Data from Selected U.S. Geological Survey National Stream Water-Quality Monitoring Networks (WQN) on CD-ROM

By Richard B. Alexander, Amy S. Ludtke, Kathleen K. Fitzgerald, and Terry L. Schertz

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PREFACE

The authors would like to acknowledge the many individuals who assisted in the development and review of the report, data sets, and graphics published on the CD-ROMs. We thank the technical reviewers Janice Ward, William Battaglin, Richard Coupe, and Randy Parker. Their recommendations greatly improved the organization and content of the report and CD-ROM data bases. We especially thank Richard Coupe for providing additional reviews of preliminary versions of the CD-ROMs and Janice Ward for providing administrative guidance during the development of the CD-ROMs. We thank Alan Lumb for administrative support that allowed Larry Briel to contribute his valuable data management skills to the project. We thank John Briggs and Timothy Miller for assistance in obtaining information on historical network operations. Thanks to Richard Smith and Gregory Schwarz for discussions and valued input on various water-quality and quality-assurance topics. Steve Glodt and Thomas Maloney of the National Water Quality Laboratory in Denver, Colorado and Herman Feltz and Bernard Malo provided important information on laboratory analytical methods used currently and historically by the USGS. Donald Dolnack performed the many daily streamflow retrievals from the USGS centralized data base, and Jerry Casile patiently retrieved water-quality data from each of the USGS District computers. Linda Geiger assisted in reviewing preliminary versions of the CD-ROMs. We thank Patricia Greene for the layout of the CD-ROM cover and inserts. Also, we thank Frances Buchanan for the production of final versions of the illustrations, Marie Nofs of the National Water Quality Assessment Program for her assistance in scanning water-quality memoranda into digital form, Dawn Fuller for her assistance in editing text and graphical data files, and Sharon Cline and Joyce Soloman for technical assistance with graphical software.

CONTENTS

FIGURES

TABLES

Page

Data from Selected U.S. Geological Survey National Stream Water-Quality Monitoring Networks (WQN) on CD-ROM

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ABSTRACT

Data from two U.S. Geological Survey (USGS) national stream water-quality monitoring networks, the National Stream Quality Accounting Network (NASQAN) and the Hydrologic Benchmark Network (HBN), are now available in a two CD-ROM set. These data on CD-ROM are collectively referred to as WQN, water-quality networks. Data from these networks have been used at the national, regional, and local levels to estimate the rates of chemical flux from watersheds, quantify changes in stream water quality for periods during the past 30 years, and investigate relations between water quality and streamflow as well as the relations of water quality to pollution sources and various physical characteristics of watersheds.

The networks include 679 monitoring stations in watersheds that represent diverse climatic, physiographic, and cultural characteristics. The HBN includes 63 stations in relatively small, minimally disturbed basins ranging in size from 2 to 2,000 square miles with a median drainage basin size of 57 square miles. NASQAN includes 618 stations in larger, more culturally-influenced drainage basins ranging in size from one square mile to 1.2 million square miles with a median drainage basin size of about 4,000 square miles.

The CD-ROMs contain data for 63 physical, chemical, and biological properties of water (122 total constituents including analyses of dissolved and water suspended-sediment samples) collected during more than 60,000 site visits. These data approximately span the periods 1962-95 for HBN and 1973-95 for NASQAN. The data reflect sampling over a wide range of streamflow conditions and the use of relatively consistent sampling and analytical methods.

The CD-ROMs provide ancillary information and data-retrieval tools to allow the national network data to be properly and efficiently used. Ancillary information includes the following: descriptions of the network objectives and history, characteristics of the network stations and water-quality data, historical records of important changes in network sample collection and laboratory analytical methods, water reference sample data for estimating laboratory measurement bias and variability for 34 dissolved constituents for the period 1985-95, discussions of statistical methods for using water reference sample data to evaluate the accuracy of network stream water-quality data, and a bibliography of scientific investigations using national network data and other publications relevant to the networks.

The data structure of the CD-ROMs is designed to allow users to efficiently enter the water-quality data to user-supplied software packages including statistical analysis, modeling, or geographic information systems. On one disc, all data are stored in ASCII form accessible from any computer system with a CD-ROM driver. The data also can be accessed using DOS-based retrieval software supplied on a second disc. This software supports logical queries of the water-quality data based on constituent concentrations, sample-collection date, river name, station name, county, state, hydrologic unit number, and 1990 population and 1987 land-cover characteristics for station watersheds. User-

selected data may be output in a variety of formats including dBASE, flat ASCII, delimited ASCII, or fixed-field for subsequent use in other software packages.

INTRODUCTION

During the past 30 years, the U.S. Geological Survey (USGS) has operated two national stream water-quality networks, the Hydrologic Benchmark Network (HBN) and the National Stream Quality Accounting network (NASQAN). These networks were begun in the 1960s and 1970s, respectively, to document stream water-quality conditions and trends for watersheds throughout the United States and to improve our understanding of the effects of the natural environment and human activities on water quality. The inactment of significant environmental legislation during these decades, including the Water Quality Act of 1965 and the Clean Water Act of 1972 and its subsequent amendments, increased the need for comprehensive water-quality monitoring data at all levels of government. The networks were designed to address these needs at the national and regional levels by providing systematically-collected information on the quality of the nation's rivers (Leopold, 1962b; Briggs and Ficke, 1975).

Since their inception, the national networks have provided water-quality data for numerous watersheds with diverse climatic, physiographic, and cultural characteristics, which has benefited efforts to investigate the causes of spatial and temporal variations in water quality (Smith and others, 1987a; Smith and Alexander, 1983). The watersheds range from the relatively small, minimally disturbed basins in the HBN to the larger, more culturally-influenced drainage basins of NASQAN. During the operation of the networks, considerable changes have occurred in terrestrial and atmospheric sources of water pollutants in the United States brought about, in part, by regulatory actions. Examples include changes in fertilizer use, atmospheric sources of sulfur and nitrogen, and wastewater discharges from municipal sewage treatment plants. The national networks have provided some of the best available information for investigating the influences of these pollutant sources on national and regional water quality (e.g., Smith and others, 1987a; Smith and Alexander, 1986; Kramer and others, 1986; Lins, 1986; Smith and others, 1993). In addition, national network data have been used to quantify trends in stream water quality (e.g., Lettenmaier and others, 1991; Smith and others, 1993), estimate the rates of chemical flux from watersheds (e.g., Alexander and others, 1996a; Peters, 1984), and investigate relations between water quality and streamflow (e.g., Smith and others, 1982) and between water quality and various physical characteristics of the watersheds (Biesecker and Leifeste, 1975; Peters, 1984). Numerous state and local investigations of stream water quality have also used NASQAN and HBN data to examine stream water-quality conditions and trends (e.g., Schertz, 1990; Schertz and others, 1994; Hay and Campbell, 1990; Hainly and Ritter, 1986).

The national networks have provided stream measurements for a relatively consistent and comprehensive set of water properties. Approximately 85 physical, chemical, and biological properties have been analyzed during more than 60,000 visits to 679 stream locations. Relatively consistent sampling and analytical methods have been used at national network sites during their operation. The water-quality data reflect sampling over a wide range of streamflow conditions. As of 1995, expenditures for the two national networks have totaled approximately $95 million, including $80 million for NASQAN and $15 million for the HBN.

Documentation and quality-assurance information on network operations and historical records of sample-collection agencies, laboratories, analytical methods, and estimates of laboratory measurement error are available to assist in the proper use of the stream water-quality data. This information is especially useful for documenting changes in network operations and sampling and analytical methods that may affect the use and interpretation of the ambient water-quality data. Much of this information is contained in USGS publications and previously unpublished USGS internal technical memoranda. Estimates of laboratory measurement error (i.e., variability and bias) have been previously published as part of the Blind Sample Program, an external USGS laboratory quality-assurance program (Maloney and others, 1994). These data have been used to systematically assess the accuracy of USGS laboratory methods and national network stream water-quality data (see for example, Maloney and others, 1994; Alexander and others, 1993).

We have assembled in an easy-to-use format on two CD-ROMs (Compact-Disk Read-Only Memory) historical water-quality and streamflow data and supporting documentation and quality-assurance information for NASQAN and HBN (these data are available on CD-ROM from the U.S. Geological Survey Digital Data Series; see Alexander and others, 1996b). The water-quality data include all measurements made at the national network stations for selected constituents during the periods of 1962-95 for the HBN and 1973-95 for NASQAN. These data on CD-ROM are collectively referred to as WQN, water-quality networks. This report provides the necessary background for understanding the characteristics of the WQN data and the retrieval system for accessing the data.

The first section of this report gives a brief overview of the purpose and content of the CD-ROMs. A list of the key features of the CD-ROM data sets is provided.

The second section of the report describes the objectives, history, and characteristics of WQN data. This section includes information on the field and laboratory methods used in the collection, processing, and analysis of the data and the procedures used to quality assure the water-quality data. We also describe the specific data selected for publication on the CD-ROMs.

The third section of the report describes the history and characteristics of a USGS quality-assurance program, the Blind Sample Program, responsible for independently monitoring the quality of laboratory analytical methods and environmental measurements since 1981. We describe the characteristics of the measurement bias and variability data produced by this program and published on the CD-ROMs.

A fourth section of the report discusses the various ways of using the Blind Sample Program data to evaluate the accuracy of national network stream water-quality data. We discuss characteristics of the quality-assurance data as they relate to those of the stream water-quality data, and describe various techniques for using the quality-assurance data to improve interpretations of the water-quality data.

In a final section, we briefly describe the organization of the WQN data sets and the characteristics of the DOS software supplied on one of the CD-ROM discs for retrieving and outputing the data.

OVERVIEW OF THE CD-ROMS

The information and data-retrieval tools provided on the CD-ROMs allow for the proper and efficient use of WQN data. The CD-ROMs are designed to allow users to efficiently input data to user-supplied software including spreadsheet, statistical analysis, or geographic information systems. The data may be extracted from the CD-ROM according to user-specified criteria using the supplied DOS retrieval software, and output in a variety of formats. Alternatively, the ASCII form of the WQN data may be accessed and manipulated by user-supplied software, such as spreadsheet or word processor.

The WQN data base contains water-quality and streamflow data collected at 679 locations in the United States including 63 HBN stations for the approximate period 1962-95 and 618 NASQAN stations for 1973-95 (two stations have belonged to both networks during the period of operations). Supporting information identifies and describes the water-quality and streamflow stations and watersheds, water-quality constituents, and the methods, remarks, laboratories, sample-collection agencies, and the laboratory measurement accuracy associated with the water-quality data. The WQN data sets on the CD-ROMs include the following elements:

- Uniformly-sampled (i.e., semi-annually to monthly) stream water-quality data for 63 physical, chemical, and biological properties of water (122 water constituents including the dissolved, suspended, and total forms). This includes physical/field measurements (e.g, temperature, instantaneous streamflow, pH, suspended sediment), major ions, nutrients, organic carbon, radiochemicals, biological measurements (e.g., fecal bacteria, phytoplankton, and periphyton), and inorganic trace elements. With the exception of the periphyton data, which reflect substrate conditions, all measurements reflect conditions in the water column.

- Daily mean values of streamflow for time periods corresponding to the water-quality records. These data can be used with the water-quality data to derive estimates of flux or load.

- Water-quality and streamflow station attributes including drainage area, latitude, longitude, the dates of station operation, county, state, and hydrologic unit code (HUC) identifiers, and drainage basin population for 1990 and land-cover statistics for 1987.

- The sample-collection agencies, laboratories, and laboratory analytical methods associated with the stream water-quality data. In addition to national network documents describing these characteristics, information on the collection agencies, laboratories, and analytical methods has been stored with the water-quality data values in digital data files since the early to mid 1980s.

- Laboratory quality-control data for 34 contstituents for water years 1985-95 (Oct. 1, 1984 to Sept. 30, 1995) for estimating the measurement bias and variability of national network stream water-quality data. The quality-control data were collected through a USGS program (the Blind Sample Program) responsible for regularly-submitting stable, homogeneous standard reference water samples to the USGS laboratory for measurement.

- Documentation of changes in field and laboratory methods, constituent coverage, network operations, reporting conventions, and sample contamination that may affect the use and interpretation of WQN stream water-quality data. The documentation includes USGS water-quality memoranda describing national network operations and important changes in field and laboratory methods.

- Copies of this Open-File Report. This report provides important background information on the national networks, characteristics of the water-quality, streamflow, and quality-assurance data, and statistical methods for using the Blind

Sample Program reference sample data to evaluate the accuracy of the stream water-quality data.

- A bibliography of publications of national network field and laboratory methods, network historical background, interpretations of network data at the national, regional, and local levels, and statistical methods and computer software that have been developed for use with data having characteristics similar to those of the national network data.

Details of the background and characteristics of the WQN data on CD-ROM are provided in the following sections.

HISTORY AND CHARACTERISTICS OF THE NATIONAL NETWORKS

This section describes the history, objectives, and characteristics of two USGS national stream water-quality monitoring networks including the field and laboratory methods and quality-assurance practices employed in the operation of the networks. The section also describes the characteristics of the stream water-quality data selected for publication on CD-ROM.

The National Stream Quality Accounting Network (NASQAN)

The need for systematic monitoring of the Nation's rivers increased in the 1960s and early 1970s with the passage of federal environmental legislation, including the Water-Quality Act of 1965 and the Clean Water Act in 1972 and its subsequent amendments. Additional monitoring was sought to provide more geographically comprehensive and uniformly-collected information on current water-quality conditions and to track changes in water quality resulting from the control of water pollution. Planning and management agencies, including the U.S. Environmental Protection Agency (EPA), interstate river-basin commissions, and selected state water agencies, were especially in need of more uniformly-collected national and regional water-quality information to address these needs. The paucity of such data complicated efforts to accurately describe river quality. Available water-quality records were often of short duration, plagued by frequent changes in the location, frequency, and methods of data collection, or lacked adequate coverage for a wide range of physical, chemical, and biological water properties (Wolman, 1971; Knopman and Smith, 1993). As a result, prior efforts to summarize the water-quality of U.S. streams and rivers were forced to rely extensively on anecdotal data (Wolman, 1971). As the lead agency responsible for assessing the Nation's water resources (U.S. Bureau of the Budget, 1964), the USGS responded to the need for improved national and regional water-quality information by initiating the NASQAN program in January 1973 (Fig. 1) to monitor the water quality of major rivers and streams in the United States (Ficke and Hawkinson, 1975).

Network objectives and station characteristics

The primary objectives of the NASQAN program are to (1) measure the quantity and quality of stream water in major watersheds of the United States, (2) describe spatial variability in stream water quality, (3) detect long-term changes in stream water quality, and (4) provide information to help guide future water-quality assessments, possibly having more temporally- and spatially-intensive components (Ficke and Hawkinson, 1975).

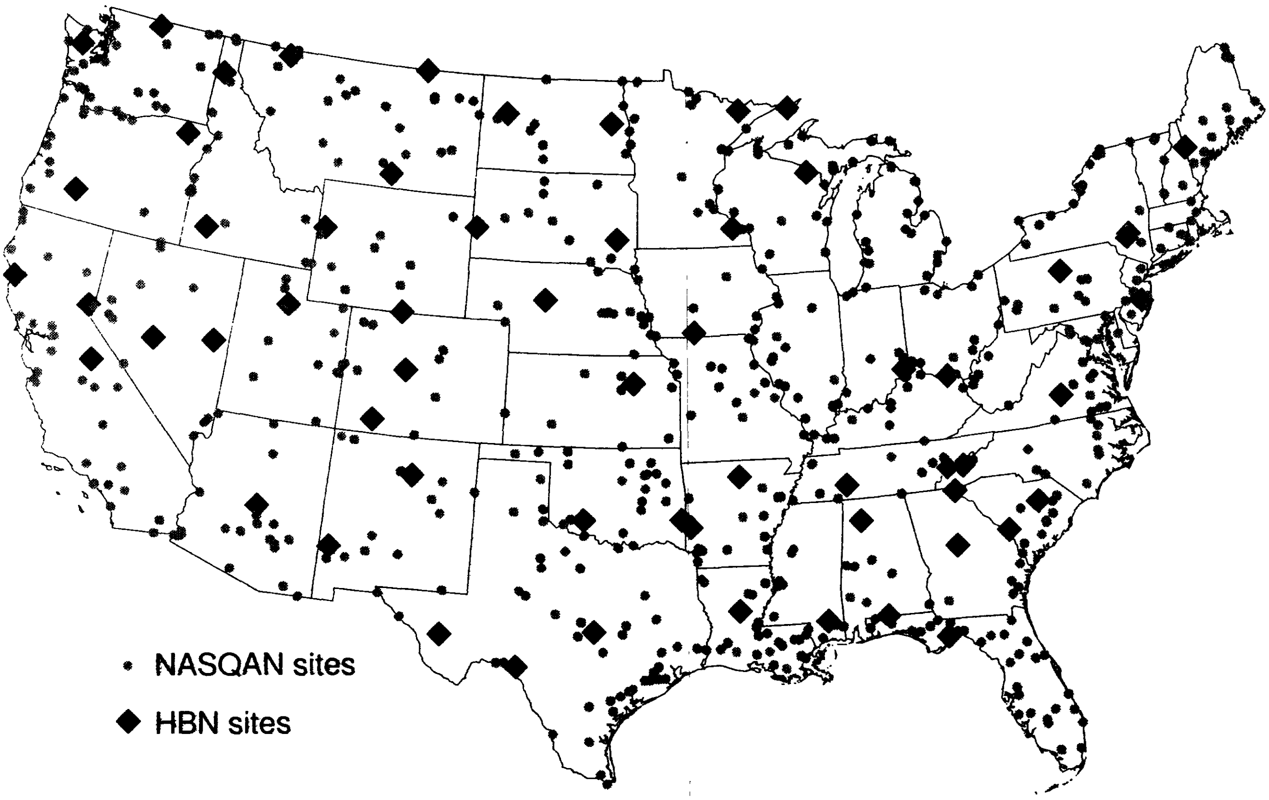

Figure 1. National Stream Quality Accounting Network (NASQAN) and Hydrologic Benchmark Network (HBN) station locations in the conterminous United States
[A total of 618 NASQAN stations were monitored from approximately 1973-95. A total of 63 HBN stations were monitored from approximately 1962-95. Stations located outside of the conterminous United States for NASQAN include 13 in Alaska, 8 in Hawaii, 6 in Puerto Rico, and 1 in Guam; HBN stations include 1 each in Alaska and Hawaii]

The selection of stream monitoring locations was aided by the Water Resources Council (WRC) hierarchial classification of hydrologic drainage basins of the United States (Seaber and others, 1987) consisting of 21 major regional drainage basins, 222 subregional basins, 352 accounting units, and 2150 cataloging units. NASQAN stations were located at the outlets of many of the accounting and cataloging units to satisfy one of the network's primary goals of accounting for chemical mass and water transported from the continent and its major interior watersheds. The median drainage area of NASQAN watersheds is about 4,000 square miles with about one-half of the watersheds (interquartile range) ranging from 1,000 to 15,000 square miles. The drainage areas of the watersheds span a considerable range from less than one square mile to over one million square miles (Table 1).

Table 1. Drainage basin size and cultural characteristics of National Stream Quality Accounting Network watersheds

[NASQAN, National Stream Quality Accounting Network. The drainage area statistics exclude 29 watersheds with interderminant area. The cultural characteristics were estimated using digital drainage boundaries for 507 NASQAN stations. Accounting unit (Seaber and others, 1987) boundaries were used for 85 NASQAN stations without digitized drainage basin boundaries. Cultural characteristics are not available for 26 stations located outside of the conterminous United States. Population data are for 1990 (U.S. Bureau of Census, 1991), and land-cover statistics are for 1987 (U.S. Soil Conservation Service, 1989)]

Characteristic	Range		Percentiles of station watersheds		
	Minimum	Maximum	25th	50th	75th
	NASQAN basins				
Drainage area (mi^2)	1	1,140,500	1,238	4,390	14,910
Population density (no./mi^2)	0.7	2,577	14.3	41.3	108.3
Crop area (%)	0	90.4	4.5	12.4	29.3
Forest area (%)	0	87.7	3.4	17.4	50.6
Urban area (%)	0	43.3	0.7	2.0	4.5
	334 accounting units in the conterminous United States				
Drainage area (mi^2)	121	47,740	4,751	7,838	11,613
Population density (no./mi^2)	1.3	3,971	13.9	47.8	118.7
Crop area (%)	0.1	81.1	5.0	14.5	31.5
Forest area (%)	0	84.5	2.0	15.8	45.4
Urban area (%)	0.1	42.9	0.7	2.3	4.7

The location of monitoring stations on rivers throughout the United States according to hydrologic criteria has generally produced more geographically representative descriptions of national and regional water quality than are available from other monitoring networks (Smith and others, 1993; Smith and others, 1987b). These hydrologic criteria have avoided the types of biases common to many monitoring networks that were frequently designed to monitor local water-pollution problems. Moreover, the similarity of the population and land-cover characteristics of the NASQAN drainage basins to those of all accounting units in the conterminous United States (Table 1) suggests that, in general, the stations broadly represent many of the cultural factors influencing water quality. For example, the crop and forest areas expressed as a percentage of the total NASQAN drainage basin area typically range from less than 10 percent to about 50 percent with medians of 12 percent and 17 percent, respectively. Very similar land-cover characteristics are noted for all U.S. accounting units (Table 1). The distribution of population density for NASQAN watersheds is also very similar to that for U.S. accounting units. The median population density of the NASQAN watersheds is about 41 persons per square mile, and typically ranges from 14 to 108 persons per square mile (Table 1). By comparison, the median population density for the accounting units is 48 persons per square mile, and typically ranges from about 14 to 119 persons per square mile.

Constituent coverage

NASQAN has provided relatively consistent monitoring for a large suite of constituents during its history. Water measurements have included a set of approximately 85 physical, chemical, and biological properties. All water properties historically monitored at NASQAN stations, with the exception of pesticides, are published on the CD-ROMs (Table 2). This includes 63 water properties or 122 constituents including dissolved, suspended, and whole-water (i.e, total) analyses of these properties. Organic pesticides were measured in the water column and bed sediments at about 160 NASQAN stations from 1975 to 1982 as part of the National Pesticide Water Monitoring Program (Feltz and others, 1971); however , these data were not included on the CD-ROMs because of space limitations and the high frequency of nondetects. These data have been previously summarized by the USGS (Gilliom and others, 1985).

Most physical and field measurements, major ions, and nutrients have been regularly monitored at NASQAN stations throughout the 1973 to 1995 period of operation. Monitoring for several other constituents began after 1973 including radiochemicals (1975 at a subnetwork of 53 sites), measures of fecal bacteria (1976), organic carbon (dissolved and suspended in 1977), and alkalinity (field determinations in 1985). Several constituents were discontinued prior to 1995 including periphyton (1980), organic carbon (1981), phytoplankton (1981), and selected trace elements in 1982 and 1991. Whole-water analyses of trace elements were discontinued in 1982 due to budget reductions. Selected dissolved trace elements, including arsenic, beryllium, cadmium, chromium, copper, lead, mercury, and zinc, were discontinued in 1991 because of concerns about the introduction of contamination during the processing of samples in the field (Windom and others, 1991; Horowitz and others, 1994). USGS investigations of trace-element sample contamination raised important concerns about the accuracy of the data for these constituents prior to 1991. These studies led to the implementation of a new sample collection and processing protocol for low-level inorganic analyses in 1994 (Horowitz and others, 1994). The results of these investigations and related documents are provided on the CD-ROMs to assist in the proper use of trace-element data collected prior to 1991 (see the section entitled "National Network Field Techniques" for additional information).

Sampling frequency

NASQAN samples have been collected according to fixed time intervals (i.e., uniform sampling). The time interval of sample collection has typically ranged from quarterly to monthly according to the constitutent and year (Table 2). Trace elements, radiochemicals, periphyton, phytoplankton, and organic carbon have typically been sampled with the lowest frequency (ranging from 1 to 7 samples per year). Samples have periodically been collected more frequently than monthly at some stations. These cases often include "continuously"-monitored field measurements (e.g., temperature, pH, specific conductance, dissolved oxygen) or supplemental monitoring of various constituents as part of USGS District cooperative projects or other federal or state programs [e.g., National Water Quality Surveillance System-NWQSS (USEPA, 1976); USGS daily suspended sediment stations].

Reductions in the sampling frequency of all constituents have occurred with time (Fig. 2) in response to budgetary constraints (see the following section "Historical changes in network operations" for a description of changes in network expenditures). Prior to 1982, monthly samples were collected at all NASQAN stations for most constituents. In 1982, most constituents were sampled bimonthly. After 1982, the sampling frequency of constituents was reduced to quarterly at many stations. The proportion of stations with

Table 2. Water properties and approximate sampling frequencies for National Stream Quality Accounting Network and Hydrologic Benchmark Network water-quality data on CD-ROM

Water properties	Frequencies[1] (samples per year)
Physical/field measurements:	
Temperature, specific conductance (field and laboratory), dissolved oxygen, pH (field and laboratory), suspended sediment, turbidity, instantaneous streamflow	4 to 12
Streamflow, daily mean	365
Major ions:	
Calcium, chloride, magnesium, potassium, silica, sodium, sulfate, fluoride, dissolved solids, hardness, alkalinity, bicarbonate, and carbonate	4 to 12
Nutrients and carbon (dissolved and total)[2]:	
Ammonia plus organic (Kjeldahl) nitrogen, ammonia, nitrite, nitrate plus nitrite, orthophosphate, phosphorus, and nitrogen	4 to 12
Organic carbon (includes suspended also)	4 to 8
Radiochemicals (dissolved, suspended sediment):	
Gross alpha and beta, radium-226, tritium, uranium	1 or 2
Biological measurements:	
Fecal coliform and streptococci	4 to 12
Periphyton (chlorophyll A and B), periphyton biomass	4
Phytoplankton (chlorophyll A and B), phytoplankton (total count), identification of predominant forms	7 to 12
Inorganic trace elements (dissolved, total):	
Aluminum, arsenic, barium, beryllium, boron, cadmium, chromium, cobalt, copper, iron, lead, lithium, manganese, mercury, molybdenum, nickel, selenium, silver, strontium, vanadium, and zinc	3 or 4

[1] The range of sample frequencies for any constituent group reflects differences in frequency among the two networks, changes in frequency with time, and differences among stations within a single network. See the section "Sampling Frequency" for a discussion of temporal changes in sampling frequency.

[2] Analyses for the "total" forms of nitrate plus nitrite, nitrite, ammonia, and orthophosphate are based on samples "decanted" in the laboratory (see the section "National Network Laboratory Techniques" for additional details). Total nitrogen is computed as the sum of total Kjeldahl nitrogen and "total" nitrate plus nitrite.

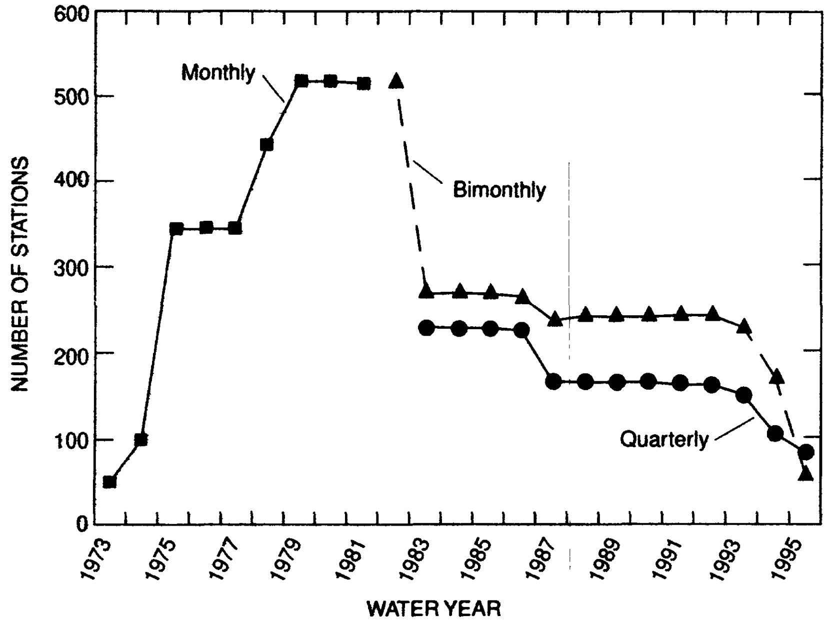

Figure 2. Number of National Stream Quality Accounting Network stations using monthly, bimonthly, and quarterly sampling frequencies by water year, 1973-95

bimonthly and quarterly sampling frequencies remained relatively constant from 1983 to 1995 with slightly more NASQAN stations sampled bimonthly than quarterly. During 1993 and 1994, in addition to the bimonthly and quarterly sampling frequencies used at most sites, samples were also collected five times per year at 81 and 120 sites, respectively. In 1995, in addition to bimonthly and quarterly sampling (107 stations), samples were collected at other frequencies (5, 3, or 2 times per year) at a total of 35 stations. NASQAN protocols established the recommended time periods for sample collection according to bimonthly and quarterly sampling frequencies as shown in Table 3.

The sampling of network sites according to fixed time intervals addresses several statistical and operational goals related to both the accuracy of trend detection methods and the efficiency of the collection of water-quality samples. The analysis and interpretation of time trends (objective 3) benefits from the use of statistically-independent water-quality observations that are equally spaced in time so as to give a temporally-unbiased representation of water-quality variations. Moreover, fixed interval sampling allows for efficient scheduling of site visits within the budgetary limits of the program. The disadvantage of fixed-interval sampling is the lack of intensive sampling during high flows, a necessary sampling feature to maximize the accuracy of estimates of the rates of constituent transport. Nevertheless, multi-year sampling at many of the NASQAN stations has produced instantaneous streamflow measurements that are approximately representative of the range of streamflow conditions at the sites (J. Weaver, U.S. Geological Survey, written communication, 1990). In addition, bias-corrected "rating-curve" load estimation techniques (Cohn and others, 1989; Gilroy and others, 1990) have been applied to instantaneous measurements and records of continuous daily streamflow at NASQAN sites to produce relatively reliable long-term estimates of annual mean flux (Cohn and others, 1992; Alexander and others, 1996a).

Table 3. National Stream Quality Accounting Network and Hydrologic Benchmark Network time periods of sample collection for bimonthly and quarterly sampling frequencies

Sample Number	Bimonthly frequency	Quarterly frequency
1	October-November	October-December
2	December-January	January-March
3	February-March	April-June
4	April-May	July-September
5	June-July	
6	August-September	

Historical changes in network operations

Changes in funding levels and network objectives during NASQAN operations have affected the number and types of stations, station sampling frequency, and the types of constituents analyzed. The following discussion provides a brief overview of historical changes in funding and network objectives.

Figure 3 displays the expenditures for NASQAN over the period 1973 to 1995 in 1987 millions of dollars. Funding for NASQAN increased rapidly from 1973 to 1980 with a corresponding increase in the number of stations (Fig. 4). NASQAN began operation in January 1973 with 51 stations. An additional 50 stations were added in 1974, with significant expansion occurring in 1975 as the network grew to 345 stations. The largest number of stations in operation in any single year was 513 stations in 1980. A concomitant increase in the number of field and laboratory analyses also occurred over this period with the total number of water-quality analyses (excluding pesticides) expanding to slightly more than 300,000 in 1980 (Fig. 5).

In 1982, a large decrease of 21 percent in expenditures (Fig. 3) was absorbed through reductions in sampling frequency (a shift from monthly to bimonthly or quarterly sampling at all sites) and constituent coverage (see the previous two sections). The number of sites remained relatively unchanged at about 500 during 1982 and in subsequent years through 1986 (Fig. 4). Reductions in sampling frequency and constituent coverage caused the total number of water-quality analyses to decline by approximately one third from 1981 to 1982 (Fig. 5). These changes were preceeded by an approximate 12 percent decrease in the total number of water-quality analyses from 1980 to 1981 (Fig. 5) resulting in part from the discontinuation of periphyton and organic carbon. Although network expenditures increased in constant dollars from 1983 to 1986 (Fig. 3) and the number of water-quality analyses increased slightly from 1983 through the late 1980s, the number of analyses performed in any year after 1980 was no more than about 50 percent of the total number of analyses performed at the peak of network operations in 1980 (Fig. 5).

In 1987, the number of stations was reduced from 495 to 408 in response to a major review of network objectives. This and other administrative changes lowered expenditures from 1986 to 1987 by 27 percent and by an additional 8 percent from 1987 to 1988 (Fig. 3). From 1987 to 1992, the number of stations remained constant at about 410, with the number of bimonthly sites representing a slightly greater percentage of the total. From 1989 to 1993, funding increased with a notable gain in 1989 (Fig. 3). During this period, the number of water-quality analyses increased slightly through 1991 and then declined through 1995 (Fig. 5). Much of the increase in water-quality analyses during the

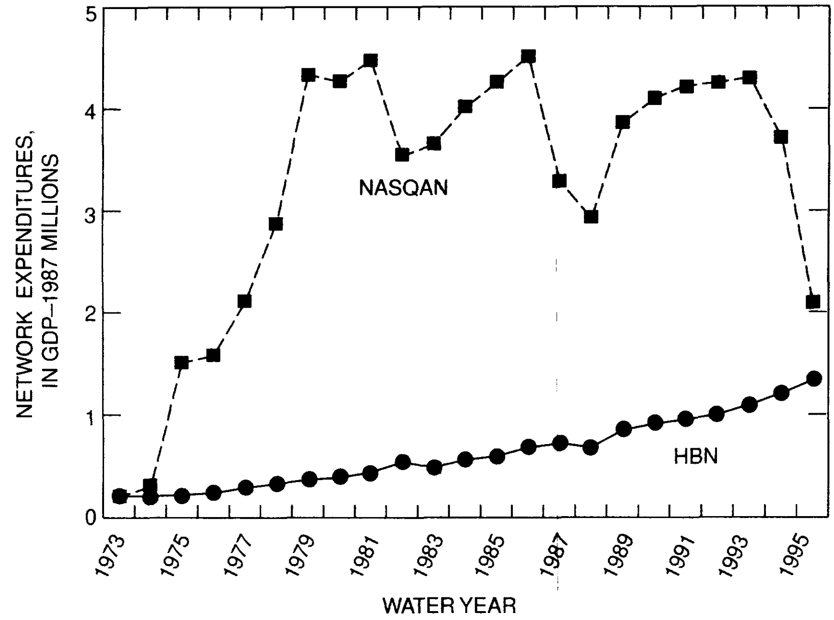

Figure 3. Total annual expenditures for National Stream Quality Accounting Network and Hydrologic Benchmark Network by water year, 1973-95 [Expenditures are expressed in 1987 millions of dollars according to the Gross Domestic Product (GDP) price-deflator]

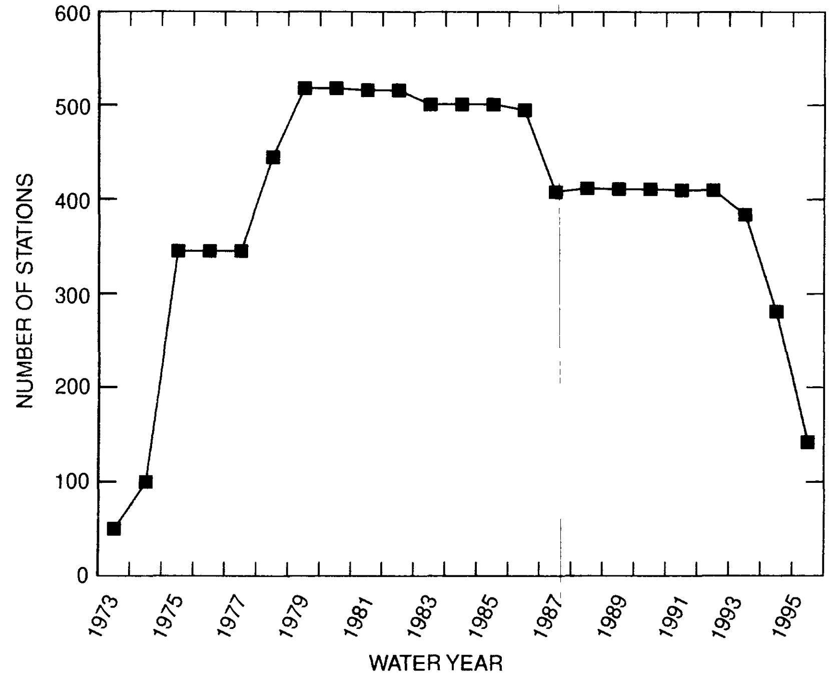

Figure 4. Number of National Stream Quality Accounting Network stations by water year, 1973-95

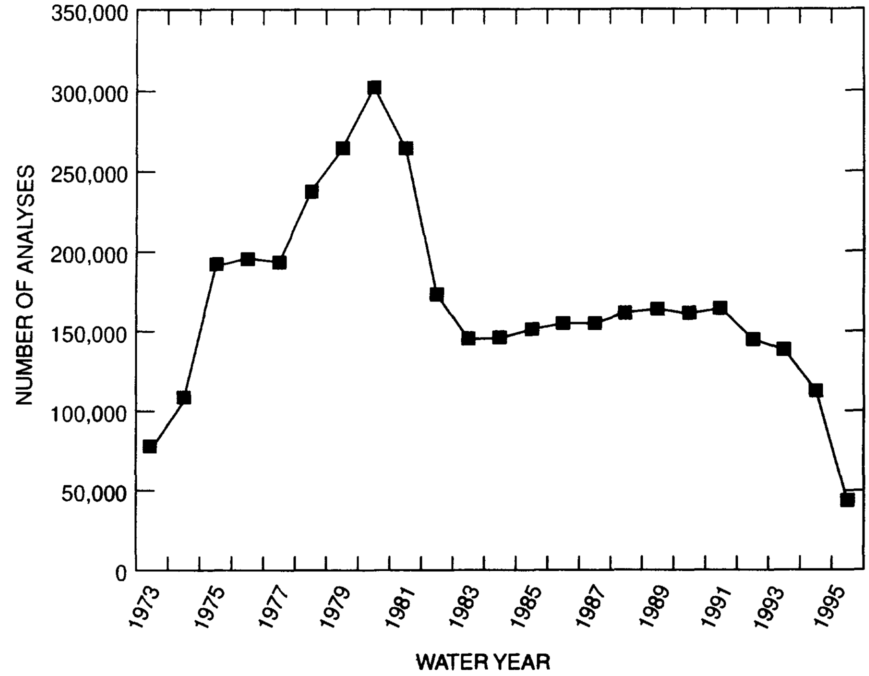

Figure 5. Number of National Stream Quality Accounting Network water-quality analyses by water year, 1973-95

late 1980s can be attributed to special high flow sampling implemented at about six stations and sampling conducted at about eight NASQAN stations as part of the pilot phase of the National Water Quality Assessment Program.

From 1993 to 1995, network expenditures declined significantly (Fig. 3) and the number of stations was sharply reduced from 384 to 142 (Fig. 4). Station operation costs also increased considerably during this period because of the implementation of an improved and more costly sampling protocol (see the section entitled "National Network Field Techniques" for more information). As a result, the number of water-quality analyses shows large declines from 1993 to 1995 (Fig. 5).

Major reviews of NASQAN in 1981, 1986, and 1995 led to various changes in network objectives, the types and number of stations, sampling frequency, and constituent coverage. Many of the changes resulting from these reviews are described in annual national network implementation memoranda (see a subsequent section entitled "National Network Field Techniques"). The 1981 review led to several changes in constituent coverage and sampling frequency beginning in 1982 and 1983, and included among other items the elimination of phytoplankton and organic carbon analyses and a modification of the nutrient schedule. The 1986 NASQAN review led to changes in the number and characteristics of the stations beginning in 1987. Network objectives were modestly revised to place greater emphasis on trend detection in smaller watersheds with more uniform land cover characteristics. The objective of accounting for mass transport was maintained although greater emphasis was placed on monitoring mass transport to major estuaries and significant fresh water bodies including the Great Lakes. The review of NASQAN led to the elimination of 90 stations that were either located downstream of certain reservoirs, located in proximity to other stations on the mainstem of large rivers, experiencing sampling problems, or located in small coastal drainages that were over-represented in the network. Thirty-one sites were added to the network in 1987 to provide better representation of certain land-cover types. The 1995 review of NASQAN led to an increased emphasis on the characterization of load for a wide range of water properties, including herbicides, in the largest drainage basins of the United States. Review recommendations were implemented in 1996 when the network was reduced to 31 stations in the Mississippi, Columbia, Colorado, and Rio Grande River Basins and five stations in major coastal drainages of the United States to accomodate a shift to more intensive sampling at each site.

Statistical analyses and interpretations of NASQAN data

Since the beginning of NASQAN, the data have been used to satisfy stream water-quality information needs at a variety of geographic levels. Many of these applications of the data appear in the publications listed in the national network bibliography in the appendix. Uses of the data have included summary and interpretative investigations at the national (e.g., Smith and others, 1987a; Lettenmaier and others, 1991; Briggs and Ficke, 1977) and regional (e.g., Alexander and others, 1996a) geographic levels. NASQAN data have also been used extensively in more spatially detailed analyses at the state (Schertz, 1990; Schertz and others, 1994; Hay and Campbell, 1990; Petersen, 1992) and accounting unit (e.g., Rinella, 1986; Graczyk, 1986; Hainly and others, 1989) levels. The publications listed in the appendix cover a range of time periods and include analyses of trends in water quality and their causes and studies of chemical flux. NASQAN data have also served as baseline information for developing and illustrating many statistical techniques (e.g., Smith and others, 1982; Hirsch and others, 1982; Hirsch and others, 1991; Alexander and others, 1993) and have aided the development of computerized water-quality data management and trend analysis systems (Crawford and others, 1983; Schertz and others, 1991).

Hydrologic Benchmark Network (HBN)

The HBN was established in 1958 by the USGS to provide a standard base of hydrologic data from minimally disturbed watersheds that could be used to investigate naturally-induced changes in streamflow and water quality (Langbein, 1968; Cobb and Biesecker, 1971). Leopold (1962a, 1962b) originally promoted the goal of establishing a baseline or "benchmark" monitoring network to investigate the influence of terrestrial and climatic factors on streamflow and water chemistry independent of the cultural effects common in most watersheds of the United States. Data from the network has served several purposes including the investigation of naturally-induced changes in hydrologic variables, the investigation of the statistical characteristics of stationary hydrologic time series, and the study of the effects of atmospherically-derived pollutants on stream water quality.

HBN watersheds were selected on the basis of the following criteria (Cobb and Biesecker, 1971):

1. No manmade storage, regulation, or diversion currently exists or is probable for many years.

2. Ground water within the basin will not be affected by pumping from wells.

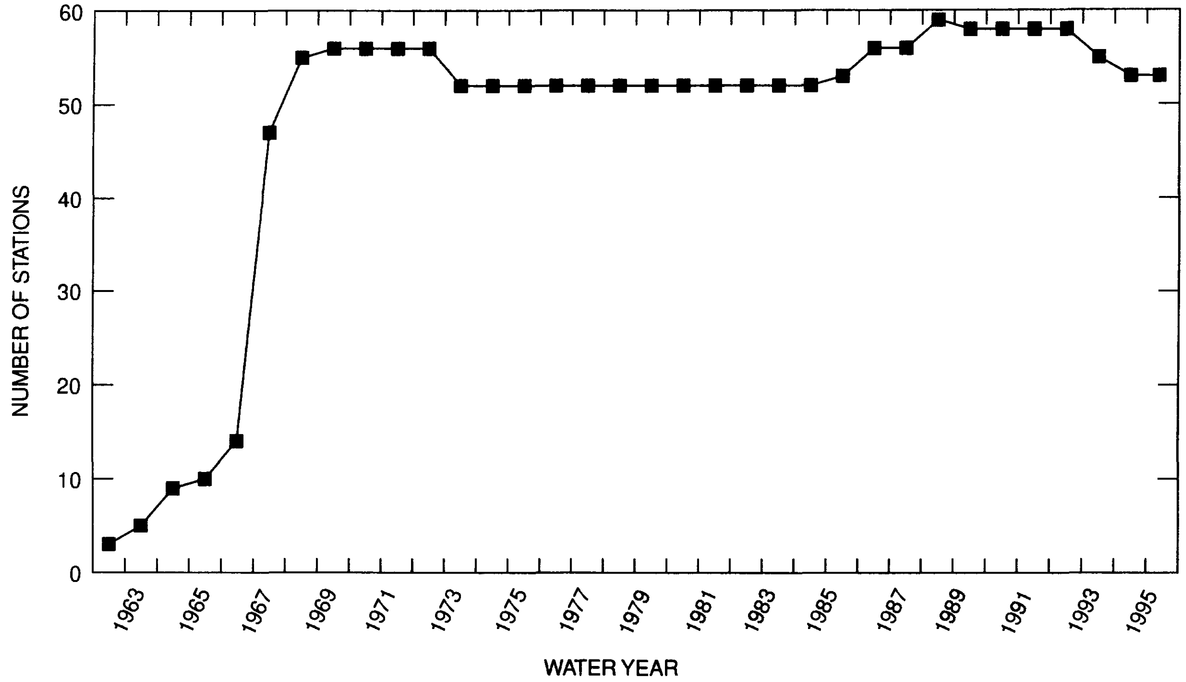

Figure 6. Number of Hydrologic Benchmark Network stations by water year, 1962-95

3. Conditions favorable for accurate measurement of streamflow, chemical and physical quality of water, ground-water conditions, and the various characteristics of weather, principally precipitation.

4. The probability is small of special natural changes due to such things as major activities of beavers, overgrazing or overbrowsing by game animals, or extensive fires.

HBN selection criteria resulted in the placement of many monitoring stations in national parks, wilderness areas, State parks, national forests, and specially-protected areas set aside for scientific investigations. A few stations were located in moderately disturbed watersheds (e.g., agriculture, logging) in cases where land use was not expected to change radically. A complete description of the watershed characteristics is provided by Cobb and Biesecker (1971) and Biesecker and Leifeste (1975).

The HBN has consisted of 63 watersheds located in 37 states (Fig. 1). Most stations began operation in the mid to late 1960's with the earliest date of water-quality data collection in 1962 (see Fig. 6). Virtually all sites were in operation by 1968 (Fig. 6). HBN watersheds represent a wide variety of natural environments including various geologic and climatic provinces and a diversity of vegetation and soils. Elevations of the watersheds range from about 100 to over 14,000 feet above sea level and vegetation ranges from sparse desert growths to dense coniferous forests (Cobb and Biesecker, 1971). In general, basins of an intermediate size were sought for the network. The median basin size is 57 square miles (25th and 75th percentiles of 24 and 99 square miles, respectively) with basin sizes ranging from 2 to 2000 square miles.

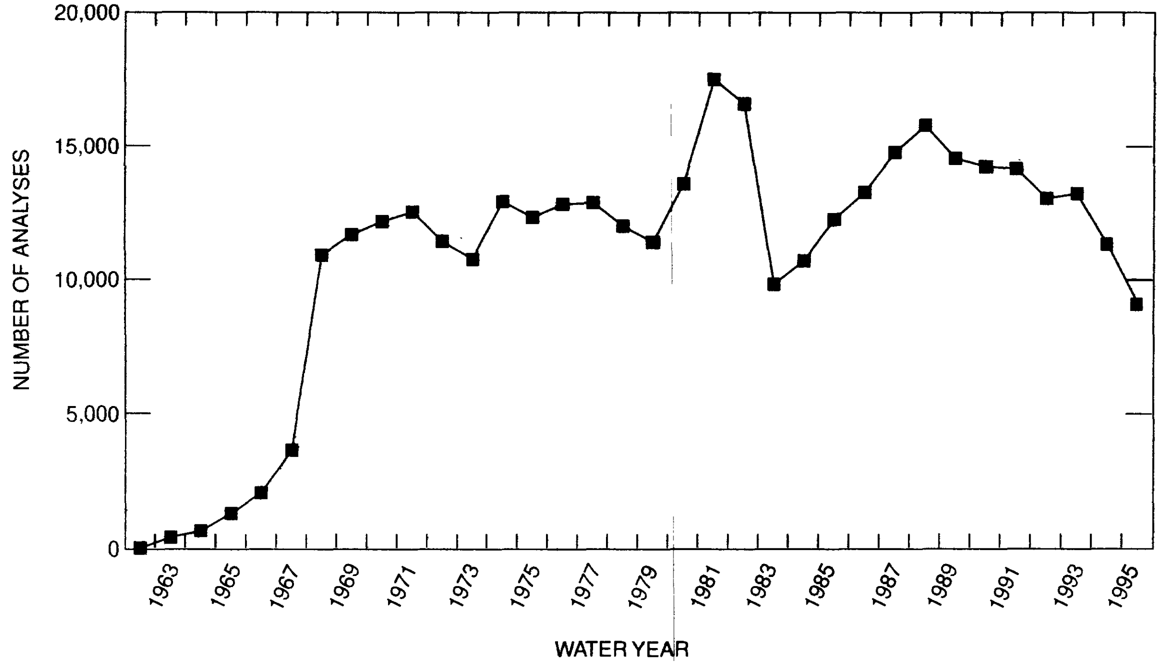

Figure 7. Number of Hydrologic Benchmark Network water-quality analyses by water year, 1962-95

The physical, chemical, and biological constituents (Table 2) and the methods of sample collection and laboratory analysis are identical to those used in NASQAN during the 1973 to 1995 period. The sampling frequency of HBN stations underwent changes in 1983 in response to funding reductions (Fig. 3). Prior to 1983, monthly samples were collected at 34 of the approximately 52 HBN stations. Bimonthly samples were collected at 14 stations and quarterly samples were collected at four stations. Beginning in 1983, most HBN stations were sampled quarterly (43 sites) with the remaining sites sampled bimonthly (10 sites) or monthly (2 sites).

Funding at HBN sites steadily increased throughout the history of the program with modest reductions occurring in 1983 and 1988 (Fig. 3). The number of water-quality analyses similarly increased over much of the period of operation (Fig. 7). A major decline in the number of analyses occurred in 1983 corresponding to the reduction in sampling frequency at network stations. Decreases in analyses in 1994 and 1995 were related to reductions in the number of sites (Fig. 6) and the number of constituents including radiochemicals and nutrients.

The network has provided excellent opportunities to investigate the effects of atmospherically-derived pollutants on stream water quality (especially sulfate and nitrogen) independent of the effects of culturally-derived land disturbances common to most watersheds (e.g., Smith and Alexander, 1986). Although the HBN stations were selected to control for the effects of anthropogenic influences on water quality, atmospherically-derived pollutants (believed to be mostly of human origin) are a major source of sulfate and nitrate in many of the watersheds (Smith and Alexander, 1983). The influence of atmospheric pollutant sources, particularly fossil fuel residuals of nitrogen and sulfur, became increasingly known after the network began, as researchers documented the effects of increasing atmospheric emissions of nitrogen and sulfur on the stream chemistry of many northeastern watersheds (Likens and others, 1980; NRC, 1983) and HBN basins (Smith and Alexander, 1983; Smith and Alexander, 1986; Kramer and others, 1986).

A detailed survey of the network was conducted in the early 1990s to evaluate the integrity of each watershed with respect to the original network objectives. This included assessments of the effects of geologically- and atmospherically-derived substances such as sulfur on stream chemistry as well as inventories of land use practices in the watersheds. In some of the watersheds, land cover changes occurred over time, most notably with respect to agriculture and logging practices, and may have affected the water chemistry measured at the stations. The survey led to the elimination of six stations and the addition of two sites in 1993 and 1994.

The national network bibliography in the appendix includes publications related to HBN. These include publications describing the origins of the network (e.g., Cobb and Biesecker, 1971; Leopold, 1962b) as well as many national and regional investigations using the data (e.g., Lawrence, 1987; Smith and Alexander, 1986; Lins, 1986). Also, many site-specific studies were conducted including several investigations of the water-quality data from McDonalds Branch in New Jersey (Johnson, 1979a; Johnson, 1979b; Lord and others, 1990, Johnsson and Barringer, 1993; Morgan, 1984; Turner and others, 1985) and other selected HBN watersheds in the northeastern United States (Hainly and Ritter, 1986; Peters and others, 1982; Stoddard, 1991).

Administration of the National Networks

The Office of Water Quality (OWQ) of the USGS's Water Resources Division has administered the NASQAN and HBN. Sample collection is conducted by USGS local District offices under the supervison of the OWQ. Samples were analyzed in USGS District laboratories prior to about 1973, and in the USGS Central Laboratory system after this date (see the following section on laboratory methods for additional details).

During the period of network operations, the OWQ periodically released protocols specifying the accepted field sampling, processing, and measurement procedures and required laboratory analytical methods for national network samples. Many of the national network field and laboratory protocols were released in the form of internal USGS technical memoranda. Also, beginning in the early 1980s, the OWQ annually communicated network protocols to the local field offices as part of the national network memoranda. These memoranda described changes in network procedures and monitoring station locations from the previous year, and provided regular updates on a wide range of network-related activities.

As part of network operations, the OWQ implemented the recommendations of periodic reviews by USGS committees of national network monitoring objectives and station design. For example, major reviews of the networks were conducted in 1981, 1986, and 1995. These reviews have resulted in adjustments in network objectives, the number and location of stations, constituent coverage, and sampling frequencies (see the discussion of selected reviews in the previous two sections). Selected changes that resulted from these reviews are documented in annual national network memoranda.

The OWQ's broader responsibilities of providing guidence to the Districts in the selection and use of USGS field and laboratory water-quality methods have also directly benefited national network operations. The OWQ has the responsibility to ensure that

District water-quality activities include the use of standard methods of data collection and analysis, the application of effective quality-assurance practices, and the training of technical personnel. The OWQ conducts regular technical reviews of District water-quality activities to evaluate these practices. For example, a program of regular evaluation of the accuracy of field determinations (pH, alkalinity, specific conductance, and dissolved oxygen) is coordinated with regional and District personnel. National, regional, and District training in water-quality sample collection and processing methods has also been coordinated by the OWQ and regional and District water-quality specialists. A detailed discussion of USGS water-quality monitoring and quality-assurance activities is provided by Friedman (1993).

The OWQ has also periodically developed and evaluated new field and laboratory methods, that are used by the national networks, to address sampling problems or to improve measurement accuracy. For example, a new sampling and processing protocol for low-level inorganic analyses was developed and implemented in 1994 in response to concerns about trace-element contamination. This method now supports many District investigations and the operations of the national networks. Other studies have also been initiated by the OWQ to evaluate nutrient preservation techniques and alkalinity determinations. Many of the historical records of actions resulting from these investigations are contained in USGS water-quality technical memoranda referenced in the next section of the report.

National Network Field Techniques

Standard methods of sample collection, processing, and field measurement have been used throughout the history of the national networks. Detailed descriptions of these methods can be found in Rainwater and Thatcher (1960), Edwards and Glysson (1988), Ward and Harr (1990), Britton and Greeson (1989), Guy and Norman (1970), Horowitz and others (1994), and USGS memorandum QW74_11, which provides field instructions for NASQAN [references to USGS memoranda in this paper are of the form XXyy_nn, where XX identifies the originating office (QW = Office of Water Quality; NL = National Water Quality Laboratory), yy is the year of release, and nn is the alphanumeric identifier for the year's memoranda]. A summary of important changes in field methods, constituent coverage, and field sample contamination during the operation of the networks is given in Table 4. A list of important USGS memoranda documenting network operations and changes in field and laboratory methods is presented in Table 5. The text and illustrations for these memoranda can be found on the CD-ROMs (see Alexander and others, 1996b).

Virtually all physical, chemical, and biological samples are collected from the water column at network stations. The exceptions include pesticides in bottom sediment samples and periphyton measurements based on the use of an artificial substrate method (see memorandum QW74_11 for details of the periphyton methods). Field measurements at network sites include instantaneous discharge, barometric pressure, water temperature, air temperature, specific conductance, pH, dissolved oxygen, fecal bacteria, and alkalinity (note changes in alkalinity procedures in Table 4). Daily mean values of streamflow are obtained from continuous river stage records, and are available for most network stations. In some cases, records of daily streamflow values are available from nearby gaging stations.

Table 4. Important changes in National Stream Quality Accounting Network and Hydrologic Benchmark Network field methods, constituent coverage, and field sample contamination from 1973-95

[NASQAN, National Stream Quality Accounting Network; HBN, Hydrologic Benchmark Network. USGS memoranda are identified by the unique number QWyy_nn where yy gives the year of the document and nn is a sequential number of the year's memoranda]

Constituent	Date	Description of change (memoranda or references)
Alkalinity	10-01-84	Field determinations of alkalinity by fixed-endpoint titration (QW84_16) required for all network samples. Alkalinity determinations between 1980 and 1984 were most likely made in the lab, but parameter code 00410 allowed for storage of field determinations (QW80_27, QW81_04, QW82_05) that may have been made by some network field personnel. Determinations prior to October 1, 1980 were made in the laboratory.
	10-01-85	Filtered samples required for field determinations of alkalinity by fixed-endpoint titration (QW85_19). Previous field determinations of alkalinity were made on unfiltered water samples.
		Field determinations of bicarbonate and carbonate in filtered samples by incremental titration method (QW85_19) implemented. Significant differences found between fixed-endpoint and incremental methods during 1984-85 study.
Biological parameters	01-01-73 - 10-01-80	Periphyton collected.
	01-01-73 - 10-01-81	Phytoplankton collected.
	10-01-77	Change in phytoplankton sampling from 12 per year to 4 samples collected in June to Sept. months and 3 samples during the remainder of the year (QW77_12).
Carbon, organic	01-01-73 - 10-01-81	Total collected.
	12-28-76	Evidence of a negative bias of unknown magnitude in total organic carbon resulting from various loss processes (e.g., adsorption to container walls, biological activity). Questionable values were deleted from the data files prior to this time (QW77_02).
	10-01-77 - 10-01-81	Dissolved and suspended collected.
Fecal bacteria	10-01-75	Began sampling.
Coliform	10-01-76	Parameter code changed from 31616 to 31625 with increase in filter pore size from 0.45 to 0.70 micrometer (QW76_25T). Studies showed that more accurate results are obtained using 0.70-micrometer pore size filters.

Table 4. Important changes in National Stream Quality Accounting Network and Hydrologic Benchmark Network field methods, constituent coverage, and field sample contamination from 1973-95--Continued

Constituent	Date	Description of change (memoranda or references)
Fecal bacteria		
Streptococci	10-01-76	Parameter code changed from 31679 to 31673 (QW76_25T) with change in media type from M-enterococcus agar to KF agar (0.45- or 0.70-micrometer filter size accepted for either parameter code; field personnel tended to use the same filter pore size as used for fecal coliform samples).
	04-15-91	A filter pore size of 0.45 micrometer is required to comply with TWRI methods (QW91_FS). A study of the effects of the two pore sizes on analytical results based on data collected at NASQAN and HBN stations in 1990 indicates no statistically significant differences in methods (QW91_FS). The differences in analytical results appear to reflect random measurement errors with no evidence of upward or downward bias based on the symmetry of the distribution of differences.
Radiochemicals	10-01-75	Began sampling.
Trace elements	04-01-78 - 02-28-79	Sample contamination with lead and cadmium from paint ring on acid ampoules (QW79_12).
	10-01-82	Discontinued analyses for total recoverable trace elements (QW82_18).
	Before 1991	Contamination detected in trace-element samples from 1989 to 1991 related to field sampling and processing procedures. Discontinued analyses for arsenic, beryllium, cadmium, chromium, copper, lead, mercury, and zinc in 1991 (QW90_13, QW91_10, QW92_05). The evidence of contamination raised important concerns about the accuracy of the data for these constituents prior to 1991.
	Before 1993	Studies beginning in 1987 showed trace-element contamination associated with the interior components of some samplers (Horowitz and others, 1994). Previously, the exterior of samplers had been routinely coated with epoxy paint to avoid contamination. The following samplers were phased out beginning in 1993: DH48, DH59, DH76, D74, P61, P63, and P72.
	10-01-93	Capsule filters (0.45 micrometer) began to be used at many stations. Higher concentrations of trace elements may be expected due to the transmission of more colloid-sized particles (QW93_05).

Table 4. Important changes in National Stream Quality Accounting Network and Hydrologic Benchmark Network field methods, constituent coverage, and field sample contamination from 1973-95--Continued

Constituent	Date	Description of change (memoranda or references)
Trace elements	02-01-94	New sampling and processing protocol implemented at some stations for low-level inorganic analyses (QW94_09, QW94_05, QW93_11). Several USGS studies documented the need for revisions in sample collection and field processing procedures for trace elements (Horowitz and others, 1994; QW93_06; QW93_05; QW93_03; QW92_13, QW92_12, QW94_13). Samplers with Teflon or plastic components (DH81, D77) were recommended for use.
Trace elements (mercury)	Period of record	Caution should be exercised in the interpretation of mercury data (QW94_10). Possible contamination sources include mercuric chloride tablets (QW80_26), manometers, thermometers, and blue-silicon seals and stoppers of Kemmerer and Van Dorn samplers.

Table 5. U.S. Geological Survey memoranda describing National Stream Quality Accounting Network and Hydrologic Benchmark Network protocols and changes in network field and laboratory methods

[NASQAN, National Stream Quality Accounting Network; HBN, Hydrologic Benchmark Network; NWQSS, National Water Quality Surveillance System; NWIS, National Water Information System; WATSTORE, National Water Data Storage and Retrieval System. The memoranda are organized chronologically from the earliest to latest dates for six topical areas, and are identified by the originating office and a unique number QWyy_nn (Office of Water Quality) and NLyy_nn (National Water Quality Laboratory), where yy gives the year of the document and nn is a sequential number of the year's memoranda. The text for the memoranda are presented on the CD-ROMs in separate ASCII files identified by the name QWyy_nn.TXT or NLyy_nn.TXT]

Memorandum number	Date	Contents
		National network implementation memoranda
QW96_02	12-04-95	National Hydrologic Benchmark Network: Fiscal Year 1996-October 1, 1995 to September 30, 1996. Outlines program status and protocol for operation of HBN for FY 1996.
QW95_01	10-28-94	National Water-Quality Networks: Fiscal Year 1995-October 1, 1994 to September 30, 1995. Outlines Program status and protocol for operation of NASQAN and HBN for FY 1995.

Table 5. U.S. Geological Survey memoranda describing National Stream Quality Accounting Network and Hydrologic Benchmark Network protocols and changes in network field and laboratory methods--Continued

Memorandum number	Date	Contents
QW93_14	09-21-93	National Water-Quality Networks: Fiscal Year1994-October 1, 1993 to September 30, 1994. Outlines program status and protocol for operation of NASQAN and HBN for FY 1994.
QW93_01	10-05-92	National Water-Quality Networks: Fiscal Year 1993-October 1, 1992 to September 30, 1993. Outlines program status and protocol for operation of NASQAN and HBN for FY 1993.
QW91_11	09-30-91	National Water-Quality Networks: Fiscal Year 1992-October 1, 1991 to September 30, 1992. Program status and protocol for NASQAN and HBN for FY 1992 are outlined. Personnel responsible for collecting NASQAN and HBN samples should read this memo.
QW90_13	09-27-90	National Water-Quality Networks: Fiscal Year 1991-October 1, 1990 to September 30, 1991. Program status and protocol for operation of the National Stream Quality Accounting Network (NASQAN) and the Hydrologic Benchmark Network (HBN) for FY 1991 are outlined. Personnel responsible for collecting NASQAN or HBN samples should read this memorandum.
QW90_02	10-04-89	National Water-Quality Networks: Fiscal Year 1990-October 1, 1989 to September 30, 1990. Program status and protocol for operation of the National Stream Quality Accounting Network (NASQAN) and the Hydrologic Benchmark Network (HBN) for FY 1990 are outlined. Personnel responsible for collecting NASQAN or HBN samples should read this memorandum.
QW88_10	09-26-88	National Water-Quality Networks: Fiscal Year 1989-October 1, 1988 to September 30, 1989. Program status and protocol for operation of the National Stream Quality Accounting Network (NASQAN) and the Hydrologic Benchmark Network (HBN) are outlined.
QW88_01	10-09-87	National Water-Quality Networks: Fiscal Year 1988-October 1, 1987 to September 30, 1988. This memorandum contains an outline of Program status and protocol for operation of the National Stream Quality Accounting Network (NASQAN) and the Hydrologic Benchmark Network (HBN) for FY 1988.

Table 5. U.S. Geological Survey memoranda describing National Stream Quality Accounting Network and Hydrologic Benchmark Network protocols and changes in network field and laboratory methods--Continued

Memorandum number	Date	Contents
QW86_10	09-30-86	National Water-Quality Networks: Fiscal Year 1987-October 1, 1986, to September 30, 1987. Program status and protocol for operation of the National Stream Quality Accounting Network (NASQAN) and the Hydrologic Benchmark Network (HBN) in FY 1987 are outlined in this memorandum.
QW86_01	03-10-86	Revisions to Field Operations for NASQAN and the HBN for FY 1986. Due to a slight budget reduction, listed are moderate changes in field and project operations for the NASQAN and HBN in FY 1986.
QW85_19	09-18-85	National Water-Quality Networks: Fiscal Year 1986-October 1, 1985, to September 30, 1986. Program status and protocol for operation of the NASQAN and the HBN in FY 1986 are outlined in this memorandum.
QW84_16	09-13-84	National Water-Quality Networks; Fiscal Year 1985-October 1, 1984 to September 30, 1985. Program status and protocol for operation of NASQAN and HBN in FY 1985 are outlined.
QW83_18	10-03-83	National Water-Quality Networks; FY 1984-October 1, 1983 to September 30, 1984. Program status and protocol for operation of NASQAN and HBN in FY 1984 are outlined.
QW82_18	09-28-82	National Water-Quality Networks; FY 1983. Protocol for NASQAN and HBN in FY 1983 are outlined.
QW82_03	11-27-81	National Water-Quality Networks; FY 1982. Protocol for NASQAN and HBN in FY 1982 are outlined.
QW81_01	10-02-80	National Water Quality Networks; FY 1981. Protocol for NWQSS program and changes in NASQAN and HBN in FY 1981 are outlined.
QW80_01	10-18-79	National Water-Quality Networks: Modification to NWQSS, NASQAN, and HBN programs and subsequent modifications to the assigned unique numbers. Important changes to the programs are discussed.

Table 5. U.S. Geological Survey memoranda describing National Stream Quality Accounting Network and Hydrologic Benchmark Network protocols and changes in network field and laboratory methods--Continued

Memorandum number	Date	Contents
QW77_11	09-15-77	Data Networks: HBN and NASQAN: water-quality program components, FY 1978. New laboratory schedule numbers have been established for NASQAN and HBN.
QW74_11	02-28-74	Data Networks, NASQAN. General field instructions for the national stream-quality accounting network for FY 1974.
		Biological methods
QW91_FS	04-15-91	Results of analysis of fecal streptococcal bacteria data collected using 0.45- and 0.7-micrometer pore-size filters. (correspondance from national network's coordinator to District and Regional water-quality specialists) Also includes a re-analysis of the raw data.
QW77_12	09-15-77	Phytoplankton sampling for NASQAN. Data-collection plans for NASQAN have been revised to take advantage of the opportunity for increased efficiency of operation suggested by results described herein.
QW76_25T	09-01-76	Analytical methods--microbiological (fecal bacteria). Describes changes in fecal coliform and fecal streptococci bacteria methods effective October 1, 1976.
		Nutrient methods
QW94_16	08-05-94	New Preservation Techniques for Nutrient Samples. Beginning October 1, 1994, the Water Resources Division of the USGS will preserve ambient water samples to be analyzed for nutrients by chilling only, with mailing to the National Water Quality Laboratory within 3 days.
QW93_04	12-02-92	Discontinuation of the National Water Quality Laboratory determinations for "total" nitrite, "total" nitrite plus nitrate, "total" ammonia, and "total" orthophosphate (using the four-channel analyzer). Effective immediately, project personnel are to discontinue requests for the listed determinations.
QW92_10	07-13-92	Phosphorus Methods and the Quality of Phosphorus Data. Describes two changes implemented at the National Water Quality Laboratory for the analysis of phosphorus and the history of total phosphorus analytical methods since 1973.

Table 5. U.S. Geological Survey memoranda describing National Stream Quality Accounting Network and Hydrologic Benchmark Network protocols and changes in network field and laboratory methods--Continued

Memorandum number	Date	Contents
QW86_06	06-16-86	Reporting Nutrient Data. The minimum reporitng level for the total Kjeldahl nitrogen analysis, nitrogen, dissolved, ammonia plus organic (mg/L as N) is 0.2 mg/L.
QW86_02	04-21-86	Evaluation of Central Laboratories Nutrient Data. Nutrient data from the Atlanta and Denver Central Laboratories was evaluated, and a special nutrient analysis study was conducted to determine whether WATSTORE files contain inaccurate nutrient analysis data and what corrective action might be taken. The evaluations prompted reconsideration of the reporting level for ammonia and total Kjeldahl nitrogen analysis.
QW85_07	01-23-85	Preservation of Nutrient Samples for Nutrient Analysis--An Update on Two Issues. An attached memorandum describes the results of tests conducted in the Denver Central Laboratory for effectiveness of five popular preservation treatments over a 16-day period. The combination of the HgCL2/NaCl tablet with chilling at 4° C is the best of the treatments tested to date. A second memorandum describes studies conducted to determine the levels of NH3-N contamination in samples stored at the Central Laboratories.
QW80_26	09-19-80	Preservation of nutrient samples by addition of mercuric chloride. Rationale for using mercuric chloride and chilling for sample preservation is summarized.
QW72_09	01-05-72	Preservation of water samples for chemical analysis. All Water Resources Division offices should stop using mercuric chloride as a preservative for water samples.
		Trace element methods
QW94_10	02-15-94	Sample Collection, Analytical Methods, and Data Interpretation for Mercury Analyses. Informs Division personnel that determinations of aqueous mercury should be carefully evaluated prior to interpretation and publication.
QW94_09	01-28-94	Revision of New Division Protocol for Collecting and Processing Surface-Water Samples for Low-Level Inorganic Analyses. The implementation date is February 1, 1994.

Table 5. U.S. Geological Survey memoranda describing National Stream Quality Accounting Network and Hydrologic Benchmark Network protocols and changes in network field and laboratory methods--Continued

Memorandum number	Date	Contents
QW94_05	12-23-93	New Division Protocol for Collecting and Processing Surface-Water Samples for Low-Level Inorganic Analyses (Superseded by QW94-09). The implementation date for the protocol is January 1, 1994.
QW93_11	07-15-93	Implementation of the Protocol for Collecting and Processing Surface-Water Samples for Low-Level Inorganic Analyses. This memo announces the implementation date for the protocol and addresses issues of concern to Water Resources Division personnel.
QW93_06	02-19-93	Trace-Element Contamination--Findings of Study on the Cleaning of Sampler Caps, Nozzles, Bottles, and Bags for Trace-Element Work at the Part-Per-Billion Level. Describes the major findings of the study.
QW93_05	01-21-93	Evaluation of Capsule Filters. Evaluation of trace-element and nutrient contamination associated with capsule filters.
QW93_03	10-29-92	Dissolved Trace-Element Data. Are dissolved trace elements lost during filtration and storage in a part-per-trillion protocol?
QW92_13	07-17-92	Trace Element Contamination: Findings of Studies on the Cleaning of Membrane Filters and Filtration Systems. Provides background for decisions the Office of Water Quality is making to provide a supportable parts-per-billion protocol for dissolved trace elements.
QW92_12	07-17-92	Trace Element Concentrations in Deionized Water Processed Through Selected Surface-Water Samplers: Study Results and Implications. The Office of Water Quality is conducting a series of studies to identify equipment, supplies, and cleaning procedures suitable for a part-per-billion protocol for dissolved trace elements.
QW92_05	03-20-92	Quality of Existing Dissolved Trace-Element Data. Describes how a number of dissolved trace elements reported in the Water Resources Division data base include contamination, and how the Division can deal with issues of uncertainty in the validity and usefulness of existing dissolved trace-element data.

Table 5. U.S. Geological Survey memoranda describing National Stream Quality Accounting Network and Hydrologic Benchmark Network protocols and changes in network field and laboratory methods--Continued

Memorandum number	Date	Contents
QW91_10	09-30-91	Dissolved Trace Element Data. Distributes report "Contamination of Dissolved Trace-Element Data: Present Understanding, Ramifications, and Issues that Require Resolution"
QW81_12	05-12-81	Trace Metals; Questionable Values for Dissolved and Total Selenium. Discusses anomalously high values of selenium in streams in the Southeast.
QW79_12	04-11-79	Questionable analytical values for lead and cadmium. Lead and cadmium concentrations reported for samples collected from April 1978 to February 1979 are questionable because of a contamination problem with the nitric acid ampoules supplied by the Central Laboratories.
		Alkalinity methods
QW88_05	10-01-88	National Water Information System (NWIS)-Global Updates to Water-Quality File. (DRAFT) Background information and detailed specification for global updates to alkalinity, and carbonate species data in the NWIS Water-Quality File are provided.
QW87_01	11-14-86	Changes to Parameter Codes for Alkalinity and the Carbonate Species. Alkalinity and carbonate species parameter codes are being consolidated by implementing the new Method Code System for these constituents. The Method Code System combines the use of a single alphanumeric character with the five digit parameter code to produce a combination code which identifies both the constituent being analyzed and the analytical methodology used to determine its value.
QW82_05	12-11-81	Provisional Method for Carbonate, Dissolved; Bicarbonate, Dissolved; and Carbonate Alkalinity, Dissolved; Electrometric Tritration, Incremental, Field. Describes a provisional method for incremental field tritrations.

Table 5. U.S. Geological Survey memoranda describing National Stream Quality Accounting Network and Hydrologic Benchmark Network protocols and changes in network field and laboratory methods--Continued

Memorandum number	Date	Contents
QW81_04	11-12-80	Assignment of parameter codes for pH, alkalinity, specific conductance and hydroxide/carbonate/ bicarbonate data. Field specific conductance and field alkalinity will be recorded in WATSTORE under parameter codes 00095 and 00410. Lab values will be recorded under 90095 and 90410.
QW80_27	09-19-80	New Parameter Codes for pH, Alkalinity, Specific Conductance, and Carbonate/Bicarbonate. Field and lab values for subject constituents will be entered into WATSTORE under separate parameter codes, with a more careful distinction made of methods used.

Miscellaneous processing, analytical, and reporting methods

Memorandum number	Date	Contents
QW94_13	04-21-94	Evaluation of the Churn Splitter for Inclusion in the Division Protocol for the Collection and Processing of Surface-Water Samples for Subsequent Determination of Trace Elements, Nutrients, and Major Ions in Filtered Water. This memo provides the justifying data and certifies the churn splitter for use with the new inorganic protocol (see QW94_09).
NL94_03	12-22-93	Change in method for determining chloride, sulfate, and fluoride.
NL93_03	12-28-92	Change in method for determination of chloride in water due to data quality problems.
QW90_04	12-28-89	Turbidimetric Sulfate Method. A positive bias in the turbidimetric method for sulfate analysis discovered by the National Water-Quality Laboratory in early March 1989 is discussed. The Office of Water Quality and the Branch of Quality Assurance are determining what adjustments can or should be made to the affected sulfate data.
QW81_22	09-08-81	WATSTORE, Remark Coded Data. Defines the 'less than' and ND remarks, reviews implications of remark codes, outlines options.

Table 5. U.S. Geological Survey memoranda describing National Stream Quality Accounting Network and Hydrologic Benchmark Network protocols and changes in network field and laboratory methods--Continued

Memorandum number	Date	Contents
QW81-18	06-29-81	Data Handling, corrections to the WATSTORE Water-Quality File. Discusses action as a result of a memo dated April 24, 1981, same subject.
QW77_04	02-07-77	Filtering of water samples. A new method for filtering water samples utilizes a backflushing plate filter which provides a 94 percent larger filtering area than the 102 millimeter filter used in most barrel filters.
QW77_02	12-28-76	Analytical methods for organic carbon. Describes procedures to insure that organic carbon data in the water quality file are as nearly correct as possible.
QW76_24T	08-16-76	Sample Splitter for Water-Sediment Samples--Introduction of new sample splitter ("churn" splitter) for use in the NASQAN program.
QW73_07	10-26-72	Teflon sediment sample splitters and plastic sieves. Method of splitting samples in the field recommended for use for NASQAN program.

Water-column samples, that are representative of the stream cross section, are collected using depth- and width-integrated sampling techniques (Edwards and Glysson, 1988). These techniques require the collection of subsamples at several locations in the stream cross section using approved depth-integrating samplers. One of two procedures (Edwards and Glysson, 1988), Equal Width Increment (EWI) or Equal Discharge Increment (EDI), are used to systematically determine these sampling locations. Network protocols recommend annual and seasonal surveys of water temperature, pH, specific conductance, and dissolved oxygen variations in the stream cross section to assist in determining the appropriate number of vertical sampling locations. The number of locations depends on the variability of water quality in the cross section and the width of the river, and can range from a few to as many as 50; however, from four to 20 sampling locations have been commonly used at most sites.

For whole-water (i.e., unfiltered) analyses, subsamples from the cross section were either composited directly into bottles for shipment to the laboratory (prior to 1972) or composited into a "splitting" device (after about 1972). A Teflon sediment sample splitter became available for use in October 1972 (QW73_07). After August 1976, a polypropylene "churn splitter" was required for sample collection at national network sites (QW76_24T). Sample bottles are filled from the churn splitter while the churn paddle is moved vertically at a specified rate to ensure the suspension of particles so that a representative sample can be obtained.

Analyses of filtered samples provide an operationally-defined determination of "dissolved" chemical constituents. Samples analyzed for "dissolved" chemical species are pumped through 0.45 membrane filtration device (Rainwater and Thatcher, 1960). Since February 1977 (QW77_04), a 142 millimeter diameter, 0.45 micrometer pore-size, tortuous-path membrane filter in a plastic plate filter has been used (Ward and Harr, 1990). In 1993, 0.45 micrometer (um) pore size capsule filters began to be used at many sites.

Fecal bacteria samples are not obtained from the splitter device, but are taken as a surface "grab" sample from the centroid of streamflow. Bacteria concentrations are measured using membrane filter techniques (Britton and Greeson, 1989). Fecal coliform counts were determined for samples filtered with a 0.45 um filter pore size prior to 1976 (Table 4). After this date, a 0.70 um filter pore size was required to ensure accurate fecal coliform counts. Either a 0.45 or 0.70 um filter pore size was acceptable for determining fecal streptococci counts, however, field personnel tended to use the same size filters as those used for fecal coliform determinations. In 1991, a 0.45 um filter pore size was required for use in fecal streptococci determinations to comply with prescribed TWRI methods (Table 4). A study of the effects of the two pore sizes on analytical results based on data collected at NASQAN and HBN stations in 1990 indicates no statistically significant differences in methods (p=0.94 for a Wilcoxon signed-ranks test) for fecal streptococci determinations (QW91_FS). The observed differences in analytical results appear to reflect random measurement errors intrinsic to the methods with no evidence of upward or downward bias based on the symmetry of the distribution of differences. For 415 pairs of fecal streptococci counts, the distribution of differences in counts has a median of zero percent (difference between counts for 0.70 filter size and counts for 0.45 filter size) and 25th and 75th percentiles of -16.5 percent and 14.6 percent, respectively.

Selected samples were stabilized with chemical treatments in the field according to laboratory specifications prior to their transport to the laboratory. Filtered and unfiltered samples analyzed for trace elements were treated with nitric acid to maintain metals in solution. A preservative was routinely added to phytoplankton samples to reduce biological activity. Similarly, nutrient samples were treated with a biocide preservative and/or chilled during most of the period of network operations. The methods of nutrient preservation have changed over time according to USGS and network guidelines (QW72_09; QW80_26; QW85_07; QW94_16; QW93_04; see also the next section entitled "National Network Laboratory Techniques"). Beginning in 1973, national network protocols required all water samples to be chilled to 4^0 C. and promptly transported to a USGS laboratory.

The analytical methods for alkalinity, bicarbonate, and carbonate have changed over time due to changes in the stage of analysis (i.e., field and laboratory), the method of determination (i.e., fixed-endpoint and incremental titration), and sample filtration (Table 4). Also, changes in guidelines for storage of the data have led to the proliferation of numerous alkalinity parameter codes, especially after 1980 when field parameter codes became available (QW81_04; QW80_27; QW82_05). In producing the CD-ROM data sets, national network data for alkalinity, bicarbonate, and carbonate were compiled from various parameter codes according to methods prescribed in memorandum QW88_05 (see also QW87_01) and records of network protocols (QW84_16; QW85_19). The data aggregation methods prescribed in these memoranda, and modified for the CD-ROM data to reflect network operations, assigns the data to the appropriate parameter and method codes to provide records suitable for statistical analysis.

Table 6 presents the parameter/method codes and time periods applicable to the alkalinity, bicarbonate, and carbonate data collected at national network stations. Fixed-

Table 6. Applicable dates and parameter/method codes used to compile National Stream Quality Accounting Network and Hydrologic Benchmark Network alkalinity, bicarbonate, and carbonate data on CD-ROM

[The assigned parameter/method codes reflect a coding of the data based on information from technical memorandum QW88_05 and records of national network protocols (memoranda QW84_16 and QW85_19). If an observation was unavailable for the indicated parameter code (column 4), the alternate parameter codes were searched for an available value according to the specified dates and parameter order. In the CD-ROM data sets, these values were assigned their corresponding parameter and method codes in column 4]

Constituent	Dates	Method of determination	Param. and method code	Alternate param. codes
		Data required by network protocols		
Alkalinity	Before 10-01-84	Lab, fixed-endpoint titration[1], unfiltered samples.	00417 A	00410, 00430, 00431, 95430, 90410, 95410, 00421
Alkalinity	10-01-84 - 09-30-85	Field, fixed-endpoint titration, unfiltered samples.	00410 A	00430, 00431
Alkalinity	10-01-85 - 09-30-95	Field, fixed-endpoint titration, filtered samples.	39036 A	00410, 00430, 00431
Bicarbonate	10-01-85 - 09-30-95	Field, incremental titration, filtered samples.	00453 B	99440, 00450
Carbonate	10-01-85 - 09-30-95	Field, incremental titration, filtered samples.	00452 B	99445, 00447
		Optional national network data		
Alkalinity	Before 10-01-85	Field, incremental titration, unfiltered samples.	00419 B	99430
Alkalinity	10-01-85 - 09-30-95	Field, incremental titration, filtered samples.	39086 B	99430, 00419
Bicarbonate	Before 10-01-85	Field, fixed-endpoint titration, unfiltered samples.	00440 A	
Bicarbonate	10-01-85 - 09-30-95	Field, incremental titration, unfiltered samples.	00450 B	99440
Carbonate	Before 10-01-85	Field, fixed-endpoint titration, unfiltered samples.	00445 A	
Carbonate	10-01-85 - 09-30-95	Field, incremental titration, unfiltered samples.	00447 B	99445

[1] A limited number of field personnel may have conducted field determinations of alkalinity by fixed-endpoint titration. These cases are coded as laboratory analyses.

endpoint titration methods were required for national network alkalinity determinations throughout the operation of the networks. Alkalinity methods incurred two changes during network operations (Table 4): (1) the stage of analysis was changed from the laboratory to the field on October 1, 1984, and (2) filtered samples were required beginning on October 1, 1985. Alkalinity determinations by incremental titration were optional for network samples. National network protocols required field determinations of bicarbonate and carbonate for filtered samples beginning on October 1, 1985 (Table 4). Bicarbonate and carbonate determinations were optionally performed on unfiltered samples by fixed-endpoint (00440A, 00445A) and by incremental (00450B, 00447B) titration methods prior to October 1, 1985.

National Network Laboratory Techniques

Standard methods of laboratory processing and analysis (Rainwater and Thatcher, 1960; Skougstad and others, 1979; Britton and Greeson, 1987; Fishman and Friedman, 1989; Faires, 1993; Patton and Truitt, 1992; Fishman and others, 1994) have been applied to network samples during the period of operations. The standard analytical schedules employed by the USGS laboratories specify the sample characteristics (e.g., filtration, treatment, and storage) required for analysis, and make available a variety of possible analyses by constituent group. The analytical schedules for national network stations are selected annually by the OWQ.

The "total" form reported for national network constituents reflect different characteristics of the analytical methods and the water-suspended sediment mixture of the samples (Table 7). Total analyses of phosphorus, Kjeldahl (organic plus ammonia) nitrogen, and carbon represent a complete digestion of the whole-water (i.e., unfiltered water-suspended sediment) sample. In contrast, analyses of four "total" nutrient species (nitrite, nitrate+nitrite, ammonia, and orthophosphate) were performed on samples "decanted" in the laboratory (Skougstad and others, 1979) to avoid measurement interferences associated with particulate material. Because the results of these analyses are not statistically separable from analytical results based on "dissolved" samples filtered in the field, "total" analyses for these four nutrient species were discontinued on October 1, 1994 (Table 8). Trace-element analyses on unfiltered samples (i.e., whole water) are based on total recoverable methods (Table 7).

Selected laboratory analytical results have changed periodically because of advances in methods related to instrumentation and processing techniques and because of changes in measurement accuracy related to sample contamination. Some of the more important method changes that may have relevance to the use and interpretation of national network data are listed in Table 8.

Prior to about 1973, national network chemical samples from the HBN were analyzed in one of 22 local District laboratories. With the advent of automated analytical equipment, these laboratories were consolidated into three centralized laboratories in 1973 (Salt Lake City, Utah; Atlanta, Georgia; and Albany, New York) to improve the efficiency of operations (Durum, 1978). In 1976, operations at the Salt Lake City laboratory, the proto-type of the USGS centralized laboratory system, were transferred to Denver, Colorado. The Salt Lake City laboratory (and later Denver) served all states west of the Mississippi River with the exception of Texas, Arkansas, Missouri, and Oklahoma. The Albany laboratory was operated as a temporary component of the centralized lab system from April, 1973 to May, 1977 (Durum, 1978; B. Malo, oral communication). This laboratory typically served the New England states of New York, Connecticut, Massachusetts, Maine, New Hampshire, Rhode Island, and Vermont. The Atlanta laboratory served states in the eastern United States, which included those served by the Albany laboratory after 1977. In April 1986, the Atlanta laboratory was closed, and the Denver lab became the National Water Quality Laboratory (NWQL), where all national network chemical samples were analyzed. A detailed history of USGS laboratories prior to about 1976 is given by Durum (1978).

Suspended sediment concentration and particle size have been analyzed during the operations of the national networks at numerous sediment laboratories located in District offices throughout the United States.

Table 7. Explanation of total constituent analyses performed on National Stream Quality Accounting Network and Hydrologic Benchmark Network water-quality samples

[The total form reflects different characteristics of the analytical methods and the water-suspended sediment mixture of the samples. Explanations are modified from USGS annual State data reports]

Term	Explanation	Applicable constituents
Total	The total amount of constituent in a representative water-suspended sediment sample, regardless of the constituent's physical or chemical form. The analytical procedure assures measurement of at least 95 percent of the constituent present in both the dissolved and suspended phases of the sample.	Nitrogen[1], phosphorus, Kjeldahl (organic plus ammonia) nitrogen, and carbon .
"Total"	The determination represents the amount of a constituent in a water sample present in the "dissolved" form. The analytical method was performed on water-suspended sediment samples "decanted" in the laboratory (Skougstad and others, 1979) to avoid measurement interferences associated with particulate material. The results of these analyses are not statistically separable from analytical results based on "dissolved" samples obtained by filtering a water-suspended sediment sample in the field using a 0.45-micrometer membrane filtration device (see memorandum QW93_04).	Nitrite, nitrate plus nitrite[2], ammonia, and orthophosphate.
Total recoverable	The amount of a given constituent remaining in solution after a representative water suspended-sediment sample has been digested by a method (usually using a dilute acid solution) that results in dissolution of only readily soluable substances. Complete dissolution of all particulate matter is not achieved by the digestion treatment, and the determination represents quantities that are less than 95 percent of the total amount.	Trace elements.

[1] Total nitrogen is calculated as the sum of total Kjeldahl nitrogen and "total" nitrate plus nitrite determinations.

[2] In cases where "total" nitrate plus nitrite laboratory analyses were not performed (i.e., beginning on 10-1-94), the results of laboratory analyses of dissolved nitrate plus nitrite were automatically substituted by the U.S. Geological Survey's water-quality data storage and retrieval system, the National Water Information System.

Analytical results of USGS laboratories are verified through an internal quality-assurance program which includes the use of proven documented methods, method validation procedures, and technician training (see Pritt and Raese, 1992 for a description of NWQL quality-assurance practices). Method validation has included the regular analysis of natural-matrix water reference samples, standard solutions, and blanks to evaluate the measurement variability and bias. Water reference samples have been part of the quality-assurance practices of USGS laboratories since 1962 when the Standard Reference Water Sample Program began a semi-annual evaluation of the analytical methods of participating laboratories (Durum, 1978). Since 1981, an external, independent quality-assurance

Table 8. Important changes in U.S. Geological Survey laboratory analytical methods, reporting conventions, and laboratory sample contamination from 1970-95

[NWQL, National Water Quality Laboratory; BSP, Blind Sample Program; SRWS, Standard Reference Water Sample; NASQAN, National Stream Quality Accounting Network. U.S. Geological Survey memoranda are identified by the originating office and a unique number QWyy_nn (Office of Water Quality) or NLyy_nn (National Water Quality Laboratory), where yy gives the year of the document and nn is a sequential number of the year's memoranda]

Constituent	Date	Description of change (memoranda or references)
Common ions	10-01-82 - 07-31-89	Sulfate showed a positive bias of about 2 mg/L for concentrations less than 75 mg/L because of interferences in the turbidimetric method that were not blank corrected (QW90_04).
	01-01-80 - 12-31-89	Residue on Evaporation (ROE)--Small, statistically significant trends detected in laboratory measurement bias based on BSP reference sample data (Alexander and others, 1993). Trend is positive for the NWQL and negative for the USGS Atlanta laboratory.
	04-01-90 - 03-31-92	Sulfate showed a positive bias on the order of 0.5-3 mg/L for samples with concentrations of 15-75 mg/L. BSP data demonstrate the bias.
	04-01-90 - 10-20-92	Chloride--Ion chromatography method showed lack of precision and positive bias on the order of one standard deviation for BSP samples. The ion chromatography method was switched to a colorimetric method in December 1992 (NL93_03).
	04-01-90 - 01-02-94	Fluoride--Ion chromatography method showed lack of precision on the order of 4 standard deviations for BSP samples. The ion chromatography method was swiched to an ion-selective electrode method in January 1994 (NL94_03).
Nutrients, major ions, and trace elements	10-01-72 - 09-30-78	Values changed in the data base to maintain consistency in reporting of non-detected ("less-than") values (QW81_18; QW81_22). Zeros were replaced with the method reporting limit and a remark code of "<". Un-remarked values equal to the method reporting limit were assigned a remark code of "<".
Nutrients	Before 1972	The methods of preservation used by field personnel are unknown, but may have included chilling of samples, sulfuric acid, or mercuric chloride. Mercuric chloride was officially recommended for use by the USGS for nitrogen analyses as early as November 1970.
	01-05-72	All field offices advised to discontinue use of mercuric chloride as a preservative for nitrogen, phosphorus, and organic carbon because of concerns about instrument interferences and problems of mercuric chloride contamination and safe disposal of wastes (QW72_09). Chilling of samples to 1-4^0 C. and rapid transport of samples are recommended alternatives.

Table 8. Important changes in U.S. Geological Survey laboratory analytical methods, reporting conventions, and laboratory sample contamination from 1970-95--Continued

Constituent	Date	Description of change (memoranda or references)
Nutrients	10-01-80	Mercuric chloride preservatives in tablet form adopted after review of the literature suggests benefits of the use of this biocide (QW80_26).
	10-01-86 - 09-30-94	Mercuric chloride preservative in liquid ampoule form adopted (E.L. Skinner, U.S. Geological Survey, written comm., 1990) because of detected ammonia contamination in tablet preservative (QW85_07).
	10-01-94	Discontinued the use of mercuric chloride preservative (QW94_16). A USGS study finds no significant differences in analytical results based on samples treated separately with mercuric chloride and chilling.
	10-01-94	Discontinued analyses of whole-water ("total") samples for nitrite, nitrate + nitrite, ammonia, and orthophosphorus (QW93_04). From 1973-1994, analyses of these constituents were performed on samples "decanted" in the laboratory. Statistical review of all 1989 data processed in the NWQL suggests that "dissolved" and "total" determinations for these four constituents are not statistically separable.
Kjeldahl (ammonia plus organic) nitrogen	10-01-78 - 09-30-91	Kjeldahl nitrogen analyzed by method I2552/I4552 without blank correction. Positive bias could average more than 0.1 mg/L.
	01-01-79 - 12-31-85	Evidence of occasional periods of positive bias based on SRWS reference sample measurements at the Denver Central Laboratory (Alexander and others, 1993).
	10-01-80 - 09-30-86	Positive bias as high as 0.5 mg/L found in blanks (Schertz and others, 1994; QW85_07) at the Denver Central Lab. The source was believed to be the tablet form of mercuric chloride preservative. High concentrations of Kjeldahl nitrogen at western NASQAN stations served by the Denver laboratory during the early 1980's (Alexander and others, 1993) may relate, in part, to this bias.
	10-01-91	Kjeldahl nitrogen "micro" method implemented (Jirka and others, 1976) with blank correction. Positive bias present in previous method no longer detected.
Phosphorus	10-01-73 - 04-30-90	Total phosphorus--Incomplete digestion in the potassium persulfate method produced negatively biased concentrations (QW92_10).
	01-01-79 - 12-31-81	Dissolved phosphorus--Evidence of occasional periods of positive bias based on reference sample measurements at the Denver Central Laboratory (Alexander and others, 1993).

Table 8. Important changes in U.S. Geological Survey laboratory analytical methods, reporting conventions, and laboratory sample contamination from 1970-95--Continued

Constituent	Date	Description of change (memoranda or references)
Phosphorus	05-01-90 - 09-30-91	Total phosphorus--Dilution procedure implemented with existing potassium persulfate method (QW92_10). Less bias observed for this method; the method may yield higher concentrations than previous method (greater than or equal to 0.01 mg/L) for samples with suspended-sediment concentrations above 50 mg/L.
	10-01-91	Total phosphorus--Kjeldahl "micro" method implemented (QW92_10). Comparative studies with the potassium persulfate method indicated that the analytical results of the new method did not display the negative bias of the old method; concentrations of the new method are likely to exceed those of the old method by more than 0.01 mg/L.
Trace elements	Before 1975	Selenium--The colorimetric diaminobenzidine method may have produced a positive bias as large as 5 ug/L (QW81_12).
	mid-1980s	Arsenic--A change in the rounding algorithm increased the frequency of nondetected values after this time. Values reported as 1.0 ug/L prior to mid-1980s were reported as less than 1.0 ug/L after this time.

program called the Blind Sample Program (BSP) has validated the analytical results of the USGS central laboratories (this program is discussed in the next section of the paper). Water reference samples from the Standard Reference Water Sample Program have also been used by the laboratory since 1981 to conduct regular internal blind evaluations of method performance. Additional discussion of historical quality-assurance practices of USGS laboratories is provided by Friedman (1993).

Laboratory analytical results for national network stations are also reviewed by District personnel responsible for the collection of the data. Analytical results are transmitted to District computers where the data are reviewed and verified for accuracy. Within approximately 30 days, the District may request the reanalysis of samples believed to contain errors; after this time samples may be discarded by the laboratory.

Selection of Water-Quality and Streamflow Data for the CD-ROMs

All available water-quality records were retrieved for 63 chemical, biological, and physical properties of water [122 properties including analyses of filtered (dissolved), unfiltered (total or total-recoverable), and particulate samples] for the approximate time periods 1973-95 for NASQAN stations and 1962-95 for HBN stations. The data include alkalinity, bicarbonate, and carbonate parameter and method codes listed in Table 6. The alkalinity data listed in Table 6 for the required network parameter and method codes are generally preferable for statistical analysis because of the larger number of observations and broader geographic coverage. We did not include laboratory determinations of bicarbonate and carbonate on the CD-ROMs. National network data on organic pesticides were excluded from the CD-ROMs because of space limitations and the high frequency of nondetected values [the user is referred to Gilliom and others (1985) for a summary of these data]. The final selection of water-quality constituents for inclusion on the CD-ROMs was based on USGS water-quality technical memoranda describing the constituents historically measured at national network stations and statistical summaries of the frequency of observations by constituent.

Water-quality data for most national network stations were retrieved from the USGS's National Water Information System (NWIS) located on local USGS District computer systems. For efficiency, selected water-quality data were obtained from the USGS's centralized data repository, the National Water Data Storage and Retrieval System (WATSTORE), located on a mainframe computer in Reston, Virginia. These additional retrievals from WATSTORE included data for most stations from January 1, 1994 to September 30, 1995, data for 1962-71 for all HBN stations, and data for selected time periods for about 30 stations. Data published on the CD-ROMs were extracted directly from these computer systems with no additional checks for outliers or unusual values.

For each water-quality value, we report the sample-collection agency, the laboratory analytical agency, the laboratory analytical method code, and relevant remark codes. For years since the early to mid 1980's, agency sample collection and analysis codes and laboratory analytical method codes may assist in identifying non-network data that may have been collected at some national network stations as part of local investigations. These agency and analytical method codes are also required to properly use the Blind Sample Program data on measurement accuracy (see the following sections for details).

The agency sample collection and agency laboratory analysis codes have been maintained in the USGS water-quality data base since the early 1980s. For years 1982 and later, these codes are available for more than 96 percent of the samples collected and analyzed. The laboratory analysis codes are also reported for 75 to 80 percent of the samples from 1979 to 1981. Agency names associated with the sample collection and laboratory analysis codes were obtained from the NWIS system (J. Briggs, U.S. Geological Survey, written communication, 1995). A single USGS laboratory analysis agency code (01028) may periodically appear in the data base prior to 1986 when more than one USGS central laboratory was operational (e.g., agency laboratory analysis code 80020 for Denver and 80010 for Atlanta). In these cases, the USGS laboratory responsible for the reported determination can only be assumed based on the approximate description of USGS laboratory jurisdictions presented in the previous section.

The laboratory analytical method codes have been maintained in the USGS water-quality data base since 1985. For years 1985 and later, the analytical method codes are reported for more than 90 percent of the analytical determinations. Descriptive information for 209 NWQL methods used to analyze 76 of the 122 constituents are published on the CD-ROM. This information, applicable to the 1985-95 time period, includes the parameter name, parameter code, analytical method name, analytical method code, laboratory method reporting limit, and the relevant USGS publication (S. Glodt, U.S. Geological Survey, NWQL, written communication, 1996). Other analytical methods not listed in this file may have been used to analyze some of these 76 constituents; however, information on these methods was unavailable at the time of CD-ROM production. The remaining 46 (of 122) constituents include 17 laboratory-analyzed parameters with codes unavailable at the time of production of the CD-ROMs, 27 field parameters, and 2 computed parameters. The 17 constituents without laboratory analytical method codes on the CD-ROMs include one trace element (vanadium), four radiochemicals, and 12 biological constituents (these predated the use of method codes). Although method codes are reported in the water-quality data base for the 27 field and two computed parameters, these codes are not officially supported and maintained by the USGS.

Daily mean values of streamflow were obtained from WATSTORE. The records published on CD-ROM were selected for time periods corresponding to the water-quality data (i.e., temperature). Daily streamflow data are available for 654 of the 679 national network water-quality stations. For 79 of these stations, the streamflow is obtained from a nearby gaging station (61 stations; 2 streamflow gages serve one NASQAN site) or, in a minority of cases, a relocated NASQAN station (19 stations). Records of daily streamflow were not available for 25 of the water-quality stations at the time of publication. For many of these stations, daily streamflow records may be available from other federal agencies (e.g., Corps of Engineers).

Information on station attributes including station name, hydrologic unit code, FIPS code, drainage area, latitude, and longitude were obtained from the WATSTORE station header file. Population data for 1990 (U.S. Bureau of Census, 1991) and land-cover statistics for 1987 (U.S. Soil Conservation Service, 1989) are reported for 507 NASQAN watersheds digitized from 1:2 million scale hydrologic unit maps. Where NASQAN watershed boundaries were unavailable in digital form or are indeterminant, the population and land-cover statistics for the accounting unit containing the NASQAN station are reported (85 of 679 stations). Population and land-cover data are not reported for 26 NASQAN stations located outside of the conterminous United States and all 63 HBN stations (watersheds in the HBN were considered to be too small to accurately report these statistics). To obtain watershed statistics on population and land cover, counties were intersected with NASQAN watershed boundaries and Water Resources Council accounting units in a geographic information system. The data were disaggregated from the county to watershed level in proportion to the area shared by both. Other information on WRC hydrologic units are also reported, and include drainage area statistics, names, and narrative (Slack and Landwehr, 1992). Information on the dates of relocation of NASQAN stations is reported on the CD-ROMs, and was obtained from national network records.

We have included on the CD-ROMs 59 selected USGS technical memoranda documenting national network operations, important changes in field and laboratory methods, and cases of sample contamination and biases in analytical results (Table 5). These previously unpublished internal memoranda provide a significant source of technical information relevant to the use and interpretation of the national network data. Many of the specific events documented by the technical memoranda are highlighted in the discussion of field and laboratory methods in the previous two sections of the report (see Tables 4 and 8).

HISTORY AND CHARACTERISTICS OF THE BLIND SAMPLE PROGRAM

National network samples have been routinely analyzed in one or more USGS operated laboratories. In addition to the internal quality-assurance practices of USGS laboratories, the USGS has operated an independent, external program of laboratory quality assurance since 1981 called the Blind Sample Program (BSP; see for example, Maloney et al., 1994). The purpose of the BSP is to monitor, assure, and improve the quality of laboratory analytical results through the use of blind quality-control samples. The BSP regularly submits to participating USGS laboratories reference water samples having known chemical concentrations and consisting of a stable, homogeneous chemical and physical matrix. The reference samples are subject to the identical laboratory handling, processing, and analytical procedures as those applied to environmental samples, and therefore, have been used by the USGS as an independent source to verify the accuracy (bias and variability) of laboratory analytical methods and ambient water-quality measurements. Regular review of the data by USGS personnel outside the laboratory allows for an independent evaluation and reporting of the status of laboratory measurement errors over time.

Users of national network data can also use BSP data as a quantitative tool for assessing the measurement bias and variability of selected laboratory methods and stream water-quality data during more recent periods of operation of the national networks. The CD-ROMs include BSP data for 34 chemical constituents analyzed at the USGS NWQL during the water years 1985 to 1995.

Estimates of the variability of laboratory analytical measurements provide quantitative information about the extent to which laboratory methods contribute to random variations in measurements of ambient stream water quality. The measurement variability indicates how well measurements can be reproduced with repeated applications of an analytical method. Random errors in measurements are intrinsic to the measurement process. These errors are by definition independent of one another, and are not reproducable over time. One important concern for a data user is whether random variations in measurements related to methods are large enough to prevent the detection of variations related to chemical processes in the environment. BSP estimates of measurement variability, determined through repeated measurements of each reference sample, are available for a wide range of concentrations, and can be used to examine this issue.

Estimates of the bias of laboratory analytical measurements provide quantitative information about the extent to which laboratory methods contribute to systematic variations in measurements of ambient stream water quality. In contrast to random measurement errors, systematic errors (i.e., measurement bias) are reproducable over time. Repeated applications of a biased analytical method would be expected to produce correlated measurement errors of a similar sign and magnitude. Such errors may be caused, for example, by sample contamination or matrix interferences. BSP data can be used to identify time periods during which laboratory analytical methods may have produced measurements with a positive or negative bias. A sufficiently large bias might lead a data user to disregard data processed at the laboratory during certain time periods or might lead a user to become overly cautious about the interpretation of environmental records that might potentially contain such errors. A data user may also question whether trends in environmental concentrations result from or are masked by changes in the measurement bias of a laboratory analytical method. BSP estimates of measurement bias can also be used to evaluate the possible effects of measurement bias on observed trends in water-quality data.

The following two sub-sections describe the characteristics of BSP samples and how estimates of the laboratory measurement bias and variability are obtained using BSP samples. A final sub-section describes the BSP data selected for publication on the CD-ROMs. The next major section of the report discusses various ways of using BSP data in the interpretation of national network water-quality data. Throughout this discussion, use of the term "environmental" data refers to stream water-quality data collected at national network stations.

Characteristics of BSP Samples

Standard reference water samples (SRWS) are used in the preparation of BSP samples (Skougstad and Fishman, 1975; Schroder and others, 1980; Janzer, 1985; Long and Farrar, 1992). SRWS are obtained from natural waters, which principally include Colorado streams. In preparing BSP samples, SRWS are used directly or are diluted with deionized water or mixed in varying proportions with other SRWS. This sample-mixing procedure produces a larger number of unique quality-control samples than would be available from the SRWS program alone.

SRWS are filtered during preparation; therefore, all constituents in the BSP are in the dissolved phase. Filtration removes most particulate material in the samples, and thus avoids subsampling problems that could produce non-representative results. Whole-water recoverable (WWR) methods are applied to the filtered reference samples in the SRWS program for selected constituents (Fishman and Friedman, 1989); however, any differences between dissolved analyses and WWR analyses are due to the digestion process associated with the WWR method rather than differences in sample source or sampling techniques.

BSP reference samples are designed to appear as much like environmental samples as possible to reduce the possibility that analysts will identify the quality-assurance samples. As with regular environmental samples, analytical request forms are completed to ensure that the user-selected analytical tests are performed on the samples.

The number of analytical determinations requested for each laboratory analytical procedure is proportional to the number of requests for the procedure from all environmental samples submitted. The BSP follows the guidelines of Friedman and Erdmann (1982) by setting the rate of submissions of external quality-assurance samples to approximately five percent of the laboratory workload for each analytical procedure. The annual workload for each analytical procedure is estimated from sample login records for the previous year. The number of BSP samples analyzed each year varies, but is approximately 200, 300, and 350 for trace elements, nutrients, and major ions, respectively.

BSP Summary Statistics

The concentration of each SRWS is estimated semi-annually through a round-robin evaluation program involving upwards of 150 laboratories [see Long and Farrar (1992) for a more detailed description]. A statistical summary of the round-robin results is prepared for each set of samples (see for example, Janzer, 1983), and includes estimates of the known concentration of each SRWS and estimates of the inter-laboratory variability in SRWS measurements. Until 1988, the SRWS concentration and inter-laboratory variability in measurements were estimated using parametric statistics of the mean and standard deviation. After 1988, nonparametric statistics of the median and F-pseudosigma (Hoaglin and others, 1983) were used. The F-pseudosigma gives an unbiased estimate of the standard deviation when the data are normally distributed. The estimate of the SRWS concentration according to the mean or median of all laboratory measurements is reported as the "most probable value" (MPV) for each constituent in SRWS summary reports. The F-pseudosigma (or standard deviation prior to 1988) is referred to as the "minimum probable deviation" (MPD) in the estimate of the known reference sample concentration.

In the Blind Sample Program, estimates of the mean or median concentration of mixtures of SRWS or mixtures of SRWS and deionized water are based on the proportion and the most probable values of the SRWS used. When deionized water is used to dilute the SRWS, a sample concentration of zero is applied to estimate the most probable value (MPV) for the proportion used.

The MPD is estimated for each SRWS chemical constituent over a continuous range of concentrations by regressing the most probable value on the MPD using the method of ordinary least squares [see Maloney and others (1994) for additional details]. SRWS program data for semi-annual round-robin studies from the previous seven years were used to derive equations for each constituent. The regression equations were updated and applied to each water year, taking into account the most recently released SRWS data.

Estimates of measurement accuracy

The laboratory analytical measurement error (E) is estimated as the difference between a laboratory measurement of a BSP reference sample (M) and the known concentration (MPV) of the sample, and contains both systematic and random sources of error. The error may be written as

$$E = M - MPV \tag{1}$$

Estimates of analytical measurement error provide a quantitative measure of the accuracy (bias and variability) of a laboratory method.

USGS laboratory procedures for reporting analytical measurements specify rounding rules that can affect the accuracy of BSP estimates of measurement error. All water-quality measurements reported by the laboratory are rounded to the nearest whole number or'decimal fraction according to the sensitivity of analytical methods as specified by the method reporting limit. As a result, the accuracy of individual estimates of error would be expected to decline as the magnitude of the error becomes smaller (i.e., as the magnitude of the error decreases relative to the size of the reporting limit). The highest levels of inaccuracy occur for error estimates that are computed to be less than the method reporting limit. For these cases, the uncertainty in water-quality measurements exceeds the magnitude of the error. Error values that are less than the method reporting limt are flagged in the CD-ROM data base. In such cases, the sign of the error value is not known with certainty, however, we report the sign resulting from differences in concentration computed according to equation 1. See the section "Statistical analysis of measurement error estimates" (p.55) for additional discussion of the effects of rounding on error estimates.

An assessment of the accuracy of analytical methods can be conducted by comparing observed error estimates with the specified limits of acceptable variability in measurement error. The Blind Sample Program defines the acceptable limits as a multiple of the inter-laboratory variability (i.e., the MPD) of the reference sample concentration. Performance of an analytical method is judged as "out-of-control" in cases where errors exceed this threshold. For purposes of assessing measurement accuracy, the BSP expresses the measurement error from equation 1 in standardized units of variability (i.e., mean of zero and standard deviation of one) called a z-value or NSD (number of standard deviations). The NSD is estimated as

$$NSD = \frac{E}{MPD} \tag{2}$$

The Blind Sample Program considers values of NSD within +/- 2 of the MPV of acceptable quality (Maloney and others, 1994). For purposes of internal laboratory quality-assurance, the NWQL specifies control limits based on values of NSD within +/- 1.5 of the MPV (Pritt and Raese, 1992).

For reference samples with very low known concentrations, located close to the method reporting limits, the reported NSD may be unrealistically large. This situation can arise because SRWS values of the most probable value are frequently reported with greater numerical precision than measurements reported by the NWQL. Thus, the regression estimates of the MPD may reflect higher precision than the NWQL analytical methods can achieve. For example, the NWQL reports values for many trace metals (based on AA analytical methods) to the nearest 10 mg/L for determinations below 100 mg/L. In contrast, the SRWS program reports values to the nearest 1 mg/L. Therefore, estimates of the MPD at very low reference sample concentrations may produce tolerance limits that are too small to be attained by the NWQL.

For constituents where laboratory rounding rules would produce a minimum NSD above one, Blind Sample Program procedures set the minimum MPD at 75 percent of the laboratory reporting limit, thereby ensuring that the minimum NSD falls within +/- 1 of the MPV. For example, manganese is reported by the NWQL to the nearest 10 mg/L. Therefore, the most accurate measurement value for a reference sample with an MPV of 25.2 mg/L would be a value of 20 or 30 mg/L. According to available regression estimates of precision, the closest reportable values of 20 and 30 mg/L would be -1.33 and 1.19 NSD units from the MPV, respectively (measurement values within +/- 1.0 NSD units of the MPV would correspond to 21.1 and 29.1 mg/L). When the minimum MPD is set to 75 percent of the laboratory reporting limit (or 7.5 mg/L), the closest reportable values of 20 and 30 mg/L would be -0.73 and 0.60 NSD units from the MPV, respectively, and thus fall within +/- 1 of the MPV.

In an extremely few cases, the laboratory has reported measurements of reference samples as "less than" the method reporting limit. This has only occurred infrequently for selected BSP samples with very low chemical concentrations. Prior to 1991, these less-than values were replaced by substituting the value of the method reporting limit. After this year, these determinations were not included as part of the BSP data base.

Estimates of measurement bias

BSP estimates of measurement error (equation 1) reflect both systematic and random sources of error. Systematic error, or measurement bias, can be isolated and quantified separately from random error by computing the mean of multiple error estimates. Measurement bias (B) is defined as

$$B = \frac{1}{n} \sum_{i=1}^{n} E_i \qquad (3)$$

where i is the ith value of laboratory measurement error for a BSP reference sample, and n is the total number of values of laboratory measurement error for a specified time period. The bias, therefore, describes a static, persistent measurement error associated with an analytical method for a specified length of time. The next major section of the report entitled "Relation of BSP Data to National Network Water-Quality Data" discusses graphical techniques for identifying bias, methods for estimating changes in bias over time, and methods for testing whether estimated bias is statistically different from zero.

Estimates of measurement variability

Estimation of random variability in analytical measurement error relies on the use of replicate measurements of a water sample. By computing the difference between replicate measurements of identical water samples spaced closely in time, systematic errors cancel, and random errors can be isolated and quantified.

In the BSP, measurement variability is estimated from replicate determinations on reference samples prepared from identical mixes of SRWS. Each BSP sample mix is analyzed repeatedly in the laboratory for approximately one year with the exception of nutrient mixes that are analyzed over about a six month period. For each unique BSP mixture and MPV concentration, the measurement variability, or variance (s^2), is estimated from all replicate determinations made during the 6 to 12 month time period as the sum of the squared differences between each measurement and the mean concentration for the period divided by the number of measurements minus one (Taylor, 1987). This estimate of measurement variability excludes any persistent long-term bias signal (i.e., mean) that may be present in analytical measurements during this time period. Any short-term variations in systematic error (bias) that may occur within this time period are included in the estimates of measurement variability. The analytical precision can be computed from estimates of measurement variability, and is defined as the inverse of the square root of the variance.

The BSP also expresses the measurement variance relative to the mean concentration of the reference sample by computing the relative standard deviation (RSD). This expression in percent is the coefficient of variation multiplied by 100, and is written as

$$RSD = \frac{\sqrt{s^2}}{X} \cdot 100 \qquad (4)$$

where X is the mean of the replicate determinations. The variance is expressed relative to the mean of NWQL determinations rather than the MPV of the reference samples to provide a consistent intra-laboratory estimate of measurement variability.

Selection of BSP Data for the CD-ROMs

The BSP data published on the CD-ROMs include NWQL analyses (laboratory analysis agency code of 80020) of 20 trace elements and 9 major dissolved ions during the water years 1985-95 (October 1, 1984 to September 30, 1995) and 5 nutrients during the water years 1986-95. These BSP data apply to all national network stream water-quality analyses made after April 1986. From October 1, 1984 to April 1986, the NWQL BSP data apply predominantly to national network stream water-quality analyses made for stations west of the Mississippi River (samples from other stations were analyzed at the Atlanta laboratory during this period; see the section entitled "National Network Laboratory Techniques" for a description of the jurisdiction of USGS laboratories). BSP data collected for water years 1981-84 at NWQL and for water years 1981-86 at the Atlanta laboratory (laboratory analysis agency code 80010) are currently being re-evaluated and are not published on the CD-ROMs. All BSP data published on CD-ROM were obtained from a USGS internal BSP data repository located in Reston, Virginia.

The BSP data published on CD-ROM were analyzed according to the NWQL method codes listed in Table 9 for the indicated water years. These methods were used in the analysis of national network stream water-quality samples. Some WQN stream water-quality data published on CD-ROM may have been analyzed in other laboratories as part of local investigations conducted at national network stations. The laboratory analysis agency code and the laboratory analytical method codes for WQN water-quality data should be examined by the user prior to use of the BSP data (see the section below "Selecting the Appropriate BSP Data").

Table 9. Blind Sample Program parameters and National Water Quality Laboratory analytical method codes selected for publication on the CD-ROM for water years 1985-95

[A water year begins on October 1 and ends on September 30. Laboratory analytical methods are specific for each unique combination of parameter and method code. See definition files provided in the CD-ROM data sets in Alexander and others (1996b) for a complete explanation of these codes]

Constituent	Codes		Water year	
	Parameter	Method	Beginning	Ending
N, ammonia, dissolved	00608	B	1985	1995
N, ammonia plus organic, dissolved	00623	A	1985	1991
	00623	C	1992	1995
N, nitrate plus nitrite, dissolved	00631	B	1985	1995
Phosphorus, dissolved	00666	B	1985	1991
	00666	C	1992	1995
Phosphorus, orthophosphate, dissolved	00671	B	1985	1995
Calcium, dissolved	00915	D	1985	1995
Chloride, dissolved	00940	H	1985	1986
	00940	E	1987	1989
	00940	J	1990	1992
	00940	E	1993	1995
Dissolved solids	70300	A	1985	1995
Magnesium, dissolved	00925	C	1985	1995
Potassium, dissolved	00935	B	1985	1995
Silica, dissolved	00955	D	1985	1995
Sodium, dissolved	00930	C	1985	1995
Sulfate, dissolved	00945	D	1985	1989
	00945	G	1990	1995
Fluoride, dissolved	00950	B	1985	1989
	00950	E	1990	1995
Aluminum, dissolved	01106	C	1985	1986
	01106	E	1987	1995
Arsenic, dissolved	01000	B	1985	1995
Barium, dissolved	01005	C	1985	1995

Table 9. Blind Sample Program parameters and National Water Quality Laboratory analytical method codes selected for publication on the CD-ROM for water years 1985-95--Continued

Constituent	Codes		Water year	
	Parameter	Method	Beginning	Ending
Beryllium, dissolved	01010	B	1985	1995
Boron, dissolved	01020	B	1985	1995
Cadmium, dissolved	01025	D	1985	1991
	01025	F	1992	1995
Chromium, dissolved	01030	B	1985	1987
	01030	F	1988	1995
Cobalt, dissolved	01035	C	1985	1995
Copper, dissolved	01040	B	1985	1989
	01040	F	1990	1995
Iron, dissolved	01046	D	1985	1995
Lead, dissolved	01049	B	1985	1989
	01049	F	1990	1995
Lithium, dissolved	01130	B	1985	1995
Manganese, dissolved	01056	C	1985	1995
Mercury, dissolved	71890	B	1985	1995
Molybdenum, dissolved	01060	A	1985	1995
Nickel, dissolved	01065	B	1985	1989
	01065	F	1990	1995
Selenium, dissolved	01145	A	1985	1995
Silver, dissolved	01075	A	1985	1989
	01075	F	1990	1995
Strontium, dissolved	01080	B	1985	1995
Zinc, dissolved	01090	B	1985	1995

The BSP data selected for publication on the CD-ROMs include measurement error data for assessing the accuracy (bias and variability) of laboratory methods and national network water-quality data. For each constituent, the measurement error data include the NWQL measurement of the BSP reference sample, the MPV of the reference sample, the NSD, the measurement error expressed as percent of the MPV, and an error remark code ("<") identifying estimates of error that are less-than the analytical method reporting limit.

The measurement error is expressed as a percentage of the MPV by dividing by the MPV and multiplying by 100. Where the error is remarked as less than the reporting limit, estimates of the percent error are computed by expressing the reporting limit as a percentage of the MPV (a negative sign is assigned to error values where a negative difference is obtained between the laboratory measurement and the MPV). For each BSP sample, the laboratory login date and the BSP sample mixture number are reported.

For BSP measurement variability data computed from replicate samples, the earliest and latest dates for laboratory analysis (i.e., login) of each BSP sample mixture are recorded. For each constituent, the data files include the MPV of the reference sample, the mean, variance, and relative standard deviation (RSD) of NWQL measurements of the BSP reference sample, and the number of observations used to compute the mean and variability statistics for the indicated time interval.

RELATION OF BSP DATA TO NATIONAL NETWORK WATER-QUALITY DATA

The use of BSP reference sample data to evaluate the laboratory measurement bias and variability of national network data requires the user to select the appropriate BSP data for analysis. To do this, the user must understand the intrinsic physical and chemical characteristics of reference samples. In the following two subsections, we highlight important characteristics of BSP data and data selection criteria that need to be considered. In the final subsection, we describe some of the ways of using BSP data to statistically evaluate the accuracy of national network environmental data.

Characteristics of BSP Samples

BSP reference samples represent a limited number of the characteristics of the stream water-quality samples collected at national network stations. As such, the error estimates obtained from the reference samples apply only to certain chemical constituents, stream environments, and stages of the measurement process.

Although BSP samples are generally representative of the range of concentrations found in natural waters for selected chemicals, the samples represent a narrower range of physical and chemical properties than those found in national network stream samples. BSP samples are mixes or dilutions of filtered, natural water matrices. The source of these natural waters is predominantly surface water in Colorado. Consequently, the chemical and physical matrix of BSP reference samples is not representative of the range of matrices found in the stream water samples analyzed at national network stations. Moreover, BSP measurements most appropriately describe the measurement accuracy associated with dissolved chemical forms because the reference samples are filtered. Organic constituents, suspended sediment, and whole water (i.e., unfiltered) samples are not analyzed in the program because stable and homogeneous matrices cannot be maintained for these constituents. Because the matrix of a sample can affect analytical results, differences between the matrices of national network stream samples and those of BSP samples could potentially lead to inaccuracies in using BSP data to estimate the measurement error associated with national network stream water-quality data. Comparisons of national network and BSP data are most appropriate using national network measurements for filtered (i.e., dissolved) stream samples.

BSP reference samples provide error estimates only for the latter stages of the measurement process beginning with the transport of samples to the laboratory. These error estimates include all sources of systematic and random errors that may originate in these stages with the exception of matrix-related errors that are not detectable in the less complex BSP sample matrix. BSP samples are not exposed to field sampling and processing methods, and thus, the effects of field methods on measurement error are not contained in BSP data. Moreover, the BSP program does not provide estimates of accuracy of field determinations including pH, dissolved oxygen, specific conductance, alkalinity, temperature, and fecal bacteria. It is important to recognize that field methods could potentially represent a significant portion of the total measurement error in environmental data, but quality-control data are not available for the national networks to quantify this source.

Selecting the Appropriate BSP Data

In selecting BSP data to estimate the measurement bias and variability of national network stream water-quality data, particular attention must be given to the laboratory and analytical methods used to analyze the reference samples, the range of chemical concentrations of the reference samples, and the time period of analysis.

The laboratory and the analytical methods used to measure BSP and environmental samples must be identical before BSP data can be used to evaluate the accuracy of the stream water-quality measurements. We have provided BSP data analyzed at the NWQL (laboratory analysis agency code 80020) during water years 1985-95. The NWQL performed all national network stream water-quality analyses after April 1986. BSP data from October 1, 1984 to April 1986 apply only to national network stream water-quality data collected at stations west of the Mississippi River; at eastern stations, BSP samples were analyzed at the Atlanta laboratory (laboratory analysis agency code 80010). From October 1, 1984 to September 30, 1995, when laboratory analysis agency codes and method codes are reported, other laboratories and analytical methods may have been used for some of the national network stream water-quality data published on the CD-ROM. These cases reflect local data collection activities that have been conducted at national network stations. To ensure proper use of the BSP data, the user should verify that the laboratory agency analysis codes and the method codes associated with the stream water-quality data agree with those of the BSP data listed in Table 9.

The proper use of BSP data requires the selection of data for a range of concentrations similar to those observed in the environmental data. This is important because the magnitude of measurement error frequently depends on the concentration of the water-quality sample. Concentration-dependent errors may be caused by, for example, interferences from the physical/chemical matrix of the sample or the adsorption of analyte to the walls of sample containers and analytical equipment. Although concentration-independent sources of error related to contaminants in laboratory solutions, instruments, and airborne particles may be detected by BSP reference samples, concentration-dependent errors are common in measurements of BSP samples (Alexander and others, 1993). Moreover, the variance of a measurement process expressed in absolute units frequently depends on the concentration of the sample (Thompson, 1988; Garden et al., 1980). Thus, users of BSP data should verify that the range of concentrations covered by the BSP and environmental data are similar to ensure that the estimates of laboratory measurement error accurately describe method performance for the environmental samples.

Finally, users should select BSP and stream water-quality data for the same years and months to ensure that the estimates of measurement error reflect method performance during the period of analysis of the environmental data. More precise pairing of BSP and environmental measurements requires assumptions about the travel time of environmental samples from the field site to the laboratory. The recorded date of the environmental samples is the date of sample collection from the stream, whereas the recorded date of the BSP samples is the date of entry (login date) at the laboratory. The travel time of environmental samples to the laboratory likely ranges from one to five days.

Statistical Evaluation of BSP Data

BSP data can be used in two ways to evaluate the accuracy of national network environmental data. First, reference sample data can be used to evaluate the laboratory measurement process. This function typically involves the use of statistical standards (e.g., multiples of the standard deviation of the method) to determine whether measurement errors in laboratory methods are sufficiently "in control" to yield precise, unbiased environmental measurements. Evidence of "out of control" behavior may lead one to suspect the validity of an analytical method during certain time periods, which may suggest the need for editing of the environmental data or at least caution in the interpretation of the environmental data.

A second function of the BSP data is to assist in the interpretation of the environmental data by providing estimates of the magnitude of variations in the environmental data caused by laboratory measurement error. Although statistical standards provide important information about the stability of the measurement process, these standards are not necessarily relevant to the magnitude of variations observed in the environmental data or the intended uses of the environmental data. A direct comparison of environmental data and BSP measurement error data can guide interpretations of the environmental observations, providing additional protection against Type I and Type II statistical errors. [In an example where the null hypothesis (or presumed real condition) is that there is no method-related contamination in a water-quality sample, the Type I error can be stated as the probability of falsely rejecting the null hypothesis and incorrectly concluding that the sample contains the contaminant. For this same example, the Type II error can be stated as the probability of falsely accepting the null hypothesis and incorrectly concluding that the sample does not contain the contaminant.]

The following two subsections discuss these two approaches to using BSP data to evaluate the accuracy of national network environmental data.

Evaluation of laboratory methods and network water-quality data

The evaluation of laboratory methods involves determining whether analytical methods provide consistent or "in control" measurements of water quality. The consistency of method performance is frequently evaluated by testing whether quality-control measurements fall within generally accepted statistical limits of control. Evaluation can be conducted using graphical methods or a variety of statistical tests.

One conventional approach is the use of a control chart. Control charts provide a graphical method for monitoring the mean and variability of a measurement process over time. Charts rely on the statistical distribution of historical measurements of quality-control samples to define an acceptable range of variability in measurement error--that is, a range that reflects variations in methods due to background noise or random variations in the

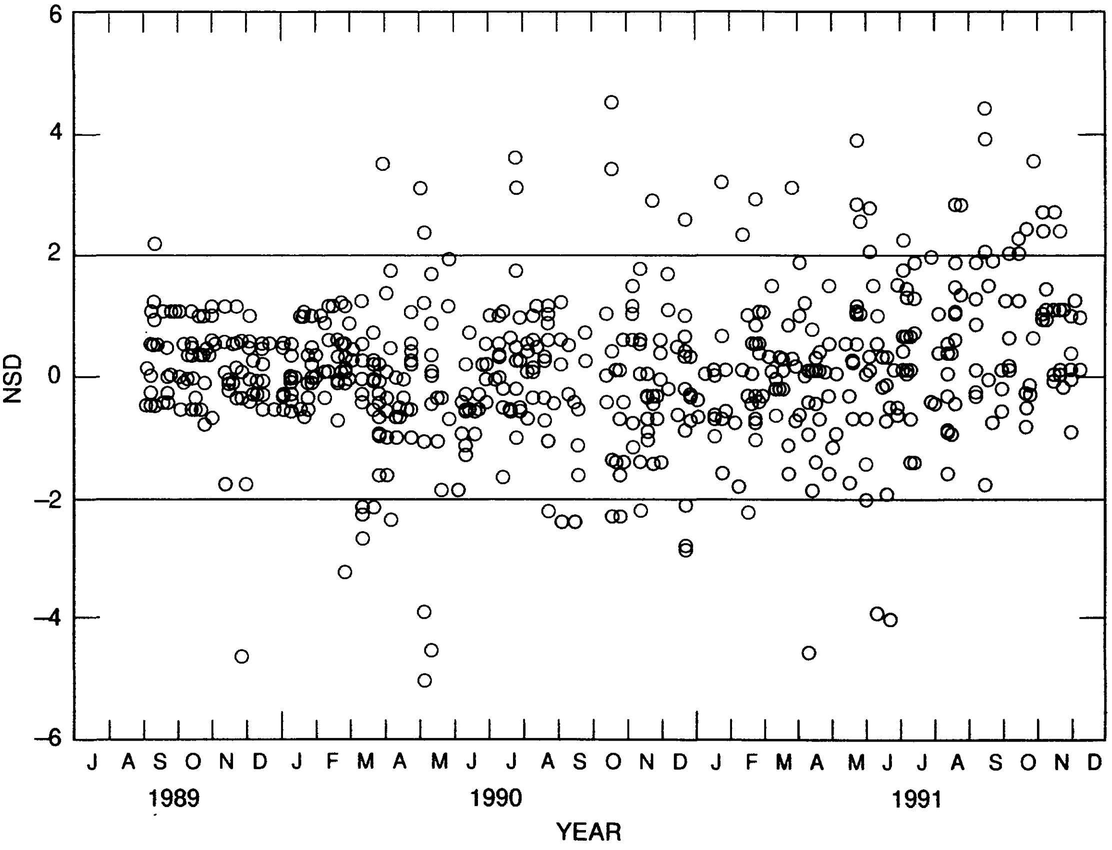

Figure 8. Number of standard deviations (NSD) from the most probable value (MPV) for Blind Sample Program measurements of sulfate, 1989-91 [The solid horizontal lines identify Blind Sample Program control limits]

analytical results. Once established, this acceptable variance can be applied graphically to determine when measurements are "in control" or "out of control." These statistical procedures effectively amount to a graphical application of a hypothesis test such as the t-test. A variety of control charts are available for identifying errors in the various components of a measurement process (see Montgomery, 1991). Many of these charts are used in combination with visual and quantitative techniques, designed to identify temporal patterns in errors that may signal the existence of bias in the measurement process or to detect changes in bias.

The statistic, NSD (number of standard deviations), reported for the BSP data gives the number of standard deviations that the measured concentration differs from the MPV, and can be used directly to assess whether the method exhibits statistical control (see Fig. 8 for an example of a control chart application of this statistic). A statistical limit of two standard deviations has been used by the BSP to specify the limit of control (see for example, Maloney, et al., 1994). The NWQL has used a limit of 1.5 standard deviations as part of their internal quality-assurance program (Pritt and Raese, 1992). Values beyond these limits may indicate time periods when laboratory methods were performing abnormally because of random or systematic errors. In the example for sulfate (Fig. 8), there is evidence of greater variance (i.e., less precision) in the analytical measurements of

BSP samples from early 1990 to late 1991 related to a change in the method of laboratory analysis, although most NSD values lie within the +/- 2 control limit. In examining a control chart, any persistent systematic behavior in the reference sample measurements may indicate a time period when bias was present in the measurement process. In the sulfate example (Fig. 8), a positive bias exist from early 1990 to the end of 1991 as indicated by the greater frequency and magnitude of NSD values above zero as compared to those below zero.

A variety of formal hypothesis tests are also available to the user to determine whether a laboratory analytical method contains statistically significant bias over a specified time period. Three of these tests are classified as matched-pairs tests, and are suitable for evaluating whether the laboratory measurement bias is significantly different from zero. The first is the paired t-test, a parametric test (Ott, 1993). Two nonparametric tests for paired data include the sign test and the signed-rank test (Helsel and Hirsch, 1992). Although not classified as a matched-pairs test, another nonparametric test, the binomial probability distribution method (Friedman, et al., 1983), can be used to test for the presence of statistically significant bias. This statistical method compares the number of analytical determinations exceeding the control limits to the number expected for a specified alpha level according to the binomial distribution. Larger than expected exceedences may be indicative of statistically significant bias in the analytical method. In using these parametric and nonparametric tests with BSP reference samples, a two sided test is recommended because prior knowledge as to whether the errors are exclusively positive or negative is unlikely to exist. It should be noted that the power of these tests to detect the presence of bias will increase with the number of error measurements.

In general, the use of parametric procedures to test for the presence of measurement bias can be problematic unless proper transformations of the data are made. Both concentration-dependent and concentration-independent measurement errors can produce distributions of measurement error that are non-normal and heteroscedastic (i.e., display nonconstant variance). These distributional characteristics violate the required assumptions of the t-test. In the case of concentration-dependent errors, considerable asymmetry can appear in the distribution of measurement errors due to changes in the magnitude of errors with different concentrations of the reference samples. In the case of concentration-independent errors (e.g., contamination), an error distribution with a lower bound of zero is not appropriately modeled as normal. Failure to satisfy the assumption of normality will lower the power of the t-test, thereby reducing the probability of detecting significant deviations of measurement bias from zero in cases where the average measurement process is actually biased. Two alternatives exist in these situations. First, logarithmic or other transformations of the estimates of measurement error can frequently yield an approximately normal distribution. Error estimates expressed as percent of the MPV may also yield a more normal distribution. Second, nonparametric tests as referenced above are not as sensitive to non-normally distributed data as parametric tests (but can be sensitive to heteroscedastic data). In cases of non-normal data, nonparametric tests have greater power than the paired t-test, expecially for small sample sizes (i.e., fewer than 30).

Tests for temporal changes in measurement bias and variability can also be important in evaluating the laboratory measurement process. In the study of long-term trends in stream water quality, it is especially important that changes in laboratory methods over time do not produce false trends or mask true trends in ambient water-quality measurements. There are examples in the literature where interpretations have been compromised by such method changes (see for example, Shapiro and Swain, 1983; Bruland, 1983; Flegal and Coale, 1989; Schertz and others, 1994). In estimating trends in measurement bias, a variety of parametric and nonparametric procedures are available to test for the presence of abrupt (i.e., step) changes (Hirsch and others, 1992) or linear and monotonic changes with time (Hirsch and others, 1992; Alexander and others, 1993).

Available tests for step changes in measurement variability include the parametric F test (Ott, 1993) for evaluating whether analytical method variances are similar for two different time periods, and the nonparametric test, the Wilcoxon-Mann-Whitney Rank-Sum test (Helsel and Hirsch, 1992), for determining whether the distribution of measurement variability has changed between two time periods. The Siegel-Tukey test (Siegel and Tukey, 1960) provides an alternative to the Rank-Sum test that is more sensitive to differences in the spread of two distributions.

Evaluation of laboratory analytical methods on the basis of statistical criteria provides important confirmation that analytical methods are producing consistent environmental measurements. The type of consistency required by users may include assurance that measurement errors are unbiased and unchanging with time. The exact nature of these requirements will ultimately depend on the intended uses of the environmental data (e.g., percent of observations detected, estimation of a mean concentration or trend in concentration). Detectable inconsistencies in laboratory methods based on statistical evaluations of BSP data may prompt a user to edit environmental data for particular time periods, disregard an entire environmental record, or simply exercise caution in interpretations of environmental data. These decisions on the part of data users are inherently subjective.

It is important to recognize that the above methods of statistical evaluation do not directly indicate the practical significance of laboratory measurement error for environmental observations. It may be of interest to know whether measurement errors (either "in-control" or "out-of-control") are sufficiently large to influence interpretations of the environmental data. Even a consistently "controlled" measurement process can exhibit subtle variations in bias that are detectable over long time periods and may have relevance to interpretations of environmental data (see, for example, Alexander and others, 1993). The effects of statistically significant measurement errors on the interpretation of environmental observations can only be evaluated through direct comparisons of estimates of measurement error and environmental data. The next section presents several ways of accomplishing this task.

Correction of water-quality data for measurement error

BSP data can assist the interpretation of national network water-quality data by providing information for evaluating and correcting the stream water-quality data for estimates of laboratory measurement error. The procedures discussed here use information on laboratory measurement bias and variability to provide additional protection against Type I and Type II statistical errors in the interpretation of the stream water-quality data. The accuracy of these correction methods will, of course, depend on how well the BSP references samples replicate the characteristics of the stream water-quality data. The intrinsic physical and chemical characteristics of the reference samples (and their limitations) as previously discussed should be considered when using the following statistical methods.

The first two methods help to identify and resolve cases where a bias-induced artifact in the stream water-quality data may be falsely interpreted as a real environmental signal (Type I error), and cases where measurement bias may prevent the detection of an environmental signal (Type II error). The first method provides a general approach to correct for the effects of measurement bias on categorical analyses of water-quality data. A second method describes a technique for computing an unbiased estimator of mean water-quality concentration or trend in concentration and for computing the variance of the estimator adjusted for measurement error. A final method evaluates laboratory measurement variability in the stream water-quality data. This method describes how to determine whether measurement variability contributes significantly to the total variability observed in the water-quality data and how to obtain an estimate of the natural variability (i.e., total variability corrrected for measurement variability).

Correction for the effects of measurement bias on categorical analyses

The first method provides a general approach to correcting individual water-quality observations for measurement bias for the purpose of classifying stream concentrations as being above or below an environmentally- or statistically-relevant threshold. Some examples of the environmental questions for which this approach may be useful for evaluating and correcting the effects of measurement bias include: (1) What fraction of the time are stream concentrations above a particular water-quality standard or criterion? (2) Is a particular water-quality contaminant present in a stream (i.e., how frequently is the concentration above the method reporting limit)? (3) Have water-quality concentrations increased or decreased over time? The bias-correction method described here is satisfactory for obtaining a general impression of the effects of measurement bias on the water-quality concentration data. Any hypothesis test conducted with the bias-corrected data would not be accurate, however, because errors in the bias estimates are not systematically incorporated in the test (see the subsequent method for addressing this issue).

In addressing the first two questions, the effects of positive bias on interpretations of the environmental data, for example, may be evaluated by lowering stream water-quality concentrations by an amount equal to the estimated bias. These adjusted concentrations may, in turn, be compared to the water-quality standard or method reporting limit for the purpose of computing exceedence statistics. Error in the estimate of measurement bias may be partially accounted for by incorporating the probability that the expected value of bias based on sample measurements differs from the true bias. To ensure that there is a very small probability that measurement bias caused a water-quality concentration to exceed the standard or reporting limit, water-quality concentrations could be adjusted downward by an amount equivalent to the expected value of positive bias plus some multiple of the expected value's standard error (e.g., the upper 95 percent confidence interval value). By accounting for error in bias in this manner, the approach is aimed at reducing the probability of a Type I error.

Investigations of the question of whether concentrations have increased or decreased over time could potentially include an evaluation and adjustment for the effects of estimated trends in measurement bias on the detection of trends in stream water-quality concentrations. The magnitude of trend declared to be statistically or environmentally significant could be increased or decreased to account for estimated trend in measurement bias. This approach is equivalent to correcting each observation for the estimated magnitude of trend in measurement bias, although the method ignores error in the estimate of trend in bias. A study of trends in dissolved solids (ROE--residue on evaporation) at USGS long-term stream monitoring sites from 1980-88 (Smith and others, 1993) adjusted the threshold for declaring significant trends to account for the effect of an estimated change in measurement bias on stream concentration trend slopes. In view of evidence of a measurement bias trend of about 2 to 3 percent at a USGS laboratory from 1981-89, statistically significant stream-concentration trend slopes less than about 3 percent were assigned to a "no trend" class. This technique provided additional protection against Type I errors by reducing the probability that a small, statistically significant trend resulting from long-term changes in laboratory measurement error would be incorrectly identified as a real trend in the dissolved solids concentration of a river. The objective of this approach is not to estimate an unbiased trend slope in water-quality concentrations (see the next section), but to reduce the probability that a trend artifact related to method changes could result in a water-quality trend being mis-classified as statistically significant.

Correction of an environmental estimator for measurement bias

A second method for correcting stream water-quality data for estimates of laboratory measurement bias can be used to compute an unbiased estimator of water-quality (e.g., mean, trend slope) and to adjust the variance of the estimator for measurement error. This approach addresses both the Type I and Type II errors associated with statistical testing of the environmental data. The approach recognizes and incorporates the effects of random measurement errors on the quantification of bias and the correction of environmental data for bias. However, if random measurement errors associated with the estimation of bias are large, it may be difficult to use BSP data to clearly identify a measurement bias signal in the environmental data.

The approach (see Alexander and others, 1993 for a detailed explanation) decomposes the laboratory measurement bias in an environmental record into two components. The first component is a persistent, long-term (multi-year) error affecting all the water-quality measurements, and can be described by a mean bias or a bias trend slope. The second bias component is sporadic, but of sufficiently long duration to affect all water-quality samples analyzed over a shorter time period, possibly spanning days or months. This component reflects random variations in measurement bias of long enough duration that a systematic error appears in all water-quality samples analyzed at the laboratory during this interval of time. In correcting the mean environmental concentration or trend slope, it is necessary to adjust for the first error component. Accounting for the second error component can lower the variability of estimates of the bias-corrected mean or bias-corrected trend slope for the environmental data. This systematic error component can be estimated by the covariance between the measurement error and environmental data. If this bias actually affects stream water-quality measurements, then a portion of the random variability in the water-quality record will be positively correlated with the estimates of measurement error.

Accordingly, an estimate of a bias-corrected mean water-quality concentration ($\hat{\mu}^{bc}$) can be computed as

$$\hat{\mu}^{bc} = \hat{\mu}_w - \hat{\mu}_b \qquad (5)$$

where $\hat{\mu}_w$ is the estimate of mean water-quality concentration and $\hat{\mu}_b$ is the estimate of mean measurement bias. The standard error of the bias-corrected mean water-quality concentration (SE^{bc}) is computed as

$$SE^{bc} = \sqrt{\frac{1}{n} \quad \hat{\sigma}_w{}^2 + \hat{\sigma}_b{}^2 - 2\ \mathrm{Cov}(w,b)} \qquad (6)$$

where $\hat{\sigma}_w{}^2$ is the estimated variance of the water-quality concentrations, $\hat{\sigma}_b{}^2$ is the estimated variance in measurement bias, and the covariance can be estimated as

$$\mathrm{Cov}(w,b) = \frac{1}{n} \sum_{i=1}^{n} (w_i - \hat{\mu}_w)(e_i - \hat{\mu}_b) \qquad (7)$$

where w_i is the water-quality concentration for the ith time period, e_i is the estimate of measurement error (equation 1) for the ith time period, and n is the number of concentration and measurement error pairs.

If random error in the measurement of bias ($\hat{\sigma}_b^2$) is large or the covariance between the environmental and measurement error data is small, the standard error of the bias-corrected mean environmental concentration may be larger than that of the biased (i.e., uncorrected) mean environmental concentration. This situation is not uncommon for national network data, and may occur for several possible reasons including difficulties in properly pairing the environmental and measurement error data (see Alexander and others, 1993). Thus, bias-correction may improve the estimate of mean water-quality, but it may also increase the variability associated with the bias-corrected mean estimate. This may lower the power of the statistical test to detect a particular signal in the environmental data. In these cases, the user must decide which type of estimate of mean concentration best satisfies their requirements--a biased, precise estimate or an unbiased, imprecise estimate.

This method can be extended to correct estimates of trend in environmental data for trend in measurement bias. The method of "seemingly-unrelated" regression (SUR) is a parametric statistical method well suited for this task. The reader is referred to Alexander and others (1993) for a detailed description of how this technique can be used with BSP data to correct water-quality trends in NASQAN data for the estimated effects of measurement bias.

Assessment of laboratory measurement variability

BSP data may also be used to assess whether variability in laboratory analytical determinations (i.e., random variations) may be large enough to have prevented the detection of an environmental signal. This information may be particularly important to the interpretation of water-quality data for streams with very low concentrations in proximity to the method reporting limit. Whether environmental observations actually measure the effects of real environmental processes is influenced by the size of the measurement variability relative to the total variability of the data. If measurement variability constitutes a sizeable fraction of the total variability observed in the environmental data, the probability of a Type II error, a failure to detect a real environmental signal, may increase. Evidence of significant measurement variability at the beginning of an investigation would normally indicate the need for improvements in methods or increased numbers of environmental samples. A retrospective statistical evaluation of variability involves comparing the total variability (as measured by stream concentrations) to the laboratory measurement variability in an F test. The presence of a significantly lower laboratory measurement variance relative to the total variance would indicate that laboratory measurement error is not likely to have accounted for the failure to detect an environmental signal in the data. Method variability related to the collection and processing of the environmental sample; however, could potentially account for an important source of variability not included in BSP estimates of measurement error.

The correction of estimates of total variability in environmental data for laboratory measurement variance could be of interest in cases where a reliable estimate of the natural variability of water quality at a stream site is required. This might include compliance monitoring situations where knowledge of the natural variability is necessary to assess the effect of incoming pollutants on stream water quality and to develop discharge limits. If measurement variability were to represent a sizeable fraction of the total variability, then a correction might be necessary. The estimated natural variability ($\hat{\sigma}_n^2$) can be computed as

$$\hat{\sigma}_n^2 = \hat{\sigma}_t^2 - \hat{\sigma}_l^2 \qquad (8)$$

where $\hat{\sigma}_t^2$ is the estimated total variance as measured by the environmental samples and $\hat{\sigma}_l^2$ is the estimated laboratory method variance as measured by BSP samples.

Statistical analysis of measurement error estimates

As indicated in the section "Estimates of measurement accuracy" (p. 41), BSP error estimates computed according to equation 1 are potentially subject to uncertainty because of the effect of laboratory rounding rules on the numerical precision of reported water-quality measurements. In reporting instrument readings, the laboratory rounds water-quality measurements to the nearest whole number or decimal fraction according to the sensitivity of analytical methods as specified by the method reporting limit. As a result, the accuracy of individual estimates of error would be expected to decline as the magnitude of the error becomes smaller (i.e., as the magnitude of the error decreases relative to the size of the reporting limit). The highest levels of inaccuracy occur for error estimates that are less than the rounding threshold, or reporting limit, because the uncertainty in water-quality measurements exceeds the magnitude of the error in this range. The sign of error values smaller than the reporting limit in size cannot be accurately determined, but is estimated according to equation 1 in reporting values of NSD and percent bias in the CD-ROM data sets.

Error estimates below the method reporting limit (denoted as "less than" the reporting limit in the CD-ROM data base) vary considerably for the chemical constituents analyzed in the BSP. The percentage of less-than nutrient error values ranges from a low of 17 percent for ammonia to a high of 75 percent for nitrate plus nitrite; approximately 20 percent of phosphorus error values fall below the reporting limit. Percentages of less-than error values for major dissolved ions range from 4 to 50 percent with most constituents displaying percentages below 20 percent. Virtually all of the percentages of less-than trace-element error values exceed 35 percent with most above 50 percent.

As the proportion of error values significantly affected by rounding (i.e., small errors and errors below the reporting limit) increases, summary statistics such as the bias (i.e., mean error), variance in bias, and measurement variance (equation 4) are likely to become increasingly less accurate. Unfortunately, the effect of rounding on the accuracy of these statistics cannot be quantified from available information. As a general guide to addressing potential inaccuracies, we advise users to exercise caution in the interpretation of error summary statistics for those constituents and time periods where a majority of the error values are less than the reporting limit. Control charts may be helpful in these cases to graphically examine variations in the measurement process, especially the infrequent occurrence of errors exceeding the reporting limit.

ORGANIZATION OF THE CD-ROMS

The water-quality and ancillary data from the USGS water-quality national networks (WQN) on CD-ROM are produced in accordance with the ISO 9660 CD-ROM standard. The data are capable of being read on any computer that has appropriate CD-ROM driver software installed. The data are provided in two forms separately on two CD-ROM discs. The ASCII disc is readable on any computer with CD-ROM driver software, and contains all WQN data in ASCII form. The DOS disc can be used to access all WQN data (except for daily streamflow values) on a DOS-compatible personal computer operating under the disc operating system (DOS). The software supplied on the DOS disc (GSSEARCH, GSMENU) allows the user to browse text files and and retrieve and output data according to user-specified criteria.

There are three first-level sub-directories on each of the CD-ROMs. Each directory contains a help file entitled "1st_read.me" that lists the sub-directories and their functions as well as the file contents of the current directory. The DOCFILES sub-directory contains ASCII files giving an overview of WQN, the authors, contacts, and references. The files DATA_ALL.TXT and DATA_DOS.TXT should be consulted by the user for a listing of the relevant ASCII and DOS data files on the CD-ROMs, respectively. The REPORT sub-directory contains the text, figures, and tables of this U.S Geological Survey Open-File Report (96-337). On the ASCII disc, the WQN sub-directory contains ASCII files of all the water-quality, streamflow, and quality-assurance data. These data are available for users unable to use the DOS-compatible search software. On the DOS disc, all data in this sub-directory, with the exception of daily streamflow values, are accessible with the supplied software, GSSEARCH and GSMENU.

On the DOS disc, an additional first-level sub-directory, DOSMENU, contains the files necessary to operate the GSMENU and GSSEARCH software, and includes the WQN data bases accessed by this software.

The following two sections describe the contents of the WQN and DOSMENU sub-directories.

WQN Directory

There are three types of data available to the user in this directory: stream water-quality data, streamflow data, and ancillary data supporting the use of these data. All data are accessible within this sub-directory on the ASCII disc. On the DOS disc, all data are accessible, with the exception of the streamflow data, using GSMENU and GSSEARCH (a single DOS accessible water-quality data file replaces the separate water-quality data sets in the regional sub-directories on the ASCII disc--see the discussion of the WQ sub-directory below).

The data in this directory are organized in three subdirectories on the ASCII disc. The sub-directory WQ contains stream monitoring data on water quality and streamflow and ancillary data on monitoring station and watershed attributes. The sub-directory BSP contains the Blind Sample Program data on laboratory measurement bias and variability. Finally, the sub-directory QASURE contains quality-assurance information on network operations and important method changes that may influence the use or interpretation of the WQN stream water-quality data. The contents of each sub-directory are described in the following sections.

WQ sub-directory

ASCII data files in this directory provide ancillary information on station and watershed attributes as well as several files describing the collection agencies, laboratories, and methods used to analyzed the water-quality data. The file "1st_read.me" provides a complete description of these data files. The format of each data file is supplied in the sub-directory FORMATS in files with the suffix "FMT." A few of the key files are highlighted here.

A listing of 121 water-quality constituents and information on the units of measure, chemical expressions, and identifying codes are described in the file WQ_PARM.DAT (instantaneous streamflow is not among the constituents listed, but the data are available in the water-quality files). Attributes of the 679 water-quality monitoring stations and the hydrologic units containing the stations are given in the file WQ_STAS.DAT. Forty-eight of these stations in the NASQAN network were relocated at some time from 1973-95. A listing of these stations, their replacement stations, and dates of station operation are given in the file WQ_RELOC.DAT. A listing of the daily streamflow station for each water-quality site is listed in WQ_FLOW.DAT. Daily streamflow records are collected at most national network sites. The file WQ_FLOW.DAT indicates a nearby alternate site for 79 of the NASQAN stations (19 sites are relocated NASQAN sites), and indicates 25 sites where no records of daily streamflow are available. The attributes of 61 alternate streamflow gaging sites (non-NASQAN) are given in the file FLOWSTAS.DAT (the streamflow record for one NASQAN site is composed of two upstream alternate streamflow sites).

The ASCII water-quality and streamflow data sets are located in 21 sub-directories corresponding to the major hydrologic regions defined by the Water Resources Council (Seaber and others, 1987). Each sub-directory has the name "REGrr" where rr is the first two digits of the hydrologic unit code (HUC) associated with the major regional watersheds (see the HUCS.TXT file for a complete explanation of hydrologic unit codes).

Within each regional sub-directory, the water-quality and streamflow data are organized in separate station and parameter files. The name of each file is "ssssssss.ttt" where "ssssssss" is the eight digit USGS station number and "ttt" refers to a three-character descriptor of the constituent group (see the WQ_PARM.DAT file for a listing of these descriptors). Each constituent has been assigned to a logical physical, chemical, or biological grouping as indicated in the WQ_PARM.DAT file. For example, station files with the suffix of "NUT" contain nutrient water-quality data and files with the suffix of "DMV" contain daily mean streamflow values. Each record in these files gives measurements for a unique date and time except the daily streamflow file where there is one record for each day of the month (31 records for each calendar year). The agency collection and agency laboratory analysis codes are also provided in the water-quality files to allow identification of the agency source of each sample (AGENCIES.DAT and LABS.DAT give explanations). These codes are available generally beginning in the early 1980s. A laboratory analytical method code and remark code is provided with each water-quality value in these files (METHODS.DAT and REMARKS.DAT give explanations of these codes). Method codes are available beginning in 1985.

BSP sub-directory

This directory provides Blind Sample Program (BSP) data for 34 dissolved chemical constituents for the water years 1985 to 1995. These constituents are listed in the file BSP_PARM.DAT with their units of measure, chemical expression, and unique identifying codes. The laboratory analytical method codes corresponding to the BSP data are listed in the file BSP_METH.DAT.

The estimates of laboratory measurement bias and variability are organized in separate files by constituent group. The name of each file is "BIAS.ttt" or "VAR.ttt" where "ttt" is a three-character descriptor of the constituent group (see the BSP_PARM.DAT file for a listing of this descriptor).

Within each measurement error file, the records are sorted by the laboratory login date, the BSP sample mixture number, and the sequential sample number designating samples of the same mixture analyzed on identical days. For each constituent, five values are recorded: the NWQL measurement of the BSP reference sample, the MPV of the reference sample, the NSD, the measurement error expressed as percent of the MPV, and a remark code to designate estimates of error that are less-than the analytical reporting limit.

Within each measurement variability file, the records are sorted by the beginning and ending dates of login of the samples to the laboratory, and the BSP sample mixture number. For each constituent, five values are recorded: the MPV of the reference sample, the mean, variance, and relative standard deviation (RSD) of NWQL measurements of the BSP reference sample, and the number of observations used to compute the mean and variance statistics for the indicate time interval.

QASURE sub-directory

This directory gives quality-assurance information on network operation and important changes in field and laboratory methods. Much of this information is documented by internal USGS memoranda provided on the discs.

The file QA_MEMOS.DAT (Table 5) gives a brief summary of 59 selected USGS water-quality technical memoranda. Documents are presented for six topical categories: national network implementation memoranda, biological methods, nutrient methods, trace element methods, alkalinity methods, and miscellaneous processing, analytical, and reporting methods. The text for the memoranda are identified by the originating office and a unique number QWyy_nn.TXT (Office of Water Quality) and NLyy_nn (National Water Quality Laboratory), where yy gives the year of the document and nn is a sequential number or character identifying the year's memoranda.

The files QA_FLD.TXT (Table 4) and QA_LAB.TXT (Table 8) give a summary of the most important changes in field and laboratory methods and sample contamination that could affect the use and interpretation of WQN data. The contents of these files are organized alphabetically by constituent type and chronologically within each constituent. For each entry, we provide a date, a brief summary of the event, and a reference to key memoranda or publications.

DOSMENU Directory

The file INSTALL.EXE in the root directory of the DOS disc is an executable program for DOS personal computers that allows the installation of the GSMENU and GSSEARCH software for browsing and searching the WQN databases and outputing data in a variety of formats. Once the CD-ROM drive is made the active drive, enter INSTALL from the keyboard. On-screen instructions allow the user to complete the installation of the software.

The GSMENU software allows the user to search the WQN data base using the program GSSEARCH. A logical query of any of the items in up to 15 datafiles may be executed. All data are retrievable from GSSEARCH or browsable from GSMENU except for the streamflow data, which can only be accessed from the ASCII disc using user-provided software. Some of the items available for searching the water-quality data include, for example, station name and other station attributes (e.g., county/state, hydrologic unit code, drainage basin 1990 population and 1987 land cover, latitude, longitude), date, constituent name, and the remark code, method code, collection agency code, laboratory analysis code, or value of the water-quality constituent. The software allows the selected data that satisfies the query conditions to be output in a variety of formats including dBASE, flat ASCII, delimited ASCII, or fixed-field. Instructions for the use of GSSEARCH are provided as text in this directory and as on-line help.

The GSMENU system may be used to browse the contents of 68 data files containing national network and quality-assurance information. These files include the water-quality memoranda in the QASURE sub-directory, several text files in the WQ sub-directory (consisting of Tables 2, 3, 6, and 7), and the files QA_FLD.TXT (Table 4), QA_LAB.TXT (Table 8), and QA_MEMOS.TXT (Table 5) in the QASURE sub-directory.

SUMMARY

Historical water-quality and streamflow data and supporting documentation and quality-assurance information for the U.S. Geological Survey's National Stream Quality Accounting Network (NASQAN) and the Hydrological Benchmark Network (HBN) have been assembled in an easy-to-use form on two CD-ROMs. The data from these networks include measurements for a set of 63 physical, chemical, and biological water properties for a time period spanning the past 30 years. Network data describe stream water-quality conditions in 679 watersheds with diverse climatic and cultural characteristics, ranging from the relatively small, minimally disturbed watersheds in the HBN to the larger, more culturally-influenced drainage basins of NASQAN. Expenditures for these two national networks have totaled approximately $95 million through 1995. Data collection has occurred during a period of significant changes in terrestrial and atmospheric sources of water pollutants in the United States stemming, in part, from the enactment of major federal legislation in the 1960's and 1970's. The national networks have provided some of the best available monitoring data for investigating the influences of these pollutant sources on national and regional water quality. Numerous studies have also used data from the national networks to investigate state and local stream water quality. Overall, national network data have been frequently used at widely-varying geographic scales to quantify trends in water quality, estimate rates of chemical flux from watersheds, and investigate the relations of water quality to the natural environment and human activities.

The CD-ROMs provide the necessary information and data-retrieval tools to allow the national network data to be accurately and efficiently used. In addition to the stream water-quality monitoring data, we include ancillary information on the objectives and characteristics of the network stations and water-quality data, historical records of network operations and sample collection and analytical methods, a bibliography of scientific investigations using national network data and other publications relevant to the networks, water reference sample data for estimating laboratory measurement bias and variability, and discussions of statistical methods for using reference sample data to evaluate the accuracy of network water-quality data.

The data structure of the CD-ROMs is designed to allow users to efficiently input the water-quality data to user-supplied software packages including statistical analysis, modeling, or geographic information systems. On one disc, all data are stored in ASCII form accessible from any computer system with a CD-ROM driver. The data can also be accessed using DOS-based retrieval software supplied on a second disc. Logical data queries of the water-quality data can be made for constituent concentrations, sample-collection date, river name, station name, county state, and hydrologic unit identifiers, and 1990 population and 1987 land-cover characteristics for station watersheds. User-selected data can be output in a variety of formats for subsequent use in other software packages.

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APPENDIX: NATIONAL NETWORK BIBLIOGRAPHY

The bibliography is arranged alphabetically and organized according to the following topical areas (number of references):

- Field sample collection, laboratory analysis techniques, and quality assurance (22)
- National network characteristics, background, and program evaluations (23)
- National and regional interpretations of National Stream Quality Accounting Network (NASQAN) data (29)
- State and local interpretations of National Stream Quality Accounting Network (NASQAN) data (52)
- National and regional interpretations of Hydrologic Benchmark Network (HBN) data (9)
- State and local interpretations of Hydrologic Benchmark Network (HBN) data (12)
- Statistical methods (14)

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