UNITED STATES

DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY

QUALITY-ASSURANCE PLAN FOR WATER-QUALITY ACTIVITIES IN THE SOUTH DAKOTA DISTRICT

July 2004

For Administrative use only
United States Department of the Interior
Geological Survey
Water Resources Discipline

CONTENTS

CONTENTS—Continued

CONTENTS—Continued

FIGURES

TABLES

TABLES—Continued

Quality-Assurance Plan for Water-Quality Activities in the South Dakota District

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Abstract

In accordance with guidelines set forth by the Office of Water Quality in the Water Resources Discipline of the U.S. Geological Survey, a quality-assurance plan has been created for use by the South Dakota District in conducting water-quality activities. This quality-assurance plan documents the standards, policies, and procedures used by the South Dakota District for activities related to the collection, processing, storage, analysis, and publication of water-quality data. The policies and procedures that are documented in this quality-assurance plan for water-quality activities are meant to complement the District quality-assurance plans for surface-water and ground-water activities and to supplement the South Dakota District quality-assurance plan.

1.0 Introduction

The U.S. Geological Survey (USGS) was established by an act of Congress on March 3, 1879, to provide a permanent Federal agency to perform the systematic and scientific "classification of the public lands, and examination of the geologic structure, mineral resources, and products of the national domain." The Water Resources Discipline (WRD) of the USGS is the Nation's principal water-resources information agency. The objectives of the WRD's Basic Hydrologic Data Program are to collect and provide unbiased, scientifically based information that describes the quantity and quality of waters in the Nation's streams, lakes, reservoirs, and aquifers. Water-quality activities in the South Dakota District are part of the WRD's overall mission of appraising the Nation's water resources.

To address quality-control issues that are related to water-quality activities, the WRD has implemented policies and procedures designed to ensure that all scientific work conducted by or for the WRD is consistent and of documented quality. The Office of Water Quality (OWQ) is responsible for providing a quality-assurance (QA) plan that documents the policies and procedures that apply to the water-quality activities in each District in the Discipline.

A QA plan is a formal document that describes the management policies, objectives, principles, organizational authority, responsibilities, accountability, and implementation procedures for ensuring quality. Quality assurance, quality control (QC), and quality assessment are all components of a QA plan. The terms are defined as follows:

Quality assurance (QA)—The systematic management of data-collection systems by using prescribed guidelines and criteria for implementing technically approved methods and policies. Quality assurance incorporates a comprehensive plan that outlines the overall process for providing a product or service that will satisfy the given requirements for quality.

Quality control (QC)—The specific operational techniques and activities used to obtain the required quality of data. Quality control consists of the application of technical procedures to achieve prescribed standards of performance and to document the quality of collected data. Quality-control data that do not meet required standards are used to evaluate and implement corrective actions necessary to improve performance to acceptable levels.

Quality assessment—The overall process of assessing the quality of environmental data by reviewing (1) the appropriate implementation of QA policies and procedures and (2) analyzing the QC data. Quality assessment encompasses both the measurable and unmeasurable factors that affect the quality of environmental data. Assessment of these factors may indicate limitations that require modifications to protocols or standard operating procedures for sample collection and analysis, or that affect the desired interpretation and use of the environmental data.

Quality-assurance, quality-control, and quality-assessment systems complement each other to provide a comprehensive QA program that ensures that quality objectives are identified and integrated into all levels of water-quality activities. By integrating these components into a discipline-wide QA guidance document, the OWQ hopes to enhance water-quality data collected by the USGS by providing for the following:

- **Consistency** in data quality across all levels of the WRD;
- **Accountability** to clients, the scientific community, regulatory agencies, and the general public;
- **Comparability** of results among samples, sites, and laboratories;
- **Traceability** from the end product back to its origins, and to all supplementary information, through written records;
- **Application** of appropriate and documented techniques that lead to similar results time and again;
- **Representativeness** of the data in describing the actual chemical composition of the biological or physical conditions at a sampling site for a given point or period in time; and
- **Adequacy** of the amount of data obtained to meet data objectives.

1.1 Purpose and Scope

The purpose of this District QA plan for water-quality activities is to document the standards, policies, and procedures used by the South Dakota District for activities related to the collection, processing, storage, analysis, and publication of water-quality data. This plan identifies responsibilities for ensuring that stated policies and procedures are carried out. The plan also serves as a guide for all District personnel who are involved in water-quality activities and as a resource for identifying memoranda, publications, and other literature that describe associated techniques and requirements in more detail.

The scope of this QA plan includes discussions of the policies and procedures followed by the South Dakota District for the collection, processing, analysis, storage, and publication of water-quality data. Although procedures and products of interpretive investigations are subject to the criteria discussed in this plan, some interpretive investigations may be required to have separate and complete QA plans. The policies and procedures documented in this QA plan for water-quality activities are intended to complement the District QA plan for surface-water and ground-water activities and supplement the South Dakota District QA plan.

2.0 Organization and Responsibilities

Quality assurance is an active process of achieving and maintaining high-quality standards for water-quality data. Consistent quality requires specific actions that are carried out systematically in accordance with established policies and procedures. Errors and deficiencies can result when individuals fail to carry out their responsibilities. Clear and specific statements of responsibilities promote an understanding of each person's duties in the overall process of ensuring the quality of water-quality data.

2.1 Organizational Chart

The South Dakota District's organizational structure is similar to those of other Districts in the Discipline, but different program requirements from one District to another contribute to the uniqueness of these organizational structures. The following chart illustrates the organization of South Dakota District personnel (fig. 2.1).

Following are specific positions related to water-quality activities in the South Dakota District, and individuals serving in those capacities:

District Office - Rapid City
District Chief - Dan J. Fitzpatrick
Chief, Hydrologic Data Collection and Analysis Section - Ralph W. Teller
Lead Hydrologic Technician, Joel A. Petersen
Chief, Hydrologic Studies Section - Dan G. Driscoll
Supervisor, District Laboratory - Ralph W. Teller
Water-Quality Specialist - Steve K. Sando
NWIS Water-Quality Database Administrator - Kathy M. Neitzert
District Reports Specialist - Janet M. Carter
District Training Officer - Linda Evensen
District Sediment Specialist - Mike J. Burr
District System Administrator - Debra K. Matthews

Subdistrict Office - Huron
Subdistrict Chief - Roy C. Bartholomay
Lead Hydrologic Technician - Mike J. Burr
Supervisor, Subdistrict Laboratory - Steve K. Sando

Field Headquarters - Pierre
Lead Hydrologic Technician - Craig E. Solberg

South Dakota District Organization Chart

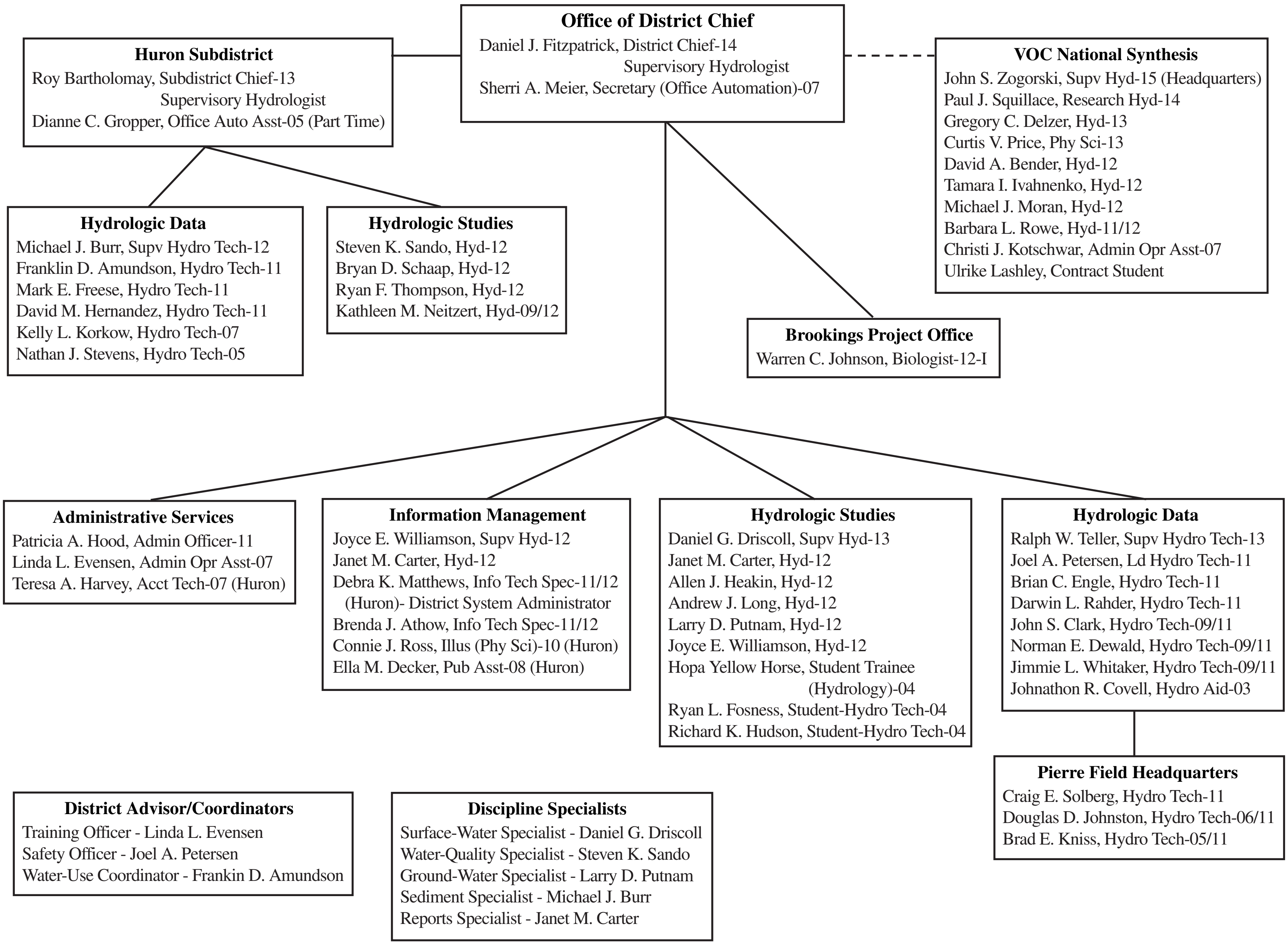

Figure 2.1. South Dakota District organizational chart, July 2004.

2.2 Responsibilities

The final responsibility for the preparation and implementation of and adherence to the QA policies that are described in this QA plan lies with the District Chief (Schroder and Shampine, 1992, p. 7).

Following is a list of responsibilities for selected District personnel who are involved in the collection, processing, storage, analysis, and publication of water-quality data.

The District Chief and designated management personnel are responsible for:

1. Managing and directing the District program, including designation of personnel responsible for managing all water-quality activities;
2. Ensuring that water-quality activities in the District meet the needs of the Federal government, the South Dakota District, cooperating State and local agencies, and the general public;
3. Ensuring that all aspects of this QA plan are understood and followed by District personnel. This is accomplished by direct involvement of the District Chief or through clearly stated delegation of this responsibility to other personnel in the District;
4. Providing final resolution, in consultation with the Water-Quality Specialist, of any conflicts or disputes related to water-quality activities within the District;
5. Keeping subordinates briefed on procedural and technical communications from regional and Headquarters offices;
6. Participating in technical reviews of all water-quality programs on a quarterly basis;
7. Ensuring that all publications and other technical communications released by District personnel are accurate and comply with USGS policy;

The District Water-Quality Specialist or designated representative is responsible for:

1. Ensuring that water-quality activities in the District meet the needs of the Federal government, the South Dakota District, cooperating State and local agencies, and the general public;
2. Preparing and implementing the District water-quality QA plan;
3. Ensuring that all aspects of this QA plan are understood and followed by District personnel. This is accomplished by the Water-Quality Specialist's direct involvement;
4. Developing and maintaining a centralized District QC profile that is a compilation and summarization of water-quality QC data collected in the District;
5. Reviewing, in a timely and thorough manner, water-quality data collected for studies or routine water-quality monitoring programs to ensure accuracy and consistency;
6. Keeping District personnel briefed on procedural and technical communications from regional and Headquarters offices;
7. Participating in technical reviews of all District water-quality programs during District project reviews;
8. Ensuring that all publications and other technical communications released by the District that relate to and include water-quality information are accurate and comply with USGS policy; and
9. Ensuring that the District QA plan is reviewed and revised at least once every 3 years to document current responsibilities, methodologies, and ongoing procedural improvements.

The project chief is responsible for:

1. Managing and directing the project's field and laboratory water-quality activities;
2. Ensuring that the project's field and laboratory water-quality activities meet the needs of the Federal government, the South Dakota District, cooperating State and local agencies, and the general public;

3. Ensuring that all aspects of this QA plan that pertain to the project's field and laboratory water-quality activities are understood and followed by project personnel;
4. Obtaining guidance, as appropriate, for project quality-assurance/quality-control (QA/QC) activities from the District Water-Quality Specialist;
5. Reviewing, in a timely and thorough manner, water-quality data collected for a given study to ensure accuracy and consistency; and
6. Ensuring that QA/QC activities are properly carried out by the project staff.

2.3 References Used for the Organization and Responsibilities Section

The following table lists reports and(or) memoranda referred to in this section. For a complete citation, refer to Section 13.0 of the report.

Table 2.3. Summary of references for organization and responsibilities related to quality assurance

Reference	Subject
Schroder and Shampine, 1992	Guidelines for preparing a quality-assurance plan.
Shampine and others, 1992	Integrating quality assurance into project workplans.

3.0 Program and Project Planning

The District Chief has primary responsibility for overall District program planning and is responsible for ensuring that District projects are supportive of District and national priorities. All water-quality projects require review and approval prior to the commencement of work. Quality-assurance requirements should be integrated into the project proposal. Whether or not a separate QA plan will be required for a water-quality project will depend on the complexity of the work, the needs of the District or cooperator, or other criteria as described in Shampine and others (1992).

3.1 Project Proposals

Project proposals are developed at the local level in response to requests by cooperating agencies, needs recognized by the WRD in working closely with other agencies, or national programs. District proposals conform to the format required by Central Region Memorandum 2001.01, "Policy--Update Procedures for Project Proposal Preparation and Submission Process - WRD, Central Region." In general, each proposal must (l) state the problem or need for the study, (2) precisely define objectives—what will be done to help solve the problem, (3) contain a statement of how the project benefits the national interests, and (4) define the approach—how work will be done to accomplish the objectives. Relevance and benefits refer to USGS goals as expressed in the USGS Strategic Plan (accessed June 24, 2003, at http://www.usgs.gov/stratplan/stratplan.pdf), or the USGS Federal-State Cooperative Program Priorities (published annually by WRD memorandum). The approach consists of a detailed outline of the data-collection activities to be carried out (if new data are needed), the QA plans, the QC information needed, and the analytical techniques to be used. Project report plans, cost estimates, time schedules, and personnel requirements also are addressed. Consultation with regional and divisional specialists is encouraged in the preparation of proposals and in the execution of projects.

Review of project proposals is given high priority. Project proposals are reviewed by the appropriate District personnel and, at the discretion of the District Chief, may be sent to other Districts for review. The Central Region provides final review and approval of all project proposals.

3.2 Project Workplan

Project workplans are developed from approved project proposals. The District requirements for the content, review, and revision of workplans are outlined below. The project chief prepares a detailed workplan that identifies all project work elements and the related technical methods and approaches that are necessary to satisfy project objectives. The workplan links project personnel, tasks, and functions with associated funds and indicates the projected dates for on-time completion of project elements and, ultimately, the project. Workplans for water-quality programs and projects, including programs and projects with water-quality components, should clearly state how the District's "Quality-Assurance Plan for Water-Quality Activities" will be implemented.

Descriptions of the methods and approaches to be used to complete the technical elements of the project are required and include, for example, the design of environmental sample collection to meet the study objectives. The plan lists the environmental sampling locations and frequency, a description of the sample types and their expected uses, and descriptions of laboratory tests.

Workplans also include a description of the design of QC sampling that is required to document bias and variability in the environmental data. The workplan lists QC sample types, the frequency of collection, and their intended uses. The types of QC samples that typically are collected include blanks and spikes to estimate bias and replicates to estimate variability (Mueller and others, 1997).

Workplans state anticipated methods for data analysis and presentation, including report plans. Accurate cost estimates are needed for personnel, materials, and services related to planned completion dates for properly budgeting the project. Assuring the availability of project personnel is often difficult and can impose serious constraints on completing project tasks; therefore, District management should be consulted to ensure adequate staff resources and to avoid the over-commitment of individuals to multiple projects. The project timeline lists major project elements and planned completion dates.

3.3 Project Review

Project reviews are conducted periodically by District management, technical advisors, and/or discipline specialists to ensure compliance with the project workplan or proposal. Project reviews are used to ensure that data collection, analysis, and reporting are being done in accordance with the workplan and with broader District policies and requirements. Quality-assurance activities with respect to project reviews are outlined in the next sections.

3.3.1 Review Schedules

The District has developed and implemented a review schedule for evaluating the technical development and progress of water-quality programs and projects. Typically, the reviews are conducted on an approximately quarterly basis. Regularly planned reviews ensure that water-quality programs or projects are conducted efficiently to produce quality products on time. Informal reviews are part of ongoing quality assurance, whereby problems and related issues are addressed as they arise.

3.3.2 Review Documentation

The District has developed a method for documenting program and project reviews. The following information should be included in program and project review documentation:

- Project name and number
- Cooperator
- Project Chief
- Report period
- Progress
- Significant findings
- Reports
- Problems
- Plans for next quarter

The District archives all review comments that address the presence or absence of project deficiencies, all actions or recommendations for fixing deficiencies, or documentation explaining why a fix cannot be made. The Hydrologic Studies Section Chief is responsible for maintaining records of all project reviews.

3.4 References Used in the Program and Project Planning Section

The following table lists reports and(or) memoranda referred to in this section. For a complete citation, refer to Section 13.0 of the report.

Table 3.4. Summary of references for program and project planning

Reference	Subject
Mueller and others, 1997	Example of QC sample design used by NAWQA for surface-water sampling.
Shampine and others, 1992	Integrating quality-assurance into project workplans.

4.0 Water-Quality Laboratories

Two of the most critical issues for a long-term, national water-quality program are data comparability and data consistency. Because of the inherent variability among laboratories, one of the best ways to provide comparability and consistency is to use a single laboratory as much as is practical.

4.1 Selection and Use of an Analytical Laboratory

The National Water Quality Laboratory (NWQL) was established as the laboratory to meet the needs of the WRD, and it is the required laboratory for use in all WRD national water-quality programs (WRD Memorandum 92.036[1]. However, there are conditions for selecting a laboratory other than the NWQL.

[1]USGS memoranda cited in this report are listed in section 13.1 USGS Memoranda.

4.1.1 Selection

Contract or cooperator laboratories can be used when the cooperative agreement designates a laboratory other than the NWQL or when analytical services are required that cannot be provided by the NWQL. Research laboratories can be used for developing analytical techniques or to provide data for research purposes, and these laboratories are generally exempt from approval requirements that other laboratories must meet (WRD Memorandum 92.035; OWQ Technical Memorandum 98.03). District laboratories generally can be used when analyses must be done within a few hours of sample collection and cannot be done conveniently in the field.

4.1.2 Requirements for Use

All laboratories that provide analytical services to the WRD for non-research purposes must meet the requirements of the WRD, as described in WRD Memorandum 92.035, before any analytical data can be stored in the WRD National Water Information System (NWIS) data base (discussed in Section 10) or published by the WRD. Laboratories affected by this policy include those that provide chemical, biological, radiochemical, stable isotope, or sediment analytical services. The District Water Quality Specialist is responsible for assuring that all laboratories providing analytical services to the District have met the requirements for approval. These laboratories must do the following:

1. Use approved and published analytical methods—Analytical methods must be approved and published by one of the following sources: USGS; U.S. Environmental Protection Agency (USEPA); American Public Health Association, American Water Works Association, and Water Environmental Federation (Standard Methods); or American Society for Testing and Materials (ASTM). The publication of the method must include documentation for the analytical techniques and chemical processes plus the expected data quality. If a specific analytical method not published by the sources listed above is requested for a specific project, it is the responsibility of the WRD office requesting the analysis to have the method approved based on requirements specified in WRD Memorandum 82.028 before the analytical data from this method are published and(or) stored in the USGS national data base.
2. Have standard operating procedures (SOP's) for analytical methods—All analytical methods must have documented SOP's that are approved in accordance with procedures contained in the laboratory QA plan.
3. Have an approved laboratory QA plan—The laboratory must have an approved QA plan that is supplied to WRD customers upon request. The laboratory QA plan should provide internal guidance and documentation that will ensure the laboratory is operating under a standardized, rigorous QA program and is producing analytical results of a known and documented quality. The laboratory QA plan should describe QA activities, QC procedures and requirements, performance acceptance criteria, and required corrective actions that will be taken if the criteria are not met.
4. Have a documented QC program that provides the data necessary to continuously track the bias and variability of analytical data. All QC information, such as QC charts, analysis of laboratory QC samples, calibration records, and analyst bench logs should be maintained for at least 3 years and be available to WRD customers.
5. Demonstrate the ability to provide the analytical services required—Laboratories can demonstrate the ability to provide the required analytical services by participation in existing USGS or non-USGS certification/evaluation/round-robin programs or by documentation of similar projects (OWQ Technical Memorandum 98.03). The USGS Standard Reference Sample (SRS) round-robin program is required for analytes included in the SRS (http://btdqs.usgs.gov/srs/) samples.

4.2 Laboratories Used by the District

The laboratories used for analytical services by District projects are shown in table 4.2. The analyses provided, the dates used, and the person who has been the primary contact at the laboratory also are provided in the table.

Table 4.2. Laboratories used for District projects

Project	Analytical laboratory	Analyses provided (by general category)	Laboratory contact	Dates used
Routine District water-quality programs and projects	USGS WRD National Water Quality Laboratory	Standard water-quality laboratory-analyzed constituents	Merle Shockey	current
Projects requiring analysis of mercury constituents in water and/or bottom sediment	USGS Wisconsin District Mercury Laboratory	Mercury constituents Organic carbon Acid-volatile sulfide	Dave Krabbenhoft	current
Projects requiring bottom-sediment trace-element analyses	USGS Geologic Division Branch of Geochemistry Laboratory	Trace-elements in bottom sediments	Paul Lamothe	current
Projects requiring suspended-sediment concentration and percent fines analyses	USGS Iowa Sediment Laboratory	Suspended-sediment concentration and percent fines	Von Miller	current
Projects requiring analyses of antibiotic compounds	USGS Ocala Water-Quality and Research Laboratory	Antibiotic compounds	Mike Meyer	current

4.3 Documentation for Laboratories Used by the District

4.3.1 National Water-Quality Laboratory

1. Methods used—The NWQL uses approved methods for determination of organic, inorganic, and radioactive substances in water, sediments, and biological tissues. The methods used include methods approved by the USGS, USEPA, the American Public Health Association, the American Water Works Association, the Water Environmental Federation, and the ASTM. A list of some analytical methods currently used at the NWQL can be found on the World Wide Web at http://wwwnwql.cr.usgs.gov/Public/ref_list.html.

Other analytical methods from the USEPA that are currently used at the NWQL can be found on the World Wide Web at http://www.epa.gov./epahome/publications.htm. Analytical methods from the ASTM that are currently used at the NWQL can be found on the World Wide Web at http://www.astm.org.

2. QA plan—The NWQL quality-assurance plan is contained in Pritt and Raese (1995). A copy of this report can be obtained by sending an Email request to nwqlqc@usgs.gov.
3. QC program—Quality control at the NWQL is monitored by three programs: (1) the internal blind sample program, (2) the external blind sample program, and (3) bench level QC samples. Information about the internal blind sample program and bench level QC samples can be obtained by sending an Email request to nwqlqc@usgs.gov. Information about the external blind sample program can be found at the following World Wide Web location: http://btdqs.usgs.gov/bsp/Fact.Sheet.html

4. Performance evaluation studies and certification programs—The NWQL participates in performance evaluation studies and laboratory certification programs. A list of the current programs and a description of each can be found by sending an Email request to nwqlqc@usgs.gov.
5. Laboratory reviews—External agencies and customer organizations audit the NWQL to assess analytical methods and QA/QC programs. A table of audits that shows the year reviewed, reviewing agency, and purpose of the review can be obtained by sending an Email request to nwqlqc@usgs.gov.
6. Miscellaneous services—Information about and access to other services offered by the NWQL can be found on the World Wide Web home page at http://wwwnwql.cr.usgs.gov/USGS/profile.html. The services offered include but are not limited to the following:

   Biological unit
   Chain-of-custody procedures
   Contract services
   External performance evaluations
   Laboratory services catalogue
   Methods Research and Development Program
   Organic spike kits
   Publications
   Quality assurance of selected field supplies
   SPiN (schedules, parameters, and network record)
   Technical memoranda

4.3.2 USGS Wisconsin District Mercury Laboratory

1. Methods used:

Methods used by the USGS Wisconsin District Mercury Laboratory are presented in table 4.3.2.

Table 4.3.2. Description of methods used by USGS Wisconsin District Mercury Laboratory

Constituent	Analytical method	Method number	Method reporting level
Unfiltered total mercury	Atomic fluorescence spectroscopy	EPA 1631	0.04 ng/L
Unfiltered methylmercury	Atomic fluorescence spectroscopy	EPA 1630, not yet approved; draft	0.05 ng/L
Filtered total mercury	Atomic fluorescence spectroscopy	EPA 1631	0.04 ng/L
Filtered methylmercury	Atomic fluorescence spectroscopy	EPA 1630, not yet approved; draft	0.05 ng/L
Filtered organic carbon	U-V promoted persulfate oxidation and infrared spectometry		0.1 mg/L
Unfiltered organic carbon	wet oxidation		0.1 mg/L
Total mercury (bottom sediment)	Atomic fluorescence spectroscopy	EPA 1631	0.04 ng/L
Methylmercury (bottom sediment	Atomic fluorescence spectroscopy	EPA 1630, not yet approved; draft	0.05 ng/L

2. Laboratory QA plan: Olson, 1997.
3. Certification/evaluation/round-robin programs: Described in Olson, 1997.
4. Dates and participants of laboratory reviews: information available from Mark Olson, USGS Wisconsin District Mercury Laboratory (mlolson; 608-821-3878)

4.3.3 USGS Geologic Division Branch of Geochemistry Laboratory:

1. Methods used:

Methods used by the USGS Geologic Division Branch of Geochemistry Laboratory are presented in table 4.3.3.

Table 4.3.3. Description of methods used by USGS Geologic Division Branch of Geochemistry Laboratory

Constituent	Analytical method	Method reporting level
Arsenic	Hydride-generated graphite-furnace atomic absorption spectrophotometry	1 mg/g
Selenium	Hydride-generated graphite-furnace atomic absorption spectrophotometry	0.1 mg/g
40-element ICP/AE scan	Inductively-coupled plasma/atomic emission spectroscopy	
Calcium		5 mg/g
Magnesium		1 mg/g
Sodium		1 mg/g
Potassium		1 mg/g
Phosphorus		0.1 mg/g
Aluminum		10 µg/g
Arsenic		50 µg/g
Barium		10 µg/g
Beryllium		0.5 µg/g
Bismuth		10 µg/g
Cadmium		2 µg/g
Cerium		5 µg/g
Chromium		2 µg/g
Cobalt		1 µg/g
Copper		2 µg/g
Europium		2 µg/g
Gallium		2 µg/g
Gold		8 µg/g
Homium		4 µg/g
Iron		10 µg/g
Lanthanum		5 µg/g
Lead		2 µg/g
Lithium		5 µg/g
Manganese		10 µg/g
Molybdenum		2 µg/g
Neodymium		5 µg/g
Nickel		1 µg/g
Niobium		5 µg/g
Scandium		1 µg/g
Silver		2 µg/g

Table 4.3.3. Description of methods used by USGS Geologic Division Branch of Geochemistry Laboratory (Cont.)

Constituent	Analytical method	Method reporting level
Strontium		10 µg/g
Tantalum		40 µg/g
Thorium		5 µg/g
Tin		5 µg/g
Titanium		10 µg/g
Uranium		100 µg/g
Vanadium		5 µg/g
Ytterbium		1 µg/g
Yttrium		5 µg/g
Zinc		5 µg/g

2. Laboratory QA plan: Arbogast, 1990.
3. Certification/evaluation/round-robin programs: Described in Arbogast, 1990.
4. Dates and participants of laboratory reviews: information available from Paul Lamothe, USGS Geologic Division Branch of Geochemistry Laboratory (plamothe; 303-236-1923)

4.3.4 USGS Iowa Sediment Laboratory

1. Methods used:

Methods used by the USGS Iowa Sediment Laboratory are presented in table 4.3.4.

Table 4.3.4. Description of methods used by USGS Iowa Sediment Laboratory

Constituent	Analytical method
Suspended sediment concentration	Filtration/evaporation, gravimetric
Percent of suspended-sediment sample that is less than 0.062 mm in diameter	Filtration/evaporation, gravimetric

2. Laboratory QA plan: Matthes and others, 1992.
3. Certification/evaluation/round-robin programs: Described in Matthes and others, 1992.
4. Dates and participants of laboratory reviews: information available from Von Miller, USGS Iowa Sediment Laboratory (vemiller; 319-358-3631)

4.3.5 USGS Ocala Water-Quality and Research Laboratory

1. Methods used:

Methods used by the USGS Ocala Water-Quality and Research Laboratory for analysis of antibiotic compounds in water are unapproved research-level techniques. Specific information concerning these methods can be obtained from Mike Meyer (mmeyer; 352-237-5514, x202).

2. Laboratory QA plan: http://owqrl.er.usgs.gov/owqrlcomp.shtml (accessed June 24, 2003).
3. Certification/evaluation/round-robin programs: Contact Mike Meyer (mmeyer; 352-237-5514, x202).
4. Dates and participants of laboratory reviews: Contact Mike Meyer (mmeyer; 352-237-5514, x202).

4.4 References Used for the Water-Quality Laboratories Section

The following table lists reports and(or) memoranda referred to in this section. For a complete citation, refer to Section 13.0 of this report.

Table 4.4. Summary of references for selecting and using water-quality laboratories

Reference	Subject
Arbogast, 1990	Quality assurance/quality control manual, GD Branch of Geochemistry Laboratory
Olson, 1997	Quality assurance/quality control manual, Wisconsin District Mercury Laboratory
Matthes and others, 1992	Quality assurance/quality control manual, Iowa Sediment Laboratory
OWQ Technical Memorandum 98.03 (USGS)	Policy for the evaluation and approval of production analytical laboratories.
Pritt and Raese, 1995	Quality assurance/quality control manual—NWQL.
WRD Memorandum 82.028 (USGS)	Acceptability and use of water-quality analytical methods.
WRD Memorandum 92.035 (USGS)	Policy for approval of all laboratories providing analytical services to the WRD for non-research purposes.
WRD Memorandum 92.036 (USGS)	Policy of the WRD on the use of laboratories by national water-quality programs.
http://btdqs.usgs.gov/srs	USGS Standard Reference Sample Program

5.0 Field Service Units and Laboratories, Mobile Labs, and Field Vehicles

The District maintains laboratory facilities, and field vehicles for use in preparing equipment for field activities, processing samples, performing sample analysis, and preparing samples for shipment to analytical laboratories. This section documents the District's criteria for maintaining and operating these facilities.

5.1 Field Service Units and Laboratories

The Rapid City District Office Service Unit consists of a designated laboratory area, a laboratory supervisor (Ralph Teller), one water-quality trailer, three water-quality field vehicles, and several hydrologists and hydrologic technicians who are involved in collection of water-quality data. The Huron Subdistrict Office Laboratory consists of a designated laboratory area, a laboratory supervisor (Steve Sando), two water-quality field vehicles, and several hydrologists and hydrologic technicians who are involved in collection of water-quality data. The Pierre Field Office Service Unit consists of a designated water-quality staging area, a water-quality field vehicle, and three hydrologic technicians who are involved in collection of water-quality data. These units assist and support water-quality activities by providing information on approved data-collection methods, field instrumentation maintenance and calibration, preparations for sample collection, and QA for these activities. The units maintain a supply of instruments, equipment, and expendable supplies needed by field personnel for water-quality sample collection and analysis.

5.1.1 Facilities

The District maintains two laboratories located in Rapid City and Huron. Both laboratories contain laboratory benches, glassware, sinks, chemical storage cabinets, and other equipment and instruments listed in table 5.1.1. Brian Engle has responsibility for maintenance of the Rapid City District Office Laboratory and QA of the equipment and instruments. Steve Sando has responsibility for maintenance of the Huron Subdistrict Office Laboratory and QA of the equipment and instruments. Both facilities are maintained in accordance with standards set forth in the South Dakota District chemical-hygiene plan (Teller, 2002; Branch of Operations Technical Memorandum 91.01).

Table 5.1.1. Equipment and instruments provided by the Rapid City District Office Laboratory and the Huron Subdistrict Office Laboratory, and quality assurance

[OWQ, Office of Water Quality; NA, not applicable]

Laboratory equipment	Quality assurance
Laboratory balance	Calibration checked periodically
Refrigerator at 4°C	Temperature monitored periodically.
Fume hood	Calibrated periodically.
Supply of deionized water	Maintained per OWQ Tech. Memo 92.01.
Ventilated acid cabinets	NA
Wash sink with drying rack	NA
Vacuum pump	NA
Drying oven	Calibration monitored periodically depending upon usage.
Autoclave	Maintained per manufacturer's instructions.
Incubators	Calibration monitored periodically depending upon usage.
Freezer	Temperature monitored periodically.
Lab pH and specific conductance meter	Calibrated each use

5.1.2 Procedures

The Rapid City District Office Laboratory and the Huron Subdistrict Office Laboratory are managed by the laboratory supervisors (Ralph Teller, and Steve Sando, respectively). These persons, or their designees, are responsible for maintaining the laboratory space, supplies, and equipment listed above. The two laboratories maintain QA records of laboratory equipment and supplies, such as calibration standards, chemical reagents, sample preservatives, and sample bottles that are provided to field personnel. Project chiefs and hydrologic technicians are responsible for repair and maintenance of project water-quality equipment and instruments. The lab supervisors and district safety officers oversee the District waste-disposal practices to ensure that procedures are in compliance with State and Federal regulations. The unit operations comply with the South Dakota District chemical-hygiene plan. The operation of the unit is reviewed every 3 years by the OWQ.

5.1.3 Equipment and Supplies

It is the responsibility of project chiefs and hydrologic technicians to order, store, and quality assure the following field equipment and supplies as needed by field personnel.

Table 5.1.3. Summary of information on supplies, equipment, and instruments in the South Dakota District

[RP, responsible party; NIST, National Institute of Standards and Technology]

Supplies, equipment, and instruments	Source and guidelines for QA	Responsible party
Sample bottles	Purchase from Water-Quality Service Unit (OWSU) in Ocala, Fla.	Project chiefs and hydrologic technicians; lab supervisor
Coolers/shipping containers	Purchase from various vendors per the guidelines of OWQ Tech. Memo 92.06.]	Project chiefs and hydrologic technicians; lab supervisor
Sample preservatives	Purchase from Water-Quality Service Unit (OWSU) in Ocala, Fla.	Project chiefs and hydrologic technicians; lab supervisor
pH calibration standards	Purchase from Water-Quality Service Unit (OWSU) in Ocala, Fla.	Project chiefs and hydrologic technicians; lab supervisor
Specific conductance calibration standards	Purchase from Water-Quality Service Unit (OWSU) in Ocala, Fla.	Project chiefs and hydrologic technicians; lab supervisor
Blank water for QA	Purchase from Water-Quality Service Unit (OWSU) in Ocala, Fla., or National Water Quality Laboratory (NWQL) in Denver, CO; NWQL Memo 92.01.]	Project chiefs and hydrologic technicians; lab supervisor
Deionized water	Produced at District facilities; Conductivity monitored weekly; QA laboratory analyses performed annually; OWQ Tech. Memo 92.01.]	Laboratory supervisors
Isokinetic water-quality samplers	Purchase Federal Interagency Sedimentation Project approved samplers from USGS ONE-STOP-SHOPPING on the Internet.	Project chiefs and hydrologic technicians; lab supervisor
Splitting devices	Purchase from Water-Quality Service Unit (OWSU) in Ocala, Fla.	Project chiefs and hydrologic technicians; lab supervisor
Specific conductance meters	Purchase from various vendors per the recommendations of the USGS Hydrologic Instrumentation Facility	Project chiefs and hydrologic technicians; lab supervisor
pH meters	Purchase from various vendors per the recommendations of the USGS Hydrologic Instrumentation Facility	Project chiefs and hydrologic technicians; lab supervisor
Multiparameter water-quality meters	Purchase from various vendors per the recommendations of the USGS Hydrologic Instrumentation Facility	Project chiefs and hydrologic technicians; lab supervisor

5.2 Water-Quality Field Vehicles

Field vehicles refer to all vehicles that are designed, designated, and outfitted for use during water-quality sample-collection and processing activities at or near sample-collection sites. The District maintains vehicles designated for water-quality sample collection and processing. If a non-designated vehicle must be used for water-quality work, portable processing and preservation chambers are used for sample processing. Refer to the National Field Manual for guidelines on procedures for collecting and processing water-quality data (Wilde and others, 1998, TWRI book 9, chaps. A1-A9).

A field vehicle is designated as a water-quality field vehicle when it meets criteria to maintain a non-contaminating environment for the constituents being sampled. The work area must be maintained to eliminate sources of sample contamination. Specifications for vehicles used when sampling for water-quality constituents are discussed by Horowitz and others (1994) and in the National Field Manual (Wilde and others, 1998a, TWRI book 9, chap. A2.3) and include the following:

- Materials used for cabinets, storage, and work surfaces must be easy to maintain, made of or covered with non-contaminating materials, and such that they can be cleaned with water or solvents as appropriate. Cargo must be restricted to equipment and supplies related to water-quality sample collection unless stored in a separate compartment. No potentially contaminating equipment or supplies, such as sounding weights, solvents, fuel, etc., may be transported in the interior compartment of the vehicle.
- A dust barrier exists between the cab and work area of the vehicle.

Project chiefs and/or hydrologic technicians designated for each vehicle are responsible for vehicle maintenance, for maintaining the suitability of the vehicle for water-quality sample collection, and for keeping the vehicle supplied.

5.3 References Used for the Field Service Units and Laboratories, Mobile Labs, and Field Vehicles Section

The following table lists reports and(or) memoranda referred to in this section. For a complete citation, refer to Section 13.0 of the report.

Table 5.3. Summary of references for Field Service Units and laboratories, mobile labs, and field vehicles

Reference	Subject
Branch of Operations Technical (OP) Memorandum 91.01 (USGS)	Safety—Chemical-Hygiene Plan.
Horowitz and others, 1994	Protocol for collecting and processing samples for inorganic analysis.
NWQL Memorandum 92.01 (USGS)	Availability of equipment blank water for inorganics and organics.
OWQ Technical Memorandum 92.01 (USGS)	Distilled/deionized water for District operations.
OWQ Technical Memorandum 92.06 (USGS)	Recommended guidelines for shipping samples to the NWQL.
Teller, 2002	South Dakota District Chemical Hygiene Plan
U.S. Geological Survey, 1997-present	National Field Manual for the Collection of Water-Quality Data, chaps. A1-A9
Wilde and others, 1998a (National Field Manual, TWRI book 9, chap. A2.3)	Guidelines for field vehicles.

6.0 Water-Quality Instruments

The South Dakota District complies with the WRD policy of providing personnel with high-quality field instruments and equipment that are safe, precise, accurate, durable, reliable, and capable of performing required tasks (WRD Memorandum 95.35). Accordingly, appropriate instruments for use in water-quality projects in the District should be selected based upon the specifications described in the USGS "National Field Manual for the Collection of Water-Quality Data" (Wilde and others, 1998, TWRI book 9, chaps. A1-A9) and the requirements of the project. The Hydrologic Instrumentation Facility (HIF), which provides analyses of precision and bias for water-quality instruments, also should be consulted for recommendations when appropriate. Consultation with the district water-quality specialist should be done if project personnel need assistance with the selection or use of equipment.

All instruments used by District personnel for water-quality measurements are to be properly operated, maintained, and calibrated. For correct operation of any field or laboratory equipment, the manufacturer's operating guidelines should be carefully followed. Most instruments will be calibrated in the field prior to making the sample measurements, as described below. Information regarding sources of calibration standards is provided in Section 5.1 of this QA plan.

Thorough documentation of all calibration activities associated with water-quality data collection is a critical element of the District QA program. Calibration and maintenance records of field equipment, including the manufacturer, make, model, and serial or property number are to be kept. A permanent calibration log book containing this information as well as records of calibration performance is maintained for each meter, and is stored with the meter in its case. For laboratory equipment, the calibration log books are stored on the lab counter next to the meter or in a nearby drawer. Information that is required to be included with the calibration and maintenance records includes the date, initials and last name of the individual performing the activity, results of calibration or equipment check, and any actions taken. Calibration and maintenance records are periodically checked for completeness and accuracy by the water-quality specialist, typically prior to publication of data.

Table 6.0. provides summary information regarding the calibration methods, acceptance criteria, calibration frequency and location, responsible persons, and references for specific instructions for the calibration and use of water-quality instruments to measure selected parameters in the South Dakota District.

Table 6.0. Summary of calibration information for water-quality instruments used to measure selected parameters in the South Dakota District

[NIST, National Institute of Standards and Technology; RP, responsible party; TWRI, Techniques for Water-Resources Investigations]

Parameter	Calibration method used	Acceptance criteria and response if not acceptable	Calibration frequency and location	Responsible person	Reference for calibration and use
Temperature	NIST-certified thermometer	For check temperatures greater than or equal to 5.0°C, field thermometer readings must be within 5 percent of NIST; for check temperatures less than 5.0°C, field thermometer readings must be within 0.5°C of NIST; non-compliance response: replace thermometer.	Every 6 months in laboratory.	Lab supervisors, or designee	Wilde and Radtke, 1998 (TWRI book 9, chap. A6.1); see manufacturer's instructions.
Specific conductance	At least two standards, bracketing expected values	Meter should be calibrated to one standard, and should be within 5 percent of the other bracketing standard; non-compliance response: clean or replace probe.	Daily in field, prior to taking measurements; if multiple sites are visited each day, the meter should be calibrated prior to measurement at the first site, and the calibration should be checked periodically during the day.	Field personnel	Wilde and Radtke, 1998 (TWRI book 9, chap. A6.3); see manufacturer's instructions.
pH	Two-point calibration, bracketing expected values	Calculated slope must be within 5 percent of theoretical slope; non-compliance response: clean or replace probe.	Daily in field, prior to taking measurements; if multiple sites are visited each day, the meter should be calibrated prior to measurement at the first site, and the calibration should be checked periodically during the day.	Field personnel	Wilde and Radtke, 1998 (TWRI book 9, chap. A6.4); see manufacturer's instructions.
Dissolved oxygen	Saturated air-calibration in chamber submersed in environmental water; or see manufacturer's instructions	Calibrate to appropriate saturation concentration; check 0 mg/L dissolved oxygen solution; meter should read less than or equal to 0.1 mg/L; non-compliance response: change membrane or replace probe.	Daily in field or laboratory, prior to taking measurements; if multiple sites are visited each day, the meter should be calibrated prior to measurement at the first site, and the calibration should be checked periodically during the day.	Field personnel	Wilde and Radtke, 1998 (TWRI book 9, chap. A6.2); see manufacturer's instructions.
Barometric pressure	Mercury barometer	Within 5 mm Hg; non-compliance response: replace barometer.	Quarterly	District water-quality specialist, or designee	See manufacturer's instructions.

6.1 References Used for the Water-Quality Instruments Section

The following table lists reports and(or) memoranda referred to in this section. For a complete citation, refer to Section 13.0 of the report.

Table 6.1. Summary of references for water-quality instruments

Reference	Subject
Wilde and others, 1998 (TWRI book 9, chap. A1-A9)	USGS Water-quality field methods.
WRD Memorandum 95.35 (USGS)	Instrumentation plan for the WRD and the hydrologic field instrumentation and equipment policy and guidelines.

7.0 Site Selection and Documentation

Deciding where to sample is an important initial step toward achieving project objectives and meeting District QA/QC requirements. Once a site is selected, thorough documentation, usually in the form of a station description, is required.

7.1 Site Selection

Site selection for sampling is important to the validity of water-quality data. Selection of a suitable site can be made only after considering a number of factors, including the need for information in a particular location, the suitability of a site for sampling, and its accessibility and safety. Specific guidelines for site selection are contained in Wilde and others (1998, chap. A1). The project chief is responsible for the selection of sampling sites, after consultation with the Water-Quality Specialist and the Surface-Water or Ground-Water Specialist, as appropriate.

7.1.1 Surface Water

If possible, water-quality stations are located at or near streamflow-gaging stations. If this is not possible, the water-quality station should be located where the stream discharge can be measured and water samples can be collected at all stages of flow to be monitored. If the water-quality station is located too close downstream from either the confluence of two or more streams or a point source of pollution, the collection of a representative sample may be difficult because of incomplete mixing. Under such conditions, the criteria for the minimum number of vertical transects sampled may need to be increased, and lateral mixing should be documented with cross-sectional surveys at various stages.

7.1.2 Ground Water

The selection of wells for ground-water sampling is dependent on many variables, including location, depth and accessibility of the well, type of well completion, availability of geologic and water-use information, and sampling purpose(s). If suitable existing wells cannot be found, new wells will need to be installed.

7.2 Site Documentation

The project chief constructs a site file containing descriptive information on location, conditions, purpose, and ancillary information for all new water-quality data-collection sites (Schroder and Shampine, 1995). Much of this information also is stored electronically in computerized site files maintained by the Data Management Section. The District Water-Quality Specialist and the Studies Section Chief are responsible for assuring that the site file is maintained for each data-collection site. Archiving of this information is discussed in Section 10.4.

7.2.1 Surface Water

A station description is prepared for each water-quality station that is sampled on a regular or periodic basis. Sites established at existing surface-water gaging stations commonly will need only supplemental information to complete the description. Other surface-water sites, such as lakes, may require varying amounts of supplemental information to complete the station descriptions. Normally, the minimum electronically stored information required for a surface-water station record is dictated by the National Water Information System (NWIS) software used by the District. The minimum information required for establishing electronic files in NWIS for surface water is listed in table 1-1 in Wilde and others (1998, chap. A1). For continuous water-quality monitoring sites, station-description requirements are presented by Wagner and others (2000).

7.2.2 Ground Water

A well file (analogous to a surface-water station description) is prepared for each well that is sampled on a regular or periodic basis. Normally, the minimum electronically stored information required for a ground-water-quality site is dictated by the NWIS software used by the District. The minimum information required for establishing electronic files in NWIS is listed in table 1-4 in Wilde and others (1998, chap. A1). Paper documents, such as agreements for use of the well between the well owner and the USGS, also should be stored in the well file.

In order to standardize and facilitate the processing of water-quality data in South Dakota, and to assure that water-quality data are entered into the proper database in a timely manner, the following procedures will be used:

- Site-header records will be established for each new site at which water-quality samples will be collected or have been collected. Header record must exist in the NWIS site file before the return of analytical data from the NWQL. New site-header data must be checked by Project or Field Office personnel. These verified records, as well as the resulting water-quality data, will be stored in the NWIS water-quality database for South Dakota. The responsibility for entry of the site-header records and maintenance of the site-header records file currently rests with project Chiefs working in conjunction with Kathy Neitzert, the NWIS data-base administrator. The pertinent information that comprises the header must be entered into the system prior to but no later than 30 days after sample collection.
- For each sample that will be sent to the NWQL for analysis, an Analytical Services Request (ASR) form will be completed by the Project or Field Office Chief with a copy (or facsimile) retained in a project file as part of the sample tracking system. For USGS employees, ASR forms can be downloaded from the NWQL (http://wwwnwql.cr.usgs.gov/USGS/USGS_srv.html) and filled out.

- The project chief is responsible for tracking all pending samples submitted for analysis. Sample status at the NWQL can be tracked from login to completion of analysis (see section 9.0).

For continuous water-quality monitoring sites, station-description requirements are presented by Wagner and others (2000).

7.3 References Used for the Site-Selection and Documentation Section

The following table lists reports and(or) memoranda referred to in this section. For a complete citation, refer to Section 13.0 of the report.

Table 7.3. Summary of references for site selection and documentation for water-quality programs

Reference	Subject
Schroder and Shampine, 1995	Guidelines for documenting new water-quality data-collection sites.
Wilde and others, 1998 (TWRI book 9, chap. A1)	Establishing electronic NWIS files for surface- and ground-water data.

8.0 Sample Collection and Processing

Water-quality data collected by the USGS are used by agencies throughout the Federal, State, and local levels to guide their decisions concerning the appropriate and efficient management of water resources for the Nation. Water-quality data are collected as part of such Federal programs as the National Stream-Quality Accounting Network (NASQAN) and the National Water-Quality Assessment (NAWQA) Program, as well as cooperative projects jointly funded by local or State agencies, and are a vital component of water-resources activities performed by the USGS and the South Dakota District.

The primary objective in collecting a water-quality sample is to obtain environmental data that are representative of the system that is being studied. Sampling and processing techniques for specific constituents may vary according to the general class of compound, such as inorganic or organic chemicals. If incorrect sampling procedures produce a nonrepresentative sample, or if the sample is contaminated or degraded before analysis can be completed, the value of the sample is limited and the data are questionable. Therefore, compliance with documented and technically approved sample-collection and processing protocols is critical to ensuring the quality of water-quality data.

It is the policy of this District that all personnel involved in collecting and processing water-quality data will be adequately informed and trained regarding water-quality data-collection and processing procedures established by the WRD. Because of rapid changes in technology, however, new and improved methods for sample collection and processing are continually being developed. All District personnel who are involved in water-quality sampling must be aware of changing requirements and recommendations. The District Water-Quality Specialist is responsible for providing current information to field personnel on the correct protocols to follow in collecting and processing water-quality samples. The District Studies Section Chief is responsible for ensuring that the correct protocols are carried out.

The Project or Field Office Chief also is responsible for seeing that field personnel take the following steps to ensure the quality and integrity of the District’s water-quality data:

Instantaneous Water-Quality Data

- Samples must be collected and processed according to prescribed WRD protocols, as described and referenced below.

- All samples must be shipped to the laboratory from the field in an expedient manner, within the required holding times for each analysis.
- All samples should be logged into NWIS (usually within 7 days of sample collection) prior to the completion of analysis and transmittal of the results back to the District.
- All analytical data must be reviewed in a timely manner and within the required holding times for each analysis (to allow time for re-analysis), and fully documented in the station analysis file.

Continuous Water-Quality Data

- The site should be vertically and horizontally well-mixed in the cross section.
- Location of the sensors must be fully documented.
- All pertinent information regarding the site, cross-sectional variability, equipment maintenance, and data shifts must be fully documented and included in the station analysis file.
- Monitors must be inspected and calibrated as frequently as required to obtain as complete a record as possible.
- Sites should be operated as described by Wagner and others (2000).

8.1 Constituents in Water

Most studies that are designed to evaluate the water quality of an aquatic system are based upon analyses of physical and chemical parameters associated with the water. Physical parameters generally are measured in the field, whereas most chemical parameters require laboratory analysis. This section of the QA plan includes an overview of relevant District and WRD policies, as well as references for specific procedures pertaining to the measurement of field parameters and the collection and processing of samples for water-quality analysis. Information in this section is drawn primarily from the National Field Manual—a TWRI that describes in greater detail the recommended and required policies and procedures for collecting and processing water-quality samples in the WRD. Additional sources of information include manuals published by the NAWQA Program (Shelton, 1994; Koterba and others, 1995). The project proposal and workplan also should be consulted for specific guidelines for field personnel regarding details of sample collection and processing.

8.1.1 Field Measurements

Routine field measurements include temperature, dissolved-oxygen (DO) concentration, specific conductance (conductivity), pH, and alkalinity. Other types of measurements that also may be necessary for specific projects include acid neutralizing capacity, reduction-oxidation potential (E_h), and turbidity. District procedures for collecting field measurements in surface- and ground-water systems are provided in chapter A6 of the National Field Manual (Wilde and Radtke, 1998). Field measurements should represent, as closely as possible, the natural conditions of the system at the time of sampling. To ensure quality of the measurements, calibration within the range of field conditions at each site is required for most instruments.

Field-measurement data must be recorded while in the field, including methods, equipment, and calibration information. Field-measurement data can be stored either electronically or on paper field forms, which may be national forms (fig. 8.1.1), or customized for a particular project. Copies of standard USGS field forms for surface-water water-quality samples can be obtained on the internet (http://water.usgs.gov/usgs/owq/SWform-04-2003.pdf). The District Water-Quality Specialist or designee is responsible for reviewing field records for completeness. To avoid the loss of data because of possible instrument malfunction, hydrologic technicians or hydrologists should ensure that backup sensors or instruments are readily available and in good working condition.

To document the quality of field measurements, all District personnel involved in the collection of water-quality data are required to participate in the National Field Quality Assurance (NFQA) Program (Stanley and others, 1992). Results of the NFQA Program are reviewed by the Regional Hydrologist and the District Water-Quality Specialist. Staff receiving an unsatisfactory rating will identify the cause of the poor measurement and participate in a follow-up round. A summary of the results for the South Dakota District staff for 2000-02 are given in the supplementary information section at the end of this document.

8.1.2 Cleaning of Sampling and Processing Equipment

Procedures for cleaning equipment used for water-quality sampling and processing are described in chapter A3 of the National Field Manual (Wilde and others, 1998). All new equipment acquired for water-quality sampling, as well as equipment that has been in long-term storage, must be cleaned in the office before being used in the field. Similarly, equipment must be cleaned as soon as possible after sample collection and before being used again to avoid cross-contamination between sampling sites. The field rinsing of equipment only with site water just prior to sample collection is not a substitute for proper cleaning.

Equipment blanks are a particular type of blank sample that is used to verify that cleaning procedures used by the field personnel are adequate for removing contamination. These blanks ensure that individual pieces of sampling equipment are not sources of detectable concentrations of constituents to be analyzed in environmental samples. An annual equipment blank, collected in the office laboratory, is required for each set of equipment used to collect water-quality samples (Horowitz and others, 1994; Wilde and others, 1998, chap. A3). Annual equipment blanks that indicate detectable levels of constituents require submission of blanks for individual components of the equipment to isolate the source of contamination. When the source of contamination has been determined, the necessary maintenance must be performed to eliminate contamination, or the equipment must be replaced. The District Water-Quality Specialist monitors the results of annual equipment blanks and ensures compliance with District standards. A compilation of results for blank samples collected by the South Dakota District for 2000-02 are given in the supplementary information section at the end of this document.

8.1.3 Surface-Water Sampling

Collecting surface-water samples that accurately represent the physical and chemical characteristics of the aquatic system requires the appropriate use of sampling equipment and methods in order to describe environmental variability and to prevent contamination or bias in the sampling process. All District personnel who are involved in water-quality studies must be well informed of the various factors that must be considered to ensure the collection of representative samples. The choice of sampling equipment and method of sample collection are based on established protocols and guidelines, depending upon the characteristics of the target constituents, study objectives, hydrologic conditions, and sampling logistics.

U.S. GEOLOGICAL SURVEY, WRD, SURFACE-WATER QUALITY FIELD NOTES BQS-2298S

Station ______ Sta.No. ______ Date ______

Sampled by ______ Agency ______ Mean Time ______

Proj. Name/No. ______ SMS Cntrl. No. ______

Record No. ______ Purpose of site visit (50280) ______ Sample purpose (71999) ______ Date samples shipped to lab ______

QC Sample Rec. No. ______ NWQL Lab ID: ______ ______ ______

FIELD MEASUREMENTS

Q. Inst. (00061) ______cfs — est. rating meas.

Gage Ht (00065) ______

Temp. water (00010) ______ °C

Temp. air (00020) ______ °C

pH (00400) ______ units

Sp. cond. (00095) ______ ÊS/cm 25 °C

Dis. oxy. (00300) ______ mg/L

DO sat. (00301) ______ %

Bar. press.(00025) ______ mm Hg

Eh (00090) ______ m volts

Alkalinity ( ) ______ mg/L

( ) ______ mg/L

Bicarbonate ( ) ______ mg/L

ANC (00410) ______ mg/L

Carbonate ( ) ______ mg/L

Hydroxide ( ) ______ mg/L

FC (31625) ______ col./100 mL; Rmk ______

E. Coli (31633) ______ col./100 mL; Rmk ______

______ col./100 mL; Rmk ______

______ col./100 mL; Rmk ______

SAMPLING CONDITIONS

Location: Wading cable ice boat bridge upstr. downstr. side bridge ft mile, above below gage and ______

Sampling site: Pool Riffle Open Channel Braided Backwater Sampler Type(80164) ______ Sampler ID ______

Method:(82398) EWI EDI OTHER ______ Nozzle size ______ Nozzle made of ______

Sample Split: Churn Cone Other ______ Made of ______ Bottle type, size ______

Sampling Time *GHT*

Start ______ ______

______ ______

______ ______

______ ______

End ______ ______

Mean ______ ______

LB ______ RB ______ Stream Width ______ Sampling Points ______ ______ ______

Bottom: Bedrock Rock Cobble Gravel Sand Silt Concrete Other ______

Stage conditions: *4)Stable, low 5)Falling 6)Stable, high 7)Peak 8)Rising 9)Stable, normal A)Not Determined*

Observations:

Codes: 0-none 1-mild 2-moderate 3-serious 4-extreme

Floating:

debris (01345) ____ Turbidity (01350) ____

garbage (01320) ____ Atms. odor (01330) ____

algae mats (01325) ____ Oil-grease (01300) ____

Detergent suds (01305) ____ Fish kill (01340) ____

Hydrologic event :

9)Routine sample 7)Flood 1)Drought 2)Spill 3)Reg. flow 4)Snowmelt A)Spg breakup B)Ice cover J)Storms

Other ______ Ice Thickness ______ Ice cover ______

Stream color(s): brown green blue gray other *Stream mixing: Excellent Good Fair Poor Unknown*

Weather: Clear Partly Cloudy est % cover Light Medium Heavy Steady Very Cold Cool

Warm Hot Intermittent Rain Snow Sleet Fog Calm Light Breeze Very Gusty Windy est speed ______

Other Observations

______

______

(Cont. p. 3,4)

LABORATORY SCHEDULES

lab-codes	added/ deleted	lab-codes	added/ deleted

Filter Type: Capsule, 0.45 ☐ Plate, 0.45 ☐ Plate, 0.10 ☐ Plate, 0.001 ☐ Other ☐ ______

☐ Preconditioned filter w/ mL Lot #

SAMPLES COLLECTED ☐ Nutrients ☐ Major Ions ☐ TOC ☐ DOC

SOC ☐ Vol. filt. ____mL ☐ BOD ☐ Turbidity ☐ COD ☐ ______

ORGANICS: ☐ Pesticide ☐ VOC ☐ BNA HCl added ______ml Final pH ______

TR. ELEMENTS: ☐ Unfiltered ☐ Filtered ☐ Suspended ☐ Bottom

☐ Sediment conc. ☐ Sediment size ☐ Sed. bot. material ☐ Sand split/break

☐ Radiochemical ☐ Isotope ☐ ______ ☐ ______

QC Samples Collected Yes ☐ ☐ No

Laboratory: ☐ NWQL ☐ Ocala Other ______

Comp by Chkd by Date

1

Figure 8.1.1. Example first page of a national field form for use in recording field-measurement data.

8.1.3.1 Equipment Selection

Guidelines for selecting equipment for sampling surface water are provided in Horowitz and others (1994) and in chapter A2 of the National Field Manual (Wilde and others, 1998). Review of equipment selection by District technical specialists occurs during proposal and workplan review and during periodic project reviews.

8.1.3.2 Sample Collection

Guidelines for the collection of surface-water samples are provided in chapter A4 of the National Field Manual (Wilde and others, 1999). Field personnel are responsible for examining the sampling site carefully and choosing the most appropriate sampling method to generate the best sample possible under the conditions at the time of sampling. The standard procedure for stream sampling is to collect the sample through the entire depth of the water column at multiple vertical transects by either the equal-discharge or equal-width increment method. These procedures generate a representative cross-sectional sample that is both flow-weighted and depth- and width-integrated (Edwards and Glysson, 1988; Ward and Harr, 1990). Occasionally, the use of non-integrated or non-flow-weighted methods may be appropriate because of hydrologic, climatic, or safety conditions, or specific project objectives. Thorough documentation of sampling equipment and methods that are used is required in field records associated with water-quality samples. The District Water-Quality Specialist or designee is responsible for timely review of field records.

Good field techniques, especially the avoidance of environmental and atmospheric inputs, are required to minimize the potential for contamination during sample collection. Standard policy of the South Dakota District is to: 1) enclose all pre-cleaned/rinsed/conditioned pump tubing, cartridge filters, sample bottles, and sampler heads, nozzles and bottles in double plastic bags for transport to the sampling site; 2) enclose pre-cleaned churn splitters in double plastic bags and a churn carrier for transport to and from the sampling site; and 3) use processing/preservation chambers during processing of samples. At the discretion of the project chief and/or the District Water-Quality Specialist, specific procedures employing two-person sampling teams using “clean hands/dirty hands” techniques may be required when sampling for trace inorganic constituents with ambient concentrations less than 10 parts per billion (ppb), as described in Horowitz and others (1994). However, two-person sampling teams are not mandatory for all sample collection. The project chief and/or the District Water-Quality Specialist are responsible for ensuring that adequate QA/QC procedures are conducted to document the appropriateness of sample collection procedures.

Review of surface-water sampling procedures for each District water-quality project is performed periodically by the District Water-Quality Specialist. An independent review of field methods, for at least one District project, is conducted once every 3 years during the Office of Water Quality District technical review.

8.1.4 Ground-Water Sampling

District ground-water sampling procedures are designed to ensure that the samples collected are representative of water in the aquifer and are not contaminated by well construction material or sampling equipment, and that the composition of the samples is not altered by physical or chemical processes during sampling. It is critical that field personnel be aware of all factors that can compromise the integrity of ground-water samples and implement consistent strategies to protect sample integrity.

8.1.4.1 Equipment Selection

Guidelines for selecting appropriate equipment for ground-water sampling are provided in the National Field Manual (Wilde and others, 1999, chap. A2). All project personnel involved in ground-water sampling for water-quality studies must understand the advantages and disadvantages of available equipment with respect to study objectives. Because of the wide range of factors involved, the ideal equipment for sample collection under some circumstances may not exist. When compromise decisions are required, the field team must thoroughly document with field notes the compromises that are made. Review of equipment selection occurs during proposal and workplan review and during periodic project reviews by District technical specialists.

8.1.4.2 Sample Collection

Guidelines, which prevent or minimize loss of sample integrity, for collecting representative water-quality samples from ground water are provided in chapter A4 of the National Field Manual (Wilde and others, 1999a). The standard procedure for ground-water sampling is to purge the well to remove at least three well volumes of standing water while monitoring field measurements for stabilization. However, exceptions to the three-well-volume rule can be made under some circumstances, depending upon project objectives or site characteristics. The project chief and/or the District Water-Quality Specialist or designee is responsible for timely review of field records.

As a rule, field personnel are required to follow a prescribed order of sample collection, described in the National Field Manual (Wilde and others, 1999a, chap. A4, table 4-5), to help ensure the quality of the data collected. For some projects, at the discretion of the project chief and/or the District Water-Quality Specialist, specific procedures employing two-person sampling teams using “clean hands/dirty hands” techniques may be required when sampling for trace inorganic constituents with ambient concentrations less than 10 parts per billion (ppb), as described in Horowitz and others (1994). However, two-person sampling teams are not mandatory for all sample collection. The project chief and/or the District Water-Quality Specialist are responsible for ensuring that adequate QA/QC procedures are conducted to document the appropriateness of sample collection procedures.

Review of ground-water sampling procedures for each District water-quality project is performed periodically by the District Water-Quality Specialist or designee and documented with a memorandum to the appropriate project chief and the District Chief. An independent review of field methods, for at least one District project, is conducted once every 3 years during the Office of Water Quality District technical review.

8.1.5 Precipitation Sampling

Precipitation samples for water-quality analysis are not routinely collected in the South Dakota District except at the Huron Well Field NADP/NTN site. Sample collection procedures at that site adhere strictly to NADP/NTN protocols. If projects develop that require collection of precipitation samples for water-quality analysis, appropriate guidelines for sample collection will be developed by the project chief and/or the District Water-Quality Specialist. Major factors that must be considered in sampling for precipitation quality include the location of the sampling station relative to human influences, the choice of sampling equipment, and special sample-handling procedures that may be necessary. Precipitation-quality sampling equipment should be composed of inert, nonabsorbent material that will not affect the typically low concentrations of ions in solution.

Guidelines regarding the collection of precipitation samples are provided in the following references:

1. Dossett and Bowersox (1999) for guidance in field and laboratory procedures in the WRD;
2. Peden and others (1986) for procedures for collecting precipitation samples recommended by the USEPA; and
3. Willoughby (1995) for a case study discussing methods of precipitation sampling and analysis.

The project proposal and workplan should be consulted for specific guidelines regarding the factors that must be considered in choosing the sample location, the sampling equipment and frequency, and the special sample handling procedures that may be necessary based upon the study objectives.

For specific questions related to precipitation sampling that are not addressed by these references, contact the Mark Nilles (303-236-1878; manilles) with NADP/NTN.

8.1.6 Sample Processing

All samples collected for water-quality analysis must be processed according to procedures in the National Field Manual (Wilde and others, 1999b, chap. A5) as soon as possible following collection. The constituents of interest and study objectives determine the specific processing procedures that are necessary, which must be described in the project workplan.

Standard policy of the South Dakota District is to: 1) enclose all pre-cleaned/rinsed/conditioned pump tubing, cartridge filters, sample bottles, and sampler heads, nozzles and bottles in double plastic bags for transport to the sampling site; 2) enclose pre-cleaned churn splitters in double plastic bags and a churn carrier for transport to and from the sampling site; and 3) use processing/preservation chambers during processing of samples. At the discretion of the project chief and/or the District Water-Quality Specialist, specific procedures employing two-person sampling teams using "clean hands/dirty hands" techniques may be required when sampling for trace inorganic constituents with ambient concentrations less than 10 parts per billion (ppb), as described in Horowitz and others (1994). However, two-person sampling teams are not mandatory for all sample collection. The project chief and/or the District Water-Quality Specialist are responsible for ensuring that adequate QA/QC procedures are conducted to document the appropriateness of sample collection procedures.

8.1.6.1 Sample Compositing and Splitting

Guidelines for using sample compositors and splitters are in the National Field Manual (Wilde and others, 1998a, chap. A2). Two types of sample splitters presently in use in the WRD are the churn splitter, which also serves as a compositing device, and the cone splitter, which requires a separate compositing vessel. Each splitter has specific advantages and disadvantages, as described in OWQ Technical Memorandum 97.06. Either splitting method can be applied to inorganic and organic constituents within the technical design limits of the device and as long as the equipment is constructed of appropriate materials.

8.1.6.2 Sample Filtration

Filtration is required for many water-quality samples in order to separate particulates from the water and constituents in solution. Selection of the appropriate filter unit and filter characteristics to be used depends on the constituent class of interest and is based on guidance provided in the National Field Manual (Wilde and others, 1998a, chap. A2). Guidelines for filtration procedures for specific constituent groups are provided in the National Field Manual (Wilde and others, 1999b, chap. A5). For surface water, the most common filtration system consists of a reversible, variable-speed battery-operated peristaltic pump and

0.45-micron pore size disposable capsule filter. For ground water, the sample is generally pumped directly from the well through a 0.45-micron pore size disposable capsule filter. Filtration of samples for analysis of trace elements in concentrations less than 10 ppb must be done in a processing chamber that encloses the filtering unit and sample bottles in a protected environment (Wilde and others, 1999-2002).

8.1.6.3 Sample Preservation

Sample preservation techniques are required for some constituent groups to prevent reduction or loss of target analytes and to stabilize analyte concentrations for a limited time. Guidelines for sample preservation are provided in the National Field Manual (Wilde and others, eds., 1999b, chap. A5), and the NWQL Services Catalog (see section 4.3.1 for location). Since some samples have a very limited holding time even when preserved, field personnel must ensure that all water-quality samples are shipped to the laboratory as quickly as possible and that time-sensitive samples are received in good condition within the appropriate holding time. For details on sample shipping requirements, refer to the next section of this QA plan.

8.2 Other Types of Water-Quality Samples

Many water-quality studies in the WRD are beginning to employ a multidisciplinary approach that relies on data from a range of sampling media. A variety of different types of biological, sediment, and radiochemical samples may be incorporated into a water-quality project in order to provide multiple lines of evidence with which to evaluate a particular aquatic system. This section of the QA plan includes an overview of standard District QA procedures and references for detailed instructions that describe the collection of biological, sediment, and radiochemical samples.

8.2.1 Biological Sampling

Routine District water-quality activities currently (2003) do not include the collection of biological samples. However, individual projects may require collection of biological samples. Specific collection and processing procedures for such projects will be developed by the project chief and/or the District Water Quality Specialist and typically will follow guidelines in the references found in table 8.2.1.

Table 8.2.1. Summary of references for collecting and processing biological samples

Reference	Sample type
Crawford and Luoma, 1994	Contaminants in tissues
Cuffney and others, 1993	Benthic invertebrates
Meador and others, 1993	Fish
Meador, Hupp, and others, 1993	Stream habitat
Myers and Sylvester, 1997 (TWRI book 9, chap. A7, section 7.1) (an update is in preparation, as is a section on fecal indicator viruses)	Fecal indicator bacteria
Delzer and McKenzie, 1999, (TWRI book 9, chap. A7, section 7.2)	Five-day biochemical oxygen demand
Porter and others, 1993	Algae

8.2.2 Suspended-Sediment and Bottom-Material Samples

District water-quality activities include the collection of suspended-sediment and bottom-material samples. Guidelines for the collection of sediment samples are described in selected WRD publications and in WRD Office of Surface Water (OSW) memoranda, which are referenced below. District personnel collect suspended sediment samples for water-quality studies by using sampling methods that include the EDI method, the EWI method, and the point sample method. Suspended-sediment samples are typically analyzed by the Iowa Sediment Laboratory for concentration and either sand and silt distribution or complete particle-size distribution. Additionally, samples for both suspended sediment and bottom sediment may be analyzed for chemical constituents, including trace elements or hydrophobic organic compounds.

Field personnel must be familiar with the factors involved in the selection of sediment-sampling equipment that are based on the type of analyses to be performed and hydraulic conditions, as well as special cleaning procedures that may be required when sampling sediment chemistry. The project workplan should be consulted for specific guidelines for sediment sampling, depending on project objectives.

Table 8.2.2. Summary of references for collecting suspended-sediment samples

Reference	Subject
Iowa District sediment laboratory QA plan	Laboratory procedures used in processing and analyzing sediment samples.
Edwards and Glysson, 1988	Field methods for measurement of fluvial sediment.
Guy, 1969 (TWRI book 5, chap. C1)	Laboratory theory and methods for sediment analysis.
Knott and others, 1992	Quality-assurance plan for collecting and processing sediment data.
OSW Memorandum 93.01 (USGS)	Instrumentation and field methods for collecting suspended-sediment data.
Radtke, 1998 (TWRI book 9, chap. A8)	Collecting and processing bottom-sediment samples.
Shelton and Capel, 1994	Collecting and processing streambed-sediment samples.
Wilde and others, 1998b (TWRI book 9, chap. A3)	Cleaning equipment for sampling suspended-sediment chemistry.
Wilde and others, 1998a (TWRI book 9, chap. A2)	Selection of equipment for sampling suspended-sediment chemistry.

8.2.3 Radiochemical

District water-quality activities occasionally include the collection of radiochemical samples. General procedures for proper collection and processing of radiochemical samples are similar to procedures for non-radioactive constituents; however, radionuclides typically occur at very low concentrations and therefore the need for appropriate preservation techniques to maintain the original condition of the sample with respect to radionuclide concentrations is particularly important. Discussion of appropriate collection and processing techniques for radiochemical samples is presented in TWRI, Book 5, Chapter A5, "Methods for determination of radioactive substances in water and fluvial sediments." Collection and processing of radiochemical samples in the South Dakota District will adhere to the guidelines presented in TWRI, Book 5, Chapter A5, and TWRI Book 9, chapters A4 and A5.

8.3 Quality-Control Samples

Quality-control samples must be collected as integral components of all District water-quality studies to determine the acceptability of performance in the data-collection process and provide a basis for evaluating the adequacy of procedures that were used to obtain data. Guidelines for the collection of specific types of QC samples and the use of QC data are provided in the National Field Manual (Wilde and others, 1999a, chap. A4). Issues of QC sample design are addressed in section 3.2 of this plan. Specific guidelines for the collection and processing of QC samples must be included in the project workplan. The project chief is responsible for reviewing QC data in a timely manner and implementing necessary modifications, when appropriate, to sampling and processing techniques. The District Water-Quality Specialist has the responsibility for advising District personnel regarding the collection and interpretation of QC samples.

8.4 Safety Issues

Because the collection of water-quality data in the field can be hazardous at times, the safety of field personnel is a primary concern. Field teams often work in areas of high traffic, remote locations, and under extreme environmental conditions. Field work involves the transportation and use of equipment and chemicals and commonly requires working with heavy machinery. Additionally, field personnel may come in contact with waterborne and airborne chemicals and pathogens while sampling. Beyond the obvious concerns regarding unsafe conditions for field personnel, such as accidents and personal injuries, the quality of the data also may be compromised when sampling teams are exposed to dangerous conditions.

So that personnel are aware of and follow established procedures and protocols that promote all aspects of safety, the District communicates information and directives related to safety to all personnel. Specific policies and procedures related to safety can be found in the South Dakota District Safety Plan.

An individual has been designated as Safety Officer by the South Dakota District. Personnel who have questions or concerns pertaining to safety, or who have suggestions for improving some aspects of safety, should direct those questions, concerns, and(or) suggestions to the Safety Officer.

Guidelines pertaining to safety in field activities are provided in the National Field Manual (Lane and Fay, 1998, chap. A9).

8.5 References Used for the Sample Collection and Processing Section

The following table lists reports and(or) memoranda referred to in this section. For a complete citation, refer to Section 13.0 of the report.

Table 8.5. Summary of references used for collecting and processing water-quality samples

Reference	Subject
Crawford and Luoma, 1994	Collecting samples of contaminants in tissue (NAWQA).
Cuffney and others, 1993	Collecting benthic invertebrate samples (NAWQA).
Edwards and Glysson, 1999	Representative sampling techniques for surface water.
Guy, 1969	Laboratory theory and methods for sediment analysis.
Horowitz and others, 1994	Protocol for collecting and processing inorganic constituents at ppb concentrations.

Table 8.5. Summary of references used for collecting and processing water-quality samples (Cont.)

Reference	Subject
Knott and others, 1992	Quality-assurance plan for collecting and processing sediment data.
Koterba and others, 1995	Collecting and processing ground-water samples (NAWQA).
Lane and Fay, 1998 (TWRI book 9, chap. A9)	Safety in field activities.
Meador and others, 1993	Collecting fish samples (NAWQA).
Meador, Hupp, and others, 1993	Characterization of streambed habitat (NAWQA).
Myers and Sylvester, 1997 (TWRI book 9, chap. A7, section 7.1) (an update is in preparation, as is a section on fecal indicator viruses)	Measuring fecal indicator bacteria.
Delzer and McKenzie, 1999 (TWRI book 9, chap. A7, section 7.2)	Five-day biochemical oxygen demand test.
OSW Memorandum 93.01 (USGS)	Instrumentation and field methods for collecting suspended-sediment data.
OWQ Memorandum 81.07 (USGS)	Field and laboratory procedures for precipitation samples.
OWQ Memorandum 97.06 (USGS)	Comparison of splitting capabilities of the churn and cone splitters.
Peden and others, 1986	Procedures for collecting precipitation samples, recommended by USEPA.
Porter and others, 1993	Collecting algal samples (NAWQA).
Radtke, 1998 (TWRI book 9, chap. A8)	Collecting and processing bottom-sediment samples.
Shelton, 1994	Collecting and processing stream-water samples (NAWQA).
Shelton and Capel, 1994	Collecting and processing streambed-sediment samples (NAWQA).
Stanley and others, 1992	National field quality-assurance program.
Ward and Harr, 1990	Representative sampling techniques for surface water.
Wilde and Radtke, eds., 1998 (TWRI book 9, chap. A6)	Well-purging procedures.
Wilde and others, eds., 1998b (TWRI book 9, chap. A3)	Cleaning equipment used to collect and process water-quality samples.
Wilde and others, eds., 1999a (TWRI book 9, chap. A4)	Collecting water-quality samples from surface and ground water.
Wilde and others, eds., 1999b (TWRI book 9, chap. A5)	Processing water-quality samples.
Wilde and others, eds., 1998a (TWRI book 9, chap. A2)	Selection of equipment used to collect and process water-quality samples.
Willoughby, 1995	Case study discussing methods of precipitation sampling and analysis.

9.0 Water-Quality Sample Handling and Tracking

All water-quality samples must be uniquely identified, documented, handled, shipped, and tracked appropriately. Following proper protocols for sample handling, shipping, and tracking ensures that samples are processed correctly and expeditiously to preserve sample integrity between the time of collection and the time of analysis. This section describes the procedures used by the South Dakota District for handling, shipping, and tracking samples from collection through transfer of the samples to an analytical facility. Receipt of analytical data from laboratories is covered in Section 10.0 (Water-Quality Data Management).

9.1 Preparation for Sampling

Ensuring that field personnel have the correct equipment and supplies on hand to perform the necessary sampling activities saves time and labor costs associated with repeated sampling trips that result from inadequate planning. Therefore, before commencing field activities, the project chief and hydrologic technician(s) are responsible for ensuring that the following preparations have been completed:

- Review the sampling instructions for each site and the list of sample types required.
- Ensure that the station site file is current.
- Prepare bottle labels for samples.
- Obtain field sheets or notebooks and analytical services request forms (ASR's).
- Ensure that necessary supplies are available, such as bottles, standards, filters, preservatives, meter batteries, waterproof markers, shipping containers, etc. (see section 5.1.3 (Equipment and Supplies).
- Ensure that all sampling equipment is thoroughly cleaned and prepared.
- Check meters and sensors for proper performance.]

9.2 Onsite Sample Handling and Documentation

During a sampling trip, it is imperative that accurate notes be taken and that sample bottles be labeled and handled appropriately for the intended analysis. Otherwise, bottle mix-ups or other errors may occur, and the samples may be wasted. The project chief and hydrologic technician are responsible for ensuring that all of the following sampling requirements are implemented:

- bottle labels must be printed clearly and should include the bottle type and volume, station id and name, analytical schedule number, and sampling date and time;
- bottle labels must be securely attached to the sample bottles;
- if, for some reason, bottle labels were not prepared prior to sampling, the required information may be printed directly on the sample bottles using a permanent marker;
- bottle caps must be securely and appropriately secured;
- appropriate preservation procedures, such as addition of a preservative or chilling, should be administered as soon as possible;
- detailed guidance on bottle labeling and preparation for shipping can be found in Chapter A5, Section 5.5 of the National Field Manual for guidance.

9.3 Sample Shipment and Documentation

Upon completion of a sampling trip, samples should be packaged and shipped to the laboratory for analysis as soon as possible. Generally, the shorter the time between sample collection and processing and sample analysis, the more reliable the analytical results will be. Before shipping samples to the laboratory, the project chief or hydrologic technician should complete the following:

1. Check that sample sets are complete and that sample bottles are labeled correctly, with all required information (see Section 9.2).
2. Complete the ASR's for all samples being sent to the NWQL. If samples are being sent to a different, approved laboratory, information similar to that required on the ASR's should be provided to the laboratory.
3. Pack samples carefully in shipping containers to avoid bottle breakage, shipping container leakage, and sample degradation. Check that bottle caps are securely sealed. Follow the packing and shipping protocols established by the USGS and the receiving laboratory (see NWQL Technical Memorandum 95.04, the National Field Manual, and NWQL Rapi-Notes 01-013, 01-023, 01-033, and 01-034 for additional information).
4. Ship samples after sample collection and the same day whenever possible.
5. Chapter A5 of the National Field Manual (Wilde and others, 1999) has tables that summarize sample processing requirements and list NWQL designation codes for commonly measured organic and inorganic constituents.

9.4 Sample Tracking Procedures

The projects maintain records of all samples collected and shipped to a laboratory for analysis to ensure the complete and timely receipt of analytical results. The project chief or hydrologic technician has responsibility for recording the required information. The project chief has responsibility for reviewing the tracking log to determine if analyses are missing and for taking corrective action(s) if necessary.

9.5 Chain-of-Custody Procedures for Samples

When chain-of-custody procedures are appropriate or required (for example, when data may be used in legal proceedings), the project chief should establish, maintain, and document a chain-of-custody system for field samples that is commensurate with the intended use of the data. A sample is in custody if it is in actual physical possession or in a secured area that is restricted to authorized personnel. Every exchange of a sample between people or places that involves a transfer of custody should be recorded on appropriate forms that document the release and acceptance of the sample. Each person involved in the release or acceptance of a sample should keep a copy of the transfer paperwork. The project chief, or designee, is responsible for ensuring that custody transfers of samples are performed and documented according to the requirements listed below.

- The means for identifying custody should be clearly understood (use of forms, stickers, etc.);
- Instructions for documenting the transfer of samples and the person responsible for this documentation must be clearly defined; and
- A plan must be in place for maintaining records in a specific location for a specific period of time (for example, in the site folder).

9.6 References Used for the Sample Handling and Tracking Section

The following table lists reports and(or) memoranda referred to in this section. For a complete citation, refer to Section 13.0 of the report.

Table 9.6. Summary of references for handling and tracking water-quality samples

Reference	Subject
NWQL Memorandum 95.04	Shipping samples to the NWQL, and instructions for filling out Analytical Services Request (ASR) forms.
NWQL Rapi-Note 01-013, 01-023, 01-033, 01-034	USGS employees can access Rapi-Notes through the NWQL in-house Web site.
Wilde and others, eds., 1999-2002 (TWRI book 9, chap. A5)	Processing water samples.

10.0 Water-Quality Data Management

Water-quality data that are collected for hydrologic investigations are recorded on paper and electronically. Data that are recorded on paper include chemical, physical, biological, and ancillary data measured in the field. This information is documented on standard USGS field forms (fig. 8.1.1) and stored in site files. Data that are recorded electronically include analytical results and continuous monitoring data transmitted over the computer network or stored by electronic data logger. Data that are recorded on paper and electronically typically are stored either in the NWIS QWDATA data base (Maddy and others, 1997) or in NWIS-ADAPS data base (Bartholoma, 1997). The NWIS is the storage medium for water-quality, streamflow, well, and water-use information collected by the USGS. Data that cannot be stored in these national data bases may be stored in other data bases, such as project data bases.

10.1 Processing Data

Sampling information, field determinations, and ancillary information are recorded on a set of water-quality field notes that are considered original record. These data are combined with analytical data from the laboratory in computer data files and paper files.

10.1.1 Continuous Monitoring Data

The South Dakota District currently (2003) collects continuous monitor water-quality data at two stations on the Big Sioux River (06482020, Big Sioux River at N. Cliff Ave. at Sioux Falls, SD; 06480000, Big Sioux River near Brookings, SD). Operation of these monitors follows guidelines presented in Wagner and others (2000). Continuous monitoring data are water-quality records collected onsite by electronic sensors and data loggers. Two methods for electronically recording data are by (1) transmitting data from a remote location by land line or radio telemetry to a central location where they are recorded on magnetic tape, disk, or solid-state memory device, and (2) recording data at a remote location on magnetic tape, disk, or solid-state memory device. Initial data processing in the office is for the purpose of obtaining a copy of the original data for archiving (see Section 10.4). Data are not manipulated by the field instrument or a computer except to convert recorded signals into data in commonly used units or to display data in a convenient format. The transfer of data from the electronic storage medium to NWIS requires thorough checking to ensure that the data have transferred successfully or that as much data as possible have been recovered and errors identified (WRD Memorandum 87.085). Continuous water-quality data are processed as described in Wagner and others (2000).

10.1.2 Analytical Data

Analytical data are results of field and laboratory chemical, physical, or biological determinations. Most water-quality samples are analyzed either in the field or at the NWQL. In some cases, samples may be analyzed by research laboratories or by laboratories outside of the USGS (see Section 4.1).

In order to enter analytical data into the NWIS data base, a site identification number must first be assigned and entered into the District site file (see Section 7.2). Field measurements are entered into the NWIS data base by the NWIS Water-Quality Database Administrator, or other individuals designated by the District Water-Quality Specialist, as soon as possible after returning from the sampling field trip. A record number is assigned by the system and is recorded on the original field form (see Section 9.4 for sample tracking.) Sample logging is required for data from the NWQL to successfully transfer the data into the data base. Environmental sample data are entered into the District database NWIS QWDATA 01; QA data are entered into the District database NWIS QWDATA 03.

All data from the NWQL are electronically transferred to the appropriate District data base by the NWIS Water-Quality Database Administrator at least once per week. Hard copies of the analytical reports (WATLIST's) are forwarded to project chiefs or designees for storage in project files. The NWIS QWDATA data base receives daily incremental backup and weekly full backup.

Data analyzed by laboratories other than the NWQL or OWSU must be entered into NWIS, if possible (Hubbard, 1992), and identified according to the analyzing laboratory. Data entry is the responsibility of the project chief. Data are entered and stored according to procedures already described for processing NWIS analytical data. Appropriate codes are used to identify the data as originating from non-USGS sources.

10.1.3 Non-National Water Information System Data Bases

Sometimes data collected by project personnel cannot be entered into the District NWIS QWDATA data base because the data are proprietary (such as data collected for some military projects) or because NWIS cannot accept the type of data that are generated by the project (for example, taxonomic data). In these cases, project data bases may be established to accommodate the data storage requirements and formats. Project data bases that are the sole repository for project data should have a written procedure for data entry, storage, and long-term backup and archival. The project chief has the responsibility for developing and implementing management of project data bases.

10.2 Validation (Records Review)

Data validation is the process whereby water-quality and associated data are checked for completeness and accuracy. After validation, data records are finalized in the District data base.

10.2.1 Continuous Monitoring Data

Following the entry of continuous monitoring data into NWIS, raw data and(or) graphs of raw data are reviewed by the lead technician, and/or project chief for anomalous values, dates, and times, and preliminary updating is done. Once the data are edited, the record is submitted to the Data Section Chief for final review and approval.

10.2.2 Analytical Data

All field notes and field measurements are reviewed for completeness and accuracy after returning from the field by individuals designated by the District Water-Quality Specialist. All chemical analyses are reviewed for completeness, accuracy, and precision as the analytical results are returned. Prompt review is necessary to allow analytical re-analysis to be performed before sample holding times have been exceeded for accuracy and precision. Every analysis entered into NWIS-QWDATA results in output (WATLIST) that includes a copy of the analyses and a report of general validation checks (Maddy and others, 1990, and Hoopes, B.C., written commun.) including but not limited to

- comparison of determined and calculated values for dissolved solids,
- comparison of dissolved constituents and total constituents,
- comparison of specific conductance with dissolved solids,
- comparison of constituents with relevant federal standards,
- comparison of sum of cations with sum of anions (ion balance).

Field and laboratory analyses, such as pH, specific conductance, and alkalinity, are compared to confirm agreement of independent measurements. If data from more than one sample are available for a site, the analysis also is compared with previous analyses within a hydrologic context to identify obvious errors, such as decimal errors, and possible sample mix-ups or anomalies warranting analytical re-analysis. These reports and comparisons are reviewed and noted on the WATLIST. If necessary, corrections or reruns are requested by the project chief.

Reruns requests to NWQL are made through the NWQL inhouse Web page (http://nwql.cr.usgs.gov/usgs/sampstatus/index.cfm), and to other laboratories in writing as stipulated in the laboratory contract. Re-analysis requests are logged and tracked by the project chief. Corrections to NWIS resulting from reruns by NWQL must be made to the laboratory database as well as the District database and are made by the project chief by email request to LABHELP. Re-analysis results are logged and tracked by the project chief or designee.

Project QA data such as blanks, replicates, blind standards, and matrix spikes, periodically are tabulated or graphed and reviewed by the project chief to facilitate identification of inaccuracies or systematic bias that may not be discernible when reviewing an individual analysis. Problems in sampling or analytical procedures that are indicated by QC sample results will be promptly dealt with by the project chief. All personnel responsible for sample collection and field analysis participate in the NFQA Program and process at least one blank sample during a given year. District QA data, including NFQA sample results and blank sample results are reviewed by the District Water-Quality Specialist and when problems are indicated appropriate corrective measures are taken. An analysis of the QA/QC data for 2000-02 is given in the supplementary information section at the end of this document.

10.3 Data Storage

In accordance with WRD policy, all water data collected as part of routine data collection by the WRD are stored in the NWIS computer data base. Data collected by others, such as cooperators, universities, or consultants, which are used to support published USGS documents and are not published or archived elsewhere, also should be entered into NWIS and identified according to analytical laboratory and collection organization. Other outside data may be entered into the data base at the discretion of the project chief in consultation with the District Water-Quality Specialist if data-collection methods and quality have been reviewed and found acceptable. Electronically stored data that cannot be entered into NWIS are stored in project data bases online or offline. The system administrator has responsibility for maintaining backups of data stored electronically in NWIS or online. Data stored electronically offline are maintained by the project chief.

In addition to electronically stored data, other project data and information, including field notes, ASR's, WATLIST's, and hard-copy results from outside labs are retained in station folders and maintained by the project chief in the District and Subdistrict Offices while the project is active.

Relatively new data, which are being compiled, modified, reviewed, and frequently used, require high levels of accessibility. As these data become older, lower levels of accessibility are typically needed. Data in the data base generally should move from areas of higher accessibility and lower security to areas of lower accessibility and higher security as the need for access diminishes and the data become finalized. As this occurs, data may be moved from online to near online or offline, as appropriate.

10.4 Records Archival

According to WRD policy, all original data that are published or support published scientific analyses shall be placed in archives (WRD Memorandum 92.059; Hubbard, 1992). Original data—from automated data-collection sites, laboratories, outside sources, and non-automated field observations—are unmodified data as collected or received and in conventional units (engineering units, generally with a decimal). Original data should be preserved in this form, no matter how they may be modified later (Hubbard, 1992). Original data on paper include field notes, field measurements, ASR's, WATLIST's, continuous water-quality monitoring records, and calibration notes. These data are archived when the project is completed or if data are more than 3 years old. It is the responsibility of the project chief to ensure that project files entered into the District archive are organized and complete. The District archive is located the Federal Archives in Denver, Colo. and is maintained by the Bureau of Archives.

10.5 References Used for the Water-Quality Data Management Section

The following table lists reports and(or) memoranda referred to in this section. For a complete citation, refer to Section 13.0 of the report.

Table 10.5. Summary of references for managing water-quality data and records

Reference	Subject
Bartholoma, S.D., 1997	NWIS ADAPS user's guide, Open-File Report 97-635.
Hubbard, 1992	Policy recommendations for managing and storing hydrologic data.
Maddy and others, 1997 (an update by Hoopes, B.C., ed., is scheduled to be available by the end of 2002)	NWIS QWDATA user's guide.
WRD Memorandum 87.085 (USGS)	Policy for collecting and archiving electronically recorded data.
WRD Memorandum 92.059 (USGS)	Policy for the management and retention of hydrologic data.
Wagner and others, 2000	Guidelines and standard procedures for continuous water-quality monitors

11.0 Publication of Water-Quality Data

Water-quality data are published in hydrologic data reports or interpretive reports. The selection of the appropriate publication outlet for water-quality data will be the responsibility of the project chief in consultation with the Studies Section Chief. A summary of USGS and WRD policies pertaining to the publication of data and interpretive reports is contained in the WRD Publications Guides (Alt and Iseri, 1986, p. 382-385; U.S. Geological Survey, 1995). Other references that should be consulted when writing reports include "Suggestions to Authors..." (Hansen, 1991) and the U.S. Government Printing Office Style Manual (U.S. Government Printing Office, 2000).

Report approval was delegated in 1995 from the Director to the Regional Hydrologists (WRD Memorandum 95.18). In addition, some USGS Districts have authority to approve some reports for publication at the District level (WRD Memorandum 92.005 and 97.002), and some Regions have delegated approval authority to teams through the team review approach. For the South Dakota District, interpretive reports, such as Water-Resources Investigations Reports, are reviewed and approved at the regional level. Non-interpretive data reports, including many Open-File Reports, are reviewed and approved within the South Dakota District.

11.1 Hydrologic Data Reports

All non-proprietary water-quality data collected during the water year are published in the WRD annual data report, "Water Resources Data, South Dakota, Water Year ___," unless the data will be published in an interpretive or separate data report. Generally, it is the policy of the South Dakota District only to publish data in one publication outlet. Hydrologic data reports make water-quality data available to users, but without interpretations or conclusions. Approval of hydrologic data reports is in accordance with applicable WRD, Region, and District policy (Alt and Iseri, 1986).

11.2 Interpretive Reports

Interpretive reports include such USGS outlets as Circulars, Professional Papers, Fact Sheets, Water-Resources Investigations Reports, and some Open-File Reports, as well as non-USGS outlets, such as scientific journals, books, and proceedings of technical conferences. The District Water-Quality Specialist, project supervisor, and outside technical specialists will provide guidance in ensuring that each water-quality report meets the highest technical standards. Approval of interpretive reports is in accordance with applicable WRD, Region, and District policy (WRD Memorandum 95.18) and is more technically rigorous than the required approval for non-interpretive data reports.

11.3 Other Data Outlets

Article 500.14.1 of the Department of the Interior Geological Survey Manual (U.S. Department of the Interior, 1992) states that data and information are released through publications; however publication is not limited to paper media (WRD Memorandum 90.030; U.S. Department of the Interior, 1993). Electronic outlets include the internet (NWISWeb at http://waterdata.usgs.gov/nwis/) and computer storage media, such as CDROM.

The term "data" refers to uninterpreted observations or measurements, usually quantitative measurements resulting from field observations and laboratory analyses of water, sediment, or biota. Data can be released to the public after preliminary review for accuracy by appropriate WRD personnel (WRD Memorandum 90.030). Constituents in water samples collected by or for the USGS that exceed USEPA drinking water maximum contaminant levels (MCL's), as specified in the National Primary Drinking Water Regulations, are promptly reported to appropriate agencies that have a need to know (WRD Memorandum 90.038).

The term "information" refers to interpretations of data or conclusions of investigations. Interpretive results or conclusions require colleague review and Director's approval for publication. Release of preliminary interpretations prior to final approval is prohibited to avoid disseminating incomplete and(or) incorrect conclusions, which are subject to change as a result of subsequent technical and policy reviews.

11.4 References Used for the Publication Section

The following table lists reports and(or) memoranda referred to in this section. For a complete citation, refer to Section 13.0 of the report.

Table 11.4. Summary of references for publishing data

Reference	Subject
Alt and Iseri, 1986	Guide for publishing WRD reports.
Hansen, 1991	Suggestions to authors of USGS reports.
U.S. Department of the Interior, 1992	Safeguard and release of USGS information.
U.S. Department of the Interior, 1993	Policy for release of computer data bases and computer programs.
U.S. Geological Survey, 1995	Guidelines on writing hydrologic reports.
U.S. Government Printing Office, 2000	Style manual for printed government documents.
WRD Memorandum 90.030 (USGS)	Policy for release of digital data.
WRD Memorandum 90.038 (USGS)	Policy for reporting maximum contaminant level exceedances.
WRD Memorandum 92.005 (USGS)	Extended delegation of authority to approve reports of certain categories for open file release.
WRD Memorandum 95.18 (USGS)	Redelegation of Director's report approval authority to Regional Hydrologists.
WRD Memorandum 97.002 (USGS)	Modification to the reports processing system
http://waterdata.usgs.gov/nwis/	NWISWeb

12.0 Water-Quality Training and Reviews

Periodic reviews of data-collection procedures are used to evaluate the effectiveness of training programs and to determine if technical work is being conducted correctly and efficiently. Such reviews also are used to identify and resolve problems before they become widespread and potentially compromise the quality of the data.

12.1 Training

Employee training is an integral part of water-quality activities allowing current employees to maintain and enhance their technical knowledge and new employees to gain the specific skills needed to adequately perform their job. A well-documented training program not only ensures that samples are collected correctly by technically competent personnel, but also lends legal credibility to data and interpretations. Training is accomplished according to the following policies and protocols.

Individual training plans are developed by the supervisor and employee at least annually as part of the performance review process. The District Training Officer is responsible for informing District staff about the availability of training—in-house, USGS, U.S. Government, and other sources of training. The Water-Quality Specialist provides recommendations and advice to supervisors and their staff as needed. The District Chief has authority and responsibility for approving training opportunities. In addition, staff are responsible for taking full advantage of the training provided.

Primary sources of water-quality training are USGS courses, usually taught at the National Training Center at the Denver Federal Center; Central Region regional training; and District seminars or in-house training courses. The Water-Quality Specialist plays an important role in providing in-District and in-house training. Training documents are maintained by the Administrative Officer in District personnel files and by the Personnel Office in Central Region.

12.2 Reviews

Reviews of water-quality data-collection activities should be conducted annually for each individual in the District who is actively involved in water-quality data collection. Reviews are conducted in the field or laboratory by the District Water-Quality Specialist or designee.

Reviews are completed in a timely manner, and comments are provided to the immediate supervisor and the reviewee. Reviews address sample collection and processing techniques, compliance with WRD, OWQ, and District policies, the condition of the work environment (for example, the field vehicle), and any other activities pertaining to the collection of good quality data. When deficiencies are noted, the reviewer, in consultation with the Water-Quality Specialist, is responsible for identifying corrective actions. The immediate supervisor is responsible for ensuring that, once identified, corrective actions are implemented and completed in a timely manner.

13.0 References

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Arvin, D.V., 1995, A workbook for preparing surface-water quality-assurance plans for Districts of the U.S. Geological Survey, Water Resources Division: U.S. Geological Survey Open-File Report 94-382, 40 p.

Bartholoma, S.D., comp., 1997, National Water Information System user's manual, chap. 3, automated data processing system: U.S. Geological Survey Open-File Report 97-635, 219 p.

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Guy, H.P., 1969, Laboratory theory and methods for sediment analysis: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. C1, 58 p.

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13.1 USGS Memoranda (Revision 1, June 2002)

The following USGS memoranda are available electronically on the Internet at the following site address (URL) http://water.usgs.gov/admin/memo/ (or for USGS employees, http://wwwoper.er.usgs.gov/memos/wrd/auto.html).

Branch of Operations Technical Memorandum 91.01, February 5, 1991, Safety—Chemical-hygiene plan.

National Water Quality Laboratory Memorandum 92.01, March 25, 1992, Availability of equipment blank water for inorganic and organic analysis.

National Water Quality Laboratory Memorandum 95.04, December 2, 1994, Shipping samples to the National Water-Quality Laboratory.

Office of Surface Water Technical Memorandum 93.01, October 8, 1992, Summary of documentation that describes instrumentation and field methods for collecting sediment data.

Office of Water Quality Technical Memorandum 92.01, December 20, 1991, Distilled/deionized water for District operations.

Office of Water Quality Technical Memorandum 92.06, March 20, 1992, Report of committee on sample shipping integrity and cost.

Office of Water Quality Technical Memorandum 97.06, May 5, 1997 (corrected May 14, 1997), Comparison of the suspended-sediment splitting capabilities of the churn and cone splitters.

Office of Water Quality Technical Memorandum 98.03, Policy for the evaluation and approval of production analytical laboratories.

Office of Water Quality Technical Memorandum 98.05, September 14, 1998, Policy for the approval of U.S. Geological Survey (USGS) water-quality analytical methods.

Office of Water Quality Technical Memorandum 02.14, April 18, 2002, Availability of universal blank water for inorganic and organic analyses.

Teller, R.W., 2002, Chemical Hygiene Plan of the South Dakota District, U.S. Geological Survey, Rapid City, South Dakota, 45 p.

Water Resources Division Memorandum 87.085, September 18, 1987, Programs and Plans—Policy for the collection and archiving of electronically recorded data.

Water Resources Division Memorandum 90.030 (revised), March 5, 1990, Programs and Plans—Policy for release of digital data.
Water Resources Division Memorandum 92.005, December 16, 1991, Publications--Extented delegation of authority to approve reports of certain categories for release to the open file.
Water Resources Division Memorandum 92.035, April 16, 1992, Policy of the Water Resources Division on the use of laboratories.
Water Resources Division Memorandum 92.036, April 16, 1992, Policy of the Water Resources Division on the use of laboratories by national water-quality programs.
Water Resources Division Memorandum 92.059, October 20, 1992, Policy for management and retention of hydrologic data of the U.S. Geological Survey.
Water Resources Division Memorandum 95.18, March 14, 1995, Publications—Redelegation of Director's report approval authority to Regional Hydrologists.
Water Resources Division Memorandum 95.35, May 15, 1995, Programs and Plans—Transmittal of an instrumentation plan for the Water Resources Division and the hydrologic field instrumentation and equipment policy and guidelines.
Water Resources Division Memorandum 97.002, November 15, 1996, Modification to the reports processing system.

14.0 Supplementary Information—Quality-Control Profile, 2000-02

This section presents and summarizes selected water-quality quality-control data collected in the South Dakota District during water years 2000-02 (hereinafter referred to as the study period). Quality-control data discussed include analytical results for equipment blank samples, replicate samples, and matrix-spike samples. The information presented only represents part of the quality-control data collected in the South Dakota District during the study period. Results are presented for constituents and equipment that are most commonly used and thus represent fairly widespread application in South Dakota District operations and give a general overview of the adequacy of sample collection and processing procedures used in the South Dakota District. Many other quality-control data are collected for individual projects where the constituents analyzed and the equipment used are less routine. For quality-control information specific to a given project, an individual should consult the final project reports or the project chief.

Quality-control data are used to assess whether contamination is routinely introduced during sample collection and processing, and also to assess the precision and accuracy of water-quality data. Blank samples are collected to assess the extent of sample contamination. Equipment blank samples are collected by passing blank water through the sampling equipment that would normally contact the environmental water during routine sample collection and processing.

Precision refers to how well measured results can be reproduced. For water-quality samples, precision typically is assessed using field-replicate samples. Two statistics generally are used to assess precision: relative standard deviation and relative percent difference. For data sets with three or more observations (that is, primary sample/replicate sample pairs), the relative standard deviation (Taylor, 1987) is used to quantify the variability between the primary environmental samples and the field replicate samples.

$$RSD = (S/X_{bar}) * 100$$

where

RSD = relative standard deviation, in percent;

S = standard deviation of the differences between results of the primary environmental samples and the field replicate samples for all sample pairs; and

X_{bar} = mean concentration for all primary and replicate samples combined.

For data sets with less than three observations, the relative percent difference is used to quantify the variability.

$$RPD = ((ABS(X_1 - X_2))/((X_1 + X_2)/2)) * 100$$

where

RPD = relative percent difference;

ABS = absolute value;

X_1 = result for primary environmental sample; and

X_2 = result for field replicate sample.

A typical data-quality objective for field replicate samples is a maximum relative standard deviation (or relative percent difference) of 20 percent (Taylor, 1987).

Accuracy refers to how close a measured result is to the “true” value. For water-quality samples, accuracy typically is assessed using matrix-spike and/or standard reference samples. In the South Dakota District during the study period, the only quality-control samples collected to assess accuracy were matrix spike samples for selected synthetic organic constituents. For these samples, accuracy was assessed by calculating the expected concentration in the spiked sample and then calculating the percent recovery (see NWQL website http://wwwnwql.cr.usgs.gov/USGS/SpikeCalc.html) using the equations:

$$C_{expd} = (C_{soln} * V_{soln})/V_{mspsample}$$

where

C_{expd} = expected concentration in the matrix-spike sample, in µg/L;

C_{soln} = concentration in the spike solution, in µg/mL;

V_{soln} = volume of spike solution added to the environmental sample, in mL; and

$V_{mspsample}$ = volume of the matrix-spike sample, in L.

$$\text{Percent recovery} = ((C_{mspsample} - C_{envsample}) * 100)/C_{expd}$$

where

$C_{mspsample}$ = concentration in the matrix-spike sample, in µg/L;

$C_{envsample}$ = concentration in the unspike environmental sample, in µg/L;

C_{expd} = calculated expected concentration in the matrix spike sample, in µg/L.

All analyses presented were performed by NWQL. For some constituents, laboratory analyses were performed using different procedures that sometimes had different laboratory reporting limits. Also, the NWQL laboratory reporting levels for some constituents varied during the study period for some specific analytical procedures. In situations where multiple laboratory reporting limits complicated the presentation and summary of results, the largest laboratory reporting level during the study period for a given constituent was assigned to be the study reporting level for that constituent. For a given constituent, any analysis that was reported to be less than a given laboratory reporting level that was smaller than the study reporting level was assigned a value of less than the study reporting level. Also, any analysis that was reported to have a detected concentration that was less than the study reporting level was assigned a value of less than the study reporting level.

14.1 Equipment Blank Samples

Equipment blank samples are collected to determine whether contamination is introduced into samples during preparation of equipment for sampling or during sample collection and processing. Equipment blank samples are collected by passing blank water through all of the equipment that would normally contact environmental water during routine sample collection and processing. The laboratory equipment blank samples discussed in this report were collected in laboratory settings in either the Rapid City District Office or the Huron Subdistrict Office. Results for these laboratory equipment blank samples help determine whether sample contamination occurs due to foreign materials that may be on or in the sampling equipment as a result of inadequate pre-sampling cleaning procedures or may actually be introduced during pre-sampling cleaning operations. Field equipment blank samples are collected in uncontrolled field settings and help determine whether sample contamination is introduced while conducting sample collection and processing activities in various environmental conditions encountered in field.

14.1.1 Laboratory Equipment Blank Samples

Summaries of analytical results for laboratory equipment blanks collected using surface-water sampling equipment during the study period for inorganic and carbon constituents are presented in tables 14.1.1-a and 14.1.1-b, respectively. These blank samples were collected using standard surface-water isokinetic samplers, including DH81, D77TM and D95 samplers, all of which had teflon caps, nozzles, and sample bottles.

Concentrations of inorganic constituents in laboratory equipment blanks for surface-water equipment (table 14.1.1-a) were all less than the study reporting level, except for calcium, sodium, aluminum, manganese, and zinc. Calcium was detected in all of the laboratory equipment blanks, and the other detected constituents each had one sample with a detection above the study reporting level. For calcium, sodium, and manganese, the detected concentrations were well below levels typically found in environmental samples from South Dakota waters. For aluminum and zinc, the detected concentrations were at levels that may occur naturally in environmental samples from South Dakota waters. However, these detections do not substantially compromise the interpretation of water-quality sampling results because: 1) for each of these constituents, there was a low frequency of detection in the blank samples (one sample out of six), which indicates that the contamination is not routine or persistent; 2) these constituents typically are not of primary concern in water-quality issues in South Dakota; and 3) the detected concentrations were not at levels that would indicate problems related to the health of humans or aquatic organisms. Concentrations of carbon constituents in laboratory equipment blanks for surface-water equipment (table 14.1.1-b) were all less than the study reporting level. In general, the laboratory equipment blanks for surface-water equipment indicate that pre-sampling cleaning procedures used in the South Dakota District are appropriate for collection of surface-water samples.

Table 14.1.1-a Summaries of analytical results for filtered[1] inorganic constituents for laboratory equipment blanks collected using surface-water sampling equipment during water years 2000-02

Constituent	Number of samples	Number of detections greater than the study reporting level	Maximum	Median	Minimum
Calcium, in mg/L	6	6	0.034	0.008	0.002
Magnesium, in mg/L	6	0	<.008	<.008	<.008
Sodium, in mg/L	6	1	0.11	<.09	<.09
Silica, in mg/L	6	0	<.13	<.13	<.13
Ammonia, in mg/L as nitrogen	6	0	<.015	<.015	<.015
Nitrite plus nitrate, in mg/L as nitrogen	6	0	<.013	<.013	<.013
Nitrite, in mg/L as nitrogen	6	0	<.002	<.002	<.002
Orthophosphate, in mg/L as phosphorus	6	0	<.007	<.007	<.007
Aluminum, in µg/L	6	1	1	<1	<1
Antimony, in µg/L	6	0	<.2	<.2	<.2
Arsenic, in µg/L	6	0	<.2	<.2	<.2
Barium, in µg/L	6	0	<1	<1	<1
Beryllium, in µg/L	6	0	<.2	<.2	<.2
Boron, in µg/L	6	0	<2	<2	<2
Cadmium, in µg/L	6	0	<.3	<.3	<.3
Chromium, in µg/L	6	0	<.8	<.8	<.8
Cobalt, in µg/L	6	0	<.2	<.2	<.2
Copper, in µg/L	6	0	<.2	<.2	<.2
Iron, in µg/L	6	0	<10	<10	<10
Lead, in µg/L	6	0	<.3	<.3	<.3
Lithium, in µg/L	6	0	<.3	<.3	<.3
Manganese, in µg/L	6	1	0.1	<.1	<.1
Molybdenum, in µg/L	6	0	<.2	<.2	<.2
Nickel, in µg/L	6	0	<.5	<.5	<.5
Selenium, in µg/L	6	0	<.3	<.3	<.3
Silver, in µg/L	6	0	<1	<1	<1
Strontium, in µg/L	6	0	<.1	<.1	<.1
Thallium, in µg/L	6	0	<.1	<.1	<.1
Uranium, in µg/L	6	0	<.2	<.2	<.2
Vanadium, in µg/L	6	0	<.2	<.2	<.2
Zinc, in µg/L	6	1	9.7	<1	<1

[1]All samples were filtered using a Gelman 0.45-µm pore-size capsule filter.

Table 14.1.1-b Analytical results for suspended[1] and filtered[2] carbon constituents for a single laboratory equipment blank collected using surface-water sampling equipment during water years 2000-02

Constituent	Concentration
Carbon, inorganic plus organic, suspended, in mg/L	<.1
Carbon, inorganic, suspended, in mg/L	<.1
Carbon, organic, suspended, in mg/L	<.1
Carbon, organic, filtered, in mg/L	<.1

[1]Suspended refers to particulate matter retained on a 0.7-µm marginal pore-size glass fiber filter.

[2]All samples were filtered by passing the sample through a 0.7-µm marginal pore-size glass fiber filter.

Analytical results for laboratory equipment blanks for ground-water sampling equipment collected in the South Dakota District during the study period for filtered inorganic constituents and properties are presented in table 14.1.1-c. These equipment blanks were collected using a Grunfos submersible pump with stainless steel fittings and plastic tubing.

Table 14.1.1-c Summaries of analytical results for filtered[1] inorganic constituents for laboratory equipment blanks collected using ground-water sampling equipment during water years 2000-02

Constituent	Number of samples	Number of detections greater than the study reporting level	Maximum	Median	Minimum
Specific conductance, in µS/cm	2	2	2	2.000	2
Calcium, in mg/L	4	1	0.020	<.01	<.01
Magnesium, in mg/L	4	0	<.008	<.008	<.008
Potassium, in mg/L	1	0	<.09	<.09	<.09
Sodium, in mg/L	4	0	<.09	<.09	<.09
Alkalinity, in mg/L as $CaCO_3$	2	2	2.00	2.000	2.00
Chloride, in mg/L	1	0	<.08	<.08	<.08
Fluoride, in mg/L	1	0	<.2	<.2	<.2
Silica, in mg/L	4	0	<.13	<.13	<.13
Sulfate, in mg/L	1	0	<.1	<.1	<.1
Dissolved solids, residue on evaporation at 180 deg. C, in mg/L	1	0	<10	<10	<10
Ammonia, in mg/L as nitrogen	4	0	<.015	<.015	<.015
Nitrite plus nitrate, in mg/L as nitrogen	4	1	0.5	<.013	<.013
Nitrite, in mg/L as nitrogen	3	0	<.002	<.002	<.002
Orthophosphate, in mg/L as phosphorus	4	0	<.007	<.007	<.007
Phosphorus, in mg/L	1	1	0.004	0.004	0.004
Aluminum, in µg/L	3	0	<1	<1	<1
Antimony, in µg/L	3	0	<.2	<.2	<.2
Arsenic, in µg/L	3	0	<.2	<.2	<.2
Barium, in µg/L	3	0	<1	<1	<1
Beryllium, in µg/L	3	0	<.2	<.2	<.2
Boron, in µg/L	3	0	<7	<7	<7
Cadmium, in µg/L	3	0	<.3	<.3	<.3
Chromium, in µg/L	3	0	<.8	<.8	<.8
Cobalt, in µg/L	3	0	<.2	<.2	<.2
Copper, in µg/L	3	0	<.2	<.2	<.2
Iron, in µg/L	4	0	<10	<10	<10
Lead, in µg/L	3	0	<.3	<.3	<.3
Lithium, in µg/L	1	0	<.3	<.3	<.3
Manganese, in µg/L	4	0	<3.2	<3.2	<3.2
Molybdenum, in µg/L	3	0	<.2	<.2	<.2
Nickel, in µg/L	3	0	<.5	<.5	<.5
Selenium, in µg/L	3	0	<.3	<.3	<.3
Silver, in µg/L	3	0	<1	<1	<1
Strontium, in µg/L	3	0	<.1	<.1	<.1
Thallium, in µg/L	3	0	<.1	<.1	<.1
Uranium, in µg/L	3	0	<.2	<.2	<.2
Vanadium, in µg/L	1	0	<.2	<.2	<.2
Zinc, in µg/L	3	0	<1	<1	<1

[1]All samples were filtered using a Gelman 0.45-µm pore-size capsule filter.

Concentrations and measurements of inorganic constituents and properties in laboratory equipment blanks for ground-water equipment (table 14.1.1-c) were all less than the study reporting level, except for specific conductance, calcium, alkalinity, nitrite plus nitrate nitrogen, and phosphorus. Specific conductance, alkalinity, and phosphorus occurred at levels above the study reporting level for all samples, but these levels were well below what is typically found in South Dakota waters. Calcium and nitrite plus nitrate nitrogen each were detected in one out of four samples. The detected concentration for calcium was well below what is typically found in South Dakota waters. The detected concentration for nitrite plus nitrate nitrogen was at a level that may occur naturally in environmental samples from South Dakota waters. However, the relatively low frequency of detection for nitrite plus nitrate nitrogen and the relatively small concentration that was detected indicates that the contamination is not routine or persistent and probably does not compromise interpretation of water-quality sampling results. In general, the laboratory equipment blanks for ground-water equipment indicate that pre-sampling cleaning procedures used in the South Dakota District are appropriate for collection of ground-water samples.

14.1.2 Field Equipment Blank Samples

Summaries of analytical results for field equipment blanks collected using surface-water sampling equipment in the South Dakota District during the study period for inorganic, carbon, and synthetic organic constituents are presented in tables 14.1.2-a, 14.1.2-b, and 14.1.2-c, respectively. These blank samples were collected using standard surface-water isokinetic samplers, including DH81, D77TM and D95 samplers, all of which had teflon caps, nozzles, and sample bottles.

Concentrations and measurements of inorganic constituents and properties in field equipment blanks for surface-water equipment (table 14.1.2-a) were all less than the study reporting level, except for specific conductance, calcium, magnesium, alkalinity, silica, dissolved solids (residue on evaporation at 180 degrees C), ammonia nitrogen, antimony, molybdenum, vanadium, and zinc. Concentrations or measurements above the study reporting level for specific conductance, calcium, magnesium, alkalinity, dissolved solids occurred at levels that were well below what is typically found in South Dakota waters. The detected concentration for ammonia nitrogen was at a level that may occur naturally in environmental samples from South Dakota waters. However, the low frequency of detection (one out of 14 samples) and the relatively small concentration that was detected indicates that the contamination is not routine or persistent and probably does not compromise interpretation of water-quality sampling results. Antimony, molybdenum, and vanadium had low frequencies of detection (one out of seven samples, each) and all of these detections were at or very near the study reporting level. Zinc had a higher frequency of detection (three out of seven samples) but all of the detections were at the study reporting level.

Concentrations of carbon constituents in field equipment blanks for surface-water equipment (table 14.1.2-b) were all less than the study reporting level, except for organic carbon in filtered samples (commonly referred to as dissolved organic carbon). Dissolved organic carbon had a relatively low frequency of detection (one out of four samples) and the concentration was at a level below what is typically found in South Dakota waters. Concentrations of synthetic organic constituents in field equipment blanks for surface-water equipment (table 14.1.2-c) were all less than the study reporting level.

In general, the field equipment blanks for surface-water equipment indicate that sample collection and processing procedures used in the South Dakota District are appropriate for collection of surface-water samples.

Table 14.1.2-a Summary of analytical results for filtered[1] and unfiltered inorganic constituents for field equipment blanks collected using surface-water sampling equipment during water years 2000-02

Constituent	Number of samples	Number of detections greater than the study reporting level	Maximum	Median	Minimum
Specific conductance, in µS/cm	18	15	9	4	<3
Calcium, filtered, in mg/L	18	11	0.02	0.02	<.01
Magnesium, filtered, in mg/L	18	1	0.016	<.014	<.014
Potassium, filtered, in mg/L	9	0	<.24	<.24	<.24
Sodium, filtered, in mg/L	16	0	<.09	<.09	<.09
Alkalinity, unfiltered, in mg/L	8	8	2	2	1
Chloride, filtered, in mg/L	9	0	<.30	<.30	<.30
Fluoride, filtered, in mg/L	9	0	<.2	<.2	<.2
Silica, filtered, in mg/L	16	1	0.5	<.5	<.5
Sulfate, filtered, in mg/L	12	0	<.3	<.3	<.3
Dissolved solids, residue on evaporation at 180 deg. C, in mg/L	7	2	22	<10	<10
Ammonia plus organic nitrogen, unfiltered, in mg/L	7	0	<.10	<.10	<.10
Ammonia nitrogen, filtered, in mg/L	14	1	0.1	<.04	<.04
Nitrite plus nitrate nitrogen, filtered, in mg/L	14	0	<.05	<.05	<.05
Nitrite nitrogen, filtered, in mg/L	13	0	<.010	<.010	<.010
Orthophosphate phosphorus, filtered, in mg/L	14	0	<.02	<.02	<.02
Phosphorus, unfiltered, in mg/L	7	0	<.06	<.06	<.06
Aluminum, filtered, in µg/L	7	0	<1	<1	<1
Antimony, filtered, in µg/L	7	1	0.51	<.30	<.30
Arsenic, filtered, in µg/L	19	0	<.3	<.3	<.3
Barium, filtered, in µg/L	6	0	<.2	<.2	<.2
Beryllium, filtered, in µg/L	7	0	<.2	<.2	<.2
Boron, filtered, in µg/L	8	0	<7	<7	<7
Cadmium, filtered, in µg/L	13	0	<.3	<.3	<.3
Chromium, filtered, in µg/L	8	0	<.8	<.8	<.8
Cobalt, filtered, in µg/L	7	0	<.2	<.2	<.2
Copper, filtered, in µg/L	13	0	<1.0	<1.0	<1.0
Iron, filtered, in µg/L	10	0	<10	<10	<10
Lead, filtered, in µg/L	13	0	<1	<1	<1
Lithium, filtered, in µg/L	7	0	<.5	<.5	<.5
Manganese, filtered, in µg/L	8	0	<3.0	<3.0	<3.0
Molybdenum, filtered, in µg/L	7	1	0.3	<.3	<.3
Nickel, filtered, in µg/L	7	0	<.5	<.5	<.5
Selenium, filtered, in µg/L	19	0	<2	<2	<2
Silver, filtered, in µg/L	12	0	<1	<1	<1
Strontium, filtered, in µg/L	9	0	<.20	<.20	<.20
Thallium, filtered, in µg/L	6	0	<.1	<.1	<.1
Uranium, filtered, in µg/L	7	0	<.02	<.02	<.02
Vanadium, filtered, in µg/L	7	1	0.2	<.2	<.2
Zinc, filtered, in µg/L	7	3	1	<1	<1

[1]Specified samples were filtered using a Gelman 0.45-µm pore-size capsule filter.

Table 14.1.2-b Summary of analytical results for suspended[1] and filtered[2] carbon constituents for field equipment blanks collected using surface-water sampling equipment during water years 2000-02

Constituent	Number of samples	Number of detections greater than the study reporting level	Maximum	Median	Minimum
Carbon, inorganic plus organic, suspended, in mg/L	3	0	<.1	<.1	<.1
Carbon, inorganic, suspended, in mg/L	3	0	<.1	<.1	<.1
Carbon, organic, suspended, in mg/L	4	0	<.1	<.1	<.1
Carbon, organic, filtered, in mg/L	4	1	0.6	<.3	<.3

[1]Suspended refers to particulate matter retained on a 0.7-µm marginal pore-size glass fiber filter.

[2]Specified samples were filtered by passing the sample through a 0.7-µm marginal pore-size glass fiber filter.

Table 14.1.2-c Summary of analytical results for filtered[1] synthetic organic constituents for field equipment blanks collected using surface-water sampling equipment during water years 2000-02

Constituent	Number of samples	Number of detections greater than the study reporting level	Study reporting level, in µg/L
2,6-Diethylaniline	5	0	0.006
Deethyl atrazine	5	0	0.006
Acetochlor	5	0	0.006
Alachlor	5	0	0.004
Alpha BHC	5	0	0.005
Atrazine	5	0	0.007
Methyl azinphos	5	0	0.05
Benfluralin	5	0	0.01
Butylate	5	0	0.002
Carbaryl	5	0	0.041
Carbofuran	5	0	0.02
Chlorpyrifos	5	0	0.005
Permethrin, cis	5	0	0.006
Cyanazine	5	0	0.018
DCPA	5	0	0.003
Diazinon	5	0	0.005
Dieldrin	5	0	0.005
Disulfoton	5	0	0.02
EPTC	5	0	0.002
Ethalfluralin	5	0	0.009
Ethoprop	5	0	0.005
Fonofos	5	0	0.003
Lindane	5	0	0.004
Linuron	5	0	0.035
Malathion	5	0	0.027
Methyl parathion	5	0	0.006
Metolachlor	5	0	0.013
Metribuzin	5	0	0.006
Molinate	5	0	0.004
Napropamide	5	0	0.007
P,P' DDE	5	0	0.006
Parathion	5	0	0.01
Pebulate	5	0	0.004
Pendimethalin	5	0	0.022
Phorate	5	0	0.011
Prometon	5	0	0.02
Pronamide	5	0	0.004
Propachlor	5	0	0.01
Propanil	5	0	0.011
Propargite	5	0	0.02
Simazine	5	0	0.011

Table 14.1.2-c Summary of analytical results for filtered[1] synthetic organic constituents for field equipment blanks collected using surface-water sampling equipment during water years 2000-02 (Cont.)

Constituent	Number of samples	Number of detections greater than the study reporting level	Study reporting level, in µg/L
Tebuthiuron	5	0	0.02
Terbacil	5	0	0.034
Terbufos	5	0	0.02
Thiobenca	5	0	0.005
Triallate	5	0	0.002
Trifluralin	5	0	0.009

[1]All samples were filtered by passing the sample through a 0.7-µm marginal pore-size glass fiber filter.

Summaries of analytical results for a single field equipment blank collected using ground-water sampling equipment in the South Dakota District during the study period for inorganic constituents are presented in tables 14.1.2-d. This equipment blank was collected using a Grunfos submersible pump with stainless steel fittings and plastic tubing. Concentrations and measurements of inorganic constituents were all less than the study reporting level, except for specific conductance, calcium, magnesium, alkalinity, dissolved solids, chromium, manganese, and zinc. Concentrations or measurements above the study reporting level for specific conductance, calcium, magnesium, alkalinity, dissolved solids occurred at levels that were well below what is typically found in South Dakota waters. The detected concentrations for chromium, manganese, and zinc were at levels that may occur naturally in environmental samples from South Dakota ground water. The single field equipment blank collected using ground-water sampling equipment also was analyzed for the organic constituents shown in table 14.1.2-c, and all constituents were determined to be less than the laboratory reporting levels. The single field equipment blank sample for ground-water equipment does not allow thorough assessment of the adequacy of sampling procedures used in the South Dakota District to collect ground water samples. The limited results may suggest that caution should be used when interpreting results for some dissolved metal constituents, including chromium, manganese, and zinc. Additional field equipment blanks using ground-water sampling equipment need to be collected.

Table 14.1.2-d Analytical results for filtered[1] and unfiltered inorganic constituents for a single field equipment blank collected using ground-water sampling equipment during water years 2000-02

[E, estimated]

Constituent	Concentration
Specific conductance, in µS/cm	3
Calcium, filtered, in mg/L	0.21
Magnesium, filtered, in mg/L	0.046
Potassium, filtered, in mg/L	<.24
Sodium, filtered, in mg/L	<.09
Alkalinity, unfiltered, in mg/L	2
Chloride, filtered, in mg/L	<.30
Fluoride, filtered, in mg/L	<.2
Silica, filtered, in mg/L	<.5
Sulfate, filtered, in mg/L	<.3
Dissolved solids, residue on evaporation at 180 deg. C, in mg/L	16
Ammonia plus organic nitrogen, unfiltered, in mg/L	<.10
Ammonia nitrogen, filtered, in mg/L	<.04
Nitrite plus nitrate nitrogen, filtered, in mg/L	<.05
Nitrite nitrogen, filtered, in mg/L	<.010
Orthophosphate phosphorus, filtered, in mg/L	<.02
Phosphorus, unfiltered, in mg/L	<.06
Arsenic, filtered, in µg/L	<2
Cadmium, filtered, in µg/L	<.3
Chromium, filtered, in µg/L	0.9
Copper, filtered, in µg/L	<1.0
Iron, filtered, in µg/L	<10
Lead, filtered, in µg/L	<1
Manganese, filtered, in µg/L	10.1
Selenium, filtered, in µg/L	<2
Zinc, filtered, in µg/L	54

[1]Specified samples were filtered using a Gelman 0.45-µm pore-size capsule filter.

14.2 Field Replicate Samples

Summaries of precision information for field replicate samples collected using surface-water sampling equipment in the South Dakota District during the study period for inorganic, carbon constituents (plus UV absorbance and chlorophyll-a), and synthetic organic constituents are presented in tables 14.2-a, 14.2-b, and 14.2-c, respectively.

All inorganic constituents had relative standard deviations of less than 20 percent except ammonia nitrogen, nitrite nitrogen, and selenium (table 14.2-a). For all of these constituents, the large relative standard deviations primarily were due to the fact that these constituents in South Dakota waters typically occur in very low concentrations that are only slightly larger than laboratory reporting levels, and sometimes actually are below laboratory reporting levels, but are reported as estimated values. At these low concentrations, relatively small differences in concentrations between primary environmental samples and replicate samples can result in large relative standard deviations, but have very little environmental significance. For example, for the 12 primary/replicate sample pairs for ammonia nitrogen, the average concentration was 0.027 mg/L, and the standard deviation of the differences was 0.010 mg/L. Most of the analytical results were reported as estimated values that were less than the most frequent laboratory reporting level of 0.04 mg/L. Thus, although the relative standard deviation for ammonia nitrogen was relatively large it does not indicate important differences between the primary and replicate samples. Similar principles also apply to the large relative standard deviation results reported for nitrite nitrogen and selenium.

Carbon constituents (plus UV absorbance and chlorophyll-a) generally had relative standard deviations or average relative percent differences that were less than 20 percent (table 14.2-b). Unfiltered organic carbon (commonly referred to as total organic carbon) and chlorophyll-a had average relative percent differences that were slightly larger than 20 percent. However, the small number of primary/replicate sample pairs for these constituents does not allow detailed assessment of the quality control data. For synthetic organic constituents (table 14.2-c), precision information is only reported for constituents with some concentrations greater than the study reporting level. All of these constituents had relative standard deviations that were less than 20 percent.

In general, the field replicate samples for surface-water equipment show good precision and indicate that sample collection and processing procedures used in the South Dakota District result in reproducible results.

Table 14.2-a Summary of precision information for filtered[1] and unfiltered inorganic constituents for field replicate samples collected using surface-water sampling equipment during water years 2000-02

Constituent	Number of replicate samples	Relative standard deviation, n percent	Average relative percent difference
pH, in standard units	15	1.3	
Specific conductance, in µS/cm	15	1.1	
Calcium, filtered, in mg/L	11	1.9	
Magnesium, filtered, in mg/L	11	2.0	
Potassium, filtered, in mg/L	8	2.4	
Sodium, filtered, in mg/L	10	3.0	
Alkalinity, unfiltered, in mg/L	10	1.0	
Chloride, filtered, in mg/L	10	2.7	
Fluoride, filtered, in mg/L	8	8.2	
Silica, filtered, in mg/L	10	2.0	
Sulfate, filtered, in mg/L	10	1.0	
Dissolved solids, residue on evaporation at 180 deg. C, in mg/L	7	0.8	
Ammonia plus organic nitrogen, filtered, in mg/L	6	12.7	
Ammonia plus organic nitrogen, unfiltered, in mg/L	9	5.1	
Ammonia nitrogen, filtered, in mg/L	12	36.1	
Nitrite plus nitrate nitrogen, filtered, in mg/L	12	7.7	
Nitrite nitrogen, filtered, in mg/L	12	28.2	
Orthophosphate phosphorus, filtered, in mg/L	12	6.6	
Phosphorus, filtered, in mg/L	12	6.8	
Phosphorus, unfiltered, in mg/L	12	6.0	
Aluminum, filtered, in µg/L	3	2.3	
Antimony, filtered, in µg/L	3	11.8	
Arsenic, filtered, in µg/L	12	5.7	
Arsenic, unfiltered, in µg/L	3	16.0	

Table 14.2-a Summary of precision information for filtered[1] and unfiltered inorganic constituents for field replicate samples collected using surface-water sampling equipment during water years 2000-02 (Cont.)

Constituent	Number of replicate samples	Relative standard deviation, n percent	Average relative percent difference
Barium, filtered, in µg/L	3	1.2	
Beryllium, filtered, in µg/L	3	0.0	
Boron, filtered, in µg/L	4	5.4	
Cadmium, filtered, in µg/L	6	4.7	
Cadmium, unfiltered, in µg/L	3	1.4	
Chromium, filtered, in µg/L	3	0.0	
Chromium, unfiltered, in µg/L	3	0.0	
Cobalt, filtered, in µg/L	3	0.8	
Copper, filtered, in µg/L	6	3.1	
Copper, unfiltered, in µg/L	3	4.1	
Cyanide, filtered, in mg/L	2	0.0	
Cyanide, unfiltered, in mg/L	3	0.0	
Iron, filtered, in µg/L	6	5.3	
Iron, unfiltered, in µg/L	6	3.0	
Lead, filtered, in µg/L	6	8.5	
Lead, unfiltered, in µg/L	3	0.0	
Lithium, filtered, in µg/L	5	3.3	--
Manganese, filtered, in µg/L	3	15.7	--
Manganese, unfiltered, in µg/L	3	6.4	--
Mercury, filtered, in µg/L	5	17.5	--
Mercury, unfiltered, in µg/L	3	0.0	--
Molybdenum, filtered, in µg/L	3	1.4	--
Nickel, filtered, in µg/L	3	13.7	--
Nickel, unfiltered, in µg/L	3	0.0	--
Selenium, filtered, in µg/L	12	25.7	--
Selenium, unfiltered, in µg/L	3	5.0	--
Silver, filtered, in µg/L	6	0.0	--
Silver, unfiltered, in µg/L	2	--	0.0
Strontium, filtered, in µg/L	5	2.7	--
Uranium, filtered, in µg/L	3	1.2	--
Vanadium, filtered, in µg/L	5	1.8	--
Zinc, filtered, in µg/L	3	19.2	--
Zinc, unfiltered, in µg/L	3	9.6	--

[1]Specified samples were filtered using a Gelman 0.45-µm pore-size capsule filter.

Table 14.2-b Summary of precision information for suspended[1] and filtered[2] carbon constituents (plus UV absorbance and chlorophyll-a) for field replicate samples collected using surface-water sampling equipment

Constituent	Number of replicate samples	Relative standard deviation, in percent	Average relative percent difference
UV absorbance (254 nm wavelength)	3	0.7	
UV absorbance (280 nm wavelength)	3	0.0	
Carbon, inorganic plus organic, suspended, in mg/L	2		4.0
Carbon, inorganic, suspended, in mg/L	2		0.0
Carbon, organic, suspended, in mg/L	3	6.5	
Carbon, organic, filtered, in mg/L	5	1.8	
Carbon, organic, unfiltered, in mg/L	2		21.9
Chlorophyll-a, in µg/L	2		23.1

[1]Suspended refers to particulate matter retained on a 0.7-µm marginal pore-size glass fiber filter.

[2]Specified samples were filtered by passing the sample through a 0.7-µm marginal pore-size glass fiber filter.

Table 14.2-c Summary of precision information for detected filtered[1] synthetic organic constituents for field replicate samples collected using surface-water sampling equipment

Constituent	Number of replicate samples	Relative standard deviation, in percent
Deethyl atrazine	5	3.0
Acetochlor	5	7.6
Atrazine	5	5.8
EPTC	4	15.3
Prometon	5	0.0
Simazine	5	17.0

[1]All samples were filtered by passing the sample through a 0.7-µm marginal pore-size glass fiber filter.

A relatively small number of field replicate samples were collected using ground-water sampling equipment in the South Dakota District during the study period. These samples were analyzed for constituents not routinely analyzed for in the District, including isotopes and volatile organic constituents. Precision information for these quality-control data can be accessed by contacting the project chiefs.

14.3 Matrix Spike Samples

Summaries of analytical results for field matrix-spike samples collected using surface-water sampling equipment in the South Dakota District during the study period results for organic constituents are presented in tables 14.3-a. These percent recovery data generally are within typical ranges reported for these constituents, and indicate that the sample collection and processing procedures used in the South Dakota District are appropriate for collection of surface-water samples.

Table 14.3-a Summary of accuracy information for filtered[1] organic constituents for field matrix-spike samples collected using surface-water sampling equipment during water years 2000-02

Constituent	Number of spike samples	Maximum recovery, in percent	Median recovery, in percent	Minimum recovery, in percent
2,6-Diethylaniline	8	131.09	104.13	82.07
Deethyl atrazine	8	93.15	48.79	33.00
Acetochlor	8	160.62	138.58	106.71
Alachlor	8	154.02	134.86	117.71
Alpha BHC	8	142.47	107.19	86.91
Atrazine	8	445.54	140.85	118.95
Methyl azinphos	8	261.28	190.24	100.76
Benfluralin	8	126.51	97.32	72.63
Butylate	8	190.32	129.85	100.74
Carbaryl	8	337.79	114.22	28.80
Carbofuran	8	200.75	126.76	72.28
Chlorpyrifos	8	125.14	95.65	83.70
Cyanazine	8	177.12	132.95	109.47
DCPA	8	140.81	118.49	98.50
Diazinon	8	143.01	117.05	100.11
Dieldrin	8	161.72	111.56	101.21
Disulfoton	6	99.01	84.52	44.00
EPTC	8	127.61	108.78	94.74
Ethalfluralin	8	151.82	102.59	82.63
Ethoprop	8	143.56	108.50	98.05
Fonofos	8	142.47	113.05	94.06
Lindane	8	157.10	106.18	86.91
Linuron	8	206.52	124.17	85.37
Malathion	8	123.76	84.07	39.67
Methyl parathion	8	151.82	131.24	93.32
Metolachlor	8	156.22	137.36	105.61
Metribuzin	8	144.11	103.08	87.76
Molinate	8	138.61	112.54	99.68
Napropamide	8	396.59	143.32	112.94
P,P' DDE	8	111.11	79.86	63.63
Parathion	8	200.22	122.14	30.34
Pebulate	8	134.21	115.79	102.86
Pendimethalin	8	183.72	121.44	87.37
Phorate	6	135.31	94.04	71.51
Prometon	7	143.01	124.05	107.07
Pronamide	8	151.27	114.97	102.86
Propachlor	8	171.07	138.09	116.65
Propanil	8	168.32	139.32	111.05
Propargite	8	200.00	135.90	103.26
Simazine	8	140.81	108.81	67.71
Tebuthiuron	7	244.57	148.46	105.26
Terbacil	8	150.17	132.73	62.84
Terbufos	6	115.51	83.42	73.68
Thiobenca	8	145.21	127.78	101.21
Triallate	8	135.86	116.59	99.56
Trifluralin	8	135.31	103.14	75.26

[1]All samples were filtered by passing the sample through a 0.7-µm marginal pore-size glass fiber filter.

14.4 Standard Reference Samples for Field Measurements

The South Dakota District participates in the USGS National Field Quality Assurance program (NFQA) administered by the USGS Ocala Water-Quality and Research Laboratory. Standard reference samples for alkalinity, pH, and specific conductance are analyzed by field personnel on an annual basis. Detailed information about the NFQA program is available on the internet at http://owqrl.er.usgs.gov/nfqa/nfqa.asp. NFQA results for the study period are summarized in table 14.4-a. In general, the South Dakota District has performed at a level comparable with the USGS Central Region as a whole. However, the South Dakota District performed poorly on alkalinity measurements for the 2002 NFQA sampling round. A large number of the alkalinity measurements performed in the Huron Subdistrict Office were unacceptable. All of these measurements were made using the same pH meter and probe. This pH meter/probe combination had not been used for a long time, and it was determined that the probe was not functioning properly. This pH meter/probe combination had not been used for actual field measurements for quite some time. Also, all of the unsatisfactory alkalinity measurements for the 2002 NFQA sampling round were made by personnel who do not routinely make alkalinity measurements in the field. To resolve the poor performance on the 2002 NFQA alkalinity measurements, the faulty pH probe was replaced. Also, it was decided that individuals that do not routinely make field alkalinity measurements would no longer be required to run NFQA alkalinities. As a result of these measures, the South Dakota District achieved 100% acceptable results for all field-measurement parameters in the NFQA results for 2003. The NFQA data indicate that methods used by the South Dakota District for field measurements are appropriate.

Table 14.4-a Summary of National Field Quality Assurance program results for field measurements for the South Dakota District for water years 2000-02

NFQA sample round	Percent acceptable results for South Dakota District (percent acceptable results for all of USGS Central Region shown in parentheses)		
	Alkalinity	pH	Specific conductance
2000	100% (95.0%)	100% (98.0%)	100% (98.4%)
2001	95.8% (94.1%)	97.8% (99.8%)	98.3% (98.1%)
2002	65.0% (94.6%)	100% (99.3%)	94.4% (96.5%)

14.5 Reference

Taylor, J.K., Quality assurance of chemical measurements: Chelsea, Mich., Lewis Publishers, 328 p.