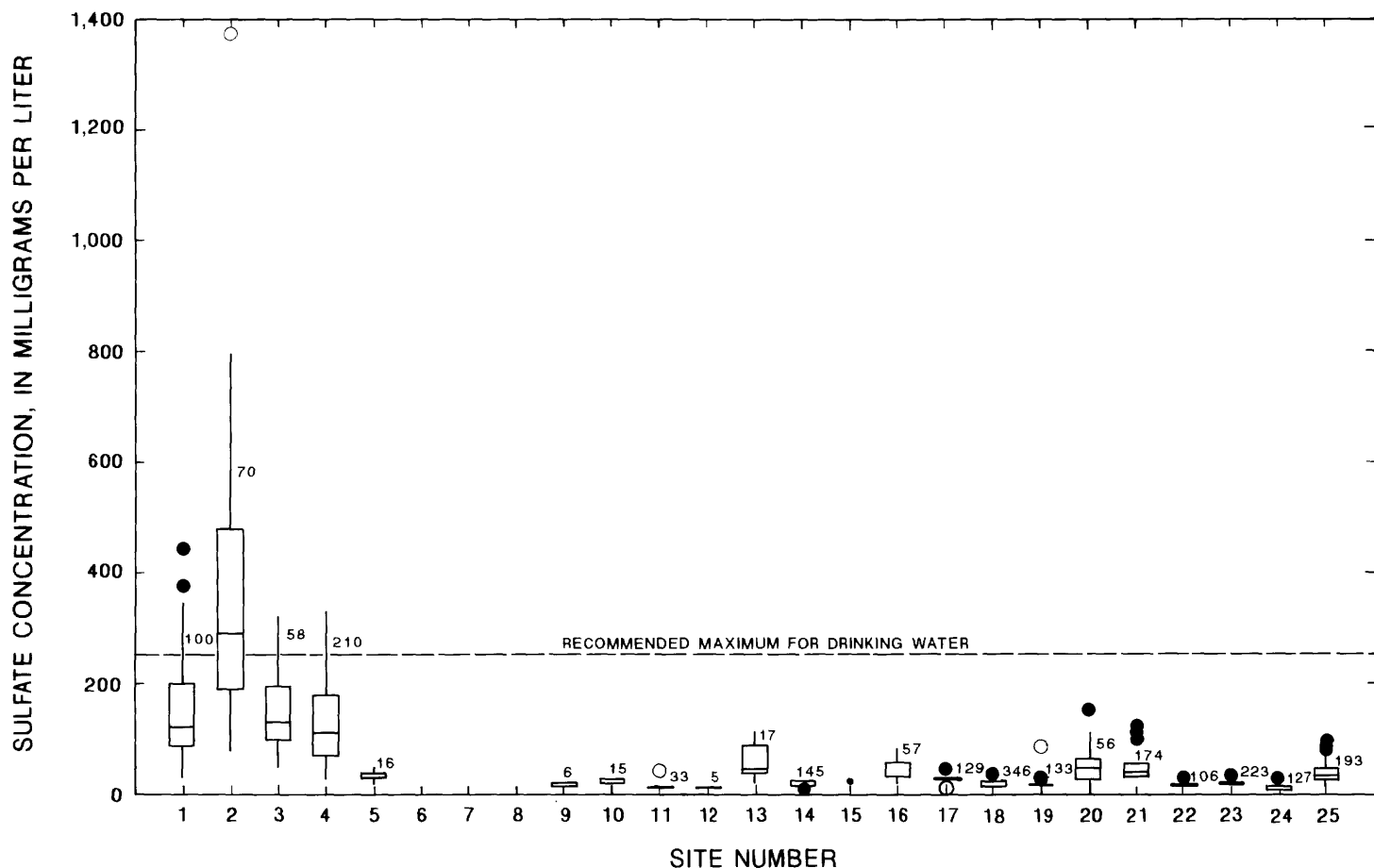


Figure 14. Distribution of chloride concentration at surface-water sites.



EXPLANATION

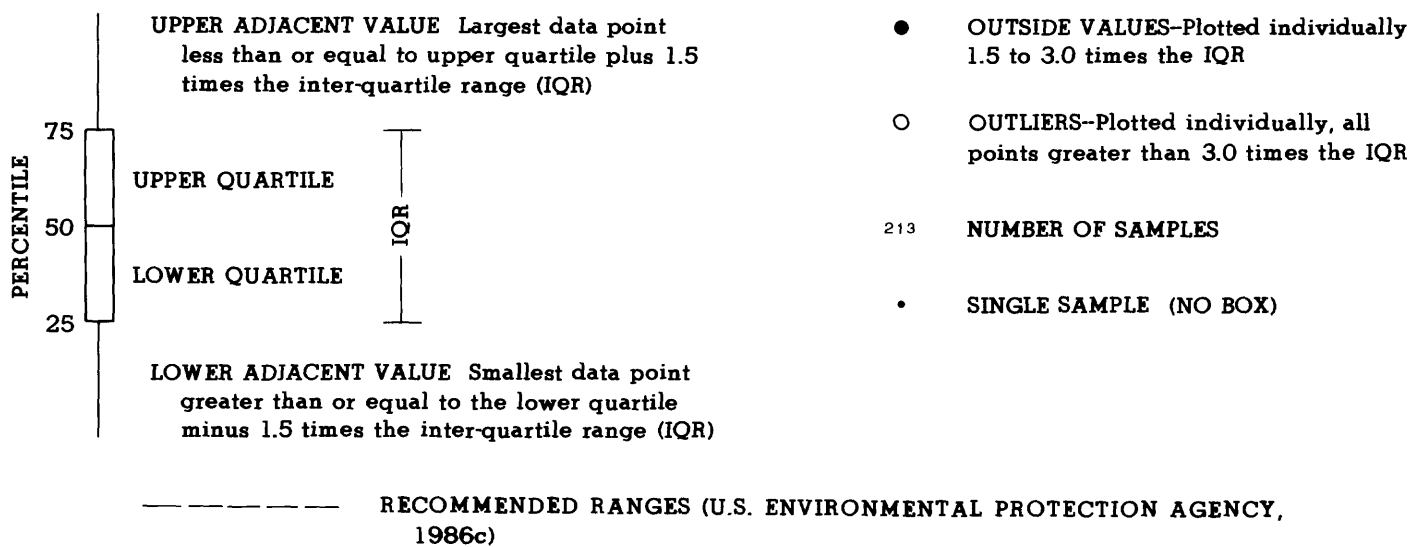


Figure 15.--Distribution of sulfate concentration at surface-water sites.

Table 6.--Summary of Seasonal Kendall test results for temporal trends for major ions

SLOPE: Slope of the trend, in milligrams per liter per year except where noted.
P: Probability that no trend exists.
NVALS: Number of values used to compute the trend.
*: p exceeds cutoff value of 0.20.
#: Logarithmic slope, expressed as percent change per year.
blank: Insufficient data used to compute trends.
+: Nonsignificant flow-concentration regression.
NASQAN: National Stream-Quality Assessment Network

Station name	Calcium				Manganese				Sodium			
	Concentration		Flow-adjusted concentration		Concentration		Flow-adjusted concentration		Concentration		Flow-adjusted concentration	
	Slope	P/NVALS	Slope	P/NVALS	Slope	P/NVALS	Slope	P/NVALS	Slope	P/NVALS	Slope	P/NVALS
1 North Branch Potomac River at Barnum, W. Va.	*		# 6.08	0.00/31	*		*		0.06	0.14/31	0.10	0.00/31
2 Georges Creek at Franklin, Md.	*		*		*		*		.23	.02/13	.25	.00/13
3 North Branch Potomac River at Pinto, Md.	*		# 1.92	.11/32	*		0.13	0.11/32	*		# 3.05	.05/32
4 North Branch Potomac River at Cumberland, Md.	*		.61	.00/73	*		# .50	.05/73	*		*	
5 Patterson Creek near Headsville, W. Va.	*				*				*		*	
6 South Branch Potomac River at Franklin, W. Va.	*				*				*		*	
7 South Branch Potomac River near Petersburg, W. Va.	*				*				*		*	
8 South Fork South Branch Potomac River at Brandywine, W. Va.	*				*				*		*	
9 South Fork South Branch Potomac River near Moorefield, W. Va.	*				*				*		*	
10 South Branch Potomac River near Springfield, W. Va.	*				*				-.70	.02/11	#-23.1	.04/11
11 Lost River at McCauley near Baker, W. Va.	*		*		*		*		*		*	
12 Cacapon River near Great Cacapon, W. Va.	*				*				*		*	
13 Potomac River at Hancock, Md.	*		# .60	.08/61	*		.08	.00/61	*		.10	.00/60
14 Conococheague Creek at Fairview, Md.	*				*				*		*	
15 Opequon Creek near Martinsburg, W. Va.	*				*				*		*	
16 Potomac River at Shepherdstown, W. Va. (NASQAN)	0.75	.02/31	+		.10	.03/31	+		.25	.12/30	+	
17 Antietam Creek near Sharpsburg, Md.	.33	.00/66	.46	.00/60	.06	.02/66	+		.12	.02/66	# 2.63	.00/60
18 South Fork Shenandoah River at Front Royal, Va.	-.14	.10/71	*		.04	.14/71	*		*		*	
19 North Fork Shenandoah River near Strasburg, Va.	-.25	.16/70	*		*		*		.25	.00/70	*	
20 Shenandoah River at Millville, W. Va. (NASQAN)	*				*		*		*		*	
21 Potomac River at Point of Rocks, Md.	*		.21	.02/74	*		.09	.00/74	*		# 1.51	.03/74
22 Monocacy River near Walkersville, Md.	*		*		.11	.09/16	#		.38	.04/16	# 3.56	.04/16
23 Monocacy River at Reich's Ford Bridge near Frederick, Md.	.22	.08/66	# 1.11	.00/60	.05	.00/66	.06	.00/60	.13	.00/65	# 2.74	.00/60
24 Seneca Creek at Dawsonville, Md.	.31	.00/69	+		.10	.00/69	+		.26	.00/68	+	
25 Potomac River at Chain Bridge at Washington, D.C. (NASQAN)	*		*		*		*		*		*	

Table 6.--Summary of Seasonal Kendall test results for temporal trends for major ions--Continued

SLOPE: Slope of the trend, in milligrams per liter per year except where noted.
P: Probability that no trend exists.
NVALS: Number of values used to compute the trend.
*: P exceeds cutoff value of 0.20.
#: Logarithmic slope, expressed as percent change per year.
blank: Insufficient data used to compute trends.
+: Nonsignificant flow-concentration regression.
NASQAN: National Stream-Quality Assessment Network

Station name	Potassium			Chloride			Sulfate		
	Concentration		Flow-adjusted concentration	Concentration		Flow-adjusted concentration	Concentration		Flow-adjusted concentration
	Slope	P/NVALS		Slope	P/NVALS		Slope	P/NVALS	
1 North Branch Potomac River at Barnum, W. Va.	0.03	0.00/31	0.05	0.00/31			*		*
2 Georges Creek at Franklin, Md.	*		*			0.22	0.04/19	# 4.50	0.01/19
3 North Branch Potomac River at Pinto, Md.	*		*			*		1.35	.00/34
4 North Branch Potomac River at Cumberland, Md.	*		*			*		*	*
5 Patterson Creek near Headsville, W. Va.	*		.02	.02/73		2.35	.13/8	*	*
6 South Branch Potomac River at Franklin, W. Va.									
7 South Branch Potomac River near Petersburg, W. Va.									
8 South Fork South Branch Potomac River at Brandywine, W. Va.									
9 South Fork South Branch Potomac River near Moorefield, W. Va.	*					*			*
10 South Branch Potomac River near Springfield, W. Va.						*			*
11 Lost River at McCauley near Baker, W. Va.	*					- .64	.14/13	# -17.55	.06/13
12 Cacapon River near Great Cacapon, W. Va.	*					*			*
13 Potomac River at Hancock, Md.	*					-1.64	.19/16	+	.08
14 Conococheague Creek at Fairview, Md.	- .06	.15/12	+	.70	.01/60	*			
15 Opequon Creek near Martinsburg, W. Va.	*					*			*
16 Potomac River at Shepherdstown, W. Va. (NASQAN)	.01	.15/30	*			.51	.05/31		.95
17 Antietam Creek near Sharpsburg, Md.	- .02	.14/66	+			.22	.00/66	*	.31
18 South Fork Shenandoah River at Front Royal, Va.	*		+			*		*	*
19 North Fork Shenandoah River near Strasburg, Va.	.02	.02/70	+			.21	.02/70	*	.31
20 Shenandoah River at Millville, W. Va. (NASQAN)	*		*			*		# -3.15	.01/37
21 Potomac River at Point of Rocks, Md.	*		*			*		*	*
22 Monocacy River near Walkersville, Md.	*		*			.44	.01/23	# 4.19	.00/23
23 Monocacy River at Reich's Ford Bridge near Frederick, Md.	*		.03	.01/60		.35	.00/74	# 3.25	.00/68
24 Seneca Creek at Dawsonville, Md.	.04	.00/68	*			.56	.00/69	+	.17
25 Potomac River at Chain Bridge at Washington, D.C. (NASQAN)	*					.20	.03/51	*	.02/50
							.31	.00/69	* .30
								-	.14/50

Few data are available for determining temporal trends for major ions in the Valley and Ridge province streams (sites 5-13). There are no apparent concentration trends for calcium, magnesium, or potassium, and large negative concentration trends in sodium (-23.1 percent per year) and chloride (-17.6 percent per year) in Lost River (site 11). The magnitude of these trends seems high because the concentration of these two constituents is low, on the order of 5 mg/L. Chloride and potassium concentrations have falling trends at the Potomac River station at Hancock, Md. (site 13).

In the Great Valley, calcium and magnesium concentration trends are rising in Conococheague Creek (site 14), the Potomac River at Shepherdstown W. Va. (site 16), and in Antietam Creek (site 17). There is a falling trend in calcium concentration and a very small rising trend in magnesium concentration in the South Fork Shenandoah River at Front Royal, Va. (site 18). The calcium concentration trend is decreasing in the North Fork Shenandoah River at Strasburg, Va. (site 17). Sodium and potassium concentrations have been rising slightly in Conococheague Creek and in the Potomac River at Shepherdstown, W. Va. Antietam Creek has a slight upward trend in sodium concentration and a slight downward trend in potassium concentration. No trends in sodium or potassium concentrations were apparent in the South Fork Shenandoah River at Front Royal, Va. Chloride concentration is increasing slightly and sulfate concentration is decreasing slightly in Conococheague Creek. Opequon Creek (site 15) has no apparent trends in chloride or sulfate concentrations. The Potomac River at Shepherdstown, W. Va., has a rising trend in both chloride and sulfate concentrations. Antietam Creek has a slight rising trend in flow-adjusted chloride concentration, and the Shenandoah River at Millville, W. Va. (site 20), has a significant downward trend in chloride concentration (-3.15 percent per year).

In the Piedmont province, the Potomac River at Point of Rocks, Md. (site 21), the Monocacy River at Reichs Ford Bridge (site 23), and Seneca Creek (site 24) have rising trends in calcium concentration. Both Monocacy River stations (sites 22, 23) and Seneca Creek have rising trends in magnesium concentration. The Potomac River at Chain Bridge (site 25) is the only station in the Piedmont with no positive trend in sodium concentration. There are small positive trends in potassium concentration at the Monocacy River at Reichs Ford Bridge and in Seneca Creek. The Potomac River at Point of Rocks, Md., has no trends in either chloride or sulfate concentration. All the other stations in the Piedmont have rising trends in chloride concentration. Seneca Creek has a small rising trend in sulfate concentration and the Potomac River at Chain Bridge has a small decreasing trend in flow-adjusted sulfate concentration.

Nutrients and Dissolved Oxygen

The USEPA (1986a) primary recommended drinking-water limit for nitrite plus nitrate (as nitrogen) is 10 mg/L. The standard was established because the reduced form (nitrite) can be toxic to infants in concentrations as low as 1 mg/L. In natural stream water, nitrate concentration greatly exceeds nitrite concentration. None of the samples at any of the 25 stations in the Upper Potomac River basin exceeded the 10 mg/L limit (fig. 16). Except for a few outliers, concentrations in the North Branch Potomac River basin (site 1-4) and the Valley and Ridge streams (sites 5-13) were less than 1 mg/L. Concentrations at most other stations were generally less than 2 mg/L.

Conococheague (site 14), Antietam (site 17), and Seneca (site 24) Creeks have median values near 4 mg/L. The Monocacy River at Reichs Ford Bridge (site 23) has a median value of about 2.8 mg/L.

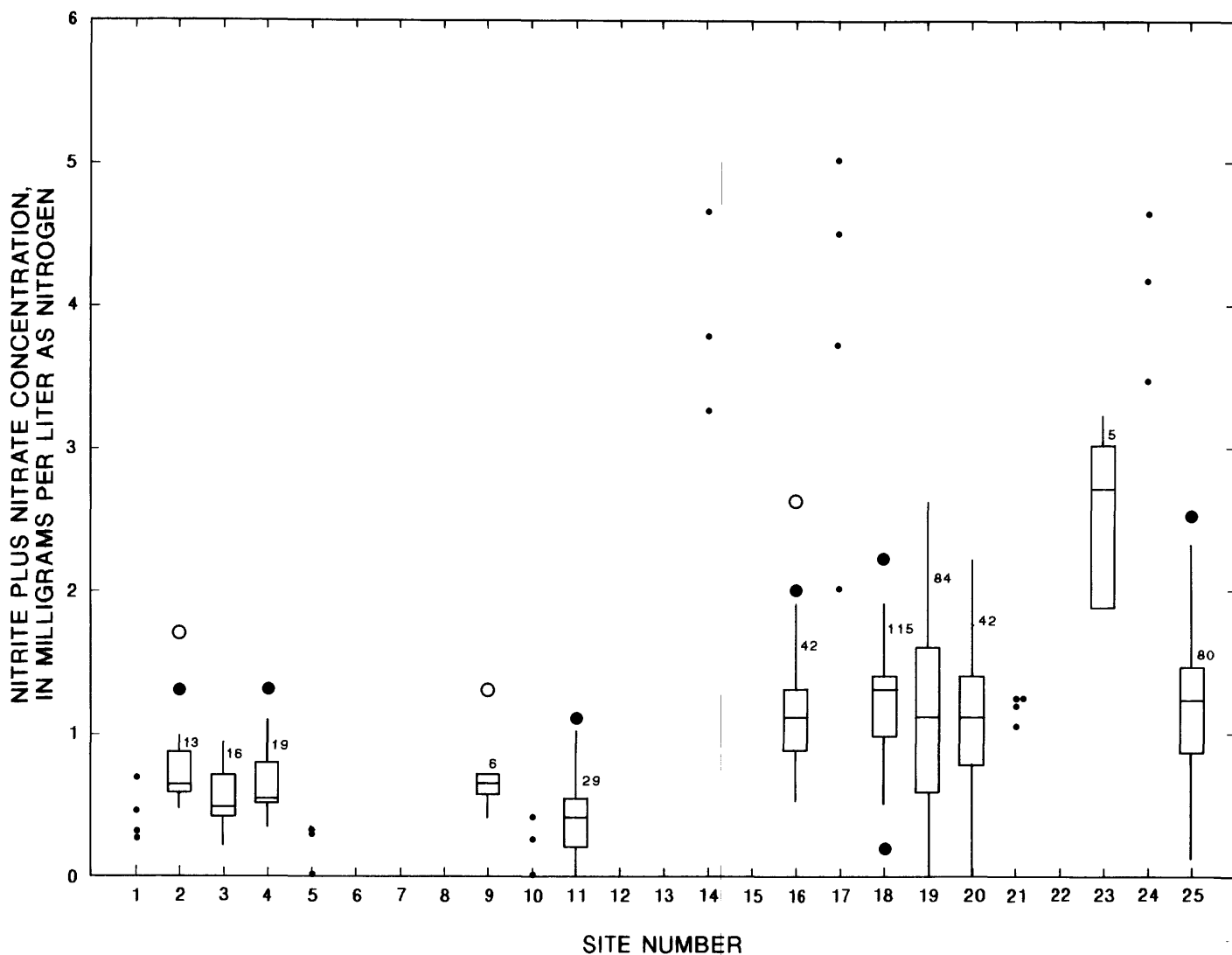
The USEPA (1986b) recommended limit for total phosphate (as phosphorus) is 0.1 mg/L for aquatic life. Higher concentrations may interfere with coagulation in water-treatment plants. To prevent excessive algal growth, the concentration should not exceed 0.05 mg/L in any stream at the point where it enters a lake or reservoir, nor should it exceed 0.025 mg/L within the lake or reservoir (U.S. Environmental Protection Agency, 1986b).

Total-phosphate data are available for 17 (fig. 17) of the 25 stations. All but one value exceeds the USEPA 0.025 mg/L recommended limit. Medians at four of the stations are less than 0.05 mg/L--two in the North Branch Potomac River basin (sites 1-2), one in the Great Valley (site 11), and the other the Potomac River at Hancock, Md. (site 13). The median total phosphate concentration at seven stations is between 0.05 and 0.1 mg/L. The median concentration exceeds 0.1 mg/L at five stations. The highest observed value of about 0.78 mg/L is on the Monocacy River (site 23). The widest interquartile ranges, which contain 50 percent of the data (about 0.2 mg/L), are in Conococheague Creek (site 14), with a median value of about 0.15 mg/L; in Antietam Creek (site 17), with a median value of about 0.3 mg/L; and in the Monocacy River at Walkersville, Md. (site 22), with a median value of about 0.2 mg/L.

The USEPA (1986b) recommended limit for dissolved oxygen for cold-water fish applies to water containing a population of one or more species in the family Salmonidae or other sensitive cold-water fish. To maintain adequate intergravel concentrations, a minimum concentration of 8 mg/L is recommended for water containing fish in early life stages, which include embryonic and larval stages and all juvenile forms to 30 days following hatching. For other life stages, a minimum concentration of 4 mg/L is recommended to prevent severe "production impairment" in the fish.

Dissolved-oxygen concentrations are generally well above the USEPA recommended minimum limit. Four of the stations have measured values less than the 4 mg/L minimum concentration (fig. 18)--the North Branch Potomac River at Cumberland, Md. (site 4), Patterson Creek (site 5), Lost River (site 11), and the Cacapon River (site 12). The median values for all of the sites exceed the 8 mg/L minimum concentration. The box part of the plot extends below 8 mg/L for six stations. The whisker part of the plot extends below 8 mg/L for all but four of the stations--the South Branch Potomac River at Franklin, W. Va. (site 6), Conococheague Creek (site 14), the North Branch Shenandoah River near Strasburg, Va. (site 19), and Seneca Creek (site 24).

Data are sufficient for 18 stations (table 7) to test for trends in nitrite plus nitrate concentration. Observed concentrations were adjusted for flow at four of these stations. The only trend in nitrite plus nitrate concentration was an increase of 0.04 mg/L per year on the South Fork Shenandoah River at Front Royal, Va. (site 18).



EXPLANATION

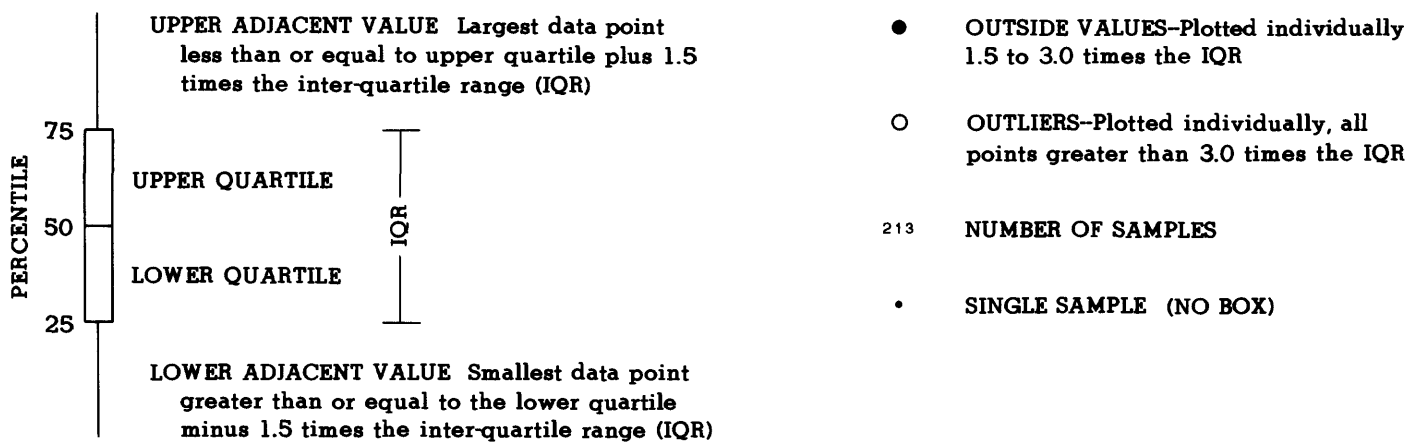
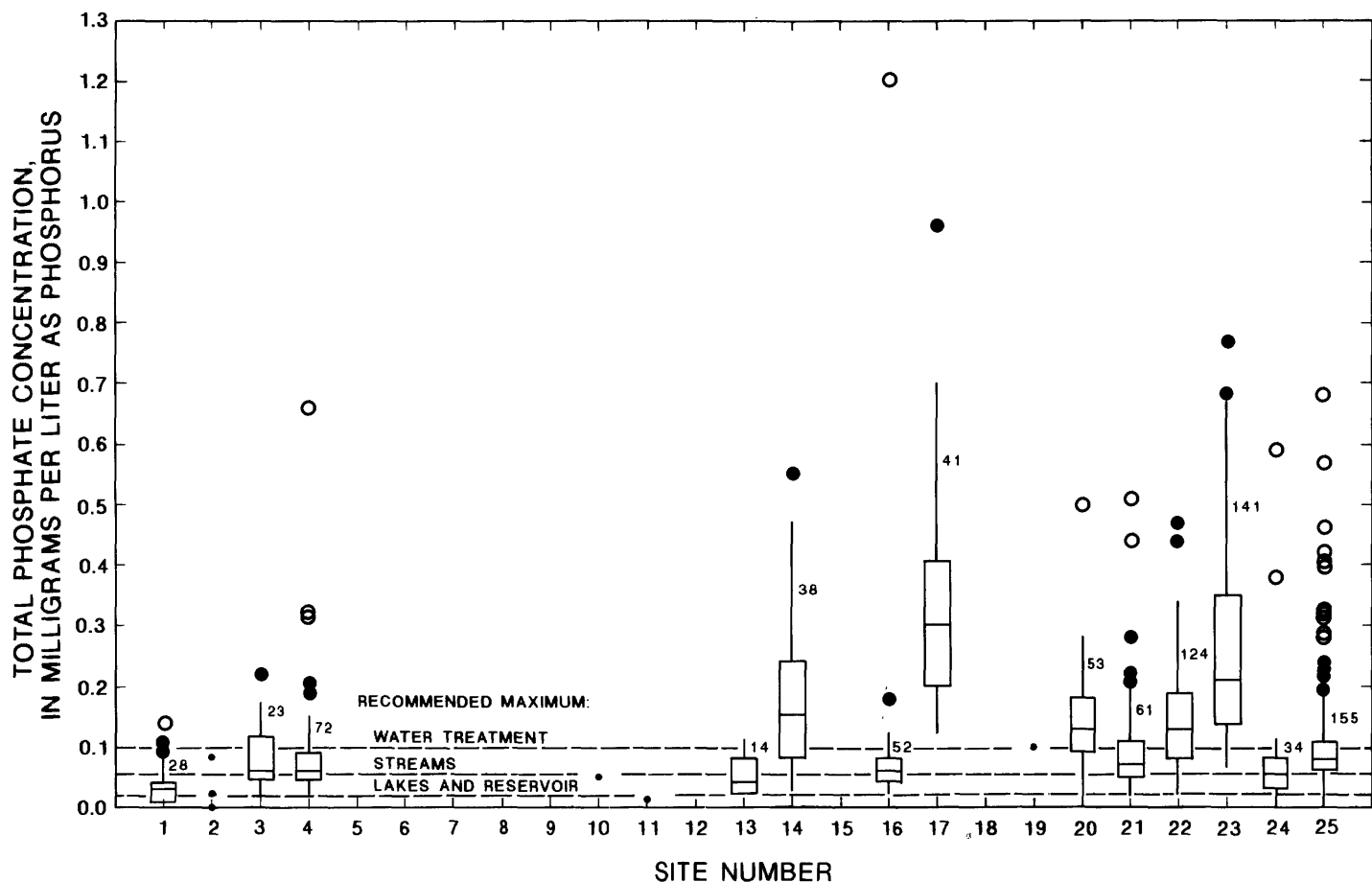


Figure 16.—Distribution of nitrite plus nitrate concentration at surface-water sites.



EXPLANATION

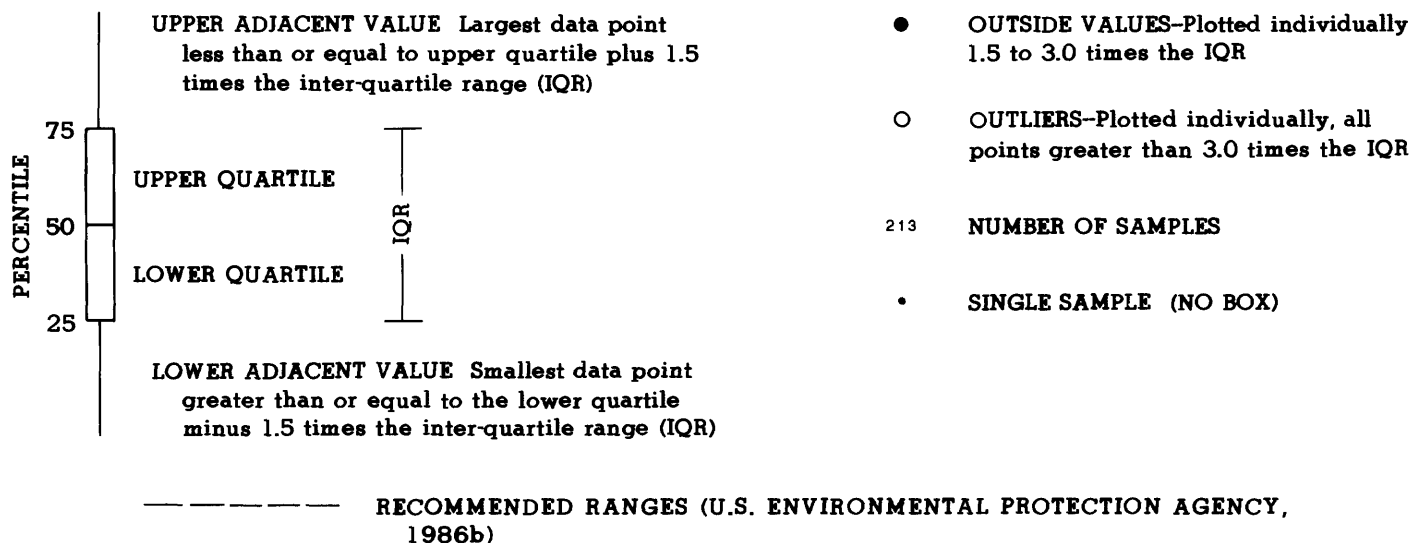
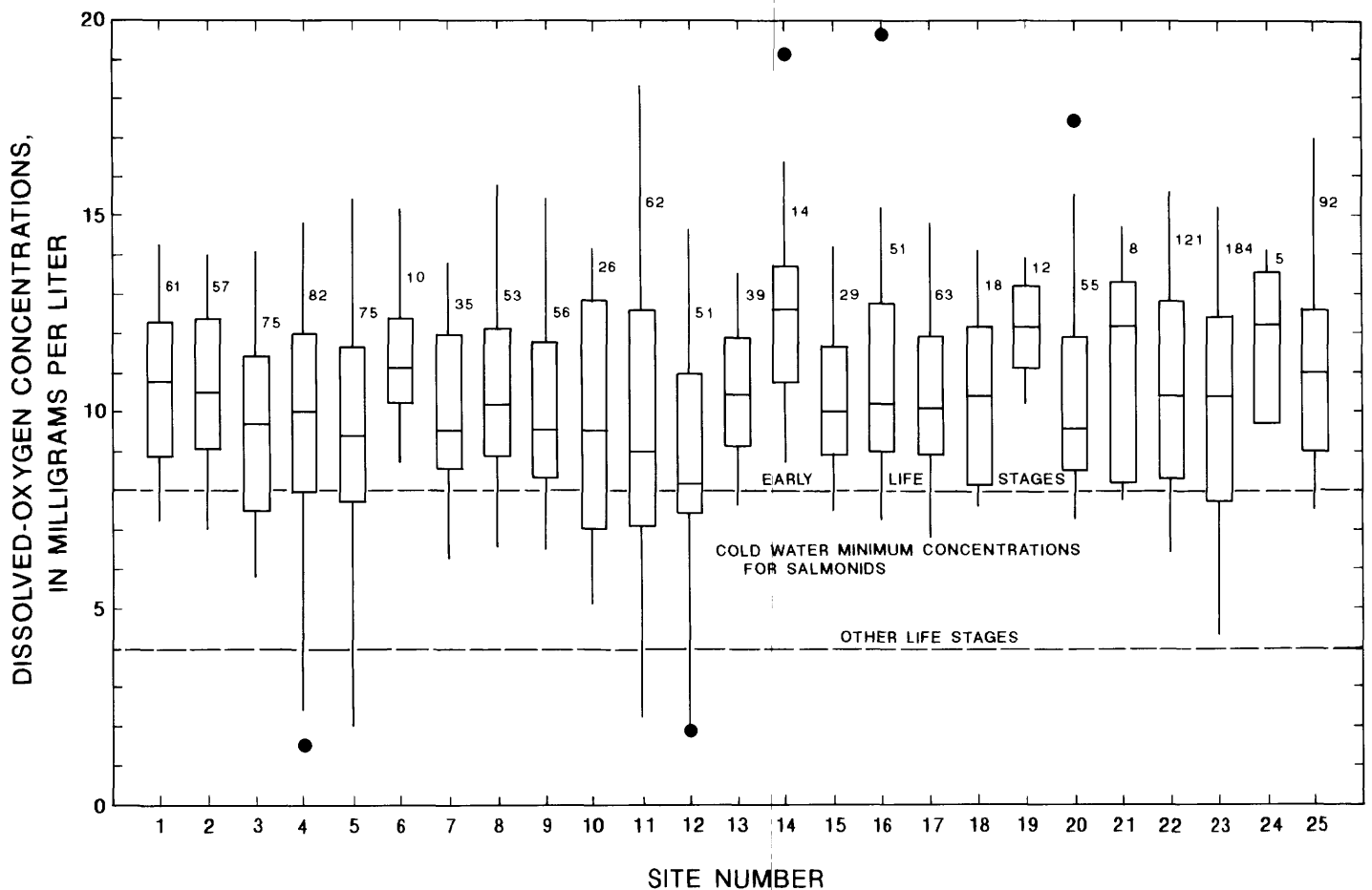


Figure 17.—Distribution of total phosphate concentration at surface-water sites.



EXPLANATION

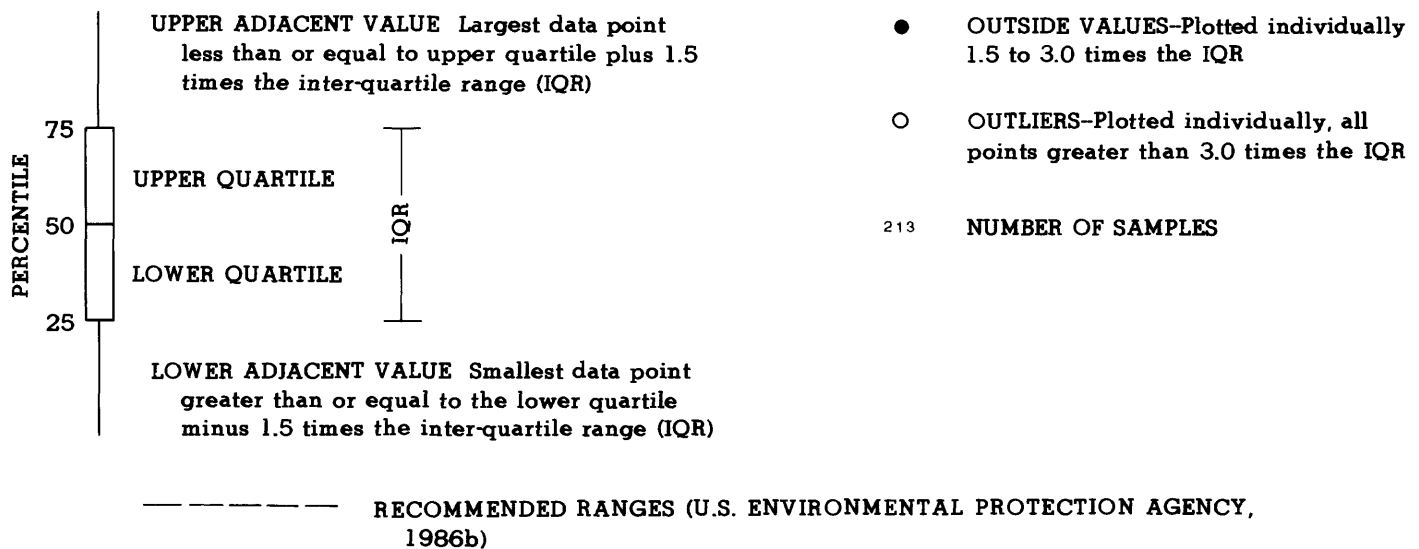


Figure 18.--Distribution of dissolved-oxygen concentration at surface-water sites.

Table 7.--Summary of Seasonal Kendall test results for temporal trends for nutrients and dissolved oxygen

SLOPE: Slope of the trend, in milligrams per liter per year except where noted.
P: Probability that no trend exists.
NVALS: Number of values used to compute the trend.
*: P exceeds cutoff value of 0.20.
#: Logarithmic slope, expressed as percent change per year.
blank: Insufficient data used to compute trends.
+: Nonsignificant flow-concentration regression.
NASQAN: National Stream-Quality Assessment Network

Station name	Nitrite plus nitrate				Total phosphate				Dissolved oxygen			
	Concentration		Flow-adjusted concentration		Concentration		Flow-adjusted concentration		Concentration		Flow-adjusted concentration	
	Slope	P/NVALS	Slope	P/NVALS	Slope	P/NVALS	Slope	P/NVALS	Slope	P/NVALS	Slope	P/NVALS
1 North Branch Potomac River at Barnum, W. Va.	*				*				0.07	0.12/25	*	
2 Georges Creek at Franklin, Md.	*				*				*		*	
3 North Branch Potomac River at Pinto, Md.	*		*		*		*		.12	.01/29	0.07	0.08/20
4 North Branch Potomac River at Cumberland, Md.	*				*				*		*	
5 Patterson Creek near Headsville, W. Va.	*								.20	.01/41	.23	.01/41
6 South Branch Potomac River at Franklin, W. Va.									*		*	
7 South Branch Potomac River near Petersburg, W. Va.									*		.13	.03/35
8 South Fork South Branch Potomac River at Brandywine, W. Va.	*				*				.15	.13/36	+	
9 South Fork South Branch Potomac River near Moorefield, W. Va.	*				*				*			
10 South Branch Potomac River near Springfield, W. Va.												
11 Lost River at McCauley near Baker, W. Va.	*		*		*				.97	.00/23	+	
12 Cacapon River near Great Cacapon, W. Va.									*			
13 Potomac River at Hancock, Md.	*				*				*			
14 Conococheague Creek at Fairview, Md.	*				0.02	0.01/26	# 5.65	0.09/26	*		-	.32
15 Opequon Creek near Martinsburg, W. Va.									*			.15/11
16 Potomac River at Shepherdstown, W. Va. (NASQAN)	*											
17 Antietam Creek near Sharpsburg, Md.	*				.04	.06/26	+	.00/33	.08	.03/28	+	
18 South Fork Shenandoah River at Front Royal, Va.	*				-	.02/33	#-6.85		.08	.10/27	+	
19 North Fork Shenandoah River near Strasburg, Va.	*		0.04	0.11/36	*				*		*	
20 Shenandoah River at Millville, W. Va. (NASQAN)	*				*				*		*	
21 Potomac River at Point of Rocks, Md.	*				*		#-4.78	.09/32	*		*	
22 Monocacy River near Walkersville, Md.	*				*		*		*		*	
23 Monocacy River at Reich's Ford Bridge near Frederick, Md.	*				*		*		.09	.08/46	*	
24 Seneca Creek at Dawsonville, Md.	*				*				*		*	
25 Potomac River at Chain Bridge at Washington, D.C. (NASQAN)	*		*		*				*		*	

Of the 18 stations with sufficient samples to compute trends in total phosphate concentration, three had trends in observed concentrations. Two stations--Conococheague Creek (site 14) and the Potomac River at Shepherdstown, W. Va. (site 16)--showed positive trends. One station--Antietam Creek (site 17)--had a downward trend in total phosphate concentration. Total phosphate concentrations were adjusted for flow at six stations. Conococheague Creek had a 5.65 percent per year increase, Antietam Creek had a 6.85 percent per year decrease, and the Potomac River at Point of Rocks, Md. (site 21), had a 4.78 percent per year decrease in total phosphate concentration. These trends in total phosphate concentration are all quite large and they should probably be evaluated more fully in the future.

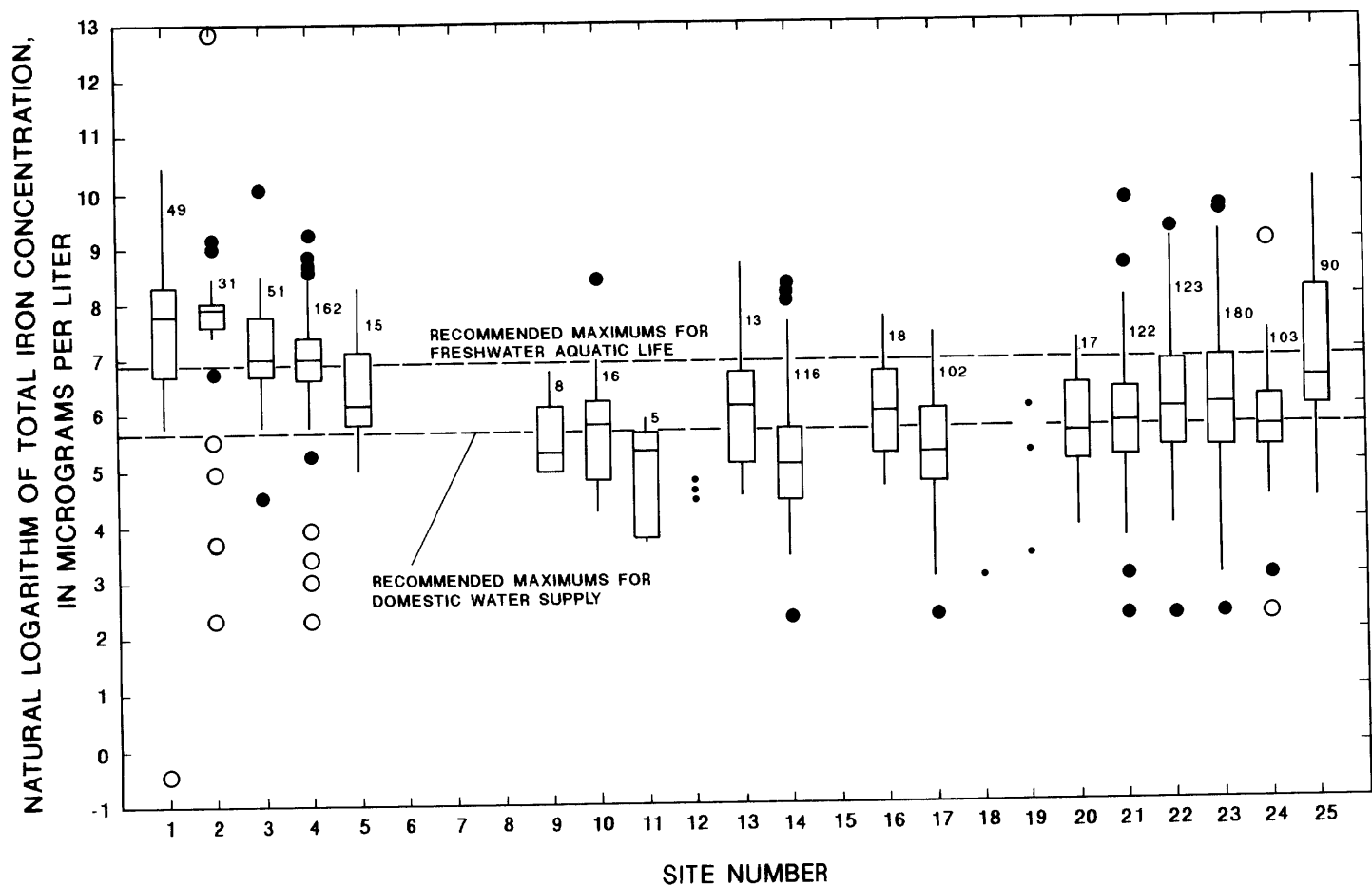
Seven stations had positive trends in observed dissolved-oxygen concentration. Only one station had a slight downward trend--Monocacy River at Reichs Ford Bridge (site 23). For flow-adjusted dissolved oxygen, this trend is not significant, but there is an upward trend in the South Fork South Branch Potomac River at Brandywine, W. Va. (site 8).

Metals

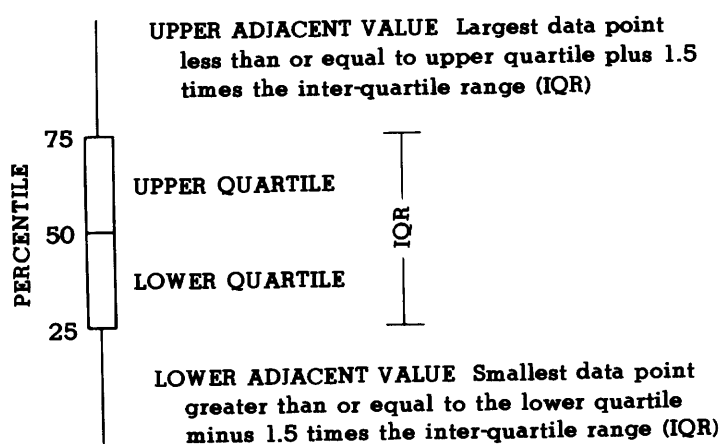
The USEPA (1986c) secondary recommended limit for total iron in domestic water supplies is 300 $\mu\text{g/L}$ (micrograms per liter). For freshwater aquatic life, the secondary recommended limit is 1,000 $\mu\text{g/L}$ (U.S. Environmental Protection Agency, 1986b). The boxplots (fig. 19) of the logarithms of total iron concentration show that the distributions are highly variable with a large number of outside and very low values. Acid-mine drainage probably causes the median concentrations in the North Branch Potomac River basin (site 1-4) to exceed the 1,000- $\mu\text{g/L}$ secondary recommended limit.

The box part of the plot extends past the 1,000- $\mu\text{g/L}$ secondary recommended limit at Patterson Creek (site 5) and the Potomac River at Chain Bridge (site 25). The whisker part of the boxplots extends past the 1,000- $\mu\text{g/L}$ limit for 9 of the remaining 15 stations sampled. The median concentration lies between the 1,000- and 300- $\mu\text{g/L}$ secondary recommended limits at eight stations. The median concentration lies below the 300- $\mu\text{g/L}$ limit at nine stations. Concentrations below 300 $\mu\text{g/L}$ were measured at all of the stations. The box part of the plot extends below 300 $\mu\text{g/L}$ at 14 of the 21 stations with measurements. The whisker part extends below 300 $\mu\text{g/L}$ for Patterson Creek (site 5) and the Potomac River at Chain Bridge (site 25).

There are only a few outliers and extreme values below 300 $\mu\text{g/L}$ at each of the North Branch Potomac River basin stations (site 1-4), where acid-mine drainage can increase dissolution of iron. Patterson Creek (site 5) and the Potomac River at Chain Bridge (site 25) are two other areas where iron concentrations are elevated. Iron concentrations are elevated throughout the basin and may need to be investigated further.



EXPLANATION



- OUTSIDE VALUES—Plotted individually 1.5 to 3.0 times the IQR
- OUTLIERS—Plotted individually, all points greater than 3.0 times the IQR
- 213 NUMBER OF SAMPLES
- SINGLE SAMPLE (NO BOX)

----- RECOMMENDED RANGES (U.S. ENVIRONMENTAL PROTECTION AGENCY, 1986b,c)

Figure 19.--Distribution of total iron concentration at surface-water sites.

The USEPA (1986c) secondary recommended drinking-water limit for manganese is 50 $\mu\text{g/L}$. Twenty-one stations (fig. 20) with measured total manganese concentrations have values that exceed the limit. In the North Branch Potomac River basin (sites 1-4), all except three very low values at Cumberland, Md. (site 4) exceed the limit. Throughout the rest of the Upper Potomac River basin, the median value at 10 stations exceeds the limit. The median at six of the other stations is less than the limit, and at three stations the entire box portion of the plot is less than the limit.

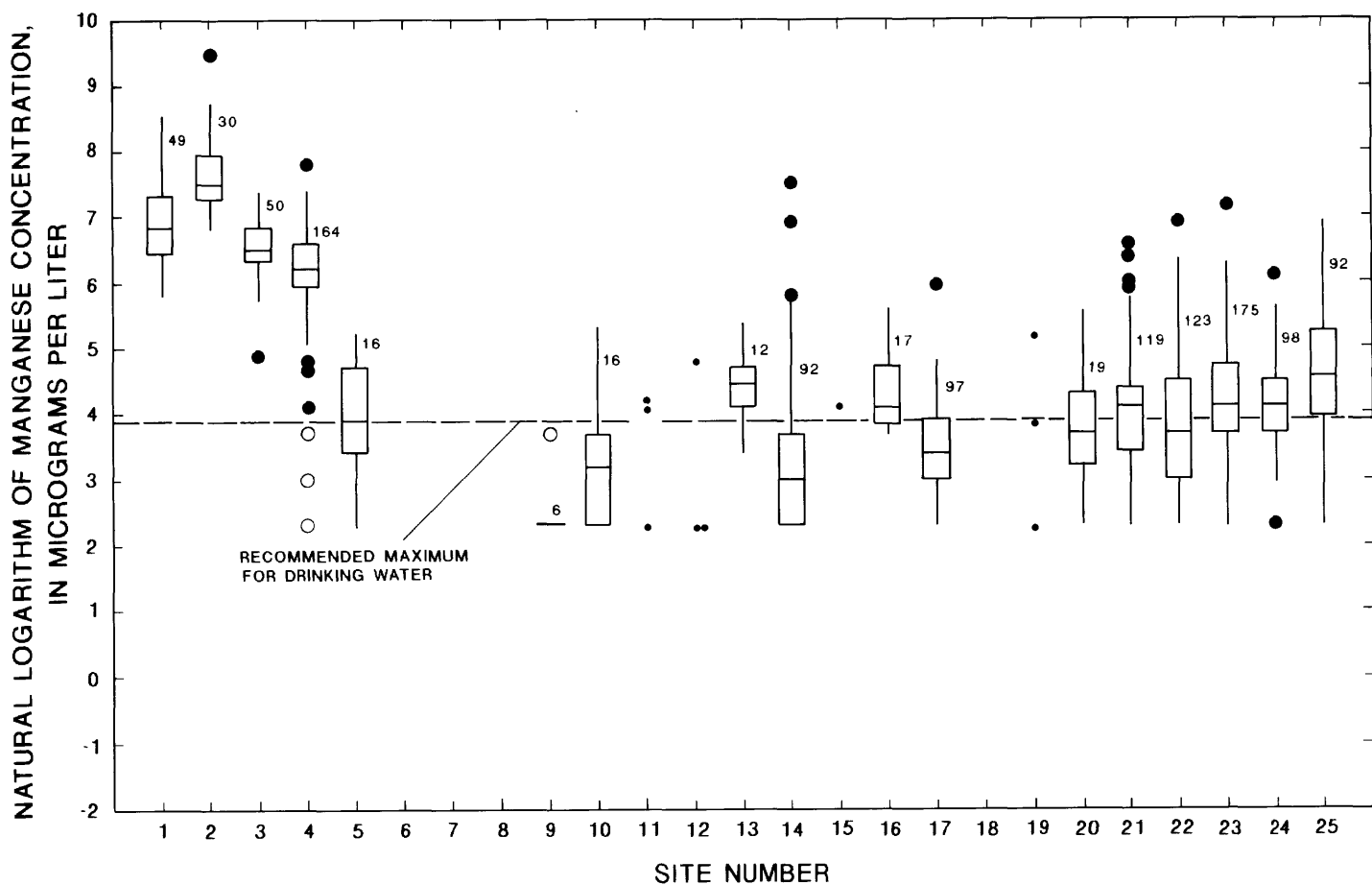
Twenty stations were tested for trends in total iron concentration (table 8). Five stations had increases of 10 to 25 $\mu\text{g/L}$ per year. However, the station at North Branch Potomac River at Pinto, Md. (site 3), had a large 65.8 mg/L per year decrease in total iron concentration. Concentrations were adjusted for flow at six stations. The Pinto station had an 8.24 percent per year decrease. Conococheague Creek (site 14) and Antietam Creek (site 17), both in the Great Valley, had increases in both observed and flow-adjusted iron concentration.

Twenty-one stations had sufficient data to test for trends in manganese concentration. The trend in manganese concentration is declining at North Branch Potomac River at Barnum, W. Va. (site 1), and at Pinto, Md. (site 3), and the Shenandoah River at Millville, W. Va. (site 20). Trends at five other stations are rising. Concentrations were adjusted for flow only on the North Branch Potomac River basin stations. The manganese concentration at the Pinto station declined 22.9 $\mu\text{g/L}$ per year.

SUGGESTED SAMPLING STRATEGY

To properly analyze the water quality at a station, water-quality samples must be representative of the water quality at the station. The sampling strategy for the three NASQAN stations combines periodic sampling with storm sampling to collect water-quality samples representative of the entire range of discharge over time. One problem with periodic sampling is that rare events can be missed. Very low flows are more likely to be sampled than very high flows because extreme low-flow conditions take a long time to develop. Extremely high flows develop rapidly during storms and decrease rapidly when the storm ends, requiring specific targeting of high-flow events for sampling.

Periodic sampling is desirable for conducting trend analysis, and sampling over the range of discharge would enhance the ability to relate concentration to discharge. An evaluation of the frequency at which periodic sampling is optimized is beyond the scope of this report. However, sampling should be maintained at a consistent rate to facilitate the proper use of trend analysis. One way to optimize sampling over the entire discharge range is to examine the number of samples already collected for each discharge.



EXPLANATION

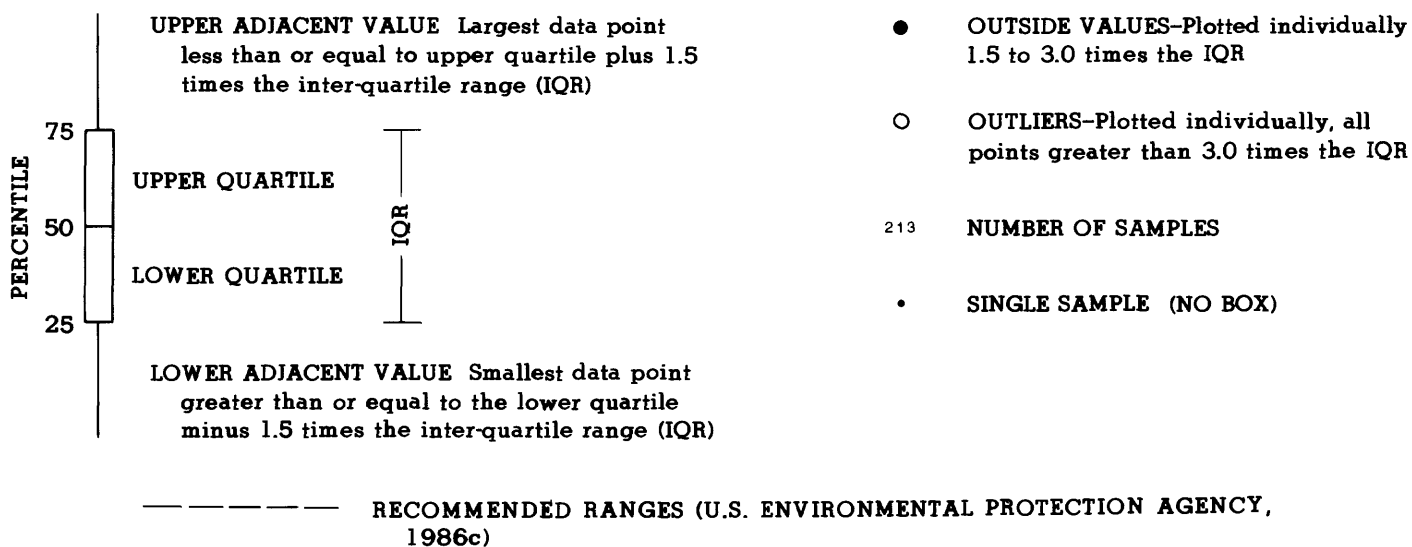


Figure 20.--Distribution of total manganese concentration at surface-water sites.

Table 8.--Summary of Seasonal Kendall test results for temporal trends for major metals

SLOPE: Slope of the trend, in milligrams per liter per year except where noted.
P: Probability that no trend exists.
NVALS: Number of values used to compute the trend.
*: P exceeds cutoff value of 0.20.
#: Logarithmic slope, expressed as percent change per year.
blank: Insufficient data used to compute trends.
+: Nonsignificant flow-concentration regression.
NASQAN: National Stream-Quality Assessment Network

Station name	Total iron				Total manganese			
			Flow-adjusted				Flow-adjusted	
	Concentration		concentration		Concentration		concentration	
	Slope	P/NVALS	Slope	P/NVALS	Slope	P/NVALS	Slope	P/NVALS
1 North Branch Potomac River at Barnum, W. Va.	*		*		-52.5	0.01/31	*	
2 Georges Creek at Franklin, Md.	*				*		*	
3 North Branch Potomac River at Pinto, Md.	-65.8	0.03/29	#-8.24	0.03/29	-28.2	.04/29	-22.9	0.01/29
4 North Branch Potomac River at Cumberland, Md.	*		*		*		*	
5 Patterson Creek near Headsville, W. Va.	*				*			
6 South Branch Potomac River at Franklin, W. Va.								
7 South Branch Potomac River near Petersburg, W. Va.								
8 South Fork South Branch Potomac River at Brandywine, W. Va.								
9 South Fork South Branch Potomac River near Moorefield, W. Va.	*				*			
10 South Branch Potomac River near Springfield, W. Va.	*				*			
11 Lost River at McCauley near Baker, W. Va.	*				*			
12 Cacapon River near Great Cacapon, W. Va.	*				*			
13 Potomac River at Hancock, Md.	*				5.00	.15/12		
14 Conococheague Creek at Fairview, Md.	10.0	.02/59	# 8.76	.00/52	.83	.00/61		
15 Opequon Creek near Martinsburg, W. Va.					*			
16 Potomac River at Shepherdstown, W. Va. (NASQAN)	*				*			
17 Antietam Creek near Sharpsburg, Md.	20.0	.00/57	#10.41	.00/51	1.34	.01/61		
18 South Fork Shenandoah River at Front Royal, Va.								
19 North Fork Shenandoah River near Strasburg, Va.	*				*			
20 Shenandoah River at Millville, W. Va. (NASQAN)	*				-7.87	.00/18		
21 Potomac River at Point of Rocks, Md.	13.8	.01/67	+		*			
22 Monocacy River near Walkersville, Md.	*				*			
23 Monocacy River at Reich's Ford Bridge near Frederick, Md.	24.3	.00/55	+		3.33	.00/58		
24 Seneca Creek at Dawsonville, Md.	20.0	2.00/59	+		3.14	.00/62		
25 Potomac River at Chain Bridge at Washington, D.C. (NASQAN)	*		*		*			

Figure 21 is an example showing the distribution of pH analyses at the three NASQAN stations for 10-percent increments of daily flow duration. Table 9 lists the flows associated with the flow increments. Samples for pH were used here only as an indicator because pH is generally measured whenever samples are collected. Daily flow duration, or exceedance probability, is the percentage of time that the daily discharge value is exceeded. Therefore, the lowest flows are in the 90- to 100-percent range and the highest flows are in the 0- to 10-percent range. The left half of figure 21 shows histograms showing the number of water-quality samples measured for pH within each 10-percent increment of flow duration. Completely random sampling would favor a similar number of samples in each 10-percent increment of flow duration.

The sampling distribution for pH at the Potomac River at Shepherdstown, W. Va. (site 16), is fairly uniform. Sampling at Shepherdstown needs to be increased at low flows, particularly in the 80- to 90-percent flow-duration range [829 to 1,210 ft³/s (cubic feet per second)] and at higher flows in the 20- to 30-percent flow-duration range (5,850 to 8,400 ft³/s). The Shenandoah River at Millville, W. Va. (site 20), needs to be sampled in the 70- to 80-percent flow-duration range (798 to 1,010 ft³/s) and in the 20- to 50-percent range (1,600 to 3,570 ft³/s). With the exception of the 80- to 90-percent flow-duration range (1,720 to 2,590 ft³/s), low-flow sampling needs to be increased at Chain Bridge (site 25). Sampling in the 10- to 20-percent flow range (16,000 to 25,400 ft³/s) also needs to be increased at Chain Bridge.

If an equal number of samples are collected within a given 10-percent increment of flow duration, fewer samples per unit of discharge will be collected as discharge increases. Therefore, the sampling frequency needs to increase with increasing discharge.

Table 9.--Flow duration data for NASQAN stations in the Upper Potomac River basin

Flow duration (percent)	Mean daily discharge, in cubic feet per second		
	Potomac River at Shepherdstown	Shenandoah River at Millville	Potomac River at Chain Bridge
-- ¹	185	194	121
90	829	605	1,720
80	1,210	798	2,590
70	1,690	1,010	3,550
60	2,330	1,270	4,820
50	3,200	1,600	6,450
40	4,270	2,060	8,560
30	5,850	2,660	11,500
20	8,400	3,570	16,000
10	13,800	5,560	25,400
-- ²	287,000	192,000	426,000

¹ Minimum.

² Maximum.

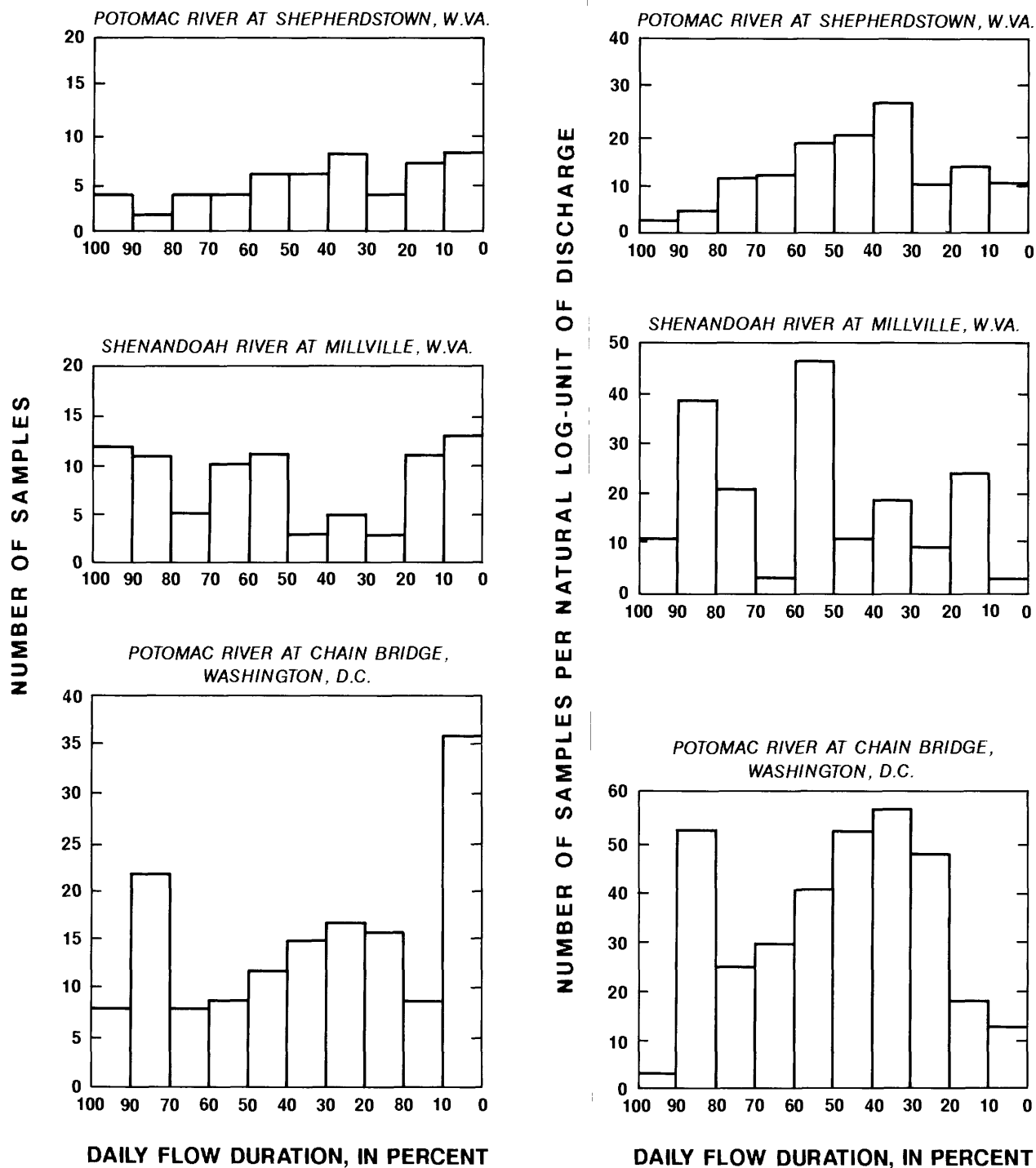


Figure 21.--Sampling distribution of pH over 10-percent increments of flow duration at the three National Stream-Quality Assessment Network (NASQAN) stations in the Upper Potomac River basin.

The right half of figure 21 shows the number of pH measurements for each log unit of discharge within each 10-percent increment of flow duration. The moderate flows at Shepherdstown, W. Va. (site 16), in the 30- to 60-percent flow-duration range (2,330 to 5,850 ft³/s) have been sampled at the expense of both the lower and higher flows. Sampling of the Shenandoah River at Millville, W. Va. (site 20) needs to be modified to smooth out the erratic sampling distribution. The high flows, with less than 20-percent flow duration (>16,000 ft³/s) as well as low flows of more than 90-percent flow duration (<1,720 ft³/s) need to be sampled at Chain Bridge (site 25).

Plotting the number of samples per log unit of discharge as a function of 10-percent increments of flow duration is needed to indicate where further sampling may be necessary or where oversampling may have occurred. Flow increments with few samples need to be evaluated more closely to determine when and where more samples need to be collected. These evaluations are not within the scope of this report. Targeting specific flows for sampling needs to be done in conjunction with periodic sampling. Targeted samples can be used to determine the flow-concentration relation. Overly sampled flow increments need to be evaluated more closely to determine what action, if any, needs to be taken.

SUMMARY

The Potomac River is the second largest tributary to the Chesapeake Bay. The Upper Potomac River basin, upstream from Chain Bridge at Washington, D.C., drains an area of 11,570 mi². The surface-water quality throughout the basin is monitored at a series of State and Federal surface-water stations. Three of these stations are National Stream-Quality Assessment Network (NASQAN) stations.

Water-quality data for 25 surface-water stations, stored on the U.S. Geological Survey's WATSTORE data-base system, were used to evaluate the water quality in the Upper Potomac River basin. Parametric and nonparametric statistical tests, including the Seasonal Kendall test for temporal trends, were used to evaluate the water-quality data for areal and temporal trends. These trends were in a few cases related to general causative factors and a sampling strategy was developed that may improve future trend analysis.

Water quality in the Upper Potomac River basin is strongly influenced by physiography. The Appalachian Plateau physiographic province is drained by the North Branch Potomac River. Streams in the North Branch Potomac River basin typically have low pH values and alkalinities and elevated concentrations of sulfate, metals, and dissolved solids resulting from acid drainage from coal mines. The use of deicing salts on the roads in winter has increased sodium and chloride concentrations above those observed in other parts of the Upper Potomac River basin. The Valley and Ridge province is characterized by the lowest concentrations of dissolved solids observed in the Upper Potomac River basin. Streams in the Great Valley have elevated concentrations of calcium, magnesium, and alkalinity resulting from the dissolution of limestone in the province. The Monocacy River, located in the Piedmont physiographic province, contains elevated concentrations of suspended sediment, possibly related to agriculture in the region.

Water quality in the Upper Potomac River basin generally has been improving over time. Alkalinity and pH have been increasing throughout the basin. This is particularly important in the Appalachian Plateau province where acid-mine drainage has been a major problem. An increase in the use of deicing salts during the winter may have caused an increasing trend in chloride concentrations in the North Branch Potomac River. Dissolved-oxygen concentration has been increasing at 7 of the 25 stations and has decreased at only one station. Concentrations of iron and manganese have declined over time in the Appalachian Plateau streams, possibly because of treatment of acid-mine drainage. Iron and manganese concentrations generally have been increasing in the Great Valley and Piedmont regions.

Water quality in each of the physiographic provinces needs to be evaluated to determine the areal water quality and water-quality trends in the Upper Potomac River basin. Sampling at one or more tributary streams entirely in a given province may reflect the overall water quality of surface water in that province. Sampling at a mainstem Potomac River station located on the downstream side of the province will indicate the quality of the water leaving the physiographic province and entering the next downstream province. Temporal trends are more easily computed when sampling is conducted at evenly spaced time intervals. Also, specific flow-duration ranges need to be targeted for sampling so that the concentration distribution over the entire flow range can be determined.

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