

QUALITY OF THE OHIO RIVER AND ATMOSPHERIC DEPOSITION AND ITS RELATION TO CORROSION OF LOCK AND DAM FACILITIES IN THE LOWER OHIO RIVER BASIN NEAR PADUCAH, KENTUCKY

By Kevin D. White

U.S. GEOLOGICAL SURVEY

Water-Resources Investigations Report 91-4050

Prepared in cooperation with the

U.S. ARMY CORPS OF ENGINEERS



Louisville, Kentucky

1991

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
2301 Bradley Avenue
Louisville, Kentucky 40217

Copies of this report may be
purchased from:

U.S. Geological Survey
Books and Open-File Reports Section
Federal Center, Box 25425
Denver, Colorado 80225

CONTENTS

	<u>Page</u>
Abstract.....	1
Introduction.....	2
Purpose and scope.....	4
Study area.....	5
Data-collection methods.....	7
Surface water.....	7
Atmospheric deposition.....	9
Corrosion product.....	10
Historical chemical data.....	10
Quality of Ohio River.....	11
Atmospheric wetfall chemistry.....	18
Quality of the Ohio River.....	22
Quality at Dam 53.....	22
Quality at Dam 52.....	31
Comparison of statistical measures of water-quality.....	34
Comparison of water-quality at Dam 53 and at Dam 52.....	34
Comparison of water-quality at Dam 53 to historical water-quality.....	44
Comparison of water quality at Dam 53 to State water-quality criteria.....	44
Quality of atmospheric deposition.....	47
Wetfall.....	47
Dryfall.....	49
Fog.....	49
Comparison of statistical measures.....	54
Comparison of atmospheric deposition quality at Dam 53 and at Dam 52.....	54
Comparison of atmospheric deposition quality at Dam 53 and at National Atmospheric Deposition Program/National Trends Network sites (1987-88).....	56
Comparison of atmospheric deposition quality at Dam 53 and at National Atmospheric Deposition Program/National Trends Network sites (historical).....	58
Corrosion of lock and dam facilities.....	58
Conclusions.....	59
References cited.....	61

ILLUSTRATIONS

	<u>Page</u>
Figure 1-2. Maps showing:	
1. Study area and location of Lock and Dams 52 and 53.....	3
2. Location of NASQAN stations on the Ohio River and National Atmospheric Deposition Program/National Trends Network stations near Dam 53.....	12
3-5. Box plots showing:	
3. Historical alkalinity concentrations at four NASQAN stations on the Ohio River.....	14
4. Historical sulfate concentrations at four NASQAN stations on the Ohio River.....	15
5. Historical suspended-sediment concentrations at four NASQAN stations on the Ohio River.....	16
6-8. Graphs showing:	
6. Resultant monthly wind direction at Paducah, Kentucky, 1987.....	21
7. Monthly median sulfate concentration in wetfall at the Southern Illinois University National Atmospheric Deposition Program/National Trends Network station, 1979-88.....	23
8. Hydrograph of the Ohio River at Metropolis, Illinois during the study period.....	32
9-17 Plots showing:	
9. Specific conductance at various points in the Ohio River at Dams 52 and 53, September 1987-February 1988.....	35
10. Specific conductance at various points in the Ohio River at Dams 52 and 53, April-August 1988.....	36
11. pH at various points in the Ohio River at Dams 52 and 53, September 1987-February 1988.....	37
12. pH at various points in the Ohio River at Dams 52 and 53, April-August 1988.....	38
13. Dissolved-oxygen concentration at various points in the Ohio River at Dams 52 and 53, September 1987-February 1988.....	39
14. Dissolved-oxygen concentration at various points in the Ohio River at Dams 52 and 53, April-August 1988.....	40
15. Oxidation/reduction potential at various points in the Ohio River at Dams 52 and 53, September 1987-February 1988.....	41
16. Oxidation/reduction potential at various points in the Ohio River at Dams 52 and 53, April-August 1988.....	42

	<u>Page</u>
17. Relation of dissolved sulfate to discharge for the Ohio River at Dam 53.....	46
18-19. Graphs showing:	
18. Monthly variations in wetfall pH at Dams 52 and 53, October 1987-August 1988.....	50
19. Monthly variations in nitrate and sulfate concentrations in wetfall at Dams 52 and 53, October 1987-August 1988.....	51

TABLES

		<u>Page</u>
Table 1.	Data-collection sites on the Ohio River.....	6
2.	Atmospheric-deposition data-collection sites.....	6
3.	Water-quality properties and constituents at the NASQAN station on the Ohio River at Dam 53.....	8
4.	Water-quality properties and constituents in wetfall, dryfall, and fog samples.....	10
5.	Statistical summary of historical water-quality data for four NASQAN stations on the Ohio River, January 1973-June 1987..	13
6.	Trend analysis on historical water-quality data, Ohio River at Dam 53, 1977-87.....	19
7.	Statistical summary of historical atmospheric wetfall quality data for three National Atmospheric Deposition Program/National Trends Network stations near Dam 53, 1979-88.....	20
8.	Trend analysis on historical National Atmospheric Deposition Program/National Trends Network data at Southern Illinois University, Carbondale, 1979-88.....	24
9.	Trend analysis on historical National Atmospheric Deposition Program/National Trends Network data at Dixon Springs, Illinois, 1979-88.....	25
10.	Trend analysis on historical National Atmospheric Deposition Program/National Trends Network data at Land Between the Lakes, Kentucky, 1984-88.....	26
11.	Raw water-quality data for the Ohio River at Dam 53.....	27
12.	Summary of water-quality data at Dam 53, August 1987-August 1988.....	30
13.	Raw water-quality data for the Ohio River at Dam 52.....	33
14.	Summary of water-quality data at Dams 52 and 53, August 1987-August 1988.....	43
15.	Statistical comparison of water-quality data at Dams 52 and 53 (nonparametric Wilcoxon-Mann-Whitney Rank Sum test, $\alpha = 0.05$).....	43
16.	Statistical comparison of current water-quality data at Dam 53 to historical data, 1973-87.....	45
17.	Comparison of water-quality data from the Ohio River at Dam 53 to Kentucky water-quality criteria.....	47
18.	Summary of atmospheric wetfall data at Dams 52 and 53, 1987-88.....	48
19.	Summary of atmospheric dryfall data at Dams 52 and 53, 1987-88.....	52
20.	Summary of atmospheric fog data at Dams 52 and 53, 1987-88...	53
21.	Statistical comparison of wetfall deposition quality at Dam 53 to Dam 52.....	54
22.	Statistical comparison of dryfall deposition quality at Dam 53 to Dam 52.....	55
23.	Statistical comparison of fog deposition quality at Dam 53 to Dam 52.....	56

	<u>Page</u>
24. Statistical comparison of wetfall deposition quality at Dam 53 to nearby National Atmospheric Deposition Program/National Trends Network stations for the same period, October 1987-August 1988.....	57
25. Statistical comparison of wetfall deposition quality at Dam 53 to historical data from nearby National Atmospheric Deposition Program/National Trends Network stations.....	59

CONVERSION FACTORS AND ABBREVIATED WATER-QUALITY UNITS

<u>Multiply</u>	<u>by</u>	<u>To obtain</u>
inch (in)	25.40	millimeter
foot (ft)	0.3048	meter
mile (mi)	1.609	kilometer
pound (lb)	0.4535	kilogram
acre	0.4047	hectare
gallon (gal)	3.785	liter
square mile (mi ²)	2.590	square kilometer
cubic foot per second (ft ³ /s)	28.32	cubic decimeter per second
gallon per minute (gal/min)	0.06309	liter per second
million gallons per day (Mgal/d)	0.04381	cubic meter per second
micromho per centimeter (μ mho/cm)	1.000	microsiemens per centimeter

Temperature in degrees Fahrenheit (°F) can be converted to degrees Celsius (°C) as follows:

$$^{\circ}\text{C} = (^{\circ}\text{F} - 32)/1.8$$

Abbreviations of Water-Quality Units

mL	milliliters
mg/L	milligrams per liter
μ g/L	micrograms per liter
μ S/cm	microsiemens per centimeter at 25 degrees Celsius
mg/kg	milligrams per kilogram

QUALITY OF THE OHIO RIVER AND ATMOSPHERIC DEPOSITION AND ITS RELATION
TO CORROSION OF LOCK AND DAM FACILITIES IN THE LOWER OHIO RIVER BASIN
NEAR PADUCAH, KENTUCKY

by Kevin D. White

ABSTRACT

Water-quality conditions and atmospheric-deposition chemistry were evaluated to determine their significance on the corrosion of Lock and Dam 53 on the lower Ohio River. Sampling activities to collect river water and atmospheric wetfall, dryfall, and fog were conducted near Lock and Dams 52 and 53, the most downstream lock and dam facilities on the Ohio River. Sample collection was coordinated with sampling activities at the U.S. Geological Survey's National Stream Quality Accounting Network station at Dam 53 and the National Atmospheric Deposition Program's wetfall-precipitation-quality stations nearby. Historical data from each of these national programs were summarized and used in comparisons with current (1987-88) conditions.

Currently, water in the lower Ohio River does not seem to be particularly corrosive on the basis of observed pH, and concentrations of alkalinity and major ions. Historical data describing these constituents indicate that the water quality at Dam 53 is better (pH nearer neutrality, higher alkalinity, and lower dissolved solids concentrations) than at locations on the Ohio River upstream. Chemical analysis of corrosion-product samples revealed typical steel-corrosion products (iron oxide and chromium oxide).

Although atmospheric-deposition quality at Dam 53 is acidic and potentially corrosive, the fact that atmospheric-deposition quality is statistically similar at Dam 52 and other nearby locations suggests that the accelerated corrosion observed at Dam 53 is not caused by atmospheric conditions alone. The median pH of wetfall was approximately 4.5 at Dams 52 and 53, and did not differ significantly from values determined in the region by the National Atmospheric Deposition Program.

Dam 53 is under water for longer periods of time than is Dam 52 because of hydrologic conditions and the elevation of the structure. Physical, electrochemical, and hydraulic conditions may contribute to the corrosion process, and these conditions exist for longer periods of time at Dam 53 than at Dam 52.

INTRODUCTION

The Ohio River Division of the U.S. Army Corps of Engineers maintains and operates two lock and dam facilities (numbers 52 and 53) on the lower Ohio River below Paducah, Kentucky (fig. 1). These facilities (hereafter referred to as Dam 52 and Dam 53) were originally constructed in 1928-29 and are scheduled to be replaced by a single lock and dam facility at Olmsted, just downstream from Dam 53. The Olmsted lock and dam is currently in the design phase.

Concerns about structural deterioration, specifically corrosion, of Dam 53 resulted in a corrosion-control survey by the U.S. Army Construction Engineering Research Laboratory (CERL). This survey, performed in 1984, concluded that abnormally rapid corrosion of the steel and galvanized steel components of Dam 53 was occurring (Myers and Riggs, 1984). On the basis of a limited amount of data, the cause of this corrosion was attributed to sulfate concentrations in the river and the presence of significant sulfate-reducing bacteria in the water column and bottom sediment near the dam site. However, a preliminary review of historical water-quality data collected at Dam 53 by the U.S. Geological Survey does not fully support these conclusions. Corrosion problems in the lower Ohio River may have implications for the Olmsted replacement dam design (such as construction materials, paint, protectant) and for the protection of other lock and dam facilities throughout the Ohio River basin.

Dams 52 and 53 can be described as "low-head" structures meaning that the lock and dam structures are under water for a significant amount of time, particularly during medium to high streamflow. The structural design and elevation of Dam 53 cause this structure to be submerged for longer periods of time than Dam 52. Because these dams are out of water or completely submerged, depending on streamflow conditions, river-quality and atmospheric-quality conditions may be contributing to the corrosion problem. Corrosion generally occurs in moist environments and can be described as a combination of two electrolytic processes: the dissolution of metal (at the anode) and, concurrently, the precipitation of metal or metal complexes (at the cathode). Highly acidic or basic environments, and (or) the presence of high concentrations of ionic contaminants can enhance the electrolytic processes and accelerate corrosion. Sulfate-reducing bacteria produce acidic and potentially corrosive hydrogen sulfide and sulfuric acid as metabolic by-products (Postgate, 1979). These bacteria are found virtually everywhere but thrive only under anaerobic conditions in the presence of sulfate and an organic food source. Atmospheric corrosion is an electrolytic process and occurs in the presence of oxygen and moisture. In the absence of oxygen or moisture, atmospheric corrosion does not occur. Atmospheric corrosion increases when the air contains pollutants, such as sulphur dioxide or corrosive salts. Furthermore, the corrosion process is enhanced if the metal surface is covered by solid particles (dust, dirt, or soot) that retain moisture and salts (Wranglen, 1985).

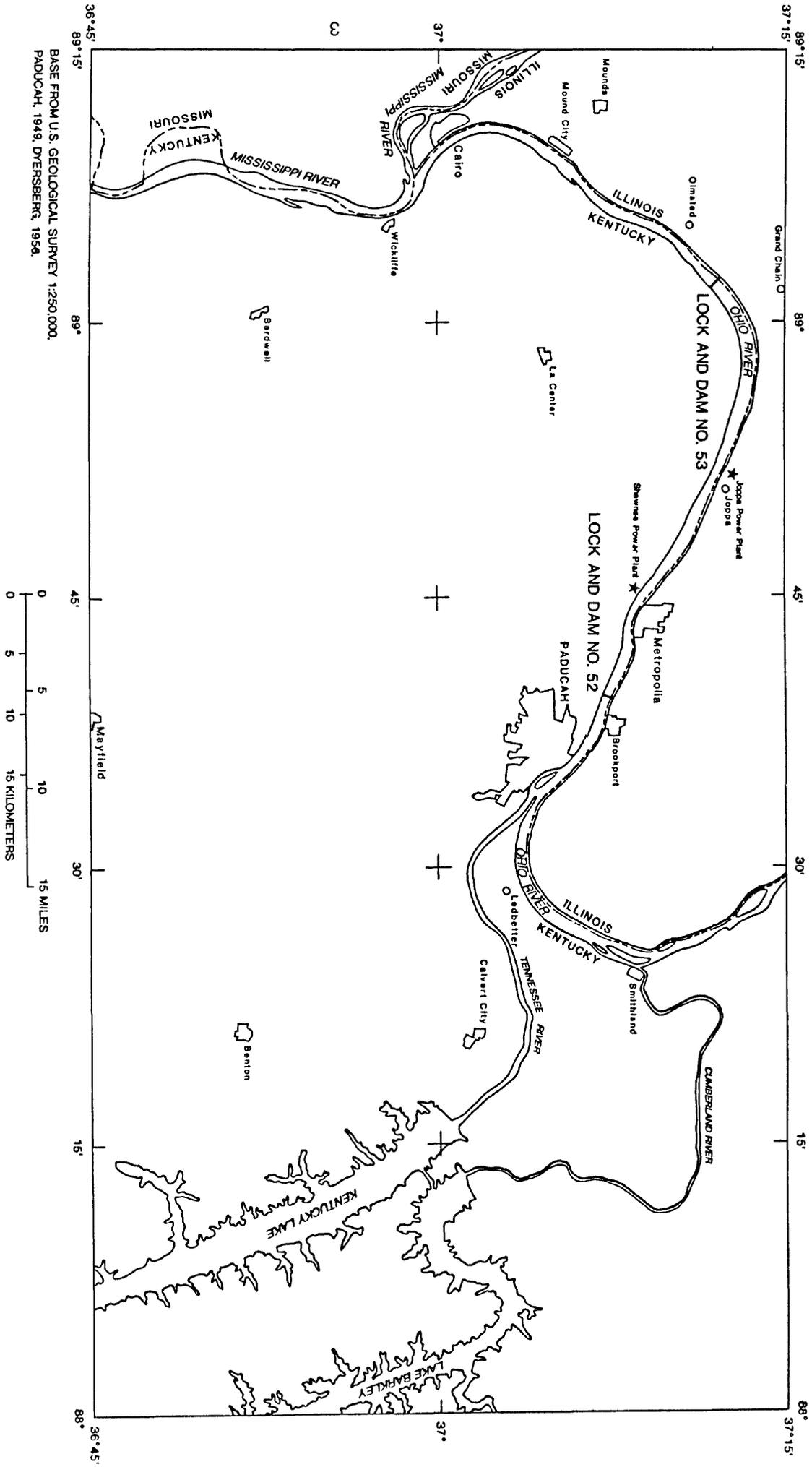


Figure 1.--Study area and location of Lock and Dams 52 and 53.

The potential for atmospheric deposition quality to affect corrosion processes at Dam 53 is significant because two coal-fired electric generating facilities are located within 10 to 15 miles of Dam 53 (fig. 1). Emissions from these facilities include sulfur dioxide and various oxides of nitrogen, which react in the atmosphere to form acid rain. Research has revealed that, under conditions of high relative humidity, the microlayer of water on metal surfaces can extract sulfur dioxide from the surrounding air to form sulfuric acid (Sereda, 1974; Brown and Masters, 1982). The conditions for this process to occur exist in the lower Ohio River basin, particularly during summer months, because of the typically high humidity levels and the proximity to sources of sulfur dioxide.

This study was performed in cooperation with the United States Department of the Army, Corps of Engineers, Louisville District. Consultations, advice, and access to the lock and dam facilities were greatly appreciated.

Purpose and Scope

The purpose of this report is to evaluate the quality of the Ohio River, atmospheric deposition, and corrosion product samples and their relation to corrosion of Lock and Dam 53 on the Ohio River near Paducah, Kentucky. Chemical determinations of river quality, atmospheric deposition, and corrosion product were performed on samples from Dam 53 and compared to similar determinations at Dam 52 (a control site 19 miles upstream) and to historical data from the region, where available. Statistical methods (summaries and applicable hypothesis tests) were used to help identify water-quality characteristics and environmental factors that have some potential for accelerating corrosion processes at Dam 53.

This investigation, begun in the late summer of 1987, consisted of three components: (1) determination of Ohio River water quality near each of the dams, (2) determination of atmospheric deposition quality (wetfall, dryfall, and fog) near each of the dams, and (3) determination of the chemical composition of the corrosion product at each of the dams. Representative Ohio River samples were collected bimonthly for a period of 1 year (August 1987-August 1988) just upstream from each of the dams. Field characteristics were measured at various depths throughout the cross-section of the river during each sampling episode. Water-quality data were evaluated to enable intersite comparisons between Dam 52 and Dam 53 and intrasite comparisons between current data collected at Dam 53 and historical data. Automatic samplers were used throughout the period of study to collect atmospheric wetfall, dryfall, and fog samples. Wetfall and fog were sampled weekly for chemical analysis, and dryfall was sampled every 8 weeks. Atmospheric data collection began in October 1987 and ended in August 1988. Atmospheric deposition data were used to determine overall deposition quality and variability, and to compare the findings at Dam 53 to Dam 52 and other atmospheric-deposition stations in the region.

Study Area

The Ohio River flows 981 miles from its head waters in Pennsylvania to its confluence with the Mississippi River near Cairo, Illinois. Draining over 203,100 mi² (7 percent of the continental United States), the Ohio River is one of the major rivers in the United States. The lower Ohio River study area is shown in figure 1. Dams 52 and 53 are the most downstream lock and dam structures on the river. Both structures were originally constructed in the 1920's, primarily to facilitate navigation. Dam 53 is at river mile 962, just 19 mi upstream from the mouth of the Ohio River, and Dam 52 is 24 mi farther upstream at river mile 938^{1/}. Paducah, Kentucky (population 34,000) is 2 mi upstream from Dam 52 on the left bank (facing downstream), and Metropolis, Illinois (population 17,000), is 4 mi downstream from Dam 52 on the right bank. Two major tributaries enter the Ohio River just upstream of Paducah-- the Cumberland River and the Tennessee River. The Cumberland River drains 17,914 mi² and enters the Ohio River at river mile 920. The Tennessee River drains 40,910 and enters the Ohio River at river mile 934.

Data-collection sites for the Ohio River were established at Dams 52 and 53, and are described in table 1. The Ohio River at Dam 53, near Grand Chain, Illinois (station number 03612500), has been sampled bimonthly since 1973 as part of the U.S. Geological Survey's National Stream Accounting Network (NASQAN). The Ohio River at Paducah (station number 03611000), upstream from Dam 52, has been sampled occasionally prior to 1977. During this investigation, river samples and measurements were taken on the upstream side of each dam. Atmospheric deposition samples were collected on the river bank near each dam at locations listed in table 2.

The U.S. Geological Survey has collected streamflow data for the Ohio River at Metropolis, Illinois (station number 03611500) since 1928. This station is at river mile 944 between Dams 52 and 53, and is further described in table 1. Average annual discharge for the period of record (1928-1987) is 271,000 ft³/s (Toms and others, 1987). The maximum discharge of record was 1,780,000 ft³/s on February 1, 1937 and the minimum was 15,000 ft³/s on July 30, 1930.

^{1/} River mile is a unit of length (1 mi) applied to the main stem of a river to denote location. Typically, the mouth of a river is designated as river mile zero and river mile length is measured upstream from this point. However, river mile zero on the Ohio River has been designated at the River's origin in Pittsburgh and river mile length is measured downstream from this point.

Table 1.--Data-collection sites on the Ohio River

Station name and location	Station number	River mile ^{1/}	Type of data collected
Ohio River near Dam 52, at Paducah, KY (lat 37°05'22" long 88°35'40")	03611000	938	Water quality
Ohio River at Metropolis, IL (lat 37°08'51" long 88°44'27")	03611500	944	Streamflow
Ohio River at Lock and Dam 53, near Grand Chain, IL (lat 37°12'11" long 89°02'30")	03612500	962	Water quality

^{1/}River mile is a unit of length (1 mi.) applied to the main stem of a river to denote location. Typically, the mouth of a river is designated as river mile zero and river mile length is measured upstream from this point. However, river mile zero on the Ohio River has been designated at the river's origin in Pittsburgh and river mile length is measured downstream from this point.

Table 2.--Atmospheric-deposition data-collection sites

Station name	Station number	Latitude	Longitude	Type of precipitation collected
Precipitation station at Dam 52	370522088354001	37°05'22"	88°35'40"	wetfall
	370522088354002	37°05'22"	88°35'40"	fog
	370522088354003	37°05'22"	88°35'40"	dryfall
Precipitation station at Dam 53	371213089022701	37°12'13"	89°02'27"	wetfall
	371213089022702	37°12'13"	89°02'27"	fog
	371213089022703	37°12'13"	89°02'27"	dryfall

DATA-COLLECTION METHODS

Surface Water

Water-quality of the Ohio River was determined by a variety of field measurements and laboratory analyses. Data-collection activities were conducted in association with routine NASQAN sampling at Dam 53. Samples were collected bimonthly (August, October, and December 1987; and February, April, June, and August 1988). Water-quality properties and constituents sampled at the NASQAN station included nutrients, major ions, and field measurements such as pH, dissolved oxygen, specific conductance, and temperature. Metals were sampled once per quarter (October, December, April, and June).

The properties and constituents determined for the NASQAN station at Dam 53 are listed in table 3. Total organic carbon (TOC) concentration was also determined at Dam 53, in addition to the NASQAN properties and constituents. For comparison, several representative constituents were determined from water samples collected at Dam 52, including dissolved sulfate, dissolved iron, and total organic carbon. All water samples were depth integrated across the sampling section, providing a representative sample of the cross section. An equal-width-increment sampling method was used (Guy and Norman, 1970).

Several field measurements were made at discrete points horizontally and vertically in the sampling section upstream from each dam to determine the existence of any water-quality stratification. These profiles were performed at the time of routine sampling by means of a portable water-quality monitor (Hydrolab model 8000)^{2/}, capable of measuring temperature, dissolved-oxygen concentration, pH, specific conductance, and oxidation/reduction potential.

Hydrogen sulfide, a metabolic by-product of sulfate-reducing bacteria, was also determined in the field by the methylene-blue, colorimetric procedure (American Public Health Association and others, 1985). Part of the representative sample collected at each dam was used for hydrogen-sulfide analysis.

Bottom sediment was collected from several locations near each dam (during low streamflow conditions) and composited to determine total organic carbon content. Bottom-sediment samples were collected by an Ekman dredge sampler, which is designed to grab a sample of surficial bottom material. Bottom-sediment samples were collected away from main flow channels in depositional areas (outside of lock walls on the upstream side of the dam). Results of sediment analysis coupled with the oxidation/reduction potential measurements with depth helped determine whether conditions favored bacterial sulfate reduction.

^{2/} The use of brand, firm, or trade names in this report is for identification purposes and does not constitute endorsement by the U.S. Geological Survey.

Table 3.--Water-quality properties and constituents at the NASQAN station on the Ohio River at Dam 53

[μ S/cm, microsiemens per centimeter; mg/L, milligram per liter; mL, milliliter; dis., dissolved; tot., total; FET, fixed endpoint titration; IT, incremental titration; μ g/L, microgram per liter; NTU, nephelometric turbidity units]

Constituent	Watstore code	Units	Where determined
Specific conductance	00095	μ S/cm	field
Specific conductance	90095	μ S/cm	lab
pH	00400	standard units	field
pH	00403	standard units	lab
Water temperature	00010	degrees Celsius	field
Air temperature	00020	degrees Celsius	field
Dissolved oxygen	00300	mg/L	field
Barometric pressure	00025	millimeters of mercury	field
Fecal coliform bacteria	31613	colonies per 100 mL	field
Fecal strep bacteria	31673	colonies per 100 mL	field
Calcium, dis.	00915	mg/L	lab
Magnesium, dis.	00925	mg/L	lab
Sodium, dis.	00930	mg/L	lab
Potassium, dis.	00935	mg/L	lab
Alkalinity, tot., FET	00410	mg/L as CaCO ₃	field
Alkalinity, tot.	00410	mg/L as CaCO ₃	lab
Alkalinity, dis.	39086	mg/L as CaCO ₃	field
Alkalinity, carbonate, IT	99430	mg/L as CaCO ₃	field
Sulfate, dis.	00945	mg/L	lab
Chloride, dis.	00940	mg/L	lab
Fluoride, dis.	00950	mg/L	lab
Silica, dis.	00955	mg/L	lab
Nitrogen, dis., NO ₂	00613	mg/L as N	lab
Nitrogen, dis., NO ₂ +NO ₃	00631	mg/L as N	lab
Nitrogen, dis., NH ₄	00608	mg/L as N	lab
Nitrogen, tot., NH ₄	00610	mg/L as N	lab
Nitrogen, tot., NH ₄ + org.	00625	mg/L as N	lab
Phosphorus, tot.	00665	mg/L as P	lab
Phosphorus, dis.	00666	mg/L as P	lab
Phosphorus, dis., ortho	00671	mg/L as P	lab
Aluminum, dis.,	01106	μ g/L	lab
Arsenic, dis.	01000	mg/L	lab
Barium, dis.	01005	μ g/L	lab
Beryllium, dis.	01010	μ g/L	lab
Cadmium, dis.	01025	μ g/L	lab
Chromium, dis.	01030	μ g/L	lab
Cobalt, dis.	01035	μ g/L	lab
Copper, dis.	01040	μ g/L	lab
Iron, dis.	01046	μ g/L	lab
Lead, dis.	01049	μ g/L	lab
Lithium, dis.	01130	μ g/L	lab
Manganese, dis.	01056	μ g/L	lab
Mercury, dis.	71890	μ g/L	lab
Molybdenum, dis.	01060	μ g/L	lab
Nickel, dis.	01065	μ g/L	lab
Selenium, dis.	01145	μ g/L	lab
Silver, dis.	01075	μ g/L	lab
Strontium, dis.	01080	μ g/L	lab
Vanadium, dis.	01085	μ g/L	lab
Zinc, dis.	01090	μ g/L	lab
Carbonate, dis., IT	00452	mg/L as CO ₃	field
Carbonate, IT	99445	mg/L as CO ₃	field
Bicarbonate, dis., IT	00453	mg/L as HCO ₃	field
Bicarbonate, IT	99440	mg/L as HCO ₃	field
Suspended sediment	80154	mg/L	lab
ROE, dis., at 180°celsius	70300	mg/L	lab
Suspended sediment	70331	percent finer than 0.062 mm	lab
Hydroxide, dis.	71834	mg/L	field
Turbidity	00076	NTU	lab

Atmospheric Deposition

Deposition of chemical constituents from the atmosphere can alter water quality and modify the natural weathering and corrosion of structures and materials. Because deposition removes many chemical constituents from the atmosphere, changes in the chemical composition of deposition are indicators of change in atmospheric composition (Bigelow and Dossett, 1988).

The National Atmospheric Deposition Program (NADP) was initiated in 1978 by the North Central Region of the State Agricultural Experiment Stations to address the problem of atmospheric deposition and its effects on agriculture, forests, and hydrologic systems. In 1980, the Federal government established the National Acid Precipitation Assessment Program (NAPAP) to broaden the scope of research into the causes and effects of acid deposition. In an effort to coordinate research, NADP was asked in 1983 to assume responsibility for coordinating the operation of the National Trends Network (NTN) of NAPAP. Utilizing common methods and laboratory, the two networks were merged and designated NADP/NTN. Currently, (1990) this precipitation network is operating in 47 States and is cooperatively supported by the State Agricultural Experiment Stations, the U.S. Department of Interior, the U.S. Department of Agriculture, the U.S. Environmental Protection Agency, the U.S. Department of Commerce, and the U.S. Department of Energy.

Methods of wetfall and dryfall collection used in this study were compatible with the methods outlined for the NADP/NTN program so that atmospheric deposition chemistry determined at Dam 53 could be compared to that determined at NADP/NTN locations in the region (Bigelow and Dossett, 1988). An automated wet/dry precipitation collector was used to collect wet and dry deposition samples continuously from October 1987 through August 1988. Composited wetfall samples were collected weekly (on Tuesdays), and composited dryfall samples were collected every 8 weeks. Deionized water (100 mL) was used to extract dryfall composites to determine field and laboratory constituents. After determining various field properties (pH, specific conductance, and precipitation volume), the samples were analyzed at a precipitation quality laboratory operated by Jake Peters of the U.S. Geological Survey's Georgia District. The constituents determined for this study are listed in table 4. Because of the compatibility in methods, the data collected during this study can be directly compared to NADP/NTN data from the region.

Fog samples also were collected on the river bank near each dam to determine quality. Atmospheric moisture in the form of condensation was collected from internally cooled metal coils by means of a commercially available dehumidifier, modified to collect up to 15 liters of water. These automated "fog" samplers were programmed to collect samples twice daily--morning and evening. A weekly composite was shipped to the precipitation laboratory operated by the U.S. Geological Survey's Georgia district office for chemical analysis. The constituents determined for fog samples are listed in table 4.

Table 4.--Water-quality properties and constituents in wetfall, dryfall, and fog samples

[dis., dissolved; mg/L, milligram per liter; $\mu\text{S}/\text{cm}$, microsiemens per centimeter at 25 degrees Celsius]

Property or Constituent	Watstore code	Units
Specific conductance, field	00095	$\mu\text{S}/\text{cm}$
Specific conductance, lab	90095	$\mu\text{S}/\text{cm}$
pH, field	00400	standard units
pH, lab	00403	standard units
Calcium, dis.	00915	mg/L
Magnesium, dis.	00925	mg/L
Sodium, dis.	00930	mg/L
Potassium, dis.	00935	mg/L
Sulfate, dis.	00945	mg/L as SO_4
Chloride, dis.	00940	mg/L
Fluoride, dis.	00950	mg/L
Bromide, dis.	71870	mg/L
Nitrogen, dis., NH_4	00608	mg/L as N
Nitrogen, dis., NO_3	00618	mg/L as N
Phosphorus, dis., ortho	00671	mg/L as P

Corrosion Product

Corrosion-product samples were collected at each lock and dam facility by physically scraping various metal structures and (or) removing various parts of the structure that showed evidence of corrosion. The corrosion-product samples were analyzed by the Stone Conservation Laboratory in the Geology Department at the University of Louisville to determine elemental and molecular composition. X-ray-diffraction techniques were used to produce molecular spectra corresponding to individual molecular species present.

X-ray-fluorescence techniques were used to determine the elemental composition of the corrosion product, thus verifying the molecular determinations made using X-ray-diffraction (K. Lal Gauri, Professor of Geology, University of Louisville, written commun., 1988).

HISTORICAL CHEMICAL DATA

Historical information on water quality and atmospheric deposition chemistry collected at or near Dam 53 was used to establish baseline conditions. Intersite and temporal comparisons of water quality and

atmospheric deposition chemistry were used to help identify unique conditions at Dam 53 that may be contributing to the observed corrosion problems occurring at the Dam.

Quality of Ohio River

Historical data were compiled from the NASQAN sampling station at Dam 53 and 3 discontinued NASQAN stations on the Ohio River. The Ohio River at Greenup Dam (river mile 342, drainage area 62,000 mi², average streamflow 91,110 ft³/s), at Markland Dam (river mile 532, drainage area 83,170 mi², average streamflow 119,200 ft³/s), and at Cannelton Dam (river mile 721, drainage area 97,000 mi², average streamflow 128,500 ft³/s) were operated as NASQAN stations during 1975-86. The NASQAN stations at Greenup Dam and Markland Dam were initiated in 1974. The Ohio River at Dam 53 (river mile 938, drainage area 203,100 mi², average streamflow 271,600 ft³/s) began operation as a NASQAN station in 1973. The relative locations of the former NASQAN stations to Dam 53 are shown in figure 2.

A historical summary (1973-87) of data for several key water-quality properties and constituents collected at the four NASQAN stations is presented in table 5. For each property or constituent, the table lists the total number of observations; the historical minimum, median, and maximum; and the fifth and ninety-fifth percentile values. The statistical summaries describing historical pH and concentrations of dissolved oxygen, alkalinity, sulfate, and dissolved solids do not support a hypothesis that water-quality conditions at Dam 53 are more conducive to corrosion than at the other three NASQAN stations on the Ohio River.

The data indicates that historical dissolved-oxygen concentrations in the Ohio River at the four NASQAN stations comply with the current ambient water-quality criteria established by the Commonwealth of Kentucky. The well-oxygenated nature of the Ohio River suggests that historical conditions, in general, were not favorable to significant sulfate reduction by bacteria. Median pH, like dissolved-oxygen concentrations, were well within Kentucky ambient criteria and differed little with location. However, some water-quality constituents did differ with location. Alkalinity, a measure of acid-neutralizing capacity, has been significantly higher at Dam 53 than at the other three stations (fig. 3). In fact, alkalinity generally increased with increasing distance downstream from Greenup Dam. Conversely, sulfate concentrations generally decreased downstream from Greenup Dam (fig. 4); the lowest median concentration was observed at Dam 53.

Suspended-sediment concentrations have historically been higher at Dam 53 than at the upstream stations (table 5 and fig. 5). The median suspended-sediment concentration at Dam 53 was 82 mg/L but only 41 mg/L at Greenup Dam. This may be significant with regard to corrosion because Dam 53 is under water for long periods of time. It is estimated that Dam 53 is submerged about 75 percent of the time, and Dam 52 is submerged less than 50 percent of the time (Tim Race, Corps of Engineers, Construction Engineering Research Laboratory, written commun., 1988). Simple abrasion of suspended sediment against the

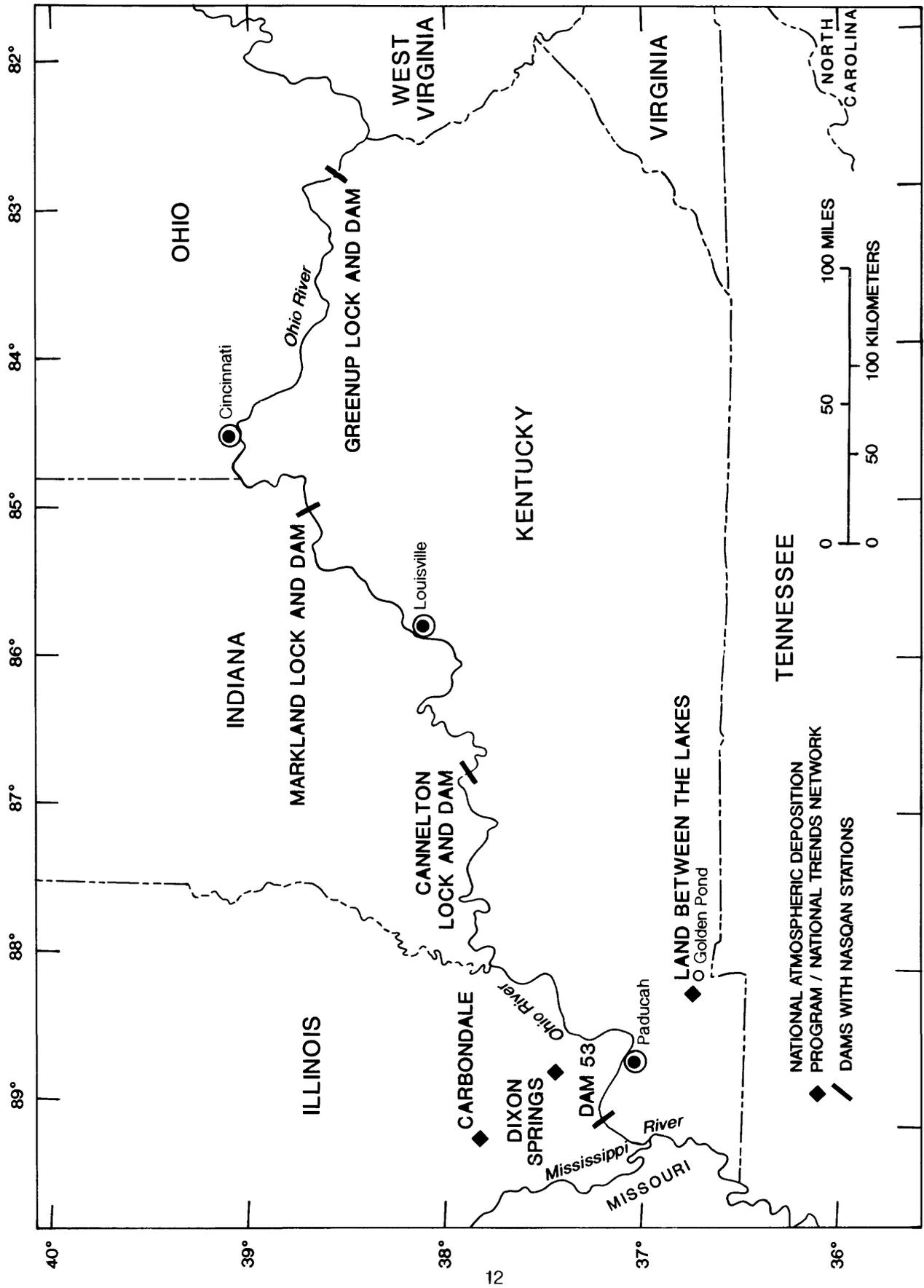
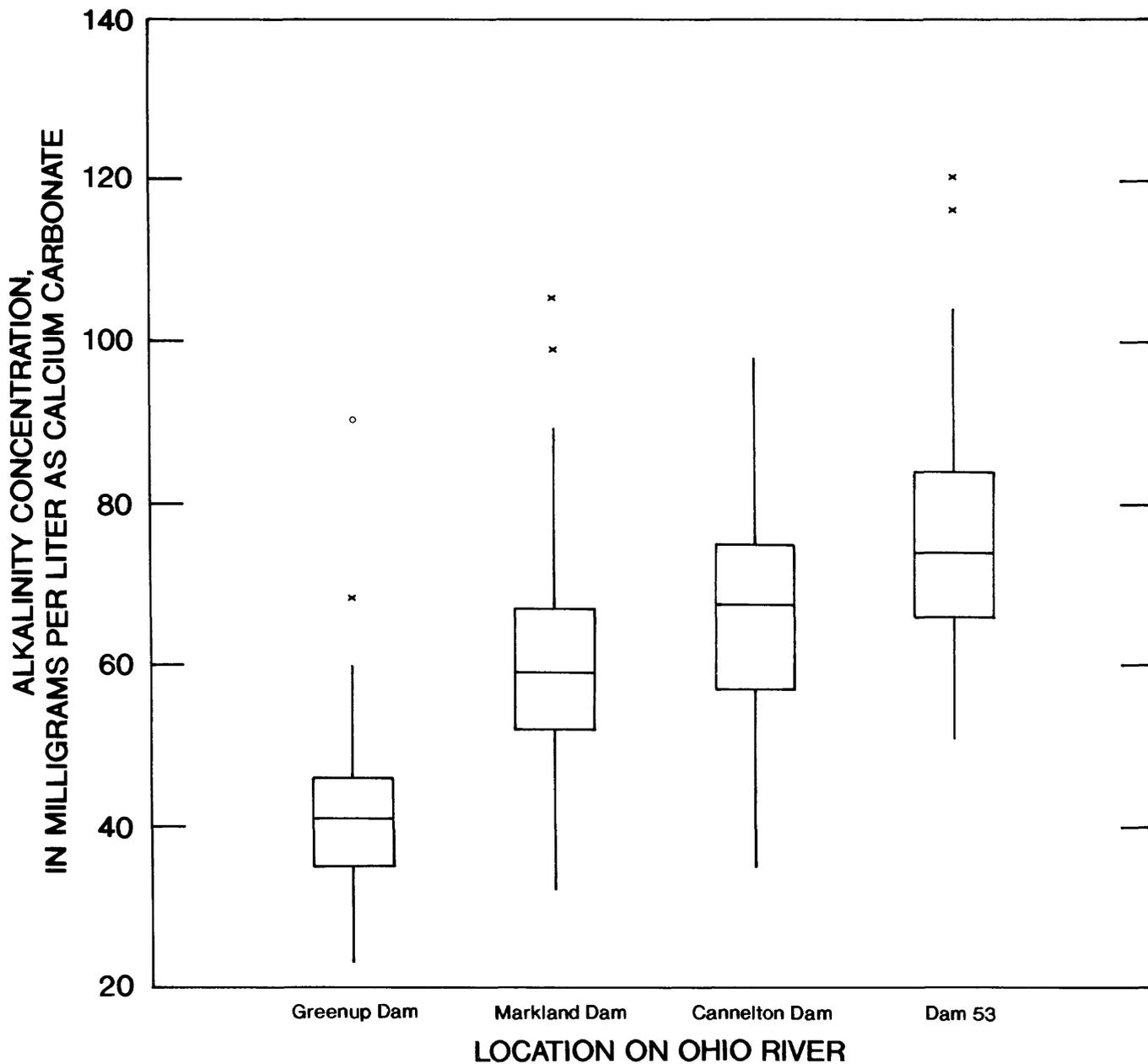


Figure 2.--Location of NASQAN stations on the Ohio River and National Atmospheric Deposition Program / National Trends Network stations near Dam 53.

Table 5.--Statistical summary of historical water-quality data for four NASQAN stations on the Ohio River, January 1973-June 1987

[N, number of observations; P5, fifth percentile; P95, ninety-fifth percentile; C, celsius; mg/L, milligram per liter; ROE, residue on evaporation; $\mu\text{g/L}$, microgram per liter; $\mu\text{S/cm}$, microsiemens per centimeter at 25 degrees Celsius]

Constituent	Station Name	N	Minimum	P5	Median	P95	Maximum
Specific conductance, field, in $\mu\text{S/cm}$	Greenup Dam	106	180	230	336	496	620
	Markland Dam	104	155	258	340	504	559
	Cannelton Dam	106	179	253	310	486	545
	Dam 53	143	190	222	300	390	500
pH, field, in standard units	Greenup Dam	104	6.1	6.4	7.2	7.8	8.2
	Markland Dam	104	6.0	6.6	7.4	8.0	8.8
	Cannelton Dam	106	6.5	6.7	7.4	7.9	8.8
	Dam 53	134	6.1	6.6	7.5	8.3	8.8
Dissolved oxygen, in mg/L O ₂	Greenup Dam	32	5.5	5.6	9.0	12.4	13.3
	Markland Dam	30	4.5	4.6	9.1	12.3	13.8
	Cannelton Dam	34	5.1	5.2	8.1	13.0	14.0
	Dam 53	57	5.3	6.2	9.1	13.2	14.8
Dissolved solids, ROE @ 180°C, mg/L	Greenup Dam	104	114	138	208	308	378
	Markland Dam	103	119	157	220	336	369
	Cannelton Dam	104	117	156	216	301	330
	Dam 53	106	120	132	184	236	302
Alkalinity, field, mg/L as CaCO ₃	Greenup Dam	78	23.0	28.0	41.0	60.0	90.0
	Markland Dam	78	32.0	39.0	59.0	84.0	106
	Cannelton Dam	80	35.0	45.0	68.0	90.0	98.0
	Dam 53	77	51.0	56.0	74.0	102	120
Sulfate, dissolved, in mg/L as SO ₄	Greenup Dam	105	43.0	48.0	75.0	120	160
	Markland Dam	104	22.0	49.0	68.0	115	130
	Cannelton Dam	105	31.0	44.0	63.0	99.0	110
	Dam 53	107	26.0	29.0	45.0	62.0	75.0
Chloride, dissolved in mg/L as Cl	Greenup Dam	105	9.70	12.5	21.0	37.0	49.0
	Markland Dam	104	8.80	12.5	21.0	39.5	57.0
	Cannelton Dam	105	8.00	11.0	21.0	35.5	42.0
	Dam 53	107	2.70	8.10	14.0	25.5	29.0
Nitrogen, NO ₂ +NO ₃ , in mg/L as n	Greenup Dam	44	0.00	.63	.98	1.4	1.5
	Markland Dam	41	.84	.85	1.30	2.0	2.0
	Cannelton Dam	43	.00	.19	1.30	2.0	2.1
	Dam 53	60	.21	.32	1.10	2.3	2.8
Iron, dissolved, in $\mu\text{g/L}$ as Fe	Greenup Dam	46	<3.00	<3.00	19.0	90.0	240
	Markland Dam	47	<3.00	<3.00	10.0	55.0	360
	Cannelton Dam	47	<3.00	<7.00	12.0	78.0	100
	Dam 53	60	<3.00	<10.0	20.0	90.0	1,200
Carbon, organic, total in mg/L as C	Greenup Dam	42	2.3	2.4	4.9	11.0	13.0
	Markland Dam	37	2.9	3.1	5.1	12.5	27.0
	Cannelton Dam	36	2.0	2.3	6.0	17.0	20.0
	Dam 53	52	.0	2.0	4.9	8.4	9.3
Sediment, suspended, in mg/L	Greenup Dam	89	5.00	6.50	41.0	404	615
	Markland Dam	93	5.00	8.00	42.0	476	937
	Cannelton Dam	86	1.00	6.00	44.0	638	1,010
	Dam 53	130	6.00	14.0	82.0	318	485



EXPLANATION
for figures 3, 4, and 5

"Whisker" indicates extent of data values, to a distance at most 1.5 interquartile ranges beyond the ends of the box. (Interquartile range is the distance between the 25th and 75th sample percentiles)

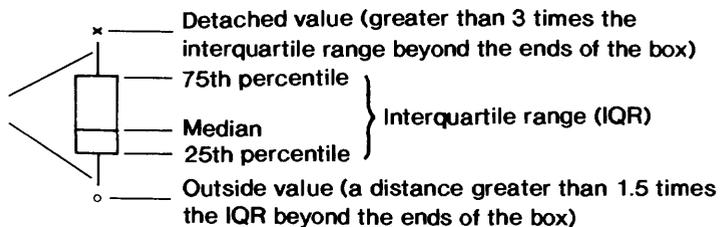
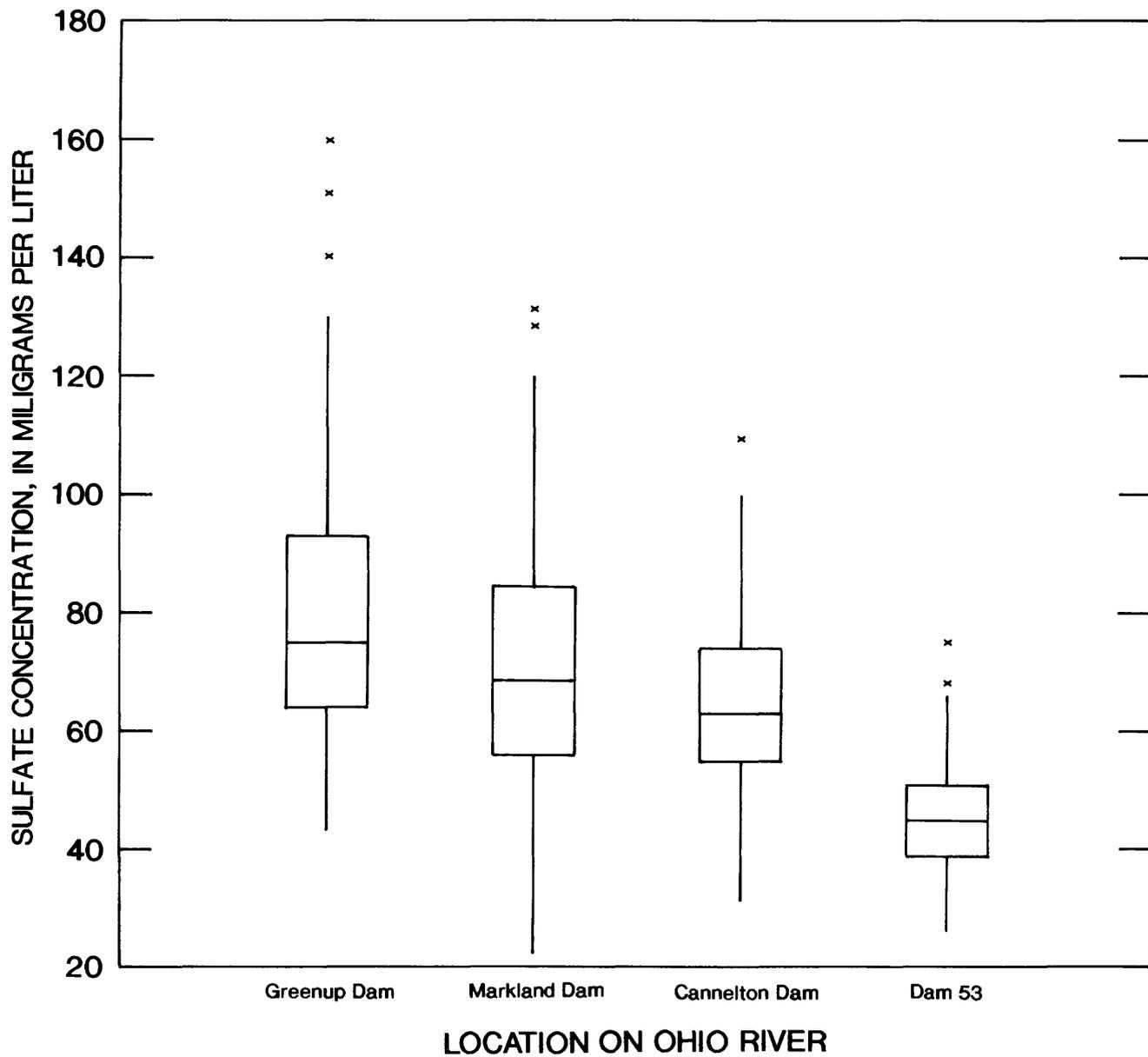
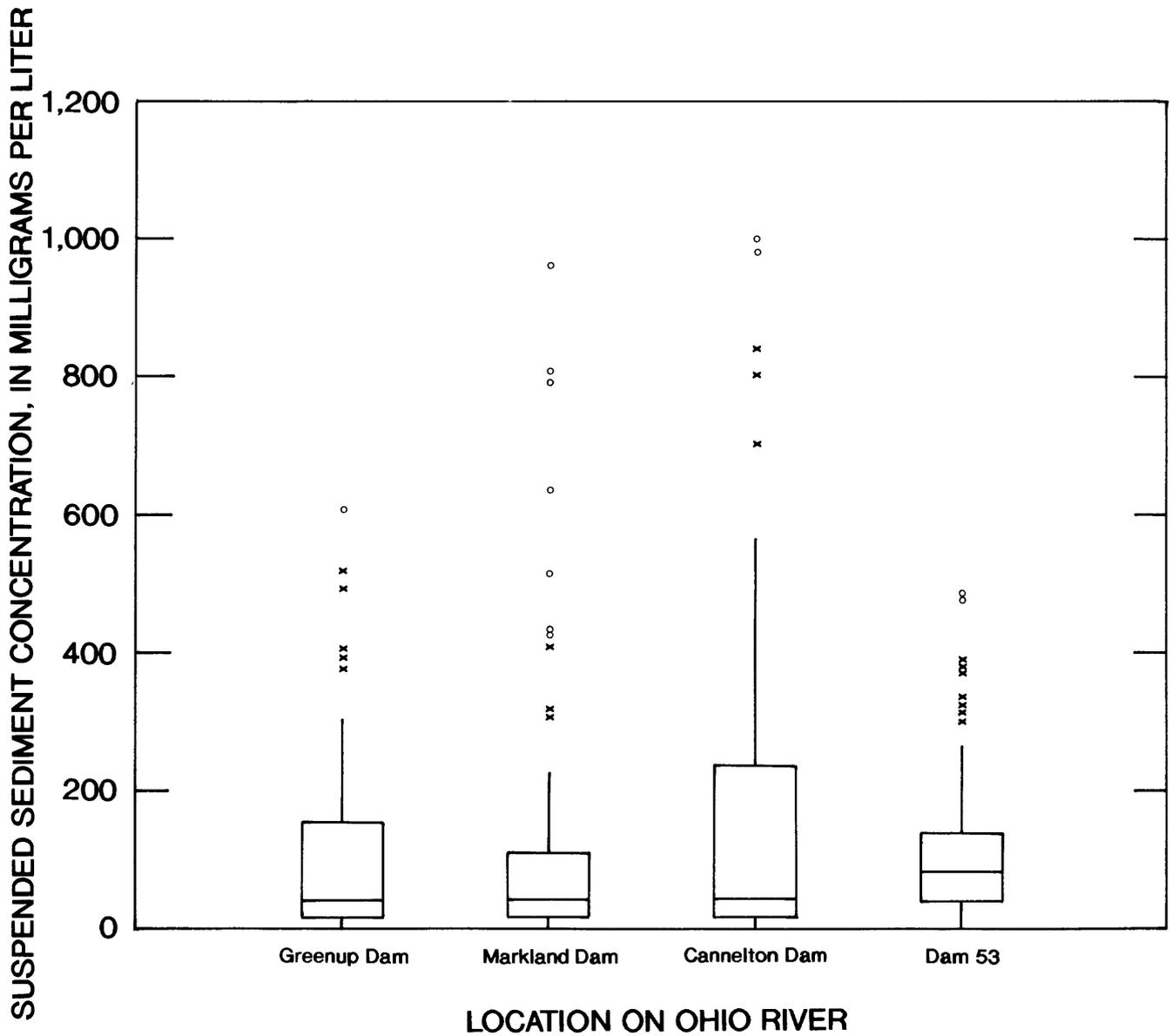


Figure 3.--Historical alkalinity concentrations at four NASQAN stations on the Ohio River.



See page 14 for detailed explanation of box and whisker plot.

Figure 4.--Historical sulfate concentrations at four NASQAN stations on the Ohio River.



See page 14 for detailed explanation of box and whisker plot.

Figure 5.--Historical suspended sediment concentration at NASQAN stations on the Ohio River.

submerged lock and dam facility may explain some of the observed corrosion at Dam 53. Galvanized steel can be particularly vulnerable to suspended-sediment abrasion because of the softness of the zinc coating. Dam 52 may be less susceptible to suspended-sediment abrasion because it is submerged for short periods of time.

Historical water-quality data from the Ohio River at Dam 53 was statistically analyzed by the seasonal Kendall test (Hirsch and others, 1982; Smith and others, 1982) to determine the existence of changes in concentrations over time (otherwise known as temporal trends). The seasonal Kendall test is a nonparametric test that detects monotonic trend and is applicable to data that exhibit some seasonality. The presence of censored data (defined as values less than some detection limit) or the existence of highly skewed data do not present problems in applying the Seasonal Kendall test because the test involves comparisons of ranks of the data. The effect of seasonality, as defined by climate or hydrologic conditions, is reduced by comparing observations from the same seasons of differing years. In this study, each year was divided into four seasons for applying the seasonal Kendall test. The test statistic (τ) has a value between -1 and +1, where negative values indicate decreasing trends and positive values indicate increasing trends. If no trend exists, then τ is zero. The null hypothesis being tested (H_0) is that no trend exists ($\tau = 0$). The level of significance, denoted by α , is the maximum acceptable probability of making a type I error--that is, the probability of rejecting the null hypothesis when it is true (Hirsch and others, 1982). The p-level is associated with an observed value of a test statistic and is the smallest level of significance that would have allowed the null hypothesis to be rejected. In this study, an α of 0.1 was chosen to denote significance. Using an "X" of 0.1 assumes a 10 percent probability of rejecting the null hypothesis when it is free, but allows for a reasonable probability for detecting statistical significance.

Because the concentration of many water-quality constituents can be related to streamflow, it is advisable to perform trend analysis on flow-adjusted data, where the relation can be defined (Langbein and Dawdy, 1964; Smith and others, 1982; Crawford and others, 1983). The effects of discharge can be minimized by deriving a best-fit relation between the constituent of interest and discharge. The seasonal Kendall test is then applied to the residuals--that is, to the difference between the actual concentration and estimated concentration determined by the best-fit equation. This is called the residuals method of flow adjustment. Some common equations used in this study to relate constituent concentration to discharge include the following (Crawford and others, 1983):

Linear	$C = a + bQ$
Log-linear	$C = a + b (\ln Q)$
Quadratic	$C = a + b_1Q + b_2Q^2$
Inverse	$C = a + b(1/Q)$
Log-log	$\ln C = a + b (\ln Q),$

where C is the constituent value,
ln C is the natural logarithm of the constituent value,
Q is discharge,
ln Q is the natural logarithm of discharge, and
a and b are coefficients of the equation.

For each constituent of interest, the best-fit equation was determined by least-square regression. The best-fit equation was chosen based on R^2 (the percentage of the variance explained) and the probability level of the regression. If no equation adequately described the relation (p-level of 0.1 or less), then flow adjustment was not performed.

The period 1977-87 was chosen for trend analysis because of data completeness and sample-collection-method compatibility. For the period 1977-87, no significant trends ($\alpha = 0.10$) were determined for any of the constituents that were tested (table 6). Where appropriate, trend analysis was also performed on the same water-quality data after adjusting for flow. Again, no significant trends ($\alpha = 0.10$) were detected (table 6). Thus, it appears that water-quality conditions did not change significantly during the period tested.

Atmospheric Wetfall Chemistry

As part of the NADP/NTN program, wetfall chemistry has been determined at many locations throughout the United States since 1978. Three of these NADP/NTN stations are near Dam 53 and yield much information describing the wetfall chemistry in the area. Wetfall-sampling stations have been operated at Southern Illinois University in Carbondale (NADP/NTN site number 143580) since July of 1979, at Dixon Springs Agricultural Center in Dixon Springs, Illinois (NADP/NTN site number 146340) since January of 1979, and at Land Between the Lakes near Golden Pond, Kentucky (NADP/NTN site number 183860) since October of 1984. Wetfall samples are collected weekly at each station and analyzed by a central analytical laboratory (part of the analytical chemistry unit of the Illinois State Water Survey, Champaign, Illinois) for a variety of chemical constituents. The relative locations of each of these NADP/NTN stations to Dam 53 are shown in figure 2.

The historical data collected at the three NADP/NTN stations near Dam 53 and data collected at Dam 53 during 1987-88 are summarized in table 7. For most properties and constituents, median values are greatest at the Dixon Springs station and smallest at the Land Between the Lakes station. Wind-direction information obtained from the National Weather Service at Paducah for 1987 show that prevailing winds generally range from south to west (fig. 6). Thus, atmospheric emissions from the two coal-fired, electric generating plants between Dams 52 and 53 would drift to the north and east, generally in the direction of the Dixon Springs NADP/NTN station and away from the Land Between the Lakes station. Median nitrate concentrations ranged from 1.28 mg/L at Land Between the Lakes to 1.47 mg/L at Dixon Springs. Median sulfate concentrations ranged from 2.05 mg/L at Land Between the Lakes to 2.79 mg/L at Dixon Springs. Exceptions to this pattern are apparent for pH and

Table 6.--Trend analysis on historical water-quality data, Ohio River
at Dam 53, 1977-87

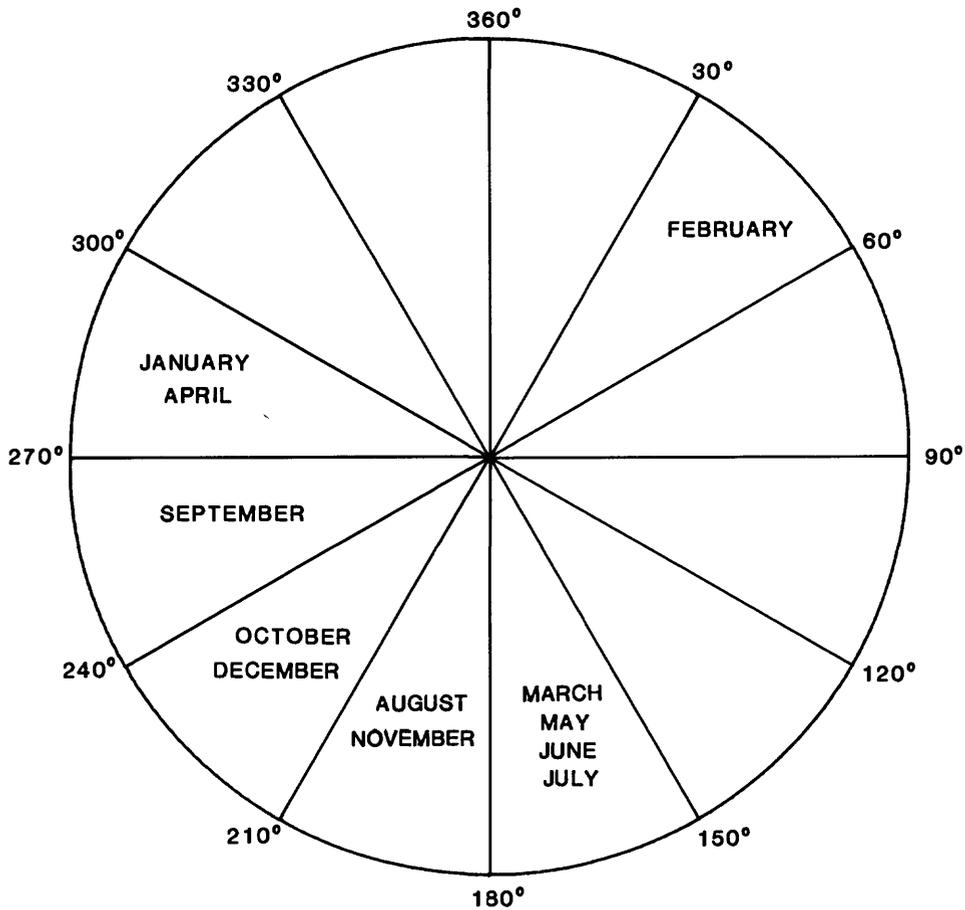
[N, number of observations; P, probability; μ S/cm, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligram per liter; μ g/L, microgram per liter. Comparison for trend tests based on four seasons. Slope is defined as constituent units per year. Trend-line slopes not significant at the 0.1 probability level are not reported]

Constituent	N	Seasonal Kendall Tests for Time Trend			
		Unadjusted for Flow		Flow Adjusted	
		P-level	Trend-line slope	P-level	Trend-line slope
Specific conductance, field, in μ S/cm	96	1.000		0.884	
pH, field, in standard units	96	.269		.210	
Oxygen, dissolved, in mg/L as O ₂	50	.699		.233	
Sodium, dissolved, in mg/L as Na	74	.308		.669	
Alkalinity, total, field in mg/L as CaCO ₃	45	.174		.542	
Sulfate, dissolved, in mg/L as SO ₄	77	.486		.694	
Chloride, dissolved, in mg/L as Cl	75	.450		.813	
Nitrogen, NO ₂ +NO ₃ , in mg/L as N	62	.774		.291	
Phosphorus, dissolved, in mg/L as P	71	.550			no significant flow relation
Iron, dissolved, in μ g/L as Fe	48	.199		.444	
Suspended Sediment in mg/L	87	.190		.853	

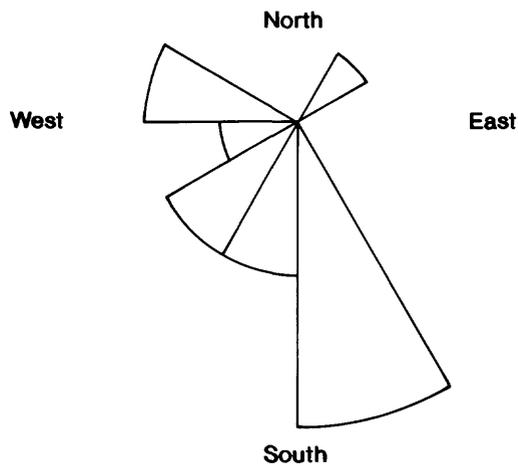
Table 7.--Statistical summary of historical atmospheric wetfall quality data for three National Atmospheric Deposition Program/National Trends Network stations near Dam 53, 1979-88

[N, number of observations; P5, fifth percentile; P95, ninety-fifth percentile; μ S/cm, microsiemens per centimeter at 25 degrees Celsius; DIX, Dixon Springs Agricultural Center, Pope County, Illinois; LBL, Land Between the Lakes, Trigg County, Kentucky; SIU, Southern Illinois University, at Carbondale, Illinois; 53, Dam 53 at Paducah, Kentucky; mg/L, milligram per liter]

Constituent	Station	N	Minimum	P5	Median	P95	Maximum
Specific conductance, in μ S/cm	DIX	362	7.7	11.5	24.0	49.9	110
	LBL	136	5.4	8.3	21.8	65.1	150
	SIU	341	4.3	8.5	22.0	52.4	117
	53	30	11.3	12.0	20.5	56.0	72.0
pH, field, in standard units	DIX	406	3.20	3.60	4.21	4.95	6.10
	LBL	139	3.47	3.93	4.38	4.89	5.33
	SIU	338	3.40	3.92	4.37	4.93	6.04
	53	31	3.76	4.11	4.54	5.72	5.85
pH, lab, in standard units	DIX	424	3.58	3.93	4.37	5.19	6.91
	LBL	156	3.50	3.99	4.41	5.28	6.63
	SIU	378	3.51	3.98	4.43	5.06	7.03
	53	32	3.76	4.11	4.54	5.72	5.85
Calcium, in mg/L as Ca	DIX	389	0.01	0.05	0.25	1.35	9.58
	LBL	150	.01	.02	.13	.88	3.18
	SIU	367	.01	.04	.22	1.17	5.14
	53	33	.06	.08	.29	1.94	2.20
Magnesium, in mg/L as Mg	DIX	389	.005	.009	.035	.192	.926
	LBL	150	.003	.005	.023	.135	.328
	SIU	367	.003	.009	.033	.202	.660
	53	32	.010	.020	.100	.180	.300
Sodium, in mg/L as Na	DIX	389	.002	.022	.110	.557	3.05
	LBL	150	.009	.024	.088	.431	.975
	SIU	367	.003	.020	.097	.533	1.47
	53	33	.010	.010	.170	.550	.570
Potassium, in mg/L as K	DIX	389	.002	.005	.030	.152	.863
	LBL	150	.003	.003	.022	.126	.740
	SIU	367	.002	.005	.025	.141	.585
	53	33	.020	.030	.150	1.36	2.00
Sulfate, in mg/L as SO ₄	DIX	389	.52	1.16	2.79	8.09	21.0
	LBL	150	.23	.75	2.05	7.44	16.4
	SIU	367	.22	1.00	2.48	6.93	24.5
	53	33	1.00	1.20	2.10	11.0	11.0
Chloride, in mg/L as Cl	DIX	389	.03	.07	.21	.76	2.75
	LBL	150	.03	.05	.16	.78	1.70
	SIU	367	.02	.05	.19	.83	2.21
	53	33	.10	.12	.52	2.00	2.50
Nitrogen, NO ₃ , dissolved, in mg/L as N	DIX	389	.03	.54	1.47	5.00	18.27
	LBL	150	.03	.34	1.28	4.72	9.09
	SIU	367	.03	.48	1.41	4.11	12.97
	53	33	.44	.53	1.14	6.20	6.64
Nitrogen, NH ₄ , dissolved, in mg/L as N	DIX	389	.02	.04	.31	1.20	4.36
	LBL	150	.02	.02	.18	.80	1.48
	SIU	367	.02	.02	.25	1.11	2.73
	53	33	.05	.06	.42	1.81	2.07
Phosphorus, ortho, dissolved, in mg/L as P	DIX	389	.003	.003	.003	.036	.370
	LBL	150	.003	.003	.010	.140	.570
	SIU	367	.003	.003	.003	.020	.300
	53	33	.031	.031	.031	.155	.372



RESULTANT WIND DIRECTION DURING MONTHS OF 1987



ROSE DIAGRAM OF PREVAILING WIND DIRECTION IN 1987

Figure 6.--Resultant monthly wind direction at Paducah, Kentucky, 1987.

ortho phosphorus. Median pH ranged from 4.21 at Dixon Springs to 4.38 at Land Between the Lakes and, if thought of as the hydrogen ion concentration, is consistent with the patterns described above. Median phosphate concentration ranged from 0.003 mg/L at Dixon Springs and Southern Illinois University to 0.01 mg/L at Land Between the Lakes. Excluding phosphate data, the historical wetfall data indicate that wetfall quality is best at Land Between the Lakes (40 miles south-southeast of Dam 53) and poorest at Dixon Springs (38 miles northeast of Dam 53).

Historical wetfall-chemistry data from the three NADP/NTN stations were statistically tested for trends with and without adjusting for precipitation volume. As before, the nonparametric seasonal Kendall test was used to test the null hypothesis that no trend exists (Smith and others, 1982; Hirsch and others, 1982). A p-level of 0.1 was chosen for significance (trend tests resulting in a p-level of less than or equal to 0.1 indicate that a significant temporal trend exists). Because of the availability of data and the seasonality observed in the historical data set (fig. 7), four seasons were used in the seasonal Kendall trend test.

As shown in table 8, several wetfall properties and constituents exhibited significant trends at the Southern Illinois University station at Carbondale, even when adjusted for rainfall volume. Trend slopes indicate that wetfall quality is generally improving at this site as noted by the negative (decreasing) trend-line slopes. Calcium and chloride concentrations (adjusted for rainfall volume) in wetfall are decreasing with time, and only ortho phosphorus concentrations are increasing. Although ortho phosphorus concentrations are increasing, the increase is almost negligible. The ortho phosphorus concentration trend slope is less than 0.001 mg/L per year. No significant rainfall-volume adjusted trends were detected for other constituent concentrations or for pH and specific conductance.

The results of trend tests performed on 10 years of data from the Dixon Springs, Illinois NADP/NTN station are shown in table 9. Only two constituents exhibited significant rainfall-volume adjusted trends. Calcium and potassium concentrations decreased slightly.

Results of rainfall-volume adjusted trend tests on historical wetfall-chemistry data collected at Land Between the Lakes (table 10) exhibited a significant downward trend in laboratory pH (slope = -0.04 units per year). Ortho phosphorus concentrations increased. The significance of trends detected at Land Between the Lakes needs to be evaluated carefully because of the relatively short period (1984-88) of data collection performed at this location.

QUALITY OF THE OHIO RIVER

Quality at Dam 53

Water-quality information collected at Dam 53 during this study is listed in table 11 and summarized in table 12. The NASQAN schedule of sampling

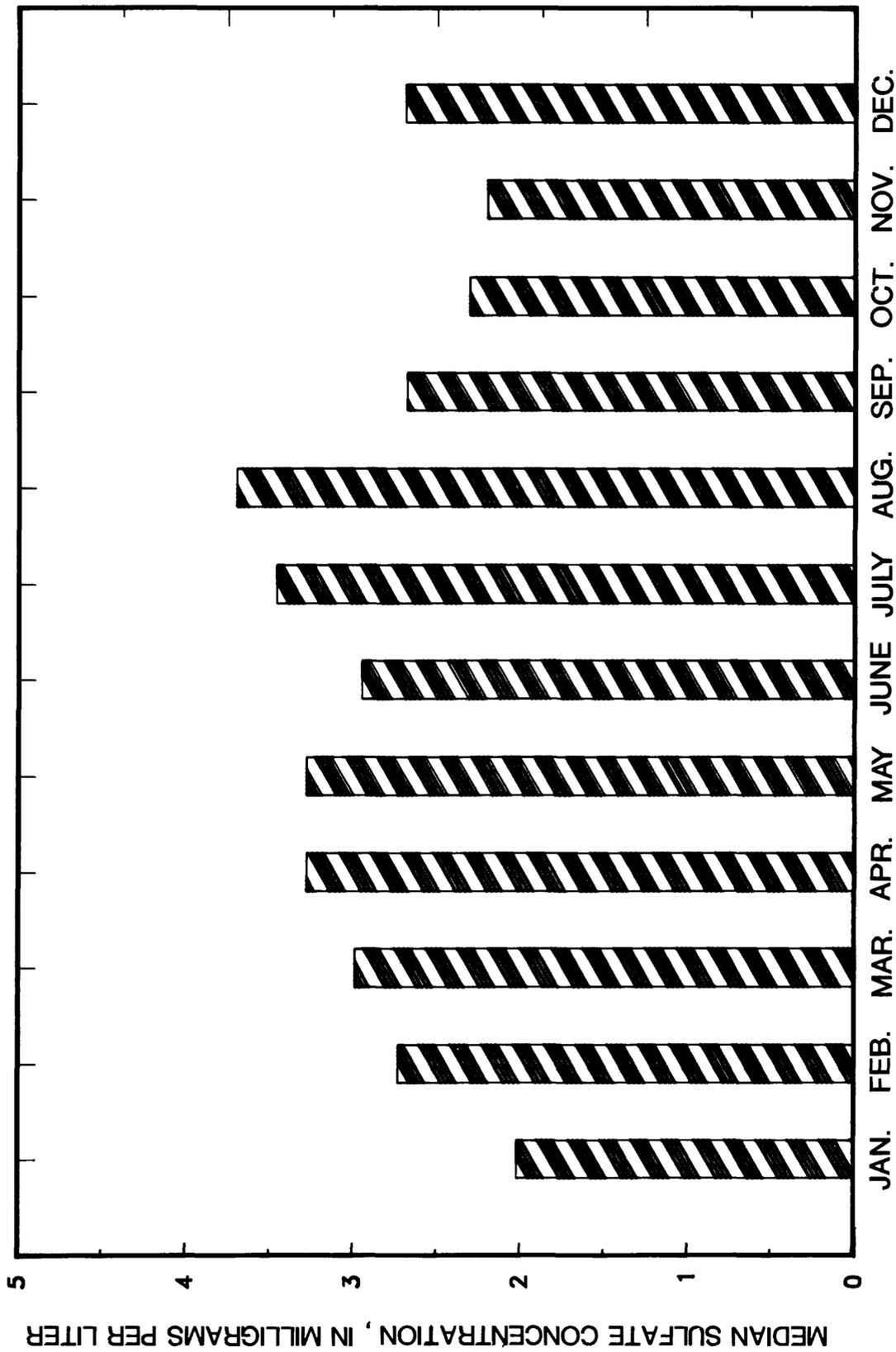


Figure 7.--Monthly median sulfate concentration in wetfall at the Southern Illinois University National Atmospheric Deposition Program / National Trends Network station, 1979-88.

Table 8.--Trend analysis on historical National Atmospheric Deposition Program/National Trends Network data at Southern Illinois University, Carbondale, 1979-88

[N, number of observations; P, probability; μ S/cm, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligram per liter. Slope is defined as constituent units per year. Trend-line slopes not significant at the 0.1 probability level are not reported]

Constituent	N	Seasonal Kendall Tests for Time Trend			
		Unadjusted for Rainfall Volume		Rainfall Volume Adjusted	
		P-level	Trend-line slope	P-level	Trend-line slope
Specific conductance, field, in μ S/cm	341	0.231		0.842	
pH, field, in standard units	338	.250		.582	
Calcium, dissolved, in mg/L as Ca	367	.018	-0.016	.016	-.020
Magnesium, dissolved, in mg/L as Mg	367	.424		.129	
Sodium, dissolved, in mg/L as Na	367	.134		.176	
Potassium, dissolved, in mg/L as K	367	.002	-.002	.151	
Sulfate, dissolved, in mg/L as SO ₄	367	.072	-.078	.194	
Chloride, dissolved, in mg/L as Cl	367	.120		.036	-.007
Nitrogen, NO ₃ , dissolved, in mg/L as N	367	.582		1.000	
Nitrogen, NH ₄ , dissolved, in mg/L as N	367	.194		.146	
Phosphorus, ortho, dissolved, in mg/L as P	367	.000	.001	.001	.000

Table 9.--Trend analysis on historical National Atmospheric Deposition Program/National Trends Network data at Dixon Springs, Illinois, 1979-88

[N, number of observations; P, probability; $\mu\text{S/cm}$, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligram per liter. Slope is defined as constituent units per year. Trend-line slopes not significant at the 0.1 probability level are not reported]

Constituent	N	Seasonal Kendall Tests for Time Trend			
		Unadjusted for Rainfall Volume		Rainfall Volume Adjusted	
		P-level	Trend-line slope	P-level	Trend-line slope
Specific conductance, field, in $\mu\text{S/cm}$	362	.816		.861	
pH, field, in standard units	406	.194		.200	
Calcium, dissolved, in mg/L as Ca	389	.104		.095	-0.011
Magnesium, dissolved, in mg/L as Mg	389	.286		.188	
Sodium, dissolved, in mg/L as Na	389	.116		.174	
Potassium, dissolved, in mg/L as K	389	.138		.093	-.001
Sulfate, dissolved, in mg/L as SO_4	389	.021	-0.061	.178	
Chloride, dissolved, in mg/L as Cl	389	.029	-.009	.140	
Nitrogen, NO_3 , dissolved, in mg/L as N	389	1.000		.471	
Nitrogen, NH_4 , dissolved, in mg/L as N	389	.266		.505	
Phosphorus, ortho, dissolved, in mg/L as P	389	.000	.001	.042	

Table 10.--Trend analysis on historical National Atmospheric Deposition Program/National Trends Network data at Land Between the Lakes, Kentucky, 1984-88

[N, number of observations; P, probability; $\mu\text{S/cm}$, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligram per liter. Slope is defined as constituent units per year. Trend-line slopes not significant at the 0.1 probability level are not reported]

Constituent	N	Seasonal Kendall Tests for Time Trend			
		Unadjusted for Rainfall Volume		Rainfall Volume Adjusted	
		P-level	Trend-line slope	P-level	Trend-line slope
Specific conductance, field, in $\mu\text{S/cm}$	136	0.062	2.008	0.234	
pH, field, in standard units	139	.234		.168	
Calcium, dissolved, in mg/L as Ca	150	.730		.610	
Magnesium, dissolved, in mg/L as Mg	150	.610		.054	-0.008
Sodium, dissolved, in mg/L as Na	150	.126		1.000	
Potassium, dissolved, in mg/L as K	150	.396		.441	
Sulfate, dissolved, in mg/L as SO_4	150	.011	0.339	.126	
Chloride, dissolved, in mg/L as Cl	150	1.000		1.000	
Nitrogen, NO_3 , dissolved, in mg/L as N	150	.234		.865	
Nitrogen, NH_4 , dissolved, in mg/L as N	150	.168		.234	
Phosphorus, ortho, dissolved, in mg/L as P	150	.002	.005	.010	.005

Table 11.--Raw water-quality data for the Ohio River at Dam 53

[°C, degrees Celsius; mm of Hg, millimeters of mercury; inst., instantaneous; ntu, nephelometric turbidity units; $\mu\text{S}/\text{cm}$, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligram per liter; wat wh tot fet, water whole total fixed end titration; --, determination not performed; g/kg, grams per kilogram; tot. in bot. mat., total in bottom material; mg/kg, milligram per kilogram; $\mu\text{g}/\text{L}$, micrograms per liter; mem. fil, membrane filtered; cols/100 mL, colonies per 100 milliliters; wat dis tot it, water, dissolved total, incremental titration; ND, not detected]

Date	Temperature water (°C)	Temperature air (°C)	Barometric pressure (mm of Hg)	Discharge, inst. cubic feet per second	Turbidity (ntu)	Specific conductance ($\mu\text{S}/\text{cm}$)	Oxygen, dissolved (mg/L)	pH (standard units)	pH lab (standard units)	Alkalinity wat wh tot fet (mg/L as CaCO_3)
AUG 1987										
10...	30.50	--	755.0	52800	3.500	305.0	--	7.330	8.100	67.00
SEP										
22...	--	--	--	--	--	--	--	--	--	--
OCT										
13...	16.80	12.70	762.0	95700	5.700	322.0	8.5	7.360	8.400	74.00
14...	--	--	--	90400	--	--	--	--	--	--
DEC										
14...	--	--	--	--	--	--	--	--	--	--
14...	7.900	3.500	756.0	126000	.700	428.0	11.4	7.360	8.100	82.00
FEB 1988										
17...	3.100	6.000	760.0	304000	64.00	282.0	12.5	7.280	7.900	60.00
18...	--	--	--	300000	--	--	--	--	--	--
APR										
13...	14.00	17.50	754.0	406000	80.00	320.0	8.7	7.380	8.200	69.00
14...	--	--	--	399000	--	--	--	--	--	--
JUN										
13...	--	--	--	61400	--	--	--	--	--	--
14...	--	--	--	--	--	--	--	--	--	--
14...	25.40	32.00	763.0	56200	2.800	378.0	8.5	7.400	7.800	--
JUL										
05...	--	--	--	--	--	--	--	--	--	--
AUG										
02...	30.20	--	758.0	--	--	340.0	6.2	7.250	--	66.00
08...	30.40	33.50	762.0	36900	5.200	315.0	6.0	7.260	8.000	68.00

Date	Nitrogen, ammonia dissolved (mg/L as N)	Nitrogen, ammonia total (mg/L as N)	Nitrogen, nitrite dissolved (mg/L as N)	Nitrogen, ammonia + organic total (mg/L as N)	Nitrogen, $\text{NO}_2 + \text{NO}_3$ dissolved (mg/L as N)	Phosphorus total (mg/L as P)	Phosphorus dissolved (mg/L as P)	Phosphorus ortho, dissolved (mg/L as P)	Carbon, organic total (mg/L as C)	Carbon, inorganic, tot in bot mat (g/kg as C)
AUG 1987										
10...	0.030	0.040	0.020	2.000	0.230	0.080	0.030	0.020	--	--
SEP										
22...	--	--	--	--	--	--	--	--	5.200	--
OCT										
13...	.090	.110	<.010	.500	.320	.360	.050	.030	--	--
14...	--	--	--	--	--	--	--	--	3.500	--
DEC										
14...	--	--	--	--	--	--	--	--	--	--
14...	.120	.130	.020	.800	1.300	.120	.060	.050	--	--
FEB 1988										
17...	.180	.150	.040	1.200	1.900	.050	.230	.060	--	--
18...	--	--	--	--	--	--	--	--	--	--
APR										
13...	.050	.070	.040	1.200	1.400	.470	.340	.040	--	--
14...	--	--	--	--	--	--	--	--	8.600	--
JUN										
13...	--	--	--	--	--	--	--	--	3.700	--
14...	--	--	--	--	--	--	--	--	--	--
14...	.060	.040	.020	.500	.330	.040	.020	<.010	--	--
JUL										
05...	--	--	--	--	--	--	--	--	--	1.700
AUG										
02...	--	--	--	--	--	--	--	--	3.600	.200
08...	.070	.080	.100	.500	.370	.030	<.010	.020	--	--

Table 11.--Raw water-quality data for the Ohio River at Dam 53--Continued

Date	Carbon, inorg + organic tot. in bot mat (mg/kg as C)	Calcium dis-solved (mg/L as CA)	Magne-sium, dis-solved (mg/L as MG)	Sodium, dis-solved (mg/L as NA)	Potas-sium, dis-solved (mg/L as K)	Chlo-ride, dis-solved (mg/L as CL)	Sulfate dis-solved (mg/L as SO ₄)	Fluo-ride, dis-solved (mg/L as F)	Silica, dis-solved (mg/L as SiO ₂)	Arsenic dis-solved (ug/L as As)
AUG 1987										
10...	--	35.00	8.700	13.00	2.200	14.00	39.00	0.200	30.00	--
SEP										
22...	--	--	--	--	--	--	55.00	--	--	--
OCT										
13...	--	30.00	9.300	21.00	2.800	23.00	54.00	.300	2.000	1.000
14...	--	--	--	--	--	--	59.00	--	--	--
DEC										
14...	--	--	--	--	--	--	88.00	--	--	--
14...	--	40.00	12.00	24.00	3.000	30.00	76.00	.200	3.400	1.000
FEB 1988										
17...	--	37.00	8.600	9.500	2.600	13.00	41.00	.300	6.100	--
18...	--	--	--	--	--	--	56.00	--	--	--
APR										
13...	--	40.00	9.500	12.00	2.500	16.00	51.00	.200	5.000	1.000
14...	--	--	--	--	--	--	55.00	--	--	--
JUN										
13...	--	--	--	--	--	--	61.00	--	--	--
14...	--	--	--	--	--	--	--	--	--	--
14...	--	34.00	11.00	16.00	1.200	18.00	64.00	.300	1.000	1.000
JUL										
05...	4.600	--	--	--	--	--	--	--	--	--
AUG										
02...	1.900	--	--	--	--	--	56.00	--	--	--
08...	--	29.00	9.500	17.00	2.300	18.00	56.00	.200	.890	--

Date	Barium, dis-solved (µg/L as Ba)	Beryl-lium, dis-solved (µg/L as Be)	Cadmium dis-solved (µg/L as Cd)	Chro-mium, dis-solved (µg/L as Cr)	Cobalt, dis-solved (µg/L as Co)	Copper, dis-solved (µg/L as Cu)	Iron, dis-solved (µg/L as Fe)	Lead, dis-solved (µg/L as Pb)	Manga-nese, dis-solved (µg/L as Mn)	Molyb-denum, dis-solved (µg/L as Mo)
AUG 1987										
10...	--	--	--	--	--	--	--	--	--	--
SEP										
22...	--	--	--	--	--	--	30.00	--	--	--
OCT										
13...	40.00	<0.500	<1.000	<1.000	<3.000	3.000	91.00	18.00	3.000	<10.00
14...	--	--	--	--	--	--	20.00	--	--	--
DEC										
14...	--	--	--	--	--	--	40.00	--	--	--
14...	46.00	<.500	<1.000	2.000	<3.000	2.000	6.000	<5.000	6.000	<10.00
FEB 1988										
17...	--	--	--	--	--	--	--	--	--	--
18...	--	--	--	--	--	--	120.0	--	--	--
APR										
13...	38.00	.700	<1.000	<1.000	<3.000	6.000	33.00	<5.000	9.000	<10.00
14...	--	--	--	--	--	--	40.00	--	--	--
JUN										
13...	--	--	--	--	--	--	20.00	--	--	--
14...	--	--	--	--	--	--	--	--	--	--
14...	44.00	<.500	<1.000	2.000	<3.000	4.000	<3.000	<5.000	1.000	<10.00
JUL										
05...	--	--	--	--	--	--	--	--	--	--
AUG										
02...	--	--	--	--	--	--	<10.00	--	--	--
08...	--	--	--	--	--	--	--	--	--	--

Table 11.--Raw water-quality data for the Ohio River at Dam 53--Continued

Date	Nickel, dissolved (µg/L as Ni)	Silver, dissolved (µg/L as Ag)	Strontium, dissolved (µg/L as Sr)	Vanadium, dissolved (µg/L as V)	Zinc, dissolved (µg/L as Zn)	Aluminum, dissolved (µg/L as Al)	Lithium, dissolved (µg/L as Li)	Selenium, dissolved (µg/L as Se)	Fecal coliform, 24-HR mem. fil (Cols./100 mL)	Streptococci, fecal, KF Agar (Cols./100 mL)
AUG 1987										
10...	--	--	--	--	--	--	--	--	22.00	29.00
SEP 22...	--	--	--	--	--	--	--	--	--	--
OCT 13...	<1.000	<1.000	160.0	<6.000	15.00	10.00	10.00	<1.000	8.000	56.00
14...	--	--	--	--	--	--	--	--	--	--
DEC 14...	--	--	--	--	--	--	--	--	--	--
14...	3.000	<1.000	210.0	<6.000	6.000	<10.00	5.000	<1.000	93.00	75.00
FEB 1988										
17...	--	--	--	--	--	--	--	--	39.00	80.00
18...	--	--	--	--	--	--	--	--	--	--
APR 13...	2.000	<1.000	160.0	<6.000	5.000	30.00	6.000	<1.000	145.0	43.00
14...	--	--	--	--	--	--	--	--	--	--
JUN 13...	--	--	--	--	--	--	--	--	--	--
14...	--	--	--	--	--	--	--	--	--	--
14...	5.000	<1.000	170.0	<6.000	6.000	<10.00	8.000	<1.000	15.00	112.0
JUL 05...	--	--	--	--	--	--	--	--	--	--
AUG 02...	--	--	--	--	--	--	--	--	--	--
08...	--	--	--	--	--	--	--	--	9.500	38.00

Date	Alkalinity, wat dis tot it field (mg/L as CaCO ₃)	Solids, residue at 180 Deg C dissolved (mg/L)	Sed. susp., sieve diam. percent finer than 0.062 mm	Mercury, dissolved (µg/L as Hg)	Sediment, suspended (mg/L)	Specific conductance, lab (µS/cm)	Alkalinity, lab (mg/L as CaCO ₃)	Hydrogen sulfide (mg/L)
AUG 1987								
10...	--	157.0	52.00	--	22	291.0	79	ND
SEP 22...	--	--	--	--	--	--	--	ND
OCT 13...	70	185.0	89.00	--	18	336.0	70	--
14...	--	--	--	--	--	--	--	ND
DEC 14...	--	--	--	--	--	--	--	ND
14...	67	243.0	93.00	--	19	427.0	79	--
FEB 1988								
17...	58	175.0	81.05	--	162	303.0	78	--
18...	--	--	--	--	--	--	--	ND
APR 13...	69	196.0	86.38	<0.100	195	336.0	84	--
14...	--	--	--	--	--	--	--	ND
JUN 13...	--	--	--	--	--	--	--	ND
14...	--	--	48.28	--	6	--	--	--
14...	--	191.0	48.28	<.100	6	340.0	78	--
JUL 05...	--	--	--	--	--	--	--	--
AUG 02...	--	--	--	--	--	--	--	ND
08...	53	189.0	65.13	--	10	319.0	66	--

Table 12.--Summary of water-quality data at Dam 53, August 1987-August 1988

[N, number of observations]

Constituent	N	Minimum	Median	Maximum
Water temperature, in degrees C	8	3.10	21.10	30.50
Turbidity, in NTU	7	.70	5.20	80.00
Specific conductance, field, in $\mu\text{S}/\text{cm}$	8	282	321	428
pH, field, in standard units	7	7.25	7.33	7.40
Dissolved oxygen, in mg/L as O_2	7	6.01	8.50	12.50
Calcium, in mg/L as Ca	7	29.00	35.00	40.00
Magnesium, in mg/L as Mg	7	8.60	9.50	12.00
Sodium, in mg/L as Na	7	9.50	16.00	24.00
Potassium, in mg/L as K	7	.00	.30	.80
Alkalinity, in $\mu\text{eq}/\text{L}$ as CaCO_3	7	60.0	68.0	82.0
Sulfate, in mg/L as SO_4	7	39.00	56.00	88.00
Chloride, in mg/L as Cl	7	13.00	18.00	30.00
Fluoride, in mg/L as F	7	.20	.20	.30
Nitrogen, NO_2 , dissolved, in mg/L as ^2N	7	.01	.02	.10
Nitrogen, $\text{NO}_2 + \text{NO}_3$, dissolved, in mg/L as ^2N	7	.23	.37	1.90
Nitrogen, NH_4 , dissolved, in mg/L as ^3N	7	.03	.07	.18
Phosphorus, total, in mg/L as P	7	.03	.08	.47
Phosphorus, dissolved, in mg/L as P	7	.01	.05	.34
Phosphorus, ortho, dis., in mg/L as P	7	.01	.03	.06
Aluminum, in $\mu\text{g}/\text{L}$ as Al	4	10.00	10.00	30.00
Barium, in $\mu\text{g}/\text{L}$ as Ba	4	38.00	42.00	46.00
Copper, in $\mu\text{g}/\text{L}$ as Cu	4	2.00	3.50	6.00
Iron, in $\mu\text{g}/\text{L}$ as Fe	7	10.00	30.00	120.00
Lead, in $\mu\text{g}/\text{L}$ as Pb	4	5.00	5.00	18.00
Lithium, in $\mu\text{g}/\text{L}$ as Li	4	5.00	7.00	10.00
Manganese, in $\mu\text{g}/\text{L}$ as Mn	4	1.00	4.50	9.00
Nickel, in $\mu\text{g}/\text{L}$ as Ni	4	1.00	2.50	5.00
Strontium, in $\mu\text{g}/\text{L}$ as Sr	4	160.00	165.00	210.00
Zinc, in $\mu\text{g}/\text{L}$ as Zn	4	5.00	7.00	15.00
Total organic carbon, in mg/L as C	5	3.50	3.70	8.60
Total organic carbon, (bottom) in mg/L as C	2	1.70	2.30	2.90
Suspended sediment, in mg/L	6	6.00	20.61	195.00
Solids, residue at 180°C , dissolved, in mg/L	7	157.00	189.00	243.00

called for field measurements and determinations of concentrations of major ions and nutrients every other month, beginning in August 1987 and ending in August 1988. Dissolved-metal concentrations were determined once per quarter (October, December, April, and June). The range of observed field determinations for pH (7.25 to 7.40 units), specific conductance (282 to 428 $\mu\text{S}/\text{cm}$), and alkalinity (60 to 82 mg/L as CaCO_3) are not indicative of water-quality problems. With the exception of concentrations of dissolved iron, dissolved phosphorus, and dissolved nitrite plus nitrate nitrogen, most laboratory determinations were not highly variable. Highest concentrations of dissolved iron (120 $\mu\text{g}/\text{L}$), dissolved phosphorus (0.34 mg/L), and dissolved nitrite plus nitrate nitrogen (1.9 mg/L as N) were observed during high streamflow conditions in February and April. Dissolved-iron concentrations were particularly variable, with large differences between samples collected on the same day. Some of the short-term variability can be explained by sampling location. Samples collected as part of NASQAN were collected in a cross section approximately 0.25 mi upstream from the lock and dam, whereas the supplemental samples used to compare with samples at Dam 52 were collected adjacent to the lock and dam. Sulfate concentration ranged from 39 to 88 mg/L and total organic carbon ranged from 3.5 to 8.6 mg/L.

Field measurements of temperature, specific conductance, pH, dissolved-oxygen concentration, and oxidation/reduction potential (ORP) were determined as a function of depth across the face of each dam during each scheduled sampling. These profiles revealed only slight water-quality stratification, even during low-flow periods. Streamflow conditions on the Ohio River at Metropolis, Illinois (station number 03611500), for the period of study are shown in figure 8. Water-quality determinations made on August 2, 1988, were made under extreme low-flow conditions. The daily mean discharge for the Ohio River at Metropolis, Illinois on that date was 28,400 ft^3/s or about 3,000 less than the 7-day, 10-year low flow at this station. Water-quality profiles during various times of the year are presented in figures 9 to 16. Although generally lower near the stream bottom, the minimum observed dissolved-oxygen concentration (5.8 mg/L) and oxidation/reduction potential (+90 mV) was indicative of oxidative conditions throughout the year. The positive ORP values observed also indicate that conditions favorable for enhanced sulfate-reducing bacteria activity (ORP less than zero) did not exist in the water column during sampling (Grant and Long, 1981). These unfavorable conditions for sulfate-reducing bacteria are substantiated by field determinations of hydrogen sulfide, a metabolic by-product and indicator of anaerobic sulfate reduction. Hydrogen sulfide was not detected in any sample collected during the study.

Quality at Dam 52

Water-quality data collected at Dam 52 are listed in table 13. For comparative purposes, water-quality properties and constituents determined at Dam 52 included only concentrations of dissolved sulfate, total organic carbon, dissolved iron, and hydrogen sulfide. The ranges of observed concentrations of dissolved sulfate (51 to 91 mg/L), TOC (3.8 to 9.2 mg/L), and dissolved iron (20 to 90 $\mu\text{g}/\text{L}$) are smaller than at Dam 53. As at Dam 53,

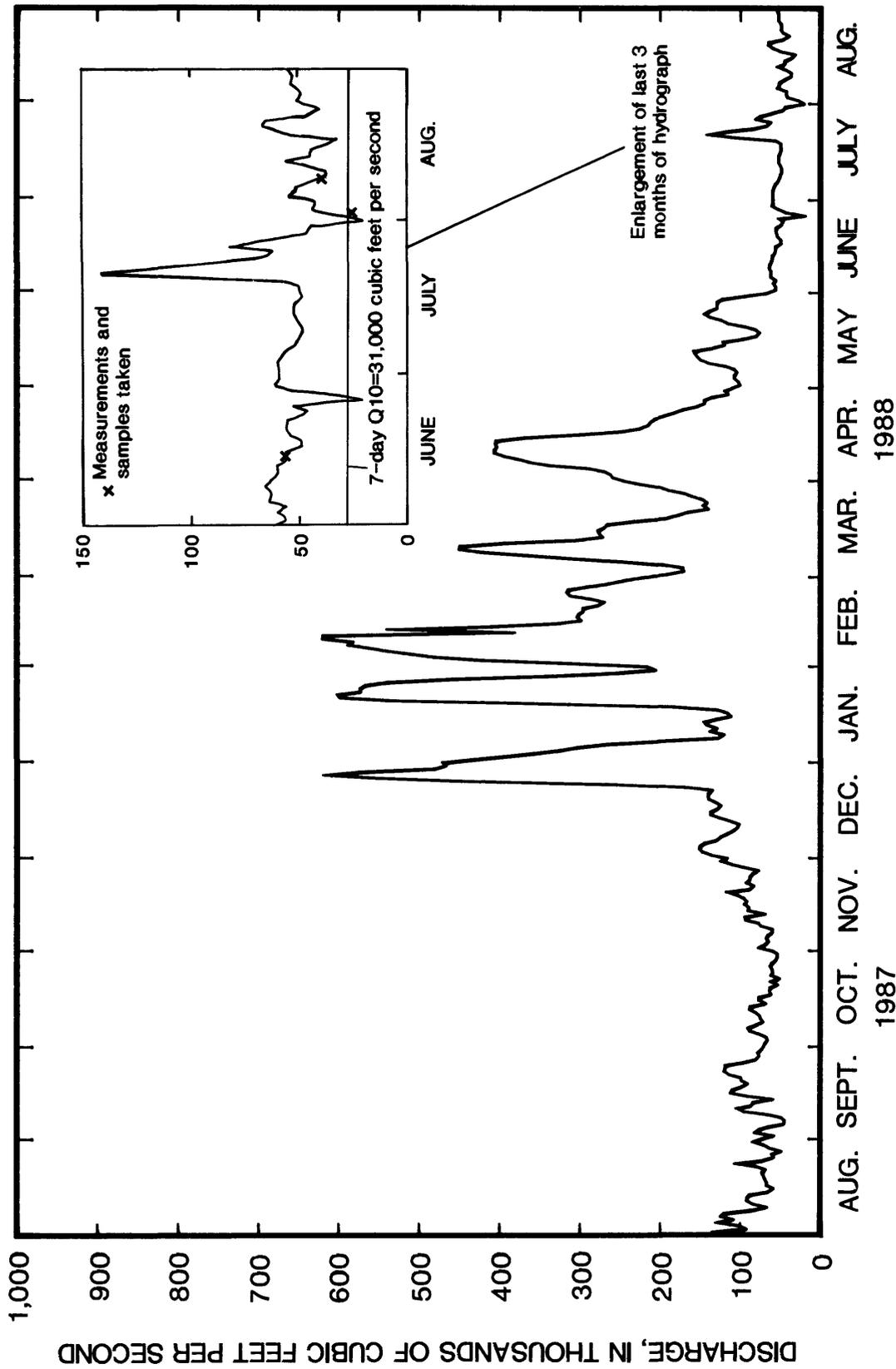


Figure 8.--Hydrograph of the Ohio River at Metropolis, Illinois during the study period. (7-day Q10 is the discharge at 10-year recurrence intervals taken from a frequency curve of annual values of the lowest mean discharge for 7 consecutive days.)

Table 13.--Raw water-quality data for the Ohio River at Dam 52

[°C, degrees Celsius; mm of Hg, millimeters of mercury; μ S/cm, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligram per liter; wat wh tot fet, water whole total fixed endpoint titration; tot in bot mat, total in bottom material; g/kg, gram per kilogram; μ g/L, microgram per liter; ND, not detected; --, determination not performed]

Date	Time	Temperature, water (°C)	Barometric pressure (mm Hg)	Specific conductance (μ S/cm)	Oxygen, dissolved (mg/L)
SEP 1987					
22...	0915	--	--	--	--
OCT					
14...	0900	--	--	--	--
DEC					
14...	1520	--	--	--	--
FEB 1988					
18...	1200	--	--	--	--
APR					
14...	1200	--	--	--	--
JUN					
13...	0915	--	--	--	--
JUL					
05...	1430	--	--	--	--
05...	1430	--	--	--	--
AUG					
02...	1205	29.70	758.0	350.0	7.000

Date	pH (standard units)	Alkalinity wat wh tot fet (mg/L as CaCO ₃)	Carbon, organic total (mg/L as C)	Carbon, inorganic, tot in bot mat (g/kg as C)	Carbon, inorg + organic tot in bot mat (mg/kg as C)	Sulfate dissolved (mg/L as SO ₄)	Iron, dissolved (μg/L as Fe)	Hydrogen sulfide (mg/L)
SEP 1987								
22...	--	--	4.900	--	--	66.00	40.00	ND
OCT								
14...	--	--	5.300	--	--	79.00	30.00	ND
DEC								
14...	--	--	4.900	--	--	91.00	50.00	ND
FEB 1988								
18...	--	--	--	--	--	58.00	90.00	ND
APR								
14...	--	--	9.200	--	--	51.00	40.00	ND
JUN								
13...	--	--	3.800	--	--	74.00	20.00	ND
JUL								
05...	--	--	--	--	--	--	--	--
05...	--	--	--	3.800	4.600	--	--	--
AUG								
02...	6.860	73.00	4.900	1.200	3.900	52.00	60.00	ND

hydrogen sulfide was not detected. A bottom material sample collected during low-flow conditions had a TOC concentration of 0.8 mg/kg.

As performed at Dam 53, field properties and constituents were measured at selected depths across the face of the dam during each scheduled sampling. Results of the water-quality profiles performed at Dam 52 are shown in figures 9 to 16. The minimum observed dissolved-oxygen concentration (4.7 mg/L) and ORP (0.127 volts) were measured outside the main river channel during periods of low-flow (June and August, respectively). Specific-conductance profiles indicate incomplete mixing of Cumberland and Tennessee River water, particularly at Dam 52. As seen in figures 9 and 10, specific-conductance values are typically lower near the left bank of river, reflecting the input of these two tributaries.

Comparison of Statistical Measures of Water Quality

Several data comparisons were made to evaluate the water-quality conditions at Dam 53 during this study. Statistical summaries (maximum, minimum, median, and mean) of the data collected at Dam 53 were compared to (1) data collected at Dam 52 during the study period, (2) historical data collected at Dam 53 from October 1974 until August 1986, and (3) appropriate State and Federal water-quality criteria.

Nonparametric statistical procedures were used to test for differences in water quality between Dam 53 and Dam 52. The Wilcoxon-Mann-Whitney Rank Sum test is a two sample t-test on ranked transformed data. The procedure does not require the assumption that the data are normally distributed and is not sensitive to the assumption of equal variances (Iman and Conover, 1983). This procedure evaluates the null hypothesis (H_0) that the mean of one set of data is equal to the mean of another set of data ($\mu_x = \mu_y$). Ranks were assigned to the two data sets jointly, using average ranks^x in the case of ties. A t-test procedure (SAS Institute, Inc., 1988) was then used to test the null hypothesis at a significance level of 0.05. Where appropriate, a paired t-test was used.

Comparison of Water-Quality at Dam 53 and at Dam 52

Water-quality information collected at Dam 53 is compared to that of Dam 52 in table 14. Results of the paired, Wilcoxon-Mann-Whitney Rank Sum test, used to indicate differences in sample means, are shown in table 15. If the difference between constituent values at Dams 52 and 53 is significant, the null hypothesis is rejected (reflected by a p-level of less than or equal to 0.1). Alternatively, if no significant differences can be determined, the null hypothesis is accepted (p-level greater than 0.1). The number of observations (N), the mean, and the standard deviation for each set of samples are also listed in table 15. Although mean concentrations of total organic carbon, dissolved sulfate, and dissolved iron appear to be slightly lower at Dam 53, there is no statistical difference between the water-quality data collected at each dam during the study period. Hydrogen sulfide was not

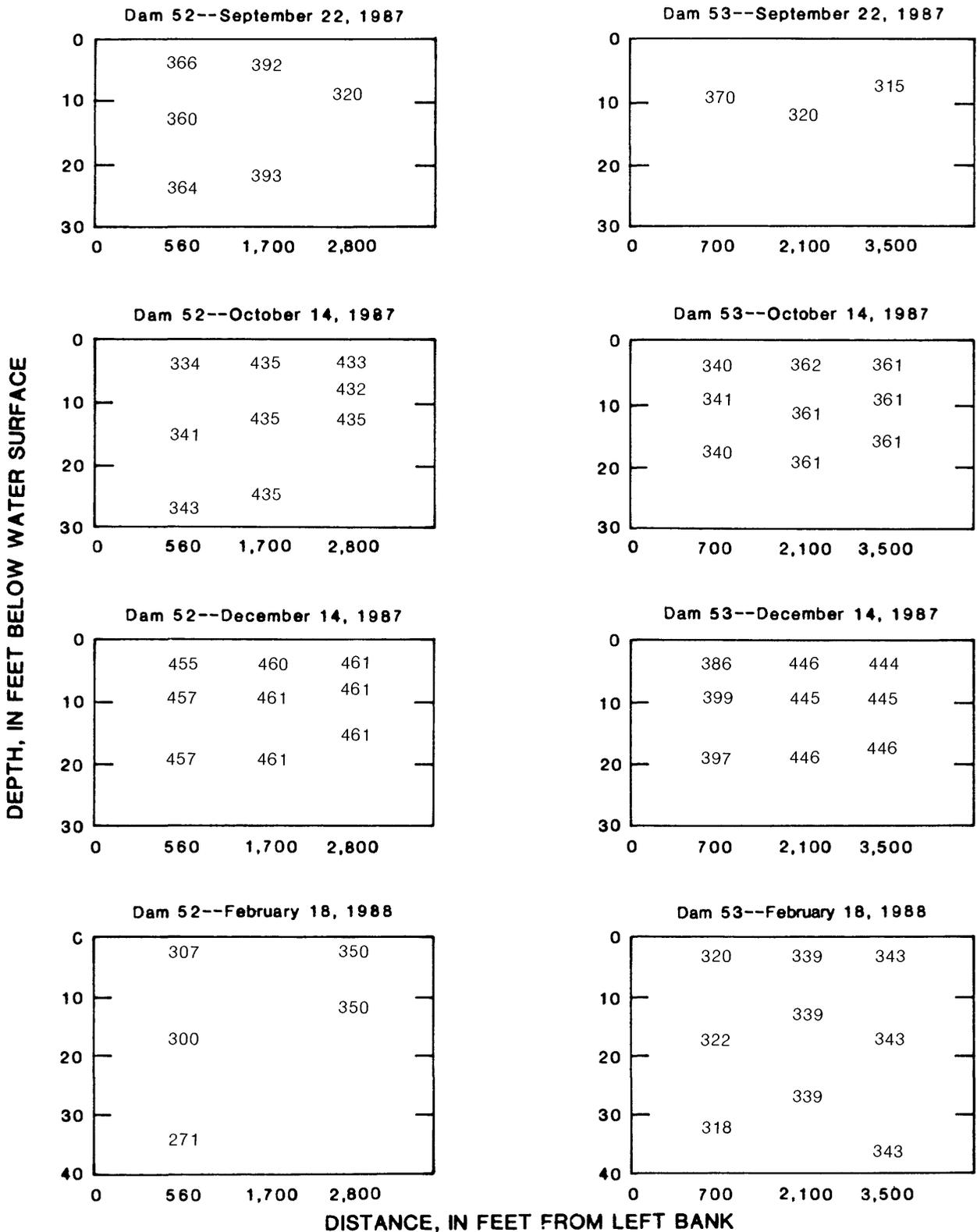


Figure 9.--Specific conductance at various points in the Ohio River at Dams 52 and 53, September 1987–February 1988. (Values are microsiemens per centimeter at 25 degrees celsius.)

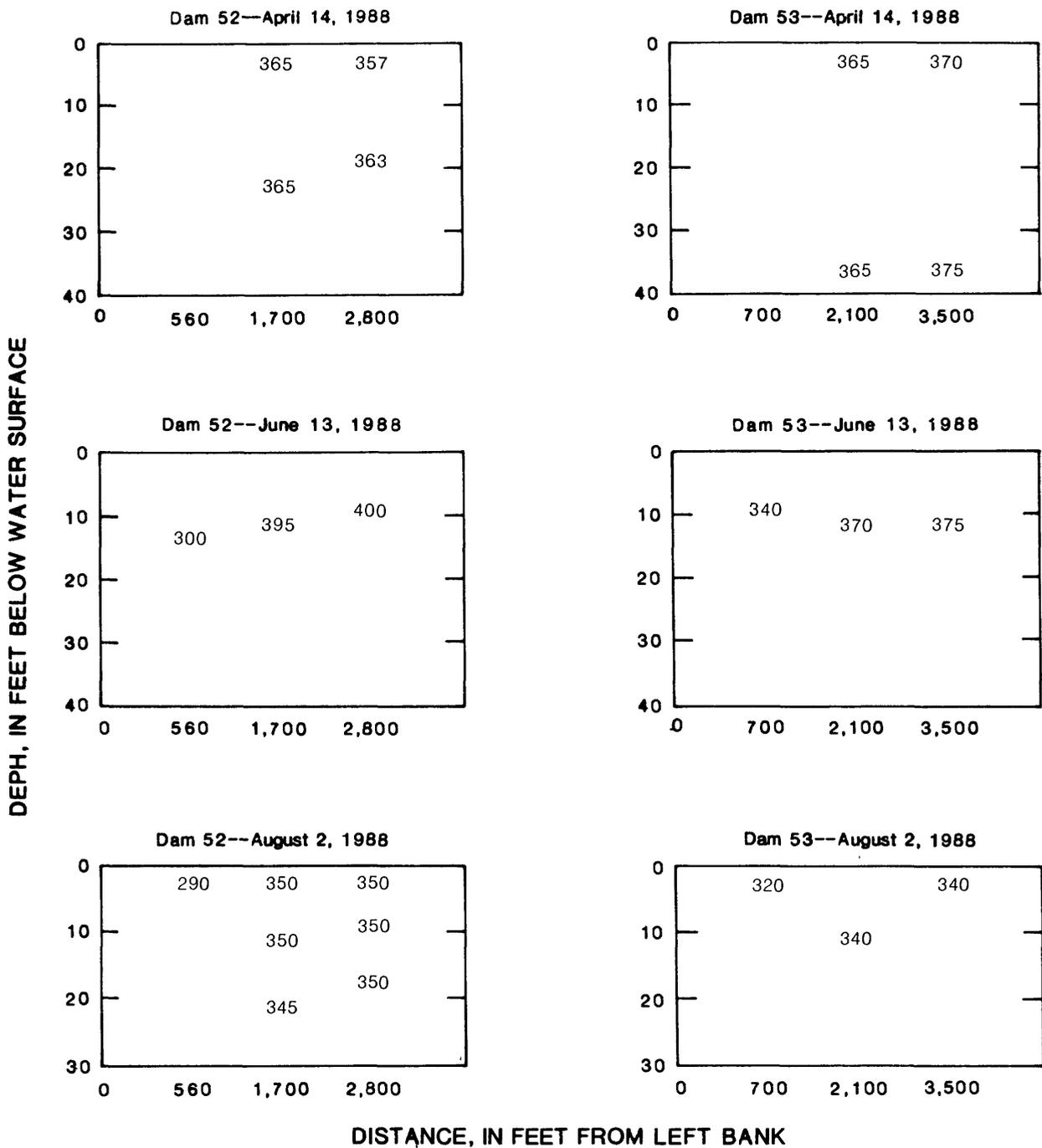


Figure 10.--Specific conductance at various points in the Ohio River at Dams 52 and 53, April–August 1988. (Values are microsiemens per centimeter at 25 degrees celsius.)

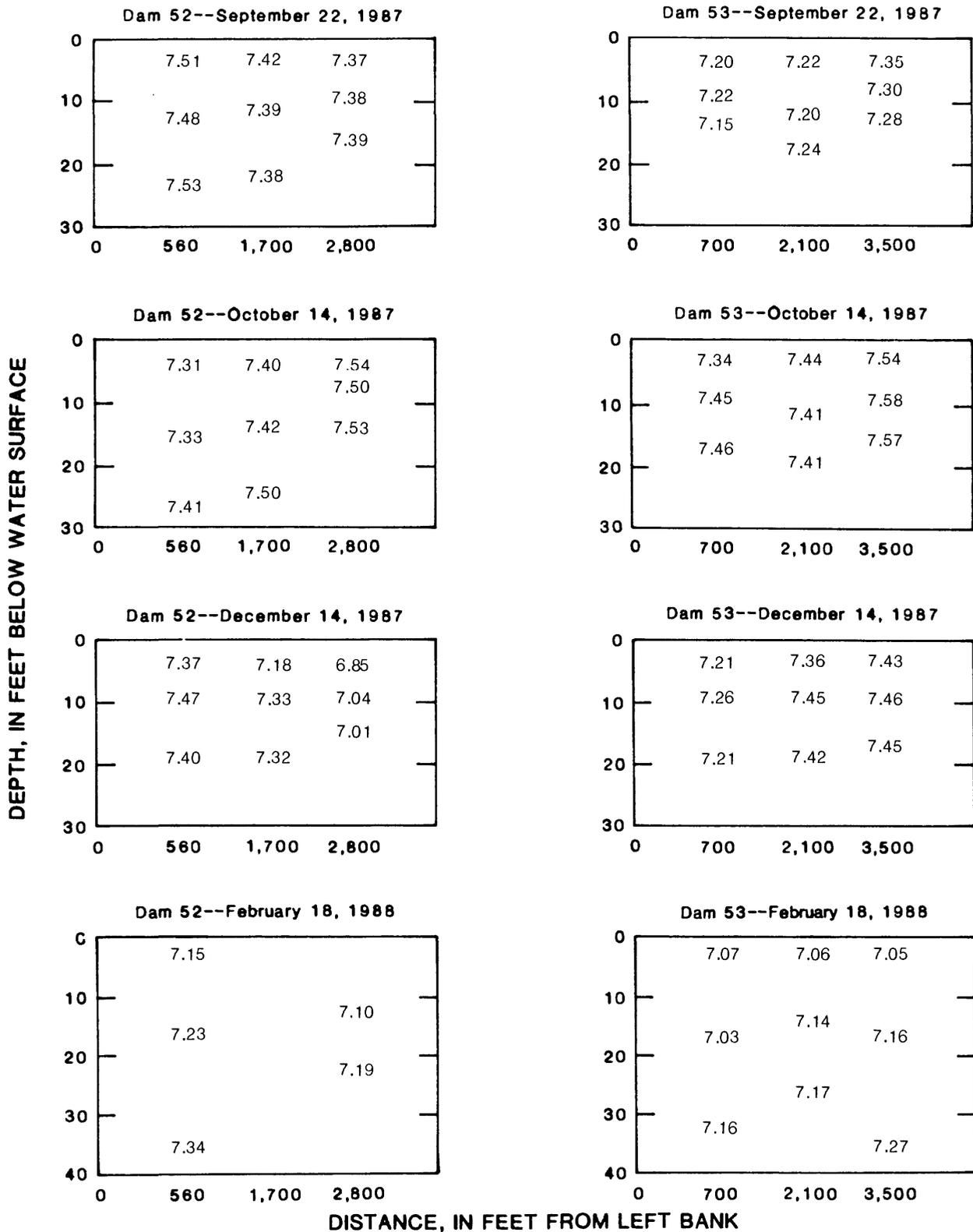


Figure 11.--pH at various points in the Ohio River at Dams 52 and 53, September 1987-February 1988. (Values are standard pH units.)

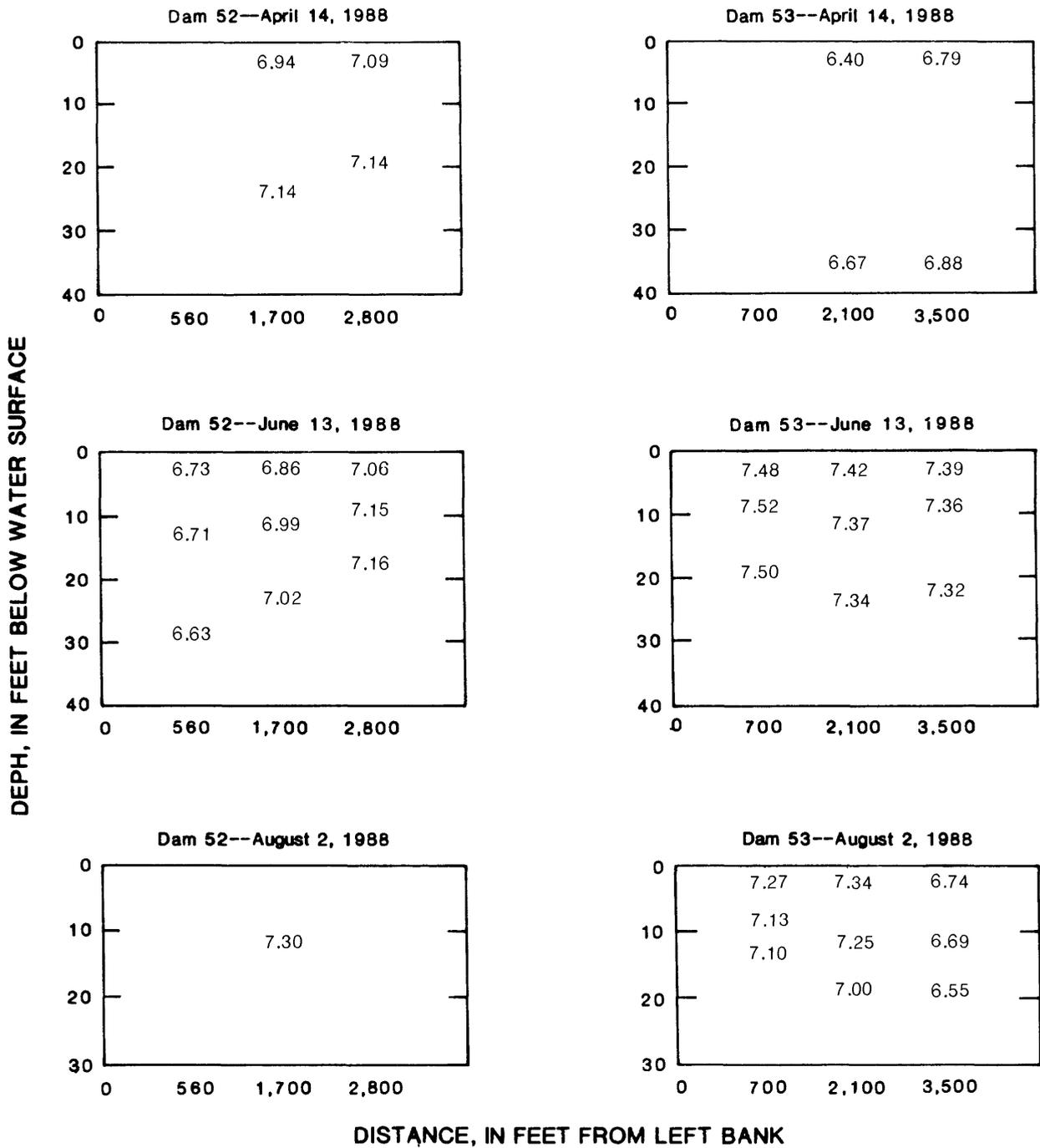


Figure 12.--pH at various points in the Ohio River at Dams 52 and 53, April-August 1988. (Values are standard pH units.)

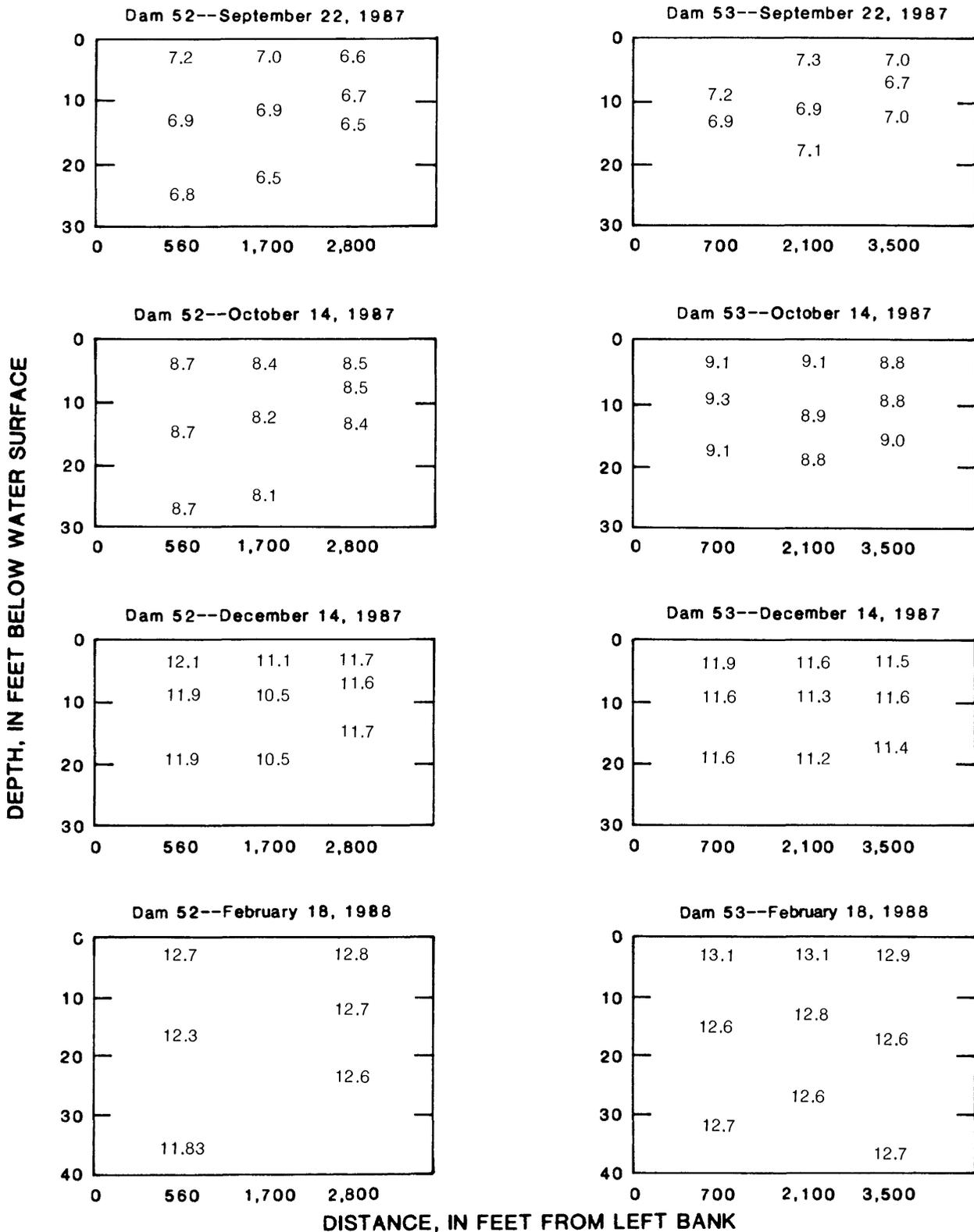


Figure 13.--Dissolved oxygen concentration at various points in the Ohio River at Dams 52 and 53, September 1987–February 1988. (Values are milligram per liter.)

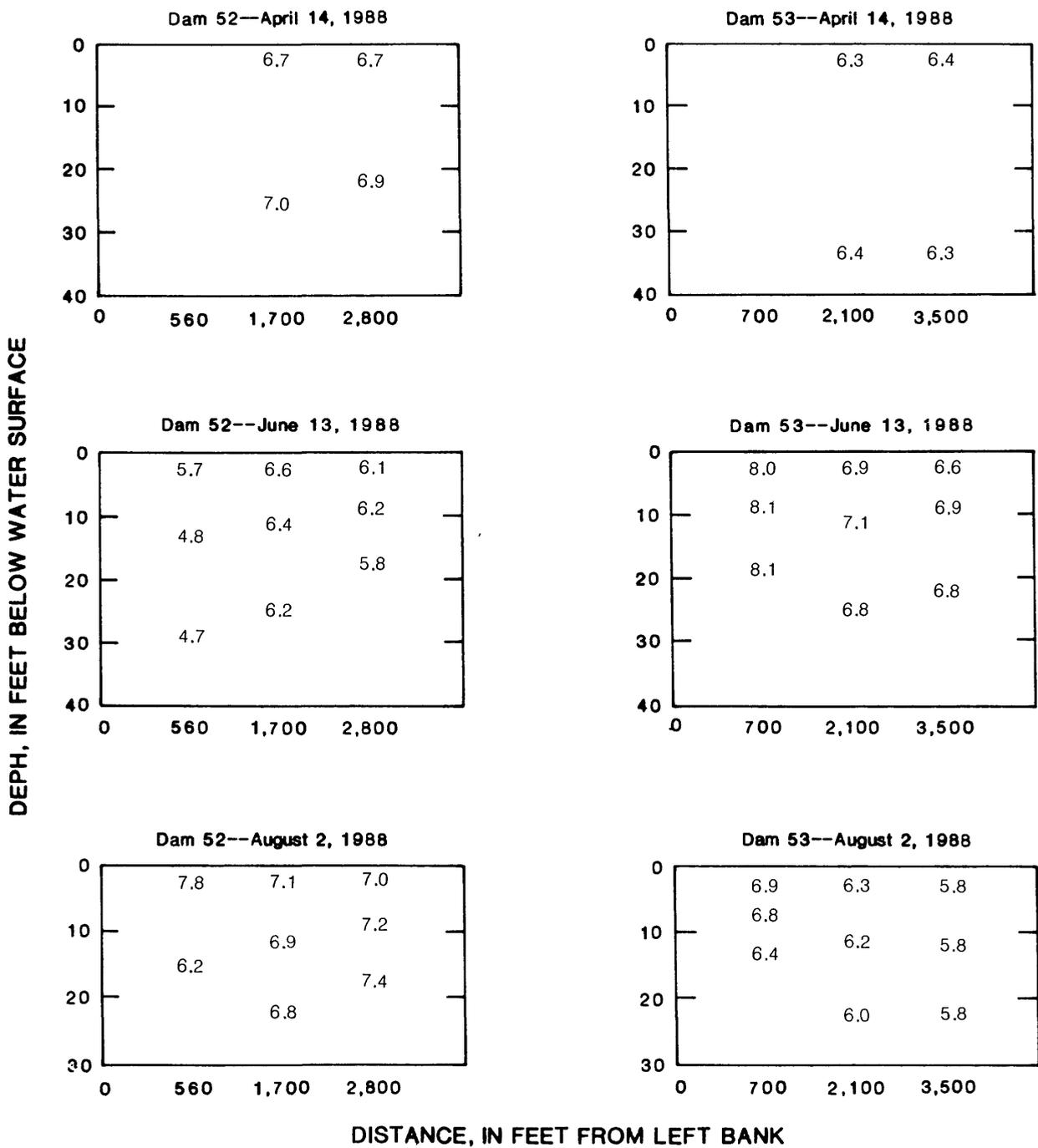


Figure 14.--Dissolved oxygen concentration at various points in the Ohio River at Dams 52 and 53, April–August 1988. (Values are milligram per liter.)

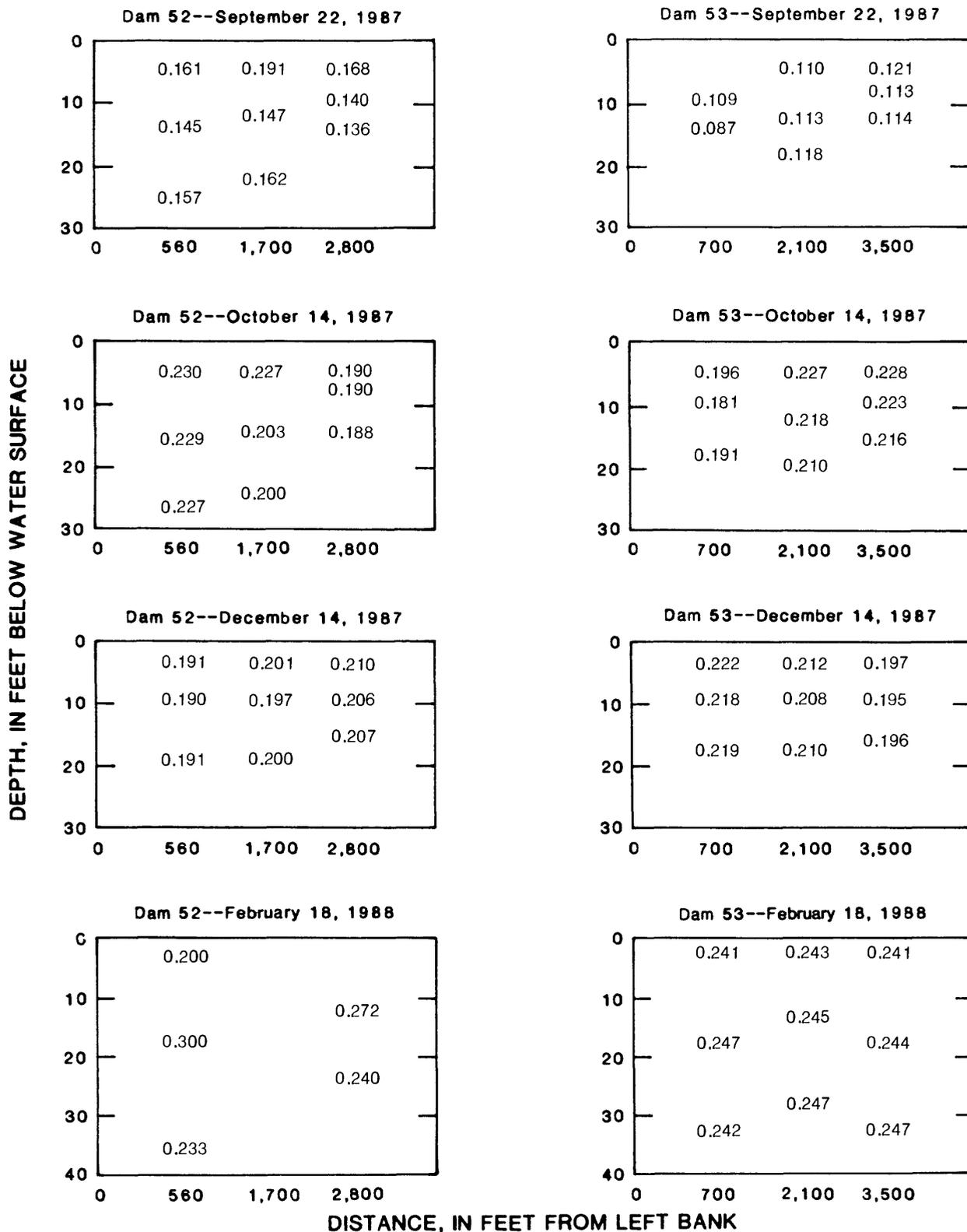


Figure 15.--Oxidation/reduction potential at various points in the Ohio River at Dams 52 and 53, September 1987-February 1988. (Values are volts.)

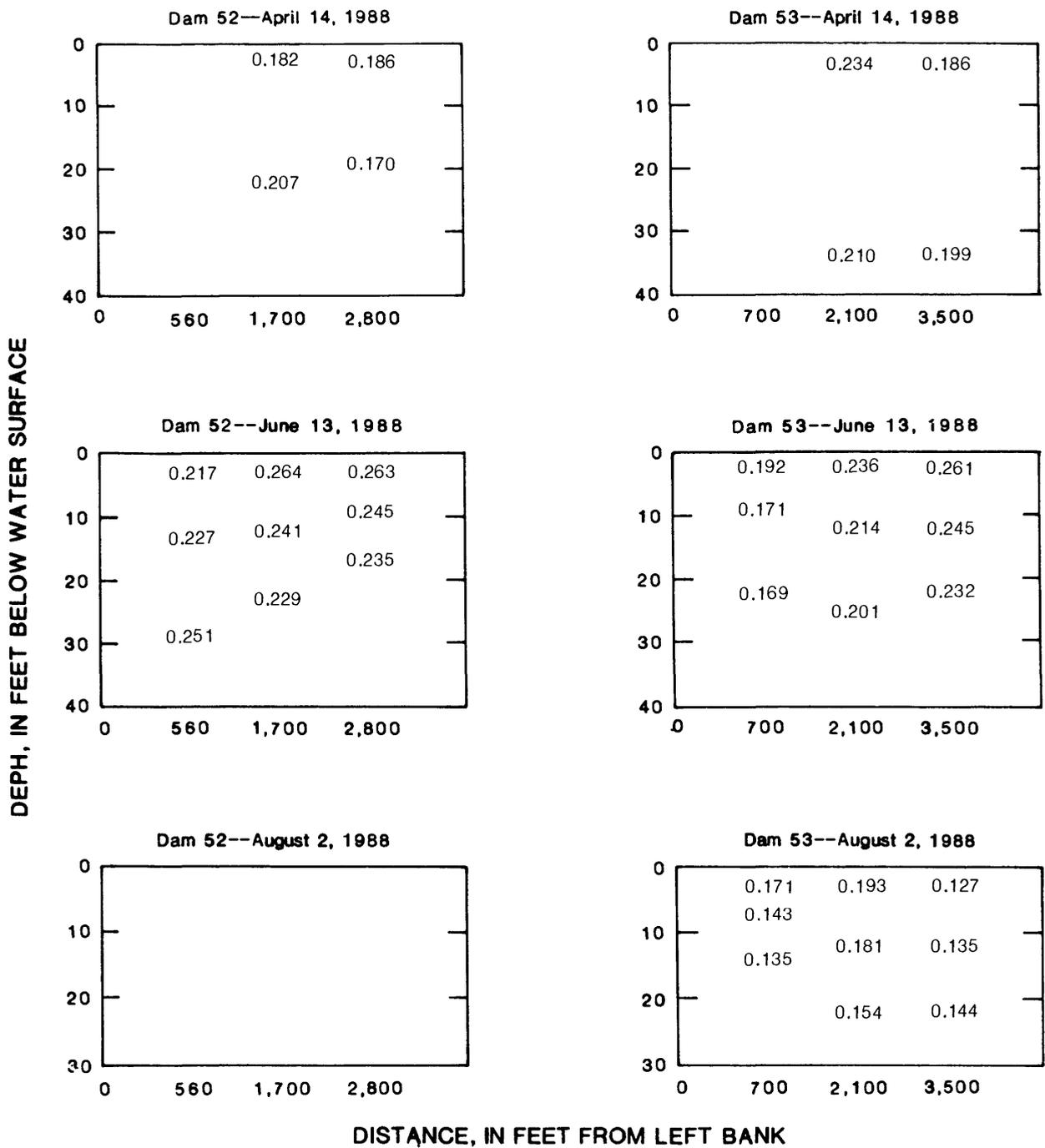


Figure 16.--Oxidation/reduction potential at various points in the Ohio River at Dams 52 and 53, April–August 1988. (Values are volts.)

detected at either location. The concentration of total organic carbon in bottom material was higher at Dam 53. However, data were not sufficient for a statistical comparison.

Table 14.--Summary of water-quality data at Dams 52 and 53, August 1987-August 1988

[N, number of observations; mg/L, milligram per liter; $\mu\text{g/L}$, micrograms per liter]

Constituent	Station	N	Minimum	Median	Maximum
Sulfate, in mg/L as SO_4	Dam 52	7	51.0	66.0	91.0
	Dam 53	7	39.0	56.0	88.0
Iron, dissolved, in $\mu\text{g/L}$ as Fe	Dam 52	7	20.0	40.0	90.0
	Dam 53	7	10.0	30.0	120.0
Total organic carbon, in mg/L as C	Dam 52	6	3.80	4.90	9.20
	Dam 53	5	3.50	3.70	8.60

Table 15.--Statistical comparison of water-quality data at Dams 52 and 53 (nonparametric Wilcoxon-Mann-Whitney Rank Sum Test, $\alpha = 0.05$)

[N, number of observations; P-value, probability, $H_0: \bar{X}_{53} = \bar{X}_{52}$, the null hypothesis that the mean at Dam 53 is equal to the mean at Dam 52; mg/L, milligram per liter; $\mu\text{g/L}$, microgram per liter]

Constituent	Station	N	Mean	Standard deviation	P-value	$H_0: \bar{X}_{53} = \bar{X}_{52}$
Sulfate, in mg/L as SO_4	Dam 52	7	67.28	14.90	0.64	Accept
	Dam 53	7	59.00	13.71		
Iron, in $\mu\text{g/L}$ as Fe	Dam 52	7	47.14	22.89	.68	Accept
	Dam 53	7	39.00	37.06		
Total organic carbon, in mg/L as C	Dam 52	6	5.50	1.88	1.00	Accept
	Dam 53	5	4.92	2.17		

Comparison of Water-Quality at Dam 53 to Historical Water-Quality

Water-quality data collected at Dam 53 during this study were compared to historical data collected at this site during 1973-87. Selected data for both periods are summarized in table 16. With the exception of dissolved-sulfate concentration, current data describing water-quality properties and constituent concentrations fall within the range of historical data. The dissolved sulfate concentration of 88 mg/L measured during this study is the highest sulfate concentration reported by the U.S. Geological Survey in the Ohio River at Dam 53 since 1973. Previously, the highest dissolved sulfate concentration measured was 75 mg/L in November 1981. In fact, 12 of the 14 samples collected during this study had dissolved sulfate concentrations greater than the historical median (45 mg/L). The large number of samples containing relatively high dissolved-sulfate concentrations is most likely attributable to the relatively low streamflow conditions when samples were collected. Streamflow was less than the historical mean of 271,600 ft³/s at 5 of the 7 independent sampling dates during this study period (August, October and December 1987; June and August 1988) (Toms and others, 1987). On the date that the highest dissolved sulfate concentration was measured (December 14, 1987), streamflow at Metropolis was 165,000 ft³/s.

Many dissolved constituents, including sulfate, are inversely related to streamflow. The relation between streamflow and dissolved-sulfate concentration, based on historical data, is illustrated in figure 17. Although variability is evident, the inverse relation shown by the regression line is readily apparent. High dissolved sulfate concentrations are generally associated with low streamflows. Residuals analysis--that is, the difference between actual determinations and predicted values (linear regression line)--indicates that six of seven independent sulfate concentrations determined were larger than predicted by the historical concentration-streamflow relation. Actual sulfate concentrations were almost 15 percent larger than predicted concentrations. Other dissolved constituents were similarly related to streamflow. Specific conductance, an indicator of the concentration of dissolved constituents, exceeded the historical median value in six of the seven independent determinations made during this study. However, all values were well within the historical range. Thus, the relatively high concentrations of dissolved sulfate and other dissolved constituents observed during the study period may be attributed to low streamflow. As noted earlier, no statistically significant trends in water-quality properties or constituents were detected in the historical data (1977-87).

Comparison of Water-Quality at Dam 53 to State Water-Quality Criteria

The State of Kentucky (Cabinet for Natural Resources and Environmental Protection, Division of Water) classifies streams for all legitimate uses. Water-quality criteria are then assigned to a particular stream on the basis of its use classification. The use classifications assigned to the Ohio River are for warmwater aquatic habitat, primary contact recreation, secondary-contact recreation, and domestic water supply (Kentucky Natural Resources and

Table 16.--Statistical comparison of current water-quality data at Dam 53 to historical data, 1973-87

[N, number of observations; $\mu\text{S}/\text{cm}$, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligram per liter; $\mu\text{g}/\text{L}$, microgram per liter; <, less than]

Constituent	Data set	N	Minimum	Median	Maximum
Specific conductance, field, in $\mu\text{S}/\text{cm}$	Current	8	282	321	428
	Historical	143	190	300	500
pH, field, in standard units	Current	7	7.2	7.3	7.4
	Historical	134	6.1	7.5	8.8
Dissolved Oxygen, in mg/L as O_2	Current	7	6.0	8.5	12.5
	Historical	57	5.3	9.1	14.8
Alkalinity, in mg/L as CaCO_3	Current	7	60	68	82
	Historical	77	51	74	120
Sulfate, in mg/L as SO_4	Current	14	39	56	88
	Historical	107	26	45	75
Iron, dissolved in $\mu\text{g}/\text{L}$ as Fe	Current	11	3.0	30	120
	Historical	60	<3.0	20	1,200
Total organic carbon, in mg/L as C	Current	5	3.5	3.7	8.6
	Historical	52	0	4.9	9.3
Suspended sediment, in mg/L	Current	6	6.0	21	195
	Historical	130	6.0	82	485

Environmental Protection Cabinet, 1987). Special water-quality criteria have been established for the main stream of the Ohio River. Water-quality criteria that pertain to determinations made during this study are listed in table 17. No water-quality determination made during this study (1987-88) exceeded any of the appropriate criteria.

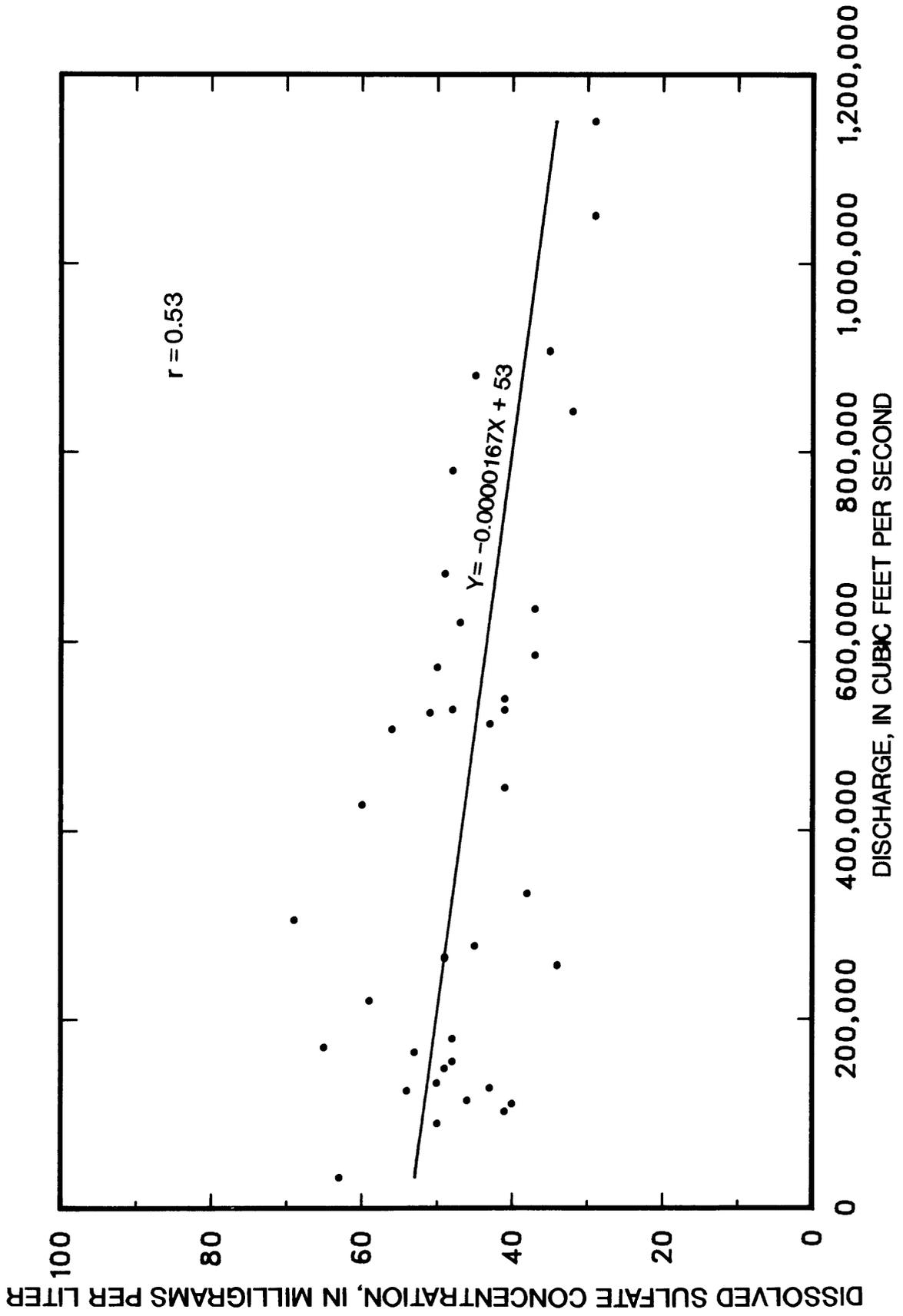


Figure 17.--Relation of dissolved sulfate to discharge for the Ohio River at Dam 53.

Table 17.--Comparison of water-quality data from the Ohio River at Dam 53 to Kentucky water-quality criteria

[mg/L, milligram per liter; -, criterion not established;
<, less than; min-max, minimum and maximum]

Constituent	Warmwater aquatic habitat criteria	Domestic water supply criteria	Ohio River criteria	Dam 53	
				observed min-max	samples exceeding criteria
Temperature, degrees Celsius	31.7	-	31.7	3.1 - 30.5	0
pH, standard units	6.0-9.0	-	-	7.25 - 7.40	0
Oxygen, dissolved, mg/L as O ₂	<4	-	<4	6.01 - 12.5	0
Sulfate, dissolved, mg/L as SO ₄	-	250	-	39 - 88	0
Chloride, dissolved, mg/L as Cl	600	250	-	13 - 30	0
Fluoride, dissolved, mg/L as F	-	1.0	-	.2 - .3	0
Total dissolved solids, mg/L	-	750	750	157 - 243	0
Nitrogen, NO ₂ , dissolved, mg/L as N	-	-	1.0	.01 - .1	0
Nitrogen, NO ₃ + NO ₂ , dissolved, mg/L as N	-	-	10	.23 - 1.9	0
Lead, dissolved, mg/L as Pb	-	-	.055	.005 - .018	0

QUALITY OF ATMOSPHERIC DEPOSITION

Wetfall

The quality of atmospheric wetfall, as determined during this study at Dams 52 and 53, is summarized in table 18. Weekly composites of wetfall were analyzed for pH, specific conductance, and major-ion concentrations. Although data variability is generally high, median values for most properties and constituents are similar at each of the study sites (Dams 53 and 52). At Dam 53, field pH ranged from 3.36 units to 6.79 units, with the median being 4.43.

Table 18.--Summary of atmospheric wetfall data at Dams 52 and 53, 1987-88

[N, number of observations; P5, fifth percentile; P95, ninety-fifth percentile; $\mu\text{S/cm}$, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligram per liter; mL, milliliter]

Constituent	Station	N	Minimum	P5	Median	P95	Maximum
Specific conductance, field, in $\mu\text{S/cm}$	Dam 52	30	12.0	12.0	22.0	51.0	58.0
	Dam 53	30	11.3	12.0	20.5	56.0	72.0
Specific conductance, lab, in $\mu\text{S/cm}$	Dam 52	31	10.0	10.0	21.0	63.0	69.0
	Dam 53	32	12.0	13.0	22.5	62.0	108
pH, field, in standard units	Dam 52	30	3.58	3.83	4.56	6.43	7.02
	Dam 53	31	3.36	3.68	4.43	5.94	6.79
pH, lab, in standard units	Dam 52	32	4.09	4.11	4.66	6.16	6.76
	Dam 53	32	3.76	4.11	4.54	5.72	5.85
Calcium, in mg/L as Ca	Dam 52	32	.04	.08	.30	1.34	5.40
	Dam 53	33	.06	.08	.29	1.90	2.20
Magnesium, in mg/L as Mg	Dam 52	32	.01	.01	.10	.16	.27
	Dam 53	32	.01	.02	.10	.18	.30
Sodium, in mg/L as Na	Dam 52	32	.01	.02	.18	.41	2.50
	Dam 53	33	.01	.01	.17	.55	.57
Potassium, in mg/L as K	Dam 52	32	.01	.02	.14	1.30	2.20
	Dam 53	33	.02	.03	.15	1.36	2.00
Alkalinity, in mg/L as CaCO_3	Dam 52	4	15.4	15.4	64.1	413.0	413.0
	Dam 53	3	24.9	24.9	41.1	99.8	99.8
Sulfate, in mg/L as SO_4	Dam 52	32	.80	.80	2.20	4.90	5.80
	Dam 53	33	1.00	1.20	2.10	11.0	11.0
Chloride, in mg/L as Cl	Dam 52	32	.04	.09	.42	1.78	2.60
	Dam 53	33	.10	.12	.52	2.00	2.50
Fluoride, in mg/L as F	Dam 52	32	.01	.01	.03	.19	.32
	Dam 53	33	.01	.01	.03	.21	.35
Nitrogen, NO_3 , dissolved, in mg/L as N	Dam 52	32	.07	.08	.27	1.07	1.64
	Dam 53	33	.10	.12	.26	1.41	1.51
Nitrogen, NH_4 , dissolved, in mg/L as N	Dam 52	32	.01	.02	.32	1.51	5.15
	Dam 53	33	.04	.05	.32	1.39	1.59
Phosphorus, ortho, dis., in mg/L as P	Dam 52	32	.01	.01	.01	.10	.52
	Dam 53	33	.01	.01	.01	.05	.12
Sample size, in mL	Dam 52	32	50.0	55.0	790	6,950	9,100
	Dam 53	33	70.0	155	970	4,300	8,800

Natural rainfall, forming and falling through the atmosphere, has a pH of about 5.6 units on the basis of its equilibrium with gaseous carbon dioxide. The seasonal pattern of wetfall pH, as observed in this study, is shown in figure 18. Generally, pH varied seasonally; the lowest values were observed during October-March. Field-determined specific conductance, an indicator of concentrations of dissolved ionic constituents, ranged from 11.3 to 72 $\mu\text{S}/\text{cm}$ at Dam 53. Median wetfall specific conductance was 20.5 $\mu\text{S}/\text{cm}$. Sulfate and nitrate concentrations in wetfall are indicators of sulfur dioxide (SO_2) and nitrous oxides (NO_x), respectively--two well-documented atmospheric pollutants. Wetfall sulfate concentrations ranged from 1.0 to 11.0 mg/L at Dam 53. Median sulfate concentration was only 2.1 mg/L. Observed nitrate nitrogen concentrations ranged from 0.1 to 1.51 mg/L at Dam 53. Nitrate and sulfate concentrations do not appear to vary seasonally (figure 19).

Dryfall

Comparatively, constituent concentrations in dryfall are much higher than in wetfall. This difference is due, in part, to the long collection period (8 weeks for dryfall compared to 1 week for wetfall) and to the relatively small volume of distilled water (100 mL) added to dryfall to create an aqueous sample. Dryfall data collected at Dams 52 and 53 during this study are summarized in table 19. Indicative of high concentrations of dissolved constituents, field specific conductance values in dryfall samples collected at Dam 53 ranged from 235 to 1,256 $\mu\text{S}/\text{cm}$. The maximum values were observed in the spring (late March to late May), possibly reflecting increased pollen counts during that time of year. Dryfall pH (field) ranged from 5.03 to 6.85 (9.3×10^{-4} to 1.4×10^{-3} mg hydrogen ion on a dry weight basis) at Dam 53 and was similar to the pH values observed at Dam 52. Median dry weight masses of sulfate (5.2 mg), chloride (0.49 mg), and nitrate (0.82 mg) collected as dryfall samples were lower at Dam 53 than at Dam 52, possibly a result of the transport of local atmospheric emissions to the north and east by prevailing winds. As discussed earlier, the presence of dissolved constituents may accelerate corrosion processes.

Fog

The location of the study area on the Ohio River ensures high atmospheric moisture conditions and the periodic formation of fog. During the study period, the collection of atmospheric moisture and fog was successful, except for periods of extreme cold weather during December-February. Water-quality data for weekly-composited fog samples (composites) collected weekly are summarized in table 20. As indicated by the median field specific-conductance value at Dam 53 (24 $\mu\text{S}/\text{cm}$), fog samples were similar to wetfall samples in total dissolved ionic species composition. Median fog pH (field) at Dam 53 (5.2 units) was significantly higher than median wetfall pH. Median values for sulfate (2.7 mg/L), nitrate (0.54 mg/L), and ammonia (0.84 mg/L) were slightly higher than median wetfall values.

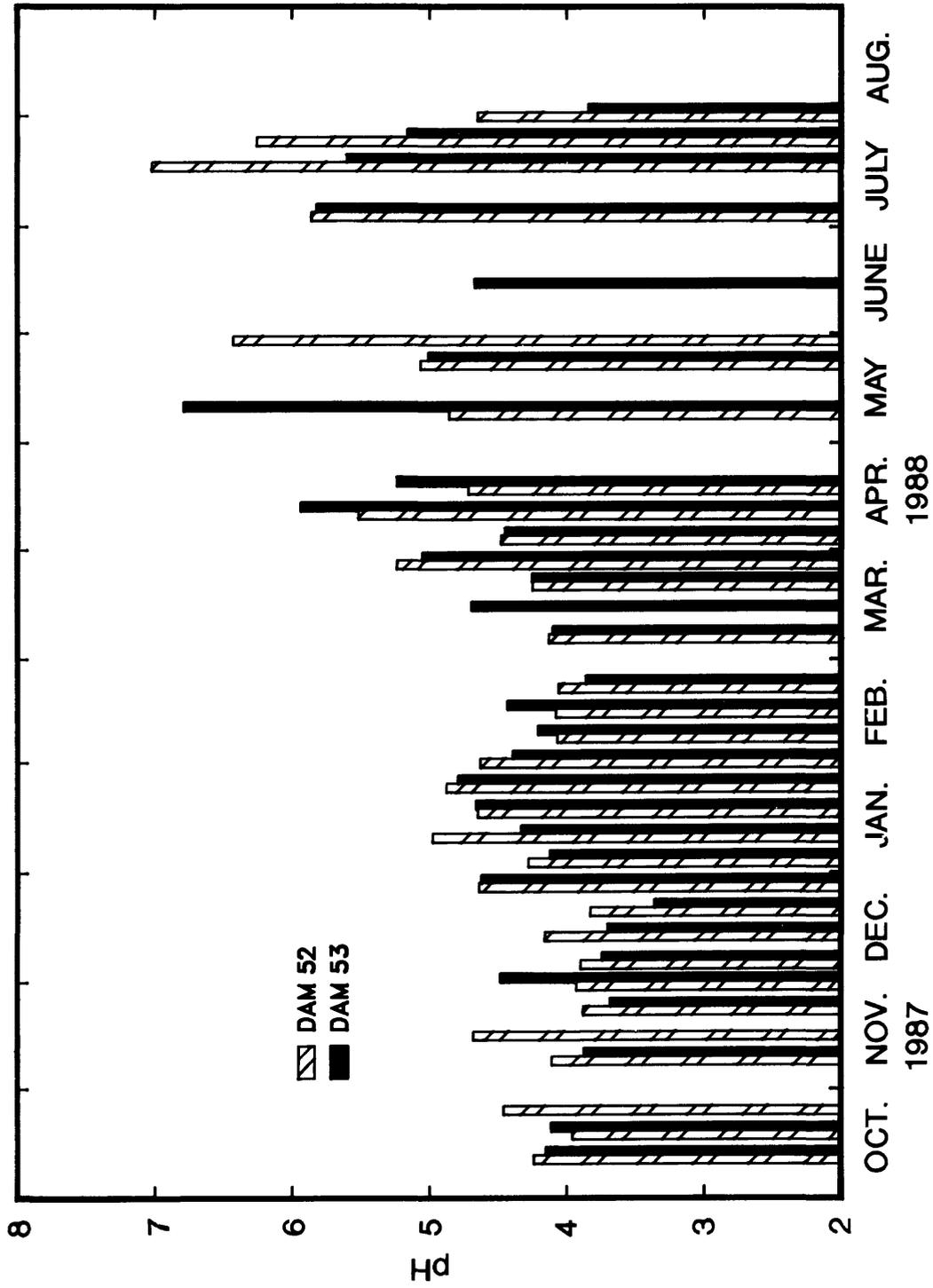


Figure 18.--Monthly variations in wetfall pH at Dams 52 and 53, October 1987--August 1988.

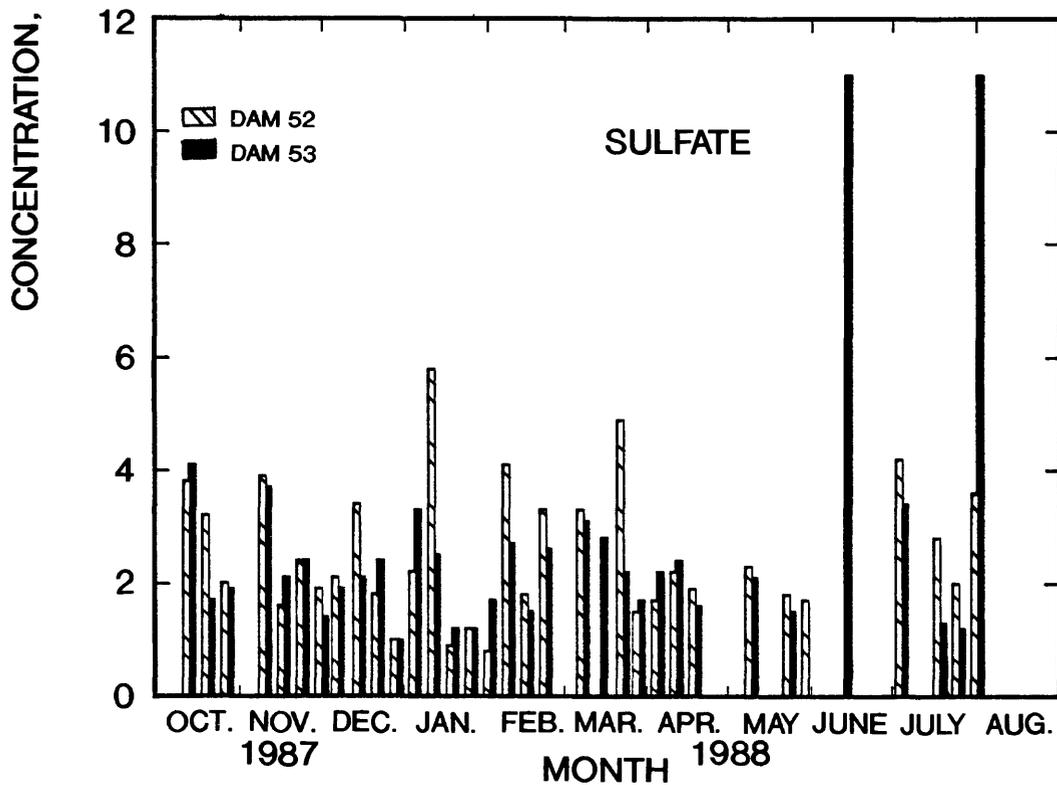
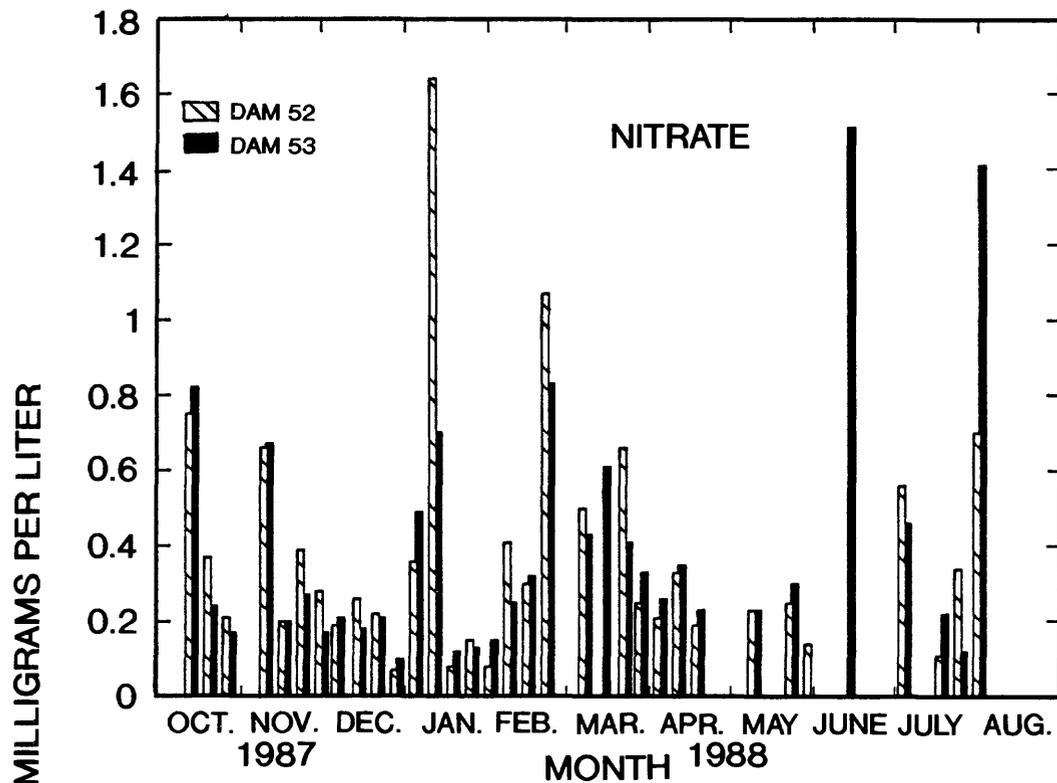


Figure 19.--Monthly variations in nitrate and sulfate concentration in wetfall at Dams 52 and 53, October 1987-August 1988.

Table 19.--Summary of atmospheric dryfall data at Dams 52 and 53, 1987-88

[N, number of observations; $\mu\text{S}/\text{cm}$, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligram per liter]

Constituent	Station	N	Minimum	Median	Maximum
Specific conductance, field, in $\mu\text{S}/\text{cm}$	Dam 52	5	275	390	872
	Dam 53	5	235	297	1,256
Specific conductance, lab, in $\mu\text{S}/\text{cm}$	Dam 52	4	305	394	557
	Dam 53	5	261	379	3,120
pH, field, in standard units	Dam 52	5	4.89	5.27	6.39
	Dam 53	5	5.03	5.58	6.85
pH, lab, in standard units	Dam 52	4	5.01	5.96	6.75
	Dam 53	5	6.10	6.40	7.71
Calcium, in mg/L as Ca	Dam 52	5	10.0	43.0	66.0
	Dam 53	5	20.2	27.0	35.0
Magnesium, in mg/L as Mg	Dam 52	5	.96	4.50	9.00
	Dam 53	5	2.80	3.30	16.0
Sodium, in mg/L as Na	Dam 52	5	1.10	11.0	54.0
	Dam 53	5	3.30	7.00	13.0
Potassium, in mg/L as K	Dam 52	5	1.58	22.0	110
	Dam 53	5	4.10	22.0	230
Sulfate, in mg/L as SO_4	Dam 52	5	25.0	60.0	130
	Dam 53	5	7.00	52.0	190
Chloride, in mg/L as Cl	Dam 52	5	5.60	17.0	81.0
	Dam 53	5	2.50	4.90	30.0
Fluoride, in mg/L as F	Dam 52	5	.04	1.10	3.00
	Dam 53	5	.25	.64	1.50
Nitrogen, NO_3 , dissolved, in mg/L as N	Dam 52	5	.04	54.56	98.56
	Dam 53	5	.04	36.08	46.2
Nitrogen, NH_4 , dissolved, in mg/L as N	Dam 52	5	1.86	5.62	137.8
	Dam 53	5	4.89	16.9	560.3
Phosphorus, ortho, dis., in mg/L as P	Dam 52	5	.03	1.55	26.66
	Dam 53	5	.25	7.13	248.0

Table 20.--Summary of atmospheric fog data at Dams 52 and 53, 1987-88

[N, number of observations; P5, fifth percentile; P95, ninety-fifth percentile; μ S/cm, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligram per liter; mL, milliliter]

Constituent	Station	N	Minimum	P5	Median	P95	Maximum
Specific conductance, field, in μ S/cm	Dam 52	27	8.90	10.3	36.9	346	571
	Dam 53	24	11.6	12.5	24.0	97.7	120
Specific conductance, lab, in μ S/cm	Dam 52	28	7.00	11.0	41.0	366	544
	Dam 53	26	7.00	11.0	23.5	182	183
pH, field, in standard units	Dam 52	27	3.86	4.08	4.84	6.93	7.28
	Dam 53	25	3.86	4.10	5.20	6.85	7.69
pH, lab, in standard units	Dam 52	28	4.61	4.65	5.12	6.14	6.22
	Dam 53	26	4.67	4.73	5.57	6.27	7.23
Calcium, in mg/L as Ca	Dam 52	28	.09	.10	.82	5.20	17.0
	Dam 53	27	.13	.21	.80	7.40	12.0
Magnesium, in mg/L as Mg	Dam 52	28	.02	.02	.10	.90	1.20
	Dam 53	27	.02	.03	.10	2.60	8.50
Sodium, in mg/L as Na	Dam 52	28	.01	.02	.11	1.20	1.50
	Dam 53	27	.01	.01	.12	1.80	2.60
Potassium, in mg/L as K	Dam 52	28	.03	.04	.24	2.99	23.0
	Dam 53	27	.01	.07	.19	3.90	11.0
Sulfate, in mg/L as SO_4	Dam 52	28	.50	.60	4.95	35.0	100
	Dam 53	27	.90	.90	2.70	27.0	36.0
Chloride, in mg/L as Cl	Dam 52	28	.01	.04	.58	14.0	41.0
	Dam 53	27	.01	.13	.50	7.40	8.70
Fluoride, in mg/L as F	Dam 52	28	.01	.04	.21	2.90	9.30
	Dam 53	27	.01	.05	.32	13.0	24.0
Nitrogen, NO_3 , dissolved, in mg/L as N	Dam 52	28	.26	.31	2.16	43.12	85.36
	Dam 53	27	.57	.57	2.38	32.56	34.1
Nitrogen, NH_4 , dissolved, in mg/L as N	Dam 52	28	.34	.35	1.11	7.54	26.0
	Dam 53	27	.22	.27	1.09	3.22	3.9
Phosphorus, ortho, dis., in mg/L as P	Dam 52	28	.03	.03	.03	.25	.31
	Dam 53	27	.03	.03	.03	.62	.78
Sample size, in mL	Dam 52	28	25.0	98.0	2,000	12,000	12,000
	Dam 53	27	6.0	50.0	2,000	12,000	15,000

Comparison of Statistical Measures

Observed atmospheric deposition quality at Dam 53 was compared to other relevant water-quality-data sets. Specifically, data collected at Dam 53 during this study were compared to the data collected at Dam 52, to data collected at nearby NADP/NTN stations for the same period (October 1987-August 1988), and to historical data collected at these same NADP/NTN sites. As before, the non-parametric Wilcoxon-Mann-Whitney Rank Sum test was used for making data set comparisons. Where appropriate, a paired t-test was used.

Comparison of Atmospheric Deposition Quality at Dam 53 and at Dam 52

Selected constituents in atmospheric deposition (wetfall, dryfall, and fog) determined during this study at Dams 53 and 52 are given in tables 21-23. Results indicate that wetfall, dryfall, and fog quality at Dam 53 was not statistically different from that at Dam 52 during the period of this study.

Table 21.--Statistical comparison of wetfall deposition quality at Dam 53 to Dam 52 (Paired Nonparametric Wilcoxon-Mann-Whitney Rank Sum test, $\alpha = 0.05$)

[N, number of observations; P, probability; $H_0: \bar{X}_{53} = \bar{X}_{52}$, the null hypothesis that the mean at Dam 53 is equal to the mean at Dam 52; $\mu\text{S/cm}$, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligram per liter]

Constituent	Station	N	Mean	Standard deviation	P-value	$H_0: \bar{X}_{53} = \bar{X}_{52}$
Specific conductance, field, in $\mu\text{S/cm}$	Dam 52	30	27.23	13.94	0.949	Accept
	Dam 53	30	26.89	15.29		
pH, field, in standard units	Dam 52	30	4.68	.84	.219	Accept
	Dam 53	31	4.55	.76		
Sulfate, in mg/L as SO_4	Dam 52	32	2.53	1.21	.249	Accept
	Dam 53	33	2.69	2.27		
Chloride, in mg/L as Cl	Dam 52	32	.60	.55	.898	Accept
	Dam 53	33	.60	.54		
Nitrogen, NO_3 , dissolved, in mg/L as N	Dam 52	32	1.67	1.41	.913	Accept
	Dam 53	33	1.76	1.50		
Nitrogen, NH_4 , dissolved, in mg/L as N	Dam 52	32	.66	1.18	.956	Accept
	Dam 53	33	.53	.48		

Table 22.--Statistical comparison of dryfall deposition quality at Dam 53 to Dam 52 (Paired Nonparametric Wilcoxon-Mann-Whitney Rank Sum test, $\alpha = 0.05$)

[N, number of observations; P, probability; $H_0: \bar{X}_{53} = \bar{X}_{52}$, the null hypothesis that the mean at Dam 52 is equal to the mean at Dam 53; $\mu\text{S/cm}$, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligram per liter]

Constituent	Station	N	Mean	Standard deviation	P-value	$H_0: \bar{X}_{53} = \bar{X}_{52}$
Specific conductance, field, in $\mu\text{S/cm}$	Dam 52	5	512.0	242.5	0.897	Accept
	Dam 53	5	477.4	437.9		
pH, field, in standard units	Dam 52	5	5.54	.68	.307	Accept
	Dam 53	5	5.75	.77		
Chloride, in mg/L as Cl	Dam 52	5	26.88	30.94	.412	Accept
	Dam 53	5	11.42	11.98		
Sulfate, in mg/L as SO_4	Dam 52	5	74.60	40.81	.962	Accept
	Dam 53	5	71.40	70.08		
Nitrogen, NO_3 , dissolved, in mg/L as N	Dam 52	5	53.94	35.33	.150	Accept
	Dam 53	5	29.39	19.23		
Nitrogen, NH_4 , dissolved, in mg/L as N	Dam 52	5	33.45	58.72	.496	Accept
	Dam 53	5	122.99	244.51		

Table 23.--Statistical comparison of fog deposition quality at Dam 53 to Dam 52
(Paired Nonparametric Wilcoxon-Mann-Whitney Rank Sum test, $\alpha = 0.05$)

[N, number of observations; P, probability; $H_0: \bar{X}_{53} = \bar{X}_{52}$, the null hypothesis that the mean at Dam 52 is equal to the mean at Dam 53; $\mu\text{S/cm}$, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligram per liter]

Constituent	Station	N	Mean	Standard deviation	P-value	$H_0: \bar{X}_{53} = \bar{X}_{52}$
Specific conductance, field, in $\mu\text{S/cm}$	Dam 52	27	75.34	119.33	0.582	Accept
	Dam 53	24	35.88	28.97		
pH, field, in standard units	Dam 52	27	5.17	.89	.657	Accept
	Dam 53	25	5.29	.85		
Sulfate, in mg/L as SO_4	Dam 52	28	10.65	19.12	.815	Accept
	Dam 53	27	6.91	8.63		
Chloride, in mg/L as Cl	Dam 52	28	2.76	7.95	.980	Accept
	Dam 53	27	1.26	2.07		
Nitrogen, NO_3 , dissolved, in mg/L as N	Dam 52	28	7.7	17.42	.981	Accept
	Dam 53	27	5.98	8.71		
Nitrogen, NH_4 , dissolved, in mg/L as N	Dam 52	28	2.47	4.86	.674	Accept
	Dam 53	27	1.46	1.07		

These results suggest that corrosion caused by atmospheric deposition quality should be no different at each of the two sites, given similar exposures.

Comparison of Atmospheric Deposition Quality at Dam 53 and at National Atmospheric Deposition Program/National Trends Network Sites (1987-88)

The data collected during this study were compared to data collected at nearby NADP/NTN stations for the same period (1987-88). Dam 53 wetfall quality was compared to the wetfall quality determined at the two NADP/NTN stations in southern Illinois and at the one station in western Kentucky (fig. 2). Results of the paired, nonparametric, Wilcoxon-Mann-Whitney Rank Sum test for pH and selected constituents are shown in table 24. Field pH and nitrate

Table 24.--Statistical comparison of wetfall deposition quality at Dam 53 to nearby National Atmospheric Deposition Program/National Trends Network stations for the same period, October 1987-August 1988. (Paired Nonparametric Wilcoxon-Mann-Whitney Rank Sum test, $\alpha = 0.05$)

[N, number of observations; P, probability; $H_0: \bar{X}_{53} = \bar{X}_{NADP}$, the null hypothesis that the mean at Dam 53 is equal to the mean at each other station; 53, Dam 53 near Grand Chain, Illinois; DIX, Dixon Springs Agricultural Center, Pope County, Illinois; LBL, Land Between the Lakes, Trigg County, Kentucky; SIU, Southern Illinois University; mg/L, milligram per liter]

Constituent	Station	N	Mean	Standard deviation	P-value	$H_0: \bar{X}_{53} = \bar{X}_{NADP}$
pH, field, in standard units	53	31	4.55	0.73		
	DIX	27	4.24	.55	0.203	Accept
	LBL	31	4.41	.30	.736	Accept
	SIU	25	4.38	.23	.226	Accept
Sulfate, in mg/L as SO ₄	53	33	2.69	2.27		
	DIX	28	2.84	1.57	.003	Reject
	LBL	32	2.59	1.84	.688	Accept
	SIU	30	2.52	1.22	.122	Accept
Nitrogen, NO ₃ , dissolved, in mg/L as N	53	33	1.75	1.47		
	DIX	28	1.80	1.17	.132	Accept
	LBL	32	1.61	1.41	.985	Accept
	SIU	30	1.54	.96	.622	Accept
Nitrogen, NH ₄ , dissolved, in mg/L as N	53	33	.53	.47		
	DIX	28	.32	.29	.005	Reject
	LBL	32	.21	.21	.000	Reject
	SIU	30	.23	.18	.000	Reject

nitrogen concentrations in wetfall at Dam 53 were not significantly different from those determined at any of the NADP/NTN sites nearby (the null hypothesis could not be rejected). Mean values of these constituents are noticeably similar. The mean ammonia nitrogen concentration at Dam 53 was statistically greater than that at any of the NADP/NTN sites for the 1987-88 period (the null hypothesis was rejected). Wetfall sulfate concentrations at Dam 53 (mean = 2.69 mg/L) were found to be significantly different (smaller) than concentrations reported at the Dixon Springs, Illinois site (mean = 2.94 mg/L).

With the exception of ammonia nitrogen concentrations, it seems that the wetfall deposition quality at Dam 53 is similar to that determined at other locations in the region. Ammonia nitrogen concentrations were greater at Dam 53. Collection methodologies and schedules used in this study were designed to be similar to those used in the NADP/NTN program, so that comparisons such as these would be relevant.

Comparison of Atmospheric Deposition Quality at Dam 53 and at National Atmospheric Deposition Program/National Trends Network Sites (historical)

The wetfall quality at Dam 53 is compared to the historical wetfall quality at each of the three nearby NADP/NTN stations in table 25. In most cases, current wetfall quality at Dam 53 (as represented by property and constituent mean values) is better (less likely to cause corrosion) than historical water-quality. The mean of the observed pH at Dam 53 was slightly higher than the historical mean of the observed pH at all three NADP/NTN sites. However, a significant statistical difference was only detected when comparing Dam 52 to the NADP/NTN site at Dixon Springs. Statistically, the mean ammonia nitrogen concentration at Dam 53 was determined to differ from historical concentrations at all NADP/NTN locations nearby. The historical mean ammonia concentration in wetfall was higher at Dam 53 (0.53 mg/L) than at the three NADP/NTN sites. Mean nitrate concentration at Dam 53 was approximately equal to or less than that determined from historical data at any of the three NADP/NTN sites. No statistical differences were detected. Statistical comparisons indicate that the mean sulfate concentration observed at Dam 53 is less than the historical mean observed at Dixon Springs. The relative location of Dam 53 to the local atmospheric emission sources (upwind) or improvements in emission-control technology over time may explain the lower sulfate and nitrate concentrations observed.

CORROSION OF LOCK AND DAM FACILITIES

Corrosion-product samples (rust and tubercle scrapings) were collected from each of the lock and dam facilities and analyzed to determine the elemental and molecular composition. Five corrosion-product samples were analyzed (three from Dam 53 and two from Dam 52). Samples collected at Dam 53 were taken from the galvanized steel grating, hydraulic piping, and the inside lock wall. Samples collected at Dam 52 were taken from hydraulic piping and the inside lock wall. X-ray-diffraction analyses revealed that the corrosion product consists of calcium carbonate, iron oxide, and chromium oxide. Results of analyses of all five samples analyzed were similar. Although calcium carbonate appears to have precipitated from the surrounding river water, the iron and chromium oxides are typical steel-oxidation (rust) products. These results were confirmed by the use of x-ray-fluorescence techniques, which determined the presence of iron, chromium, and calcium. No extraneous substances were identified that could have contributed to the corrosion process (K. Lal Gauri, Professor of Geology, University of Louisville, written commun., 1988).

Table 25.--Statistical comparison of wetfall deposition quality at Dam 53 to historical data from nearby National Atmospheric Deposition Program/National Trends Network stations (Nonparametric Wilcoxon-Mann-Whitney Rank Sum test, $\alpha = 0.05$)

[N, number of observations; P, probability; $H_0: \bar{X}_{53} = \bar{X}_{NADP}$, the null hypothesis that the mean at Dam 53 is equal to the mean at each NADP station; 53, Dam 53 at Paducah, Kentucky; DIX, Dixon Springs Agricultural Center, Pope County, Illinois; LBL, Land Between the Lakes, Trigg County, Kentucky; SIU, Southern Illinois University; mg/L, milligram per liter]

Constituent	Station	N	Mean	Standard deviation	P-value	$H_0: \bar{X}_{53} = \bar{X}_{NADP}$
pH, field, in standard units	53	31	4.55	0.73		
	DIX	393	4.25	.42	0.032	Reject
	LBL	208	4.39	.30	.604	Accept
	SIU	338	4.40	.35	.696	Accept
Sulfate, in mg/L as SO ₄	53	33	2.69	2.27		
	DIX	424	3.55	2.63	.002	Reject
	LBL	225	2.76	2.29	.866	Accept
	SIU	367	3.09	2.28	.094	Accept
Nitrogen, NO ₃ , dissolved, in mg/L as N	53	33	1.75	1.47		
	DIX	424	1.99	1.92	.534	Accept
	LBL	225	1.72	1.43	.769	Accept
	SIU	367	1.81	1.40	.371	Accept
Nitrogen, NH ₄ , dissolved, in mg/L as N	53	33	.53	.47		
	DIX	424	.43	.45	.000	Reject
	LBL	225	.26	.27	.000	Reject
	SIU	367	.35	.35	.000	Reject

CONCLUSIONS

The data collected during this study do not clearly define an environmental cause for the observed accelerated corrosion occurring at Dam 53. Current and historical data were used to evaluate the quality of the Ohio River water and atmospheric deposition. Statistical tests were used to detect potential differences between the conditions observed at Dams 53 and 52, as well as other locations in the region. Procedures for detecting temporal trends were also used in an effort to explain the observed conditions.

Ohio River water quality does not seem to be particularly corrosive, on the basis of the pH, alkalinity, and major ion determinations made during this study and on the basis of historical data. Analyses of historical data indicates that water-quality conditions at Dam 53 have been equal to or better than other upstream locations at Greenup, Markland, and Cannelton Dams. This implies that similar facilities upstream should be experiencing corrosion problems equal to or worse than that at Dam 53 if the corrosion were due to water-quality conditions. Water-quality analyses did not detect hydrogen sulfide (indicative of sulfate reduction by bacteria) and showed that anaerobic conditions were not prevalent. The observed dissolved-oxygen conditions (concentrations not less than 4.0 mg/L) indicate that bacterial sulfate reduction is unlikely. Comparisons of water-quality data collected during this study from Dam 53 to Dam 52 detected no significant differences. The water quality of the Ohio River at Dam 53 meets all applicable ambient water-quality criteria established by the State of Kentucky for use as a warmwater aquatic habitat, a domestic water-supply source, and a primary- and secondary-contact recreational water body.

Atmospheric deposition (wetfall, dryfall, and fog) was acidic and contained significant concentrations of several chemical constituents. Although potentially corrosive, the atmospheric-deposition quality at Dam 53 was statistically no different than that determined at Dam 52 or at 3 locations in the region where wetfall-deposition-quality stations are operated by the NADP/NTN program. Some slight differences were noted between current Dam 53 data and historical data collected at the NADP/NTN stations. However, the observed differences indicate that the current wetfall quality is slightly better than the historical wetfall quality in the region.

Chemical analyses of the corrosion product collected from each lock and dam failed to detect any extraneous substance that could have accelerated the corrosion process. The iron oxide and chromium oxide that were found are typical of steel oxidation, and calcium carbonate appears to have precipitated from river water.

One fact was noted during this study that may be significantly affecting the corrosion process at Dam 53. The length of time that Dam 53 is under water (annually) is longer than the length of time that Dam 52 is under water; Dam 53 is under water about 75 percent of the time, whereas Dam 52 is under water less than 50 percent of the time. Conditions favorable for corrosion occur when a structure is under water and these conditions are met more frequently at Dam 53 than at Dam 52. In addition, hydraulic and possibly suspended-sediment abrasion may be contributing to the corrosion process by physically wearing away protective coatings on the Dam structures. The galvanized coating on gratings, railings, pipe and other metallic components may be particularly vulnerable to this type of abrasive process because of its relative softness compared to other types of coatings or protectants.

REFERENCES CITED

- American Public Health Association, American Water Works Association, and Water Pollution Control Association, 1985, Standard methods for the examination of water and wastewater: Washington, D.C., 623 p.
- Bigelow, D.S. and Dossett, S.R., 1988, Instruction manual, NADP/NTN site operation: National Atmospheric Deposition Program, Natural Resource Ecology Laboratory, Colorado State University, Fort Collins, CO, 110 p.
- Brown, P.W. and Masters, L.W., 1982, Factors affecting the corrosion of metals in the atmosphere, in Ailor, W.H. (ed.), Atmospheric Corrosion: New York, John Wiley and Sons, pp. 31-49.
- Crawford, C.G., Slack, J.R., and Hirsch, R.M., 1983, Testing for trends in water-quality data using the statistical analysis system: U.S. Geological Survey Open-File Report 83-550, 102 p.
- Grant, W.D. and Long, P.E., 1981, Environmental Microbiology: London, Halsted Press, 206 p.
- Guy, H.P. and Norman, V.W., 1970, Field methods for measurement of fluvial sediment: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 3, Chapter C2, 59 p.
- Hirsch, R.M., Slack, J.R., and Smith, R.A., 1982, Techniques of trend analysis for monthly water quality data: Water Resources Research, v. 18, no. 1, p. 107-121.
- Iman, R.L. and Conover, W.J., 1983, A modern approach to statistics: New York, John Wiley and Sons, 497 p.
- Kentucky Natural Resources and Environmental Protection Cabinet, 1987, Kentucky Water Quality Regulations, Kentucky Administrative Regulations, Title 401, Chapter 5: Frankfort, Kentucky, Department for Environmental Protection, Division of Water, 17 p.
- Langbein, W.B. and Dawdy, D.R., 1964, Occurrence of dissolved solids in surface waters in the United States: U.S. Geological Survey Professional Paper 501-D, D115-D117.
- Myers, J.R. and Riggs, W.L., 1984, Corrosion control survey: Shelbyville Dam, Carlyle Dam, Kaskaskia Lock and Dam, Lock and Dam 52, and Lock and Dam 53: a report to the U.S. Army Construction Engineering Research Laboratory, 31 p.
- National Atmospheric Deposition Program, 1987, NADP/NTN annual data summary: deposition chemistry in the United States, 1986: Fort Collins, CO, Natural Resource Ecology Laboratory, Colorado State University, 363 p.
- Postgate, J.R., 1979, The Sulphate-Reducing Bacteria: London, Cambridge University Press, 210 p.
- SAS Institute, Inc., 1985, SAS Users Guide: Statistics, version 5 edition: Cary, N.C., SAS Institute, Inc., 956 p.
- Sereda, P.J., 1974, Weather Factors Affecting Corrosion of Metals: in Corrosion in Natural Environments, ASTM STP 558, American Society for Testing and Materials, pp. 7-22.
- Smith, R.A., Hirsch, R.M., and Slack, J.R., 1982, A study of trends in total phosphorus measurements at NASQAN stations: U.S. Geological Survey Water-Supply Paper 2190, 34 p.

Toms, S.G.; Sholar, C.J.; and Zettwoch, D.D.; 1987, Water Resources Data, Kentucky, Water Year 1987: U.S. Geological Survey Water-Data Report KY-87-1, 356 p.

Wranglen, G., 1985, An Introduction to Corrosion and Protection of Metals: New York, Chapman and Hall, 288 p.