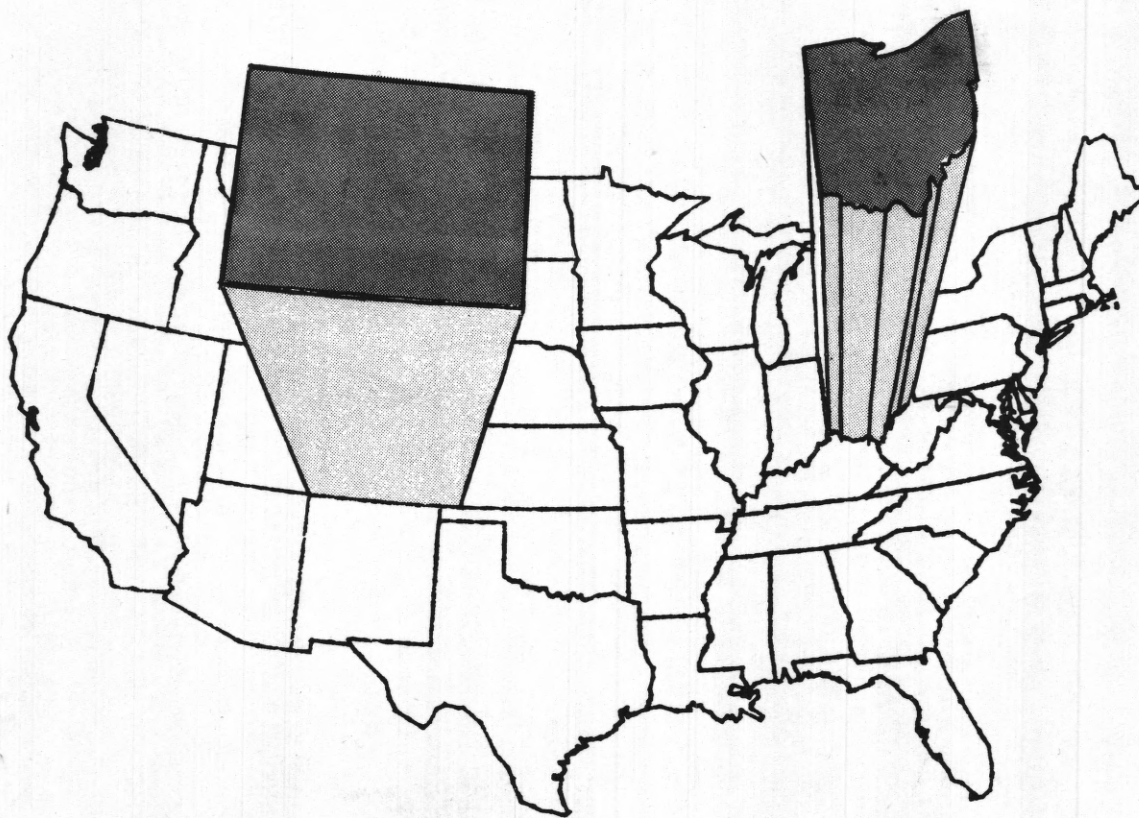


# WATER-QUALITY DATA-COLLECTION ACTIVITIES IN COLORADO AND OHIO: PHASE II--EVALUATION OF 1984 FIELD AND LABORATORY QUALITY-ASSURANCE PRACTICES

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U.S. GEOLOGICAL SURVEY

OPEN-FILE REPORT 87-33







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By Carolyn J. Oblinger Childress, Thomas H. Chaney, Donna Myers,  
J. Michael Norris, and Janet Hren

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Columbus, Ohio

1987

DEPARTMENT OF THE INTERIOR  
DONALD PAUL HODEL, Secretary  
U.S. GEOLOGICAL SURVEY  
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## FOREWORD

One of the great challenges faced by the Nation's water-resources scientists is the need for reliable information that will guide the protection of our water resources. That challenge is being addressed by Federal, State, interstate, and local water-resource agencies, and by academic institutions. Many of these agencies are collecting water-quality data for a host of purposes, including compliance with permits and water-supply standards; development of remediation plans for specific contamination problems; operational decisions on industrial, wastewater, or water-supply facilities; and research on water quality. Prominent is the need for information of regional and national scope, and on the trends and causes of water-quality conditions. Without this information, policy decisions may be based on information from a few localized problems. Conversely, a lack of information may lead to a false sense that some problems do not exist. In the past two decades, billions of dollars have been spent on water-quality data-collection programs. However, only a small part of the data collected for these programs has been obtained specifically to assess the status, trends, and causes of water-quality conditions on regional and national scales. Also, in some instances, the utility of these data for present and future regional and national assessments is limited by such factors as the areal extent of the sampling network, frequency of sample collection, and the types of water-quality characteristics determined.

Water-quality data collected for permits and for compliance and enforcement purposes constitute a sizable source of information that may be suitable for regional and national assessments. Such data must, however, be carefully screened before use. The needs, uses, and types of water-quality data vary widely, and data collected for one purpose are not necessarily suitable for other purposes. In fact, the use of unsuitable data in regional or national assessments can be much worse than a lack of information, because the use of such data can lead to incorrect conclusions having far-reaching consequences.

Accordingly, the U.S. Geological Survey, with cooperation from other agencies and from universities, has undertaken a three-phase study in Colorado and Ohio to determine the characteristics of existing Federal and other public-agency water-quality data-collection programs and to evaluate the suitability of the data bases from these programs for use in water-quality assessments of regional and national scope. This report describes results of the second phase of the study. This study does not imply that past and present data-collection programs have failed or are inappropriate for their intended purposes. The data from those programs may fully meet individual agency needs and fulfill their mandated requirements, yet may have only limited relevance to water-quality questions of regional and national scope.

This study has depended heavily on cooperation and information from many Federal, State, regional, and local agencies and academic institutions. The assistance and suggestions of all are gratefully acknowledged.

A handwritten signature in black ink, appearing to read "Philip Cohen". The signature is fluid and cursive, with the first name "Philip" and last name "Cohen" clearly distinguishable.

Philip Cohen  
Chief Hydrologist

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## CONVERSION FACTORS

For the benefit of readers who prefer to use metric (International System) units, conversion factors for inch-pound units used this report are listed below:

<u>Multiply inch-pound unit</u>	<u>By</u>	<u>To obtain metric unit</u>
inch (in.)	25.4	millimeter (mm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
cubic foot per second (ft <sup>3</sup> /s)	28.32	liter per second (L/s)
million gallons per day (Mgal/d)	0.04381	cubic meter per second (m <sup>3</sup> /s)



## GLOSSARY

The following are definitions of selected technical terms as they are used in this report; they are not necessarily the only valid definitions for these terms. Terms defined in the glossary are in **bold print** where first used in the main body of this report.

**Accuracy**.--The degree of agreement of the value, obtained by using a specific analytical method or procedure, with the true value. The concept of accuracy includes both bias (systematic error) and precision (random error).

**Ambient water-quality conditions**.--The general, prevailing physical, chemical, and biological characteristics of water in a given stream reach or part of an aquifer. Ambient water-quality conditions may or may not include effects from human activities.

**Analyte**.--A substance or chemical compound to be determined by field or laboratory analysis.

**Bias**.--A tendency for estimated or measured values to be predominantly more than or less than the true value.

**Calibration**.--The adjusting and checking of a measuring instrument to assure accurate readings.

**Control sample**.--A sample containing a predetermined amount of the substance of interest; used to monitor the quality of an analysis by assessing precision or bias, or both.

**In situ**.--In the original location or position; refers to measurements made while instrument sensors are in the water body being studied.

**Interlaboratory testing**.--The distribution and testing of control samples among laboratories conducting similar types of work, for a variety of purposes including validation of a method, proficiency testing, or collaborative testing.

**Intralaboratory testing**.--Testing, within one laboratory, of control samples (the characteristics of which are not known to the analyst) for the purpose of providing an objective assessment of quality-control activities.

**Organic substances**.--Any compound containing carbon linked in chains or rings, usually containing hydrogen, oxygen, or nitrogen; for example, phenols, polychlorinated biphenyls, methylene-blue-active substances, and atrazine.



Percent recovery.-- A measure of the amount of a substance previously added to a sample that is reclaimed through analysis of the sample, expressed as a percent. Percent recovery is used to determine the degree of bias in the analytical measurement.

Precision.--The degree of agreement of repeated measurements of a homogeneous sample expressed in terms of the variance of those measurements about the mean.

Property.--A characteristic of water such as temperature, pH, turbidity, and specific conductance.

Quality assurance.--A program of testing that encompasses all facets of data collection, laboratory analysis, and reporting to establish the reliability of results.

Quality control.--The routine use of specific procedures to define the level of quality and reliability of a specific analytical or measurement activity.

Reference material.--A substance for which the composition and properties are established, which is used to calibrate a chemical analyzer or to validate an analytical or measurement process.

Sediment.--Fragmental material that originates from disintegration of rocks and biological material and is transported by or suspended in water or that has been deposited by water.

Spiked sample.--A sample to which a known amount of a constituent has been added for the purpose of determining how accurately the constituent can be measured.

Standard additions, method of.--A laboratory technique in which different known amounts of a constituent of interest are added to equal volumes of sample for the purpose of determining the concentration of the constituent of interest in the sample when a substance is present that interferes with the analysis.

Standard solution.--A sample containing a known concentration of a constituent, used to calibrate an instrument or verify the accuracy of a measurement or analysis.

Water-quality sample.--A volume of water, collected from a stream, lake, reservoir, aquifer, or effluent discharge, that may be analyzed for a number of different constituents.



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EXECUTIVE SUMMARY

Serious questions have been raised by Congress about the usefulness of water-quality data for addressing issues of regional and national scope and, especially, for characterizing the current quality of the Nation's streams and ground water. In response, the U.S. Geological Survey has undertaken a pilot study in Colorado and Ohio to (1) determine the characteristics of current (1984) water-quality data-collection activities of Federal, regional, State, and local agencies, and academic institutions; and (2) determine how well the data from these activities, collected for various purposes and using different procedures, can be used to improve our ability to answer major broad-scope questions, such as:

- A. What are (or were) natural or near-natural water-quality conditions?
- B. What are existing water-quality conditions?
- C. How has water quality changed, and how do the changes relate to human activities?

Colorado and Ohio were chosen for the pilot study largely because they represent regions with different types of water-quality concerns and programs.

The study has been divided into three phases, the objectives of which are:

Phase I--Inventory water-quality data-collection programs, including costs, and identify those programs that met a set of broad criteria for producing data that are potentially appropriate for water-quality assessments of regional and national scope.

Phase II--Evaluate the quality assurance of field and laboratory procedures used in producing the data from programs that met the broad criteria of Phase I.

Phase III--Compile the qualifying data and evaluate the adequacy of this data base for addressing selected water-quality questions of regional and national scope.

Water-quality data are collected by a large number of organizations for diverse purposes ranging from meeting statutory requirements to research on water chemistry. Combining these individual data bases is an appealing and potentially cost-effective way to attempt to develop a data base adequate for regional or national water-quality assessments. However, to combine data from diverse sources, field and laboratory procedures used to produce the data need to be equivalent and need to meet specific quality-assurance standards. It is these factors that are the focus of Phase II, which is described in this report.

In the first phase of this study, an inventory was made of all public organizations and academic institutions that undertook water-quality data-collection activities in Colorado and Ohio in 1984. Water-quality programs identified in Phase I were tested against a set of broad screening criteria. A total of 44 water-quality programs in Colorado and 29 programs in Ohio passed the Phase-I screen and were examined in Phase II. These programs accounted for an estimated 165,000 analyses in Colorado and 76,300 analyses in Ohio for 20 selected constituents and properties. Although qualifying programs included both surface- and ground-water sampling, they emphasized surface waters and produced few ground-water analyses (3,660 for Colorado and 470 for Ohio).

For Phase II, information about field and laboratory quality-assurance practices was provided by each organization and its supporting laboratories through questionnaires. This information was evaluated against a set of specific criteria for field and laboratory practices. The criteria were developed from guidelines published by public agencies and professional organizations such as the American Public Health Association, the U.S. Environmental Protection Agency, and the U.S. Geological Survey. Each of the eight criteria that comprise the Phase-II screen fall into one of two major categories--field practices or laboratory practices.

#### Field practices:

- Use of documented sample-collection techniques
- Collection of samples representative of stream or aquifer conditions
- Use of other established field practices
- Use of established sample-handling and sample-preservation procedures
- Use and maintenance of analytical instruments in the field in accordance with established procedures

## Laboratory practices:

- Maintenance of a quality-assurance program
- Maintenance of laboratory quality-control procedures
- Use of appropriate analytical methods

## Results and Conclusions

1. Screening results--Relatively few of the analyses inventoried in Phase I of the study met all the screening criteria for both Phase I and Phase II. As the accompanying table shows (box A), the percentage of those analyses that passed both screening steps amounted to about 11 percent for Colorado and 14 percent for Ohio. That is, for both States, less than 15 percent of the analyses met the conditions (screening criteria) judged necessary for the data to be included in a consistent data base appropriate for addressing fundamental water-quality issues of regional and national scope.

The numbers and percentages in the table exclude analyses from more than 170,000 water samples for Colorado and more than million for Ohio, initially inventoried in Phase I, that were collected for purposes other than to represent ambient water conditions.

2. Screening criteria--The screening criteria pertaining to field practices had a greater effect on the number of analyses passing the Phase-II screen than did the laboratory-practices criteria.

Compared to all other criteria, the representative-sampling criterion was met by the smallest percentage of analyses (see table, box B). Analyses that failed this criterion were from stream samples that could not be verified as being representative of the entire stream cross section. Generally, these were point (or "grab") samples; that is, samples collected from a single point near the water surface. Point samples may be collected for several reasons, but savings of time and cost probably are dominant factors. Grab samples are much less expensive because they take much less time to collect than do samples that represent water throughout a stream's cross section. A representative stream sample is best obtained by combining depth-integrated samples collected at several locations in the stream cross section. For Colorado, about 115,000 surface-water analyses met all of the field- and laboratory-practices criteria except the representative-sample criterion. For Ohio, about 18,000 analyses met all the criteria except this one. The sample-handling and sample-preservation criterion, which addressed field procedures for preparing and preserving samples for shipment to the laboratory, was met by the second smallest percentage of analyses for both States.



Summary of Phase II Statistics

Selected data	Colorado		Ohio	
<u>Analyses and measurements at different phases :</u>	<u>Number</u>	<u>Per- cent- age</u>	<u>Number</u>	<u>Per- cent- age</u>
Inventoried in Phase I	240,000	100	242,000	100
Passing Phase-I screen	165,000	69	76,300	32
A. Passing Phase-I and Phase-II screen	26,400	11	34,900	14

Percentages of analyses and measurements meeting each Phase-II screening criterion

Field-practices criteria:

	<u>Percentage</u>	<u>Percentage</u>
Documented sample-collection techniques	100	96
B. Collection of representative samples	18	67
Other sample-collection practices	99	89
Sample handling and preservation	91	72
Field-instrument use and maintenance	100	84

Laboratory-practices criteria:

Quality assurance	96	75
Quality control	100	99
Analytical methods	94	93

Numbers of analyses and measurements passing Phase-I and Phase-II screens:

Surface water	23,900	34,400
C. Ground water	2,530	470
Totals, rounded to nearest 100	26,400	34,900

The information shown in this table represents the sums of individual analyses or measurements for only the 10 constituents and properties of interest in Phase II (for example, pH, lead, phosphorus, and so forth). The information presented by Hren and others (1987) represents the sums of samples analyzed for groups of constituents and properties (for example, nutrients, trace-element analyses, and so forth). In addition, because only the analyses and measurements that met all of the Phase-I criteria were evaluated in Phase II, only those analyses and measurements associated with ambient water-quality conditions are included in the sums shown in this table. In contrast, Hren and others (1987) present the sums of all of the samples inventoried in Phase I, which include both the numbers of samples associated with ambient water-quality conditions and with nonambient water-quality conditions (such as samples of effluents and treated drinking water).

Because of these differences, the screening results presented in this table cannot readily be compared with the results of the Phase-I screen as presented by Hren and others (1987). Thus, the sums of analyses inventoried in Phase I that are reported here have been adjusted from those reported in Hren and others (1987) to allow for a meaningful comparison. For Colorado, 338,000 ambient and nonambient samples were inventoried in Phase I (Hren and others, 1987); when adjusted for comparison to Phase II, 240,000 ambient analyses and measurements of the 20 constituents of interest in Phase II were inventoried in Phase I. For Ohio, 1,198,000 ambient and nonambient samples were inventoried in Phase I (Hren and others, 1987); when adjusted for comparison with Phase II data, 242,000 ambient analyses and measurements of the 20 constituents of interest in Phase II were inventoried in Phase I.

In contrast, except for the quality-assurance criterion for Ohio, more than 90 percent of analyses met each of the laboratory-practices criteria. This is due, in part, to the more detailed description and widespread publication of guidelines for laboratory practices compared with guidelines for field practices, particularly for collection of representative samples. The laboratory guidelines most commonly cited by programs evaluated in this study contain detailed quality-assurance procedures, whereas the field-practices guidelines most commonly cited do not describe sample-collection procedures in detail. None of these guidelines emphasizes the need for, or methods of, collecting representative samples. Furthermore, very little has been published about the sources and magnitude of errors associated with collection of water samples for chemical analysis.

This study highlights the need for additional emphasis, by organizations collecting water-quality data, on field procedures, especially concerning collection of representative water samples. Improvements in this regard could result in a large increase in the amount of water-quality data applicable to regional and national water-quality assessments. Maintaining high quality-assurance standards in the laboratory is equally important, but there is little benefit from precise analyses if the samples are unreliable.

3. Character of the data base--After Phase-I and Phase-II screening was completed, most of the data that passed both the Phase-I and Phase-II screens were for constituents and properties that broadly characterize water quality; that is, pH, alkalinity, specific conductance, and dissolved oxygen. Therefore, the Colorado and Ohio data bases contain a relatively large number of analyses that are needed to address issues of long-standing concern such as sanitary quality and salinity (data on inorganic constituents and physical properties). The fewest analyses that passed the Phase-I and Phase-II screens were for trace constituents; that is, atrazine, polychlorinated biphenyl, and lead. As a result, the data bases for Colorado and Ohio contain relatively few analyses for constituents that are needed to address issues of most recent regional and national concern, such as contamination of waters by potentially toxic organic compounds and trace metals.

4. Ground-water data--For Colorado, of the 26,400 analyses remaining after the Phase-II screening, 2,530 are ground-water analyses (see table, box C). For Ohio, of the 34,900 analyses remaining, only 470 are ground-water analyses. Few ground-water analyses were identified in Phase I of this study, and the Phase-II screening had little effect on those numbers; 69 percent of the ground-water analyses for Colorado and 100 percent of those for Ohio passed the Phase-II screen. There probably are too few ground-water analyses in the data base, especially for Ohio, to make a valid assessment of regional ground-water quality conditions.

5. Data storage--Data from several programs that met all Phase-I criteria except the criterion requiring that the data be stored in computer files were evaluated in Phase II. These programs were screened out in Phase I only because time constraints precluded transferring all the pertinent data to computer files. Any of these data that met the Phase-II criteria could be added to the data base if the data were entered into computer files. However, none of these analyses and measurements passed the Phase-II screen. This indicates that at least a preliminary field and laboratory quality-assurance screening needs to be conducted before time and effort are expended to transfer existing water-quality data from paper files to computer files.



## INTRODUCTION

National awareness of the importance of clean water has increased greatly in the last two decades. Several environmental laws have been passed that address the issues associated with protecting water quality, including the Clean Water Act (1972, amended 1977 and 1981); the Safe Drinking Water Act (1974, amended 1986); the Resource Conservation and Recovery Act (1976); the Toxic Substances Control Act (1976); the Surface Mining Control and Reclamation Act (1977); and the Comprehensive Environmental Response, Compensation, and Liability Act (1980). A summary of the water-quality issues addressed by these and other legislative acts and agreements is shown in table 1. In addition, Federal, State and local agencies and industry have made significant commitments to the protection of water quality. Expenditures for water-pollution abatement and control during the 1970's have been estimated at more than \$100 billion (The Conservation Foundation, 1982, p. 32-35). Water-quality data-collection programs alone undoubtedly have accounted for a few billions of dollars during the last two decades. The purposes of these programs may range from meeting legal requirements to research in water chemistry. The result is a large amount of water-quality data generated by a diverse group of organizations for widely differing purposes.

Questions have been raised by Congress about the usefulness of these water-quality data for addressing issues of regional and national scope and, especially, for characterizing the current quality of the Nation's surface and ground water (Blodgett, 1983). In spite of the seemingly large amounts of data being compiled, it has been difficult to make a reliable assessment of national and regional water-quality conditions. One reason is that the water-quality data that have been obtained specifically for such broad-scope assessments constitute a relatively small part of the total available water-quality data. The water-quality data collected for other purposes constitute a sizable potential source of additional data for application to regional and national assessments, but such data must be selected and used carefully. The needs, uses, and types of water-quality data differ greatly, and data collected for one purpose are not necessarily suitable for other purposes. If data from different programs are to be aggregated, it becomes very important to ensure that available data have been produced with comparable sample-collection and analysis methods. In fact, the use of unsuitable data in regional or national assessments can be much worse than a lack of data, because it can lead to incorrect conclusions having far-reaching consequences.

Insufficient information has been available to determine the benefits and problems associated with aggregating available water-quality data for regional and national assessments. Consequently, the U.S. Geological Survey has undertaken a study of water-quality data collected by various agencies and academic institutions in Colorado and Ohio to determine the suitability of these data for use in water-quality assessments of regional and national scope.

## Project Objectives and Approach

The objectives of this study are to: (1) Determine the characteristics of current (1984) water-quality data-collection activities of Federal, regional, State, and local agencies, and academic institutions; and (2) determine how well the data from these activities, collected for various purposes and using different procedures, can be used to improve our ability to answer broad-scope questions, such as:

- A. What are (or were) natural or near-natural water-quality conditions?
- B. What are existing water-quality conditions?
- C. How has water quality changed, and how do the changes relate to human activities?

A three-phase approach was used; the objectives of these phases are:

Phase I--Inventory water-quality data-collection programs, including costs, and identify those programs that met a set of broad criteria for producing data that are potentially appropriate for water-quality assessments of regional and national scope.

Phase II--Evaluate the **quality assurance**<sup>1</sup> of field and laboratory procedures used in producing the data from programs that met the broad criteria of Phase I.

Phase III--Compile the qualifying data and evaluate the adequacy of the resultant data base for addressing selected water-quality issues of regional and national scope.

Two States, Colorado and Ohio, were chosen to serve as a small sampling of the Nation. These States represent regions with different types of water-quality issues and programs. Colorado, which has a population of about 3 million (U.S. Bureau of the Census, 1981a), is a lightly industrialized western State with 36 percent federally owned lands (U.S. Bureau of Land Management, 1983). During 1980, freshwater withdrawals in Colorado averaged 16 billion gallons per day (81 percent surface water, 19 percent ground water) for public supply, rural domestic and livestock, industrial, and irrigation uses (Solley and others, 1983, p. 38).

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<sup>1</sup> To assist readers who may not be familiar with all the technical terms associated with water-quality studies, a glossary is provided before the main part of this report. Terms defined in the glossary are in bold print where first used in the main body of the report.

Eighty-eight percent of this water was used for irrigation and 6 percent for industry (thermoelectric and other industries included). Major water-quality concerns in Colorado include salinity from irrigation-return flows, contamination from potentially toxic trace metals from mining, sedimentation from land disturbances such as mining and agriculture, and sanitary quality of surface- and ground-water supplies.

Ohio, which has a population of about 10.8 million (U.S. Bureau of the Census, 1981b), is an industrialized eastern State with only about 1 percent federally owned lands (U.S. Bureau of Land Management, 1983). In Ohio, freshwater withdrawals in 1980 averaged 14 billion gallons per day (93 percent surface water, 7 percent ground water) (Solley and others, 1983, p. 38). Eighty-six percent was for industrial uses (thermoelectric and other industries included). Less than 1 percent of the water was used for irrigation. Major water-quality concerns in Ohio include contamination from potentially toxic trace metals and synthetic **organic substances** sometimes associated with industrial or municipal waste discharge; sedimentation from agricultural, mining, and other activities that disturb the land surface; and sanitary quality of surface- and ground-water supplies.

#### Summary of Phase I

Results of Phase I of this study are presented in a report by Hren and others (1987). Major results include:

Agency involvement--Phase I of the study identified 115 water-quality data-collection programs by 48 organizations for Colorado and 88 programs by 42 organizations for Ohio. Federal agencies operated the largest group of data-collection programs in each State, accounting for about 50 percent of all programs identified in Colorado and 32 percent of those in Ohio. In addition, many of the State and local programs received funding and other support from Federal agencies.

Sources of samples--More than 90 percent of all water samples collected in each State were surface-water samples. Ground-water samples represented only about 9 percent of the samples reported from Colorado and 4 percent of those from Ohio. Much of the sampling in both States was for mandated purposes, such as meeting permit requirements for monitoring wastewater effluent or drinking water. Only about 42 percent of the samples for Colorado and 15 percent of those for Ohio reportedly were for characterizing **ambient water-quality conditions**.

Screening criteria--The water-quality data-collection programs were tested against a set of criteria selected to evaluate the potential applicability and availability of their data for addressing water-quality issues of regional and national scope:

1. Do the data characterize ambient surface- or ground-water conditions, as opposed to wastewater effluent or treated water?
2. Are the data available for public use?
3. Can sampling sites be readily located?
4. Is quality-assurance documentation available?
5. Are the data in computer files?

Only 34 percent of all samples reported for Colorado and 5 percent reported for Ohio met all five criteria. Most samples that failed to meet Phase I were permit-required samples of waste effluent or treated water and, therefore, could not be considered to represent ambient water-quality conditions in streams.

Costs--About \$63 million was estimated to have been spent in the two States during 1984 for just the laboratory analyses of water-quality samples. Only about 36 percent of the analytical costs for Colorado and 6 percent for Ohio were for samples that met all the screening criteria. Laboratory costs generally amount to less than one-half of the total cost of a water-quality data-collection program, but the actual total costs for programs in the two States could not be discerned in this study.

Properties and constituents--Reported sample analyses and measurements were segregated into 11 major groups of water properties and constituents. Of the samples that met all the screening criteria, relatively few had analyses in the groups most pertinent to concerns about toxic pollution, for which analytical data are expensive to obtain.

### Purpose and Scope of Phase II

Phase II of the study, described in this report, evaluates current (1984) field and laboratory practices of organizations in Colorado and Ohio that produced data that met the Phase-I screening criteria. Because all of the many water-quality characteristics of potential interest could not be evaluated, the Phase-II evaluation was limited to selected constituents and properties that relate to issues of concern in Colorado or Ohio (table 1). The data from samples that were found to have been collected and analyzed or measured in accordance with standard methods and with appropriate quality-assurance procedures constitute the data set that will be evaluated in Phase III.



Table 1.--*Selected water-quality issues, possible causative factors, related policy and legislation, and some related water-quality constituents and properties*

[Constituents in boldface type were selected for consideration in Phase II]

Issues (Water occurrence to which the issue pertains)	Some possible causes or sources	Examples of related policy and legislation	Water-quality properties, constituents, and constituent categories
Acid rain----- (Surface water)	Industrial and auto emissions, natural sources.	Clean Air Act and amendments.	pH, alkalinity, acidity, dissolved sulfate, nitrate, aluminum, trace metals.
Eutrophication---- (Surface water)	Runoff from agricultural and urban areas, septic tanks, wastewater discharges.	Clean Water Act and amendments, Great Lakes Water- Quality Agreement.	Water transparency, phosphorus, organic and inorganic nitrogen, silica, chlorophyll a.
Salinity----- (Surface and ground water)	Road salt, irrigation return flow, mine discharges, evap- oration, natural sources (such as geochemical compo- sition of soils and mineral- ized ground water).	Clean Water Act and amendments, Surface Mine Control and Re- clamation Act, Colo- rado River Basin Sa- linity Control Act.	Specific conductance dissolved solids, dissolved chloride, sodium, calcium, other major minerals.
Soil erosion/ sedimentation--- (Surface water)	Agricultural practices, surface mines, natural processes.	Watershed Protection and Flood Prevention Act, Surface Mining Control and Reclamation Act, Clean Water Act and amendments.	Suspended sediment, bed sediment.
Toxic contamination--- (Surface and ground water)	Municipal and industrial waste, pesticides, landfills, runoff from urban areas, natural sources, irrigation return flows.	Resource Conservation and Recovery Act; Toxic Substances Control Act; Comprehensive Environ- mental Response, Comp- ensation and Liability Act (Superfund); Clean Water Act and amend- ments; Great Lakes Water Quality Agreement.	Priority pollutants (organic and inorganic compounds, pesticides, industrial chemicals, toxic trace metals).

Table 1.--*Selected water-quality issues, possible causative factors, related policy and legislation, and some related water-quality constituents and properties*--Continued

Issues (Water occurrence to which the issue pertains)	Some possible causes or sources	Examples of related policy and legislation	Water-quality properties, constituents, and constituent categories
Mine drainage----- (Surface and ground water)	Coal mines, mineral and gravel mines, mill tailings.	Surface Mine Control and Reclamation Act, Clean Water Act and amendments.	Specific conductance, pH, dissolved solids, sulfate, iron, manga- nese, uranium, suspen- ded sediment, heavy metals.
Sanitary quality/ water supplies-- (Surface and ground water)	Municipal and industrial waste effluents, feedlots, runoff from urban areas, natural sources.	Clean Water Act and amendments, Safe Drinking Water Act	Dissolved oxygen, bio- chemical oxygen de- mand, ammonia- nitrogen, nitrate- nitrogen, iron, manga- nese, methylene-blue- active substances, sus- pended solids, dis- solved solids, total and fecal coliform bacteria, fecal strep- tococcus bacteria.

## Quality Assurance

Variability in analytical results, caused by errors in the sample-collection and analysis process, always occur even under rigorously controlled field and laboratory conditions. For example, errors can be introduced into sample results through: (1) Selection of a sampling location or method that produces a sample that fails to represent the conditions of interest; (2) improper use of instruments; (3) contamination of the sample; and (4) inappropriate methods of analysis. These errors can be so small that they cannot be measured, or so large that their presence is obvious. Quality-assurance programs are used to detect and control these errors and to maintain and document the reliability of results. A quality-assurance program needs to evaluate all aspects of sample collection, analysis, and reporting.

**Quality control**, an essential component of quality assurance, encompasses routine and specific procedures that determine the quality of an individual measurement activity. Quality-control procedures performed at each step in sample collection and analysis help ensure that sample-collection practices produce samples that represent actual environmental conditions, that sample handling preserves sample integrity, and that analytical methods are appropriate.

A common goal of quality-assurance programs is to minimize sources of error to the extent required by the goals of the program. Thus, different levels of quality assurance may be appropriate for data-collection programs with different goals and objectives. For example, the level of quality assurance appropriate for the routine characterization of effluents from wastewater-treatment operations may be less than the level of quality assurance needed to detect changes in concentrations of constituents that typically occur in trace amounts.

The water-quality data evaluated in this study were collected and analyzed for a variety of purposes requiring different ranges of analytical certainty as well as different methods of sample collection and analysis. The data from these programs may fully meet the needs of the program for which they were collected, yet may have only limited applicability to water-quality issues of regional and national scope.

Several organizations have developed policies and procedures for quality assurance in efforts to ensure that water-quality data are reliable and legally defensible. For example, the U.S. Environmental Protection Agency requires programs within that agency, as well as programs operated by regional, State, and local pollution-control organizations with funds from that agency, to establish quality-assurance plans (U.S. Environmental Protection Agency, 1983). Specific quality-assurance practices for monitoring effluents and surface and ground water affected by effluents are documented by the U.S. Environmental Protection Agency (1979b, 1982).

The U.S. Geological Survey's policies and procedures for planning and conducting quality-assurance activities in water-resource investigations are described in manuals by the Office of Water Data Coordination (1977) and Friedman and Erdmann (1982). In addition, U.S. Geological Survey offices in individual States have developed written guidelines for collection and field analysis of samples under conditions specific to those States. The U.S. Geological Survey's efforts toward standardization of practices have focused on ambient-water-quality analysis (Cable, 1982).

The National Bureau of Standards recently published a handbook that contains concepts of quality assurance, quality control, and use of standard **reference materials**. These concepts may be applied to many broad categories of physical and chemical analysis, including water samples (Taylor, 1981).

Most of the other Federal agencies involved in water-quality data collection--including the U.S. Army Corps of Engineers, U.S. Forest Service, U.S. Bureau of Reclamation, and others--endorse the use of quality-assurance practices and procedures similar to those recommended by the U.S. Environmental Protection Agency and the U.S. Geological Survey.

Professional organizations such as the Water Pollution Control Federation and the American Chemical Society's Subcommittee on Environmental Analytical Chemistry also have encouraged the development and use of quality-assurance and quality-control practices through conferences and published guidelines (Freeman, 1980; Keith and others, 1983).

The quality-assurance practices and procedures cited above are broadly applicable to water-quality data-collection programs. Accordingly, these practices and procedures were used extensively to develop criteria for evaluations during Phase II of this study.

#### METHODS OF ACQUIRING, COMPILING, AND EVALUATING INFORMATION

The main sources of information for this report were two questionnaires developed by the U.S. Geological Survey and completed through interviews with public agencies and academic institutions having programs that met the Phase-I criteria. (See the Supplemental Information section at the back of this report.) The first questionnaire addressed field practices and was discussed with organizations whose programs met the five screening criteria used in Phase I. The second questionnaire addressed laboratory-analytical practices and quality assurance, and was discussed with each laboratory that performed sample analyses for those organizations. The questions primarily pertained to practices and procedures in 1984, and, because of the large number of constituents of potential interest, were limited to selected constituents that relate to issues of concern for each State (table 1).



Although the questionnaires focused on an organization's quality-assurance practices for water-quality sample-collection and analysis programs, they were not intended to provide a detailed evaluation of these practices. A detailed evaluation would require on-site inspection, extensive interviews with program personnel, and detailed examination of records, all of which would go far beyond the scope of this study.

For each constituent and property addressed in Phase II, the total number of analyses or measurements was estimated using information about frequency of sampling (reported in Phase I) together with information about which constituents and properties were analyzed (reported in Phase II). The numbers of analyses and measurements evaluated and results of the Phase-II screening process are reported as the sums of individual analyses or measurements of only the 20 constituents and properties of interest in Phase II (that is, the sum of measurements or analyses for pH, lead, phosphorus, and so forth). This method of tallying differs from the method used in Phase I. The results of Phase I (Hren and others, 1987) are presented as sums of samples analyzed for groups of constituents and properties (for example, nutrients, trace-element analyses, and so forth). In addition, because only the analyses and measurements that met all of the Phase-I criteria were evaluated in Phase II, the numbers presented in Phase II include only those analyses and measurements associated with ambient water-quality conditions, whereas the numbers presented in Phase I include all of the samples inventoried; that is, both the numbers of samples associated with ambient water-quality conditions and with nonambient water-quality conditions. Nonambient water-quality samples are permit-required samples of effluents, samples collected to monitor compliance with effluent or drinking-water regulations, or samples collected for enforcement of effluent and drinking-water regulations.

Because of these differences and to allow for a meaningful comparison between the results of the two Phases, the total numbers of analyses and measurements reported in the tables that follow, as inventoried in Phase I, were adjusted using the Phase-II method of tallying. Thus, for Colorado, 338,000 ambient and nonambient samples were reported as inventoried in Phase I by Hren and others (1987); when adjusted for comparison to Phase II, 240,000 ambient analyses and measurements of the 20 constituents of interest in Phase II were inventoried in Phase I. For Ohio, 1,198,000 ambient and nonambient samples were inventoried in Phase I (Hren and others, 1987); when adjusted for comparison with Phase-II data, 242,000 ambient analyses and measurements of the 20 constituents of interest in Phase II were inventoried in Phase I.

### Field-Practices Questionnaire

The field-practices questionnaire was developed from sample-collection guidelines published by the U.S. Geological Survey (Brown and others, 1970), the Office of Water Data Coordination (1977), the U.S. Environmental Protection Agency (1979a, 1982, 1984a), the American Public Health Association and others (1981), and the Ohio River Valley Water Sanitation Commission (1984). The questionnaire had four parts. In the first part, information was requested to determine which constituents were analyzed or measured; in what computer data base the data are stored; whether field practices used by the organization are documented; which laboratory analyzed the samples; and the period during which each laboratory was used.

In the second part of the questionnaire, information was requested concerning the location of each site sampled and whether the purpose of the site was for measurement of ambient water quality or of the effects of contamination sources.

The third part of the questionnaire addressed procedures for obtaining a representative sample. For surface-water programs, respondents were asked if instream-mixing conditions were known before sample collection. If instream-mixing conditions were not known, they were asked to indicate the technique that was used to ensure that the samples were representative of the stream cross section. For ground-water programs, respondents were asked if selected ancillary information about the well and equipment significant to sample characteristics (such as pump type and well-casing material) was known and recorded. They also were asked if standing water was evacuated from well casings before sample collection.

The fourth part of the questionnaire addressed field practices or procedures that are specific to the constituents selected for study in Phase II. These included questions about sample-collection procedures, sample handling and preservation, and use and maintenance of field instruments.

In Colorado, the field-practices questionnaire was provided to 13 organizations representing 44 programs (31 surface water, 13 surface and ground water) (table 2). Only two questionnaires were not completed.

In Ohio, the field-practices questionnaire was provided to eight organizations with 29 programs (24 surface water, 3 surface and ground water, and 2 ground water). Only two questionnaires were not completed. For Ohio, all the programs sampling ground water were U.S. Geological Survey programs (table 2).

Table 2.--Numbers of organizations and programs contributing analyses and measurements to Phase II of the study, by organizational category, Colorado and Ohio

Organizational category	Colorado				Ohio			
	Surface water		Ground water		Surface water		Ground water	
	Number of organizations	Number of programs	Number of organizations	Number of programs	Number of organizations	Number of programs	Number of organizations	Number of programs
Federal agencies:								
U.S. Geological Survey-----	1	19	1	6	1	11	1	5
Other-----	6	16	3	7	3	4	--	--
Regional agencies-----	2	3	--	--	1	3	--	--
State agencies-----	1	3	--	--	1	7	--	--
Local agencies-----	2	2	--	--	1	1	--	--
Academic institutions--	1	1	--	--	1	1	--	--
	--	--	--	--	--	--	--	--
Totals-----	13	<sup>1</sup> 44	4	<sup>1</sup> 13	8	<sup>1</sup> 27	1	<sup>1</sup> 5

<sup>1</sup>Some programs included sample collection from both surface water and ground water.

### Laboratory-Practices Questionnaire

The laboratory-practices questionnaire was developed from quality-assurance guidelines published by the U.S. Environmental Protection Agency (1979b, 1984b) and the U.S. Geological Survey (Friedman and Erdmann, 1982). The questionnaire was organized into two parts. The first part addressed laboratory quality-assurance practices and quality-control practices specific to the selected constituents. Laboratories were expected to have a documented quality-assurance plan or guidelines, and were asked to respond concerning the use of 11 specific quality-control practices. Information also was requested regarding participation in interlaboratory and intralaboratory testing.

The second part of this questionnaire addressed the specific physical, chemical, and microbiological methods of analysis used to measure the constituents of interest in surface and ground water, the period during which those methods were used, and when any method changes were made. Most of the specified analytical methods are listed in the Federal Register as adopted by the U.S. Environmental Protection Agency (1984a) and include references to specific procedures such as those from the American Public Health Association, U.S. Geological Survey, U.S. Environmental Protection Agency, American Society for Testing and Materials, Association of Official Analytical Chemists, and various other publications and manuals on water-quality testing.

Analytical methods for suspended **sediment**, uranium, and coliform bacteria, which are not cited in the Federal Register, are described respectively in Guy (1969), Thatcher and others (1977, p. 81-95), and Greeson and others (1977).

Because many of the programs used the same laboratories, there were fewer laboratories than programs to contact. Thus, for Colorado, only 12 laboratories were contacted. For Ohio, 17 different laboratories were contacted.

### Screening Procedure and Criteria

The eight criteria (as represented by the questions in the two questionnaires) that were developed to screen the data were grouped into the two categories of field practices and laboratory practices (table 3). As table 3 shows, most of the criteria do not apply to all the constituents of interest. Therefore, the numbers of analyses and measurements applicable to each criterion had to be considered. Accordingly, in accompanying tables showing the percentages that met the various criteria (tables 5, 8, 9, and 10), the corresponding applicable numbers of analyses and measurements also are presented. The percentage values meeting the different criteria are comparable only in this context.

Table 3.--Screening criteria that are applicable to the specific constituents and properties selected for study

[X indicates criterion is applicable to all analyses or measurements unless noted otherwise]

Chemical constituents and physical properties	Categories of Criteria							
	Field practices					Laboratory practices		
	Docu- mented sample- collec- tion tech- niques	Collec- tion of repre- sentative samples	Other sample- collec- tion prac- tices	Sample handling and preser- vation	Field instru- ment use and mainten- ance	Qual- ity assur- ance	Qual- ity con- trol	Analy- tical methods
Surface water								
Dissolved oxygen-----	X	X	X	X <sup>1</sup>	X <sup>2</sup>	X <sup>1</sup>	X <sup>1</sup>	X <sup>1</sup>
pH-----	X	X			X <sup>2</sup>	X <sup>1</sup>	X <sup>1</sup>	X <sup>1</sup>
Specific conductance-----	X	X			X <sup>2</sup>	X <sup>1</sup>	X <sup>1</sup>	X <sup>1</sup>
Alkalinity-----	X	X		X		X	X	X
Sulfate-----	X	X				X	X	X
Chloride-----	X	X				X	X	X
Dissolved solids-----	X	X	X			X	X	X
Total phosphorus-----	X	X		X		X	X	X
Nitrate-----	X	X		X		X	X	X
Lead-----	X	X	X	X		X	X	X
Polychlorinated biphenyl--	X	X	X	X		X	X	X
Atrazine-----	X	X	X	X		X	X	X
Suspended sediment-----	X	X	X					X
Fecal coliform bacteria---	X	X		X		X	X	X
Ground water								
Dissolved solids-----	X	X	X			X	X	X
Iron-----	X	X		X		X	X	X
Manganese-----	X	X		X		X	X	X
Uranium-----	X	X		X		X	X	X
Nitrate-----	X	X		X		X	X	X
Phenol-----	X	X		X		X	X	X
Methylene-blue-active substances-----	X	X		X		X	X	X
Total coliform bacteria---	X	X	X	X		X	X	X

<sup>1</sup>Not applicable to analyses and measurements made in the field.

<sup>2</sup>Not applicable to analyses and measurements made in the laboratory.



Two of the field-practices criteria were general and pertained to all constituents and properties. The first was for use of documented sample-collection techniques by program personnel. This criterion was met if there were established guidelines for field practices, either written by the organization or obtained from published sources. The second criterion was for assurance that samples were representative of conditions in the stream or aquifer. For stream samples, this criterion was met if samples were collected with a depth-integrating sampler at multiple points in the stream cross section, or by a similar method of sample integration. (See later section on Collection of Representative Samples.) This criterion also was met if samples were collected at a single point in the stream cross section (grab sample), provided that (1) an accurate relationship between grab samples and depth-width-integrated samples had been established for the full range of flow conditions sampled; or, (2) data were recorded that demonstrated that the stream was well mixed when sampled. For lakes and reservoirs, samples collected at single points were accepted. (See later section on Collection of Representative Samples.) For ground water, the representative-sample criterion was met if specified information was available about sampling depth, well construction, and well-casing material. In addition, standing water must have been evacuated from the well casing prior to sample collection.

Each of the remaining three field-practices criteria was specific to certain constituents and properties or groups of constituents and properties (table 3). The criterion for other sample-collection practices addressed a considerable range of activities important for obtaining a reliable sample, such as use of correct sampling equipment. The criterion for sample handling and preservation addressed sample-preparation procedures for storing and shipping samples before laboratory analysis. The criterion for field-instrument use and maintenance pertained to the calibration and use of analytical instruments in the field.

There were three laboratory-practices criteria. The first criterion, quality assurance, pertained to general laboratory practices such as proper sample-identification procedures, inter-laboratory and intralaboratory testing programs, and corrective actions for any data-quality problems. The second criterion, quality control, pertained to requirements for statistical **precision and accuracy** controls. These requirements varied depending on the constituent and the analytical method, but generally included procedures such as **calibration, percent recovery of spiked samples or standard solutions**, the use of internal or external standards, use of surrogate standards, and **standard additions**. These two laboratory-practices criteria were applied to all constituents and properties measured in the laboratory except suspended sediment (table 3).

The quality-assurance and quality-control policies cited for sediment analyses were different from those typically cited by water-quality laboratories. Most of the work in developing policies for quality assuring sediment analyses has been done by the Federal Interagency Sedimentation Project, a cooperative project sponsored by the Interagency Advisory Committee on Water Data, Subcommittee on Sedimentation. The resultant quality-assurance practices for sediment analyses focus on evaluations of sediment records through review of the data for consistency and reasonableness, rather than evaluations of laboratory practices. The entire sediment record, which includes data on suspended-sediment concentration, corresponding streamflow rates, and particle-size analysis, may be reviewed in the quality-assurance step.

Because suspended-sediment analyses are quality-assured through data review, no interlaboratory or intralaboratory testing is conducted and no reference materials for testing are available. Additional, detailed evaluation would be needed to determine whether quality-assuring the sediment records is equivalent to quality-assuring the laboratory analyses. However, such detailed evaluation is beyond the scope of the present study, and sediment data that were reported to be quality-assured by data review passed the Phase-II screen.

The third laboratory-practices criterion, analytical methods, addressed the physical, chemical, and microbiological methods of analysis used for specific constituents. This criterion was met if the method used is currently published in one or more of the references cited previously (see preceeding section on Laboratory-Practices Questionnaire) and is applicable to analysis of ambient water-quality samples.

#### FIELD QUALITY-ASSURANCE PRACTICES

Use of comparable field practices that adhere to quality standards is a desirable goal among different organizations so that diverse data bases can be compared and possibly combined. It is an essential goal within a single program for which the data are aggregated to meet a single objective.

##### Use of Documented Sample-Collection Techniques

Assurance of uniformity of field practices and adherence to data-quality standards by personnel within an organization can be greatly enhanced by establishing written and clearly stated guidelines and by establishing an organizational policy that those guidelines be followed. Accordingly, respondents to the field-practices questionnaire were asked if such written guidelines existed within their organization and to cite published references used to guide the organization's sample-collection practices.

Most agencies in Colorado and Ohio reported use of field practices described by the U.S. Environmental Protection Agency (1982) or the American Public Health Association and others (1981). Two agencies developed and used their own written guidelines; only one agency indicated that no written guidelines were used; analyses from this agency accounted for only about 1 percent of the total analyses from both States.

### Collection of Representative Samples

In water-quality studies, as in many other types of studies, it is not possible to analyze the whole water body--a stream, lake, reservoir, or aquifer. The objective of water-quality sampling is to collect a portion of the water body small enough in volume to be conveniently transported to and handled in the laboratory while also representing adequately the whole or desired part of the water body being sampled. If a constituent of interest were distributed uniformly throughout a water body (well mixed), obtaining a representative sample would be relatively simple; a single water-quality sample collected anywhere would be representative. In reality, such uniform distribution is unusual and a suitable sampling method must be selected that will account for the non uniform distribution.

#### Surface Water

The quality of lake and reservoir water may vary considerably because of natural causes such as rainfall, inflowing runoff, seasonal water-density stratification, and effects of wind. The low velocities of lakes and reservoirs preclude the use of depth-integrating samplers designed for use in flowing waters; thus, special sampling devices need to be used to obtain samples from distinct points, both areally and with depth. A single, representative sample may be obtained by compositing these point samples, or the point samples may be analyzed separately. The choices of location, depth, and frequency of sampling need to be based on the physical conditions of the lake as well as on the purposes of sampling.

In a stream, water-quality conditions at any instant may vary with distance from the stream bank and with depth. The uniformity of water-quality conditions (degree of mixing) at any cross section depends on many factors, such as streamflow characteristics (velocity, turbulence), stream-channel characteristics (width, depth, slope, and roughness), characteristics of the constituent of interest (in solution or attached to particles), and distance from sources of a constituent of interest (tributaries, industrial or municipal effluents, storm drains, irrigation drainage ditches, and so forth). All these factors determine the method of stream



sampling needed to characterize the actual water-quality conditions throughout the stream cross section. Vertical mixing may be rapid if the stream is highly turbulent. Lateral, cross-stream mixing occurs more slowly unless the stream's width is relatively small in relation to its depth (Fisher and others, 1979, p. 104; Ward, 1973, p. 1075). The distance from the source of a constituent (for example, from a tributary or effluent entering the stream at one side) to the point downstream of the source where that constituent is both vertically and laterally well mixed with the stream water, is known as the mixing length. For many streams, the mixing length may be many miles.

Examples of estimated mixing lengths for different flow conditions in two river reaches--Roaring Fork River at Glenwood Springs, Colorado and Maumee River near Waterville, Ohio--are presented in table 4. Roaring Fork River is a steep, fast-flowing stream draining western slopes of the Colorado Rocky Mountains, whereas the Maumee River is a flat, slow-moving river draining part of northwestern Ohio. Mixing lengths were estimated using a method described by Ward (1973) (table 4), and represent the estimated distance required for 95-percent mixing throughout the stream cross section at a specified flow condition. Estimated mixing lengths for Roaring Fork River, over a range of flows typically measured in that reach, ranged from about 3.5 to 13 miles. Estimated mixing length for Maumee River, which is considerably wider than Roaring Fork River (table 4), ranged from about 58 to 180 miles, also for a range of flows commonly measured at the site.

In addition to consideration of stream characteristics in determining mixing conditions for stream sampling, recognition of the role of suspended sediment also is important. Many constituents of interest in water-quality data-collection programs are transported on suspended sediment. For example, in waters of near-neutral pH, phosphorus and many potentially toxic trace elements are largely transported on suspended sediment. Sediment is maintained in suspension because of stream velocity and turbulence. These factors vary within the stream cross section; velocity generally is highest near the water surface and lowest near the streambed. Sediment concentration varies also from the water surface to the streambed, and generally is lowest near the water surface and greatest near the streambed. Figure 1 shows the cross section of a typical sand-bed channel, and illustrates variability in the vertical and lateral distribution of sediment in a cross section. Fine sediment (silt and clay) is readily kept in suspension and commonly is maintained in a relatively uniform distribution throughout the depth of flow (fig. 1A). Larger particle sizes, such as sand, require greater energy to maintain suspension high in the water column. Consequently, the average size of sediment in suspension is smaller near the water surface than near the streambed, and most sand is carried near the streambed (fig. 1B).

Table 4.--Estimated stream lengths required for thorough mixing of water downstream an effluent source, for various conditions of width, depth, and streamflow, for reaches of Roaring Fork River, Colorado, and Maumee River, Ohio

Stream site	Average width (feet)	Average depth (feet)	Width-to- depth ratio	Instantaneous discharge (cubic feet per second)	Mixing <sup>1</sup> length to 95-percent homogeneity (miles)
Roaring Fork River at Glenwood Springs, Colorado	156	1.1	140	331	13
	165	1.6	100	652	9.8
	170	4.7	36	5,690	3.5
Maumee River near Water- ville, Ohio	462	.9	510	201	140
	630	1.3	480	1,160	180
	800	6.4	120	2,800	58

<sup>1</sup>Mixing length calculated using Ward's equation (Ward, 1973, p. 1074):

$$x = \frac{K B^2}{0.02d}$$

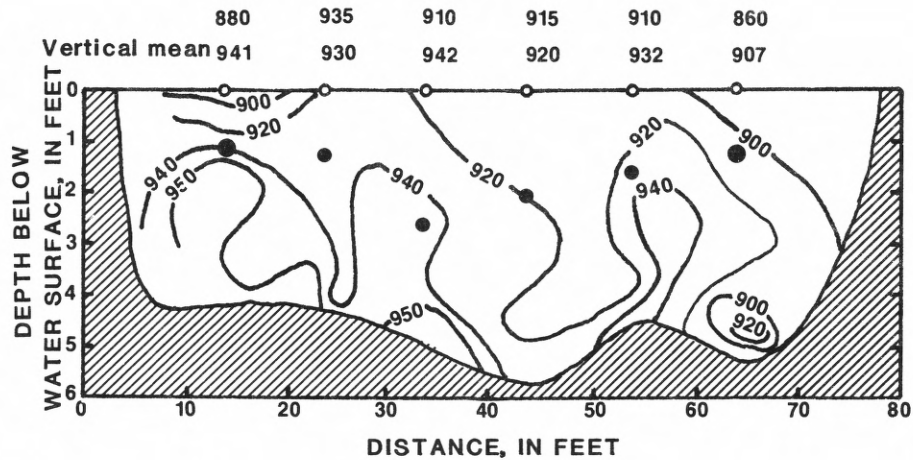
where x is mixing length in a straight channel to achieve 95-percent mixing, in meters;

B is average width of the stream reach, in meters;

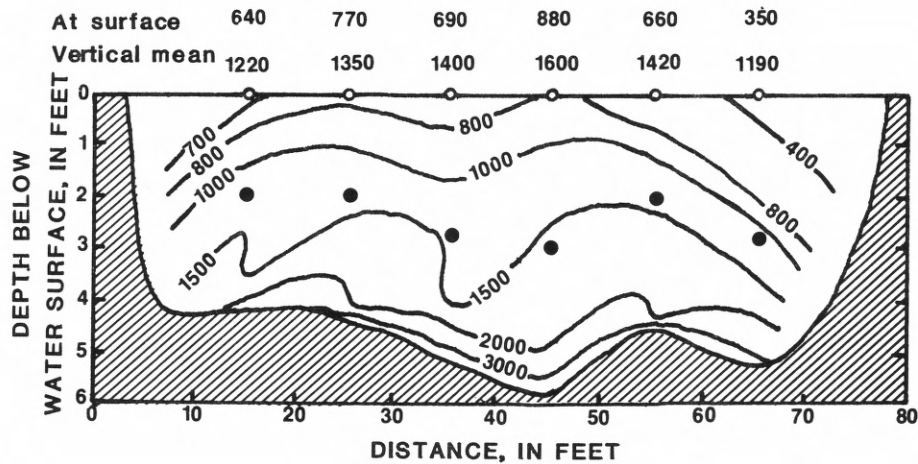
d is average depth of the stream reach, in meters; and

K is a factor describing dispersion and mixing in the width direction from an inflow point at one side.

### A. Silt and clay concentrations



### B. Sand concentrations



### EXPLANATION

- 1000 — LINE OF EQUAL SUSPENDED-SEDIMENT CONCENTRATION—  
Interval, in milligrams per liter, is variable
- HORIZONTAL POSITION OF SAMPLING LOCATIONS
- APPROXIMATE DEPTHS OF MEAN CONCENTRATIONS

Water discharge = 1280 cubic feet per second.

Mean velocity = 4.41 feet per second

Medium diameter of bed material = 0.33 millimeters

Figure 1.—Measured variations in concentrations of suspended (A) silt and clay, and (B) sand in the Rio Grande conveyance channel near Bernardo, New Mexico (from Feltz and Culbertson, 1972).

A sampling procedure that is most appropriate for the collection of all samples cannot be specified in absolute terms because of the varied purposes for and conditions under which samples are collected. The method selected for sampling streams, like the sampling of lakes and reservoirs, should be guided by the physical conditions and the objectives of data collection.

Stream-water-quality samples often are collected manually from a single point in the stream, usually just below the water surface. This method of sampling is known as point, dip, or grab sampling. Automatic sampling devices also are used to collect point samples, especially if resources are limited and sequential samples are desired to determine temporal variation in water-quality conditions. Point sampling has the advantages of being relatively quick and inexpensive, and requiring (except for automatic samplers) no special equipment or training. A disadvantage, as figure 1 shows, is that point samples will not represent the average water-quality conditions in the cross section unless the constituents of interest are uniformly distributed. For example, Feltz and Culbertson (1972, p. 175) estimated that a composite of individual point samples, collected at the six surface points across the cross section shown in figure 1, would represent only about 68 percent of the total suspended-sediment load. Thus, the sample collected by this method also may underrepresent the constituents attached to suspended sediment.

One sampling technique that can be used to collect a composite sample of the water-sediment mixture flowing through a stream cross section employs a depth-integrating sampler. The sampler is moved from the water surface to the streambed and back at a constant rate. The rate at which water enters the sampler is a function of stream velocity; therefore, the sample from each vertical traverse not only contains water from the surface to the streambed, but also integrates the variation in velocity. A number of these depth-integrated samples are collected at selected locations in the stream cross section and may be combined into a single composite sample that is representative of the water-sediment mixture flowing in the entire cross section (Guy and Norman, 1970, p. 27). This method, although slower and, therefore, more expensive to employ than point sampling, provides assurance of a representative sample of the entire cross section if the stream is poorly mixed or if mixing conditions are unknown.

With point samples, collected manually or automatically, the mean concentration of a constituent in a stream can be estimated if a reliable relation can be established between the concentrations of the constituent at the sampling point and the mean concentrations of the same constituent throughout the entire cross section (Porterfield, 1972, p. 11). The relations between mean concentrations and point-sample concentrations need to be established for the full range of streamflow conditions to be sampled and for each constituent of interest.

For Colorado, only 16 percent of all surface-water analyses evaluated in Phase II were from samples judged to be representative of the cross section (fig. 2A; table 5). These were either (1) samples collected with a depth-integrating sampler at multiple vertical traverses in the cross section, (2) samples for which the mean concentrations were estimated using established relations between the constituent concentrations at a point in the cross section and the mean concentration of the same constituent for the range of flow conditions sampled, or (3) samples collected from cross sections that were well mixed.

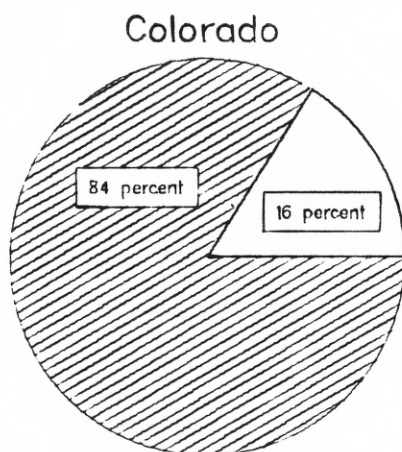
For Ohio, 67 percent of the surface-water analyses were from samples judged to represent mean concentrations in the cross sections of the sampled streams (fig. 2A; table 5). Fewer analyses met the representative-sample criterion than any of the other Phase-II criteria. For 71 percent of the surface-water analyses in Colorado and 23 percent in Ohio, this criterion is the only constraint limiting the further use of the data in this study (fig. 3).

There are several possible reasons for the small number of analyses that met this criterion. One reason seems to be a relative lack of emphasis on the need for obtaining a representative sample, as compared to the emphasis placed on laboratory precision and accuracy. The two references most frequently cited in this study as guiding field practices (U.S. Environmental Protection Agency, 1982; American Public Health Association, 1981) do not offer detailed discussion of procedures or equipment for collecting a representative sample. Other possible reasons include training deficiencies of field personnel and the greater time and cost involved in collecting a representative sample rather than a point sample.

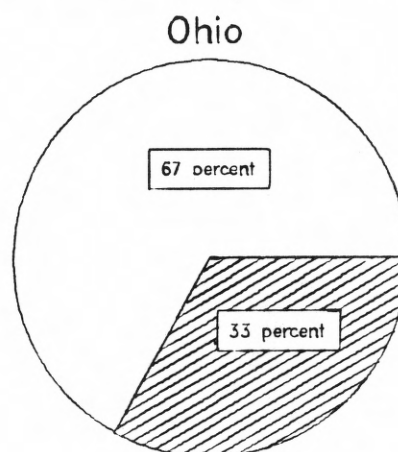
The data from point samples where mixing conditions were unknown were judged to be provisional, because some point-sample data possibly could be considered for use in the Phase-III water-quality assessment, if the bias for each sample could be retrospectively determined. However, the bias associated with the data depends on the mixing characteristics at each individual site, and therefore would have to be determined on a site-by-site basis for the full range of flow conditions sampled. Also, even if these detailed field studies were done, stream conditions may have changed over time (for example, the location and number of effluent sources), so that establishing past mixing conditions in the reach would be difficult.



## A. Surface water

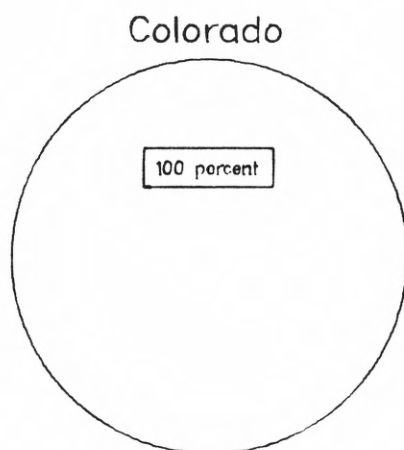


Total = 161,000 analyses  
and measurements

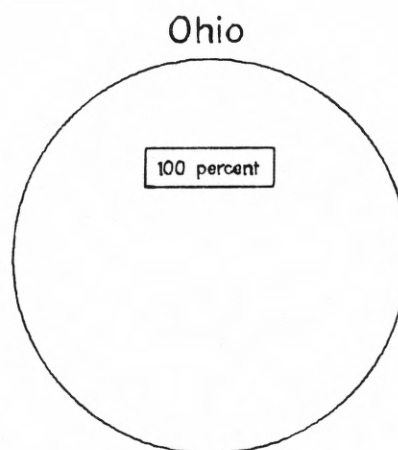


Total = 75,800 analyses  
and measurements



## B. Ground water



Total = 3660 analyses



Total = 470 analyses

- EXPLANATION**
-  ANALYSES AND MEASUREMENTS MEETING THE REPRESENTATIVE-SAMPLE CRITERION
  -  ANALYSES AND MEASUREMENTS NOT MEETING THE REPRESENTATIVE-SAMPLE CRITERION

**Figure 2.--Percentages of (A) surface-water analyses and measurements and (B) ground-water analyses that met or failed to meet the representative-sample criterion for Colorado and Ohio.**

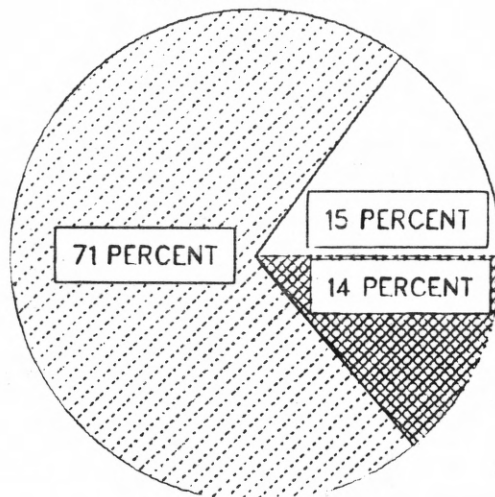
Table 5.--Numbers of analyses or measurements pertaining to each screening criterion, and percentages meeting each criterion, Colorado and Ohio

[Dash indicates no data available. N/A indicates criterion or percentage not applicable. Details by organizational category are shown in tables 8-10].

<u>Criteria for field practices</u>										
	<u>Documented sample-collection techniques</u>		<u>Collection of representative samples</u>		<u>Other sample-collection practices</u>		<u>Sample handling and preservation</u>		<u>Field instrument use and maintenance</u>	
	Num- ber	Per- cent	Num- ber	Per- cent	Num- ber	per- cent	Num- ber	per- cent	Num- ber	Per- cent
Colorado:										
Surface water-----	161,000	100	161,000	16	26,200	99	85,000	91	63,800	100
Ground water-----	3,660	100	3,660	100	40	100	2,100	100	0	N/A
Totals (rounded), Colorado -----	165,000	100	165,000	18	26,200	99	87,100	91	63,800	100
Ohio:										
Surface water-----	75,800	96	75,800	67	28,200	89	41,000	72	33,300	84
Ground water-----	470	100	470	100	0	N/A	370	100	0	N/A
Totals (rounded), Ohio -----	76,300	96	76,300	67	28,200	89	41,400	72	33,300	84
<u>Criteria for laboratory practices</u>										
	<u>Quality assurance</u>		<u>Quality control</u>		<u>Analytical methods</u>		<u>All field- and laboratory-practices criteria (percent)</u>			
	Num- ber	Per- cent	Num- ber	Per- cent	Num- ber	Per- cent				
Colorado:										
Surface water-----	74,800	97	74,800	100	77,900	94			15	
Ground water-----	3,660	88	3,660	96	3,660	86			69	
Totals (rounded), Colorado -----	78,500	96	78,500	100	81,500	94			16	
Ohio:										
Surface water-----	36,100	75	36,100	99	42,000	93			45	
Ground water-----	470	100	470	100	470	100			100	
Total (rounded), Ohio -----	36,600	75	36,600	99	42,500	93			46	

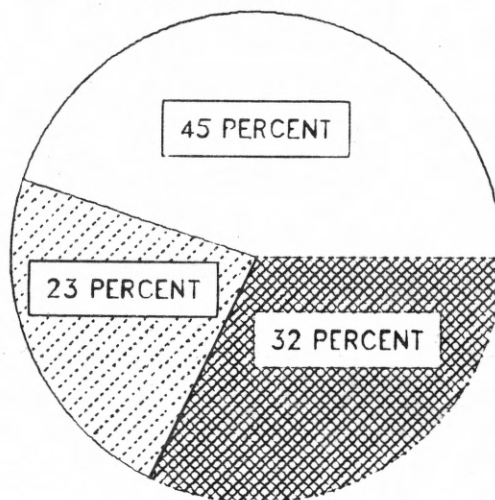


*A.* Colorado



Total = 161,000 analyses and measurements

*B.* Ohio



Total = 75,800 analyses and measurements

EXPLANATION




-  ANALYSES AND MEASUREMENTS MEETING ALL CRITERIA
-  PROVISIONAL ANALYSES, MEETING ALL BUT THE REPRESENTATIVE-SAMPLE CRITERION
-  ANALYSES AND MEASUREMENTS NOT MEETING OTHER CRITERIA

Figure 3.--Phase-II screening results for surface-water analyses and measurements for (A) Colorado, and (B) Ohio.

## Ground Water

The issue of representative sampling is equally important for ground-water samples, but the factors affecting the collection of such samples are considerably different and are more difficult to control than they are for surface-water sampling. In contrast to lakes, reservoirs, and streams, where the water is in well-defined basins or channels, ground water occurs in permeable soil and rock materials (aquifers) that may have indefinite, largely undefined boundaries. At many places, the ground water occurs in not just one, but in a sequence of shallow and deeper aquifer zones that contain water of somewhat different quality characteristics and that have some degree of hydraulic interconnection. In collecting ground-water samples, the objective usually is to sample water from a specific aquifer zone. Therefore, collection of representative ground-water samples is best ensured if guided by considerable knowledge of the local aquifer system and the characteristics of the wells sampled (Claassen, 1982; Scalf and others, 1981).

Not all wells are constructed in a manner such that water samples from them will be representative of a discrete aquifer. A municipal water-supply well, for example, may have been designed to take water from two or more aquifer zones to maximize well yield. Thus, water from the well is a mixture from the two zones and does not represent conditions in any one aquifer. Similarly, irrigation-supply wells often are constructed with little regard to the possibility of water from the land surface entering the well; thus, samples from those wells may have constituent concentrations that are not representative of the water in the aquifer. A well casing that penetrates more than one aquifer zone and is not completely sealed against the rock materials at depth might allow entry of water from an aquifer zone other than the one intended for sampling. This would result in a mixture of water that is not representative of any one aquifer.

Because of the potential for such sample-reliability problems, it is important to have available lithologic, well-construction, and well-completion data to define the aquifer or the part of an aquifer that is represented by a water sample. The lithologic data indicate the rock materials penetrated by the well and provide specific information on the characteristics of the aquifer and adjacent zones so that water-quality data can be related to the local hydrologic system. Information on well completion refers to activities that take place after drilling is completed, including cleanout of the well and installation of the casing. The methods and the materials used in construction and completion activities determine the source of water entering the well and can add contaminants to the well water. For example, if drilling fluid is used in well construction, it can affect the representativeness of the water being sampled by reducing permeability of parts of the aquifer or by introducing contaminants into the water. The factors to be considered in obtaining representative

ground-water samples are discussed in more detail in Claassen (1982) and Scalf and others (1981).

The actual collection of a ground-water sample for water-quality analysis presents another set of requirements. The procedures used depend on the water-quality constituents that will be analyzed. The most generally accepted procedure is to pump the well to remove a volume of water equal to at least three well-casing volumes or until successive measurements register consistent values for properties such as specific conductance and pH (Claassen, 1982, p. 38). Other, more complex sampling procedures may be required for certain classes of constituents such as organic compounds or dissolved gases. The above references also provide guidance for these procedures.

For evaluation of programs containing ground-water data, respondents were asked to identify a few key factors relevant to the water well being sampled. It was assumed that, if knowledge about these key factors were available for sample-site selection, the corresponding samples are representative of aquifer conditions. These factors included aquifer name, lithologic unit, well casing, and method of sealing the annulus (space between casing and rock materials). Respondents also were asked if an amount of water equivalent to at least three times the casing volume of the well was pumped before sampling. (See Field-Practices Questionnaire, part 3c, Ground-Water Sites, in the Supplemental Information section.) The analyses met the representative-sample criterion for ground water if the responses to all of these questions were positive. Results for this criterion are summarized in figure 2B and table 5. For both Colorado and Ohio, 100 percent of all ground-water analyses evaluated in Phase II met this criterion, even though only a few (largely Federal) organizations were represented (table 2).

#### Other Sample-Collection Practices

The criterion for other sample-collection practices pertains to procedures or equipment that ensure sample integrity or aid in the interpretation of water-quality analyses. These procedures include selection of sampling equipment appropriate for the constituents of interest, use of standard equipment-cleaning procedures, and concurrent measurement of relevant environmental conditions. Selection of appropriate sampling equipment includes consideration of the equipment's sorptive or leaching characteristics, particularly if the constituent of interest is expected to be present in trace concentrations. For example, if trace metals are to be analyzed, the use of a sampler having metal surfaces that may contaminate the sample would be inappropriate. Sampling equipment needs to be as free of contamination as possible before use; for example, pumps and delivery tubes used to obtain ground-water samples need to be thoroughly cleaned and rinsed between well samplings to prevent cross contamination. For some con-

stituents, ancillary data are needed to enhance interpretation. For example, water temperature is important for interpretation of dissolved-oxygen concentrations because of the relation of water temperature to the solubility of dissolved gases in water. The need for ancillary data pertained, in this study, to analyses of dissolved oxygen, dissolved solids, lead, polychlorinated biphenyl, atrazine, suspended sediment, and total coliform bacteria (table 3).

The criterion for other sample-collection practices was met by 99 percent of analyses for Colorado and 89 percent for Ohio (table 5). For both Colorado and Ohio, most of the samples that did not meet this criterion were samples for the analysis of lead and suspended sediment that were not collected with appropriate equipment. That is, potentially contaminating sampling devices were used to collect samples for lead analyses, and suspended-sediment samples were collected without depth-integrating sampling devices.

#### Sample Handling and Preservation

The criterion for sample handling and preservation consists of procedures used to maintain the chemical, physical, and (or) biological characteristics of a sample as nearly as possible to the characteristics at the time of sampling. Procedures of sample handling differ with the constituent of interest, and may include limits on holding time between sample collection and analysis, requirements for the composition and preparation of sample containers, and techniques for filling sample containers. Procedures of sample preservation are limited to cooling to 4°C, addition of chemicals, pH adjustment, or freezing (American Public Health Association and others, 1981, p. 41). The appropriate sample-preservation procedures also depend on the constituent of interest.

The composition of the sample container can affect the chemistry of the sample. Organic substances may leach from plastic containers and cap liners, so that the containers are unsuitable for samples to be analyzed for trace concentrations of organic substances. Similarly, borosilicate-glass or plastic containers need to be used in preference to ordinary soda-lime glass (also called soft glass) containers for collection of samples for analysis of trace metals because of the undesirable leaching characteristics of soda-lime glass.

Sample containers need to be cleaned using standard procedures to prevent contaminating the sample with residue remaining from previous samples or from contact with the environment. For example, containers that will be used to hold samples for the analysis of trace metals need to be rinsed with dilute acid followed by deionized water to remove residues. Similarly, containers that will be used to collect samples for the analysis of bacteria need to be sterilized.



Without preservation, most constituents in a water sample undergo chemical or biological change--some almost immediately and others during the time the sample is being held for laboratory analysis. For example, metals may be lost from solution through chemical changes or by adsorption to container walls. Therefore, samples for the analysis of metals need to be acidified immediately after collection to prevent such losses. Similarly, microbiological activity can cause changes in relative concentrations of nitrate, nitrite, and ammonia unless microbiological activity is decreased or stopped through addition of a preservative or by refrigeration, or both.

Even with sample preservation, all constituents in a sample cannot be completely stabilized for an indefinite time, although some are more likely to change than others. As a result, limits on holding times have been recommended by the Office of Water Data Coordination (1977) and the U.S. Environmental Protection Agency (1982, 1984a), among others. Examples of maximum recommended holding times for properly preserved samples are 6 hours for bacteriological samples, 48 hours for nitrite-nitrogen samples, and as much as 6 months for most metals.

In the screening process for this study, the sample-handling and sample-preservation criterion was applied to all properties and constituents surveyed except pH, specific conductance, sulfate, chloride, dissolved solids, and suspended sediment (table 3). This criterion was met by the second fewest of analyses of any of the criteria; however, 91 percent of the analyses reported for Colorado and 72 percent reported for Ohio met the sample-handling and sample-preservation criterion (table 5). Procedures that did not meet the criterion included: (1) The use of containers that had not been acid-rinsed for samples to be analyzed for lead; (2) collection of microbiological samples that were not treated with a chelating or dechlorinating agent when relatively large concentrations of metals or chloride were suspected to be present; and (3) samples that were collected with automatic samplers and not preserved immediately after collection.

#### Field-Instrument Use and Maintenance

The criterion for field-instrument use and maintenance consists of calibration and proper operation of instruments used to make analytical measurements in the field, as well as maintenance of instruments. Constituents and properties such as temperature, dissolved oxygen, and pH may change rapidly after sample collection and, under certain conditions, specific conductance, total acidity, and total alkalinity also may change. Therefore, prompt measurement is desirable for accurate characterization of water-quality conditions. Unlike other unstable constituents that cannot be readily measured on site and need to be sampled and preserved for laboratory analysis, these constituents and properties can be readily measured at the sampling site with analytical instruments designed for field use.



Field analyses need to be subject to quality controls similar to those applied in the laboratory. These include at least daily calibration of instruments when they are in use, and the use of standard solutions for calibration. Measurements of temperature, pH, dissolved oxygen, and specific conductance made by continuous monitoring systems also require stringent quality-control practices similar to those for laboratory or other field applications.

The criterion for field-instrument use and maintenance was applied to measurements of pH, dissolved oxygen, and specific conductance made in the field. For Colorado, 100 percent of the measurements met the criterion and, for Ohio, 84 percent met the criterion (table 5). No single reason accounted for the few analyses that did not meet the field-instrument use and maintenance criterion; however, failure to calibrate dissolved-oxygen meters was reported, as were use of only one standard solution to calibrate pH meters and failure to compensate specific-conductance measurements to the standard of 25°Celsius.

#### LABORATORY QUALITY-ASSURANCE PRACTICES

Laboratory practices need to be guided by programs for testing and evaluation of all facets of quality assurance, quality control, and laboratory analytical methods, to define the reliability of results. These laboratory practices, when effectively used, minimize the errors introduced into sample results by sample-analysis procedures.

##### Quality Assurance

The criterion for quality assurance comprises interlaboratory and intralaboratory testing, adequate training of laboratory personnel, adequate instruments and supplies, and corrective actions in response to problems in data results.

Interlaboratory and intralaboratory testing and evaluation are independent ways to evaluate the effectiveness of quality-assurance programs. Laboratories periodically analyze samples with predetermined compositions that are not known to the laboratory analysts. Results of analysis of these samples are reported to an independent testing agency, or to a designated quality-assurance individual within the laboratory, for evaluation. These testing programs help to determine laboratory quality-assurance programs that need to be improved.

The provision for adequately trained personnel and well maintained, up-to-date instruments and supplies are fundamental to a quality-assurance program. For example, guidelines specifying quality of instrumentation and reagents, instrument-

operation practices, levels of analyst training, and other concerns are published in manuals and handbooks of the U.S. Environmental Protection Agency (1979b) and the U.S. Geological Survey (Friedman and Erdmann 1982). Laboratories need to incorporate and use guidelines such as these in daily operations. Adherence to laboratory-practices guidelines, either from published sources such as the two cited above or through a laboratory's own documentation, is considered essential to establishing and maintaining standard operating procedures.

Corrective actions taken in response to deviations from standard procedures or errors in analytical results are needed to avoid misinterpretation because of erroneous data. Corrective actions may involve, for example, re-collection and reanalysis of samples, improvements in techniques or analytical methods, or some combination of these. Although corrective actions are an important part of a laboratory quality-assurance program, they commonly are overlooked.

The laboratory quality-assurance criterion was applied to all constituents and properties in the Phase-II evaluation except suspended sediment and field measurements of dissolved oxygen, pH, and specific conductance (table 3). (See section on Screening Procedure and Criteria.) The criterion was met by 96 percent of the analyses for Colorado and 75 percent for Ohio (table 5); for Ohio, one laboratory was responsible for all but 2 percent of the analyses that did not meet this criterion. No distinctions can be made, relative to laboratory-practices criteria, between ground-water and surface-water analyses because ground-water and surface-water samples are not handled differently in the laboratory.

Quality-assurance programs were similar among water-quality laboratories participating in this study. Nearly all water-quality laboratories that were queried reported that they participated in interlaboratory and intralaboratory testing. Most often, the participation cited was either in the U.S. Environmental Protection Agency's Performance Evaluation Program or the U.S. Geological Survey's Standard Reference Water Sample Program. The U.S. Environmental Protection Agency commonly was cited as a source for reference materials for intralaboratory testing.

All participating water-quality laboratories responded that they used some documented guidelines for establishing quality-assurance programs and good laboratory practices. References most commonly cited were U.S. Environmental Protection Agency (1979b) and Friedman and Erdmann (1982). Additionally, laboratories funded by the U.S. Environmental Protection Agency cited their own quality-assurance program guidelines.

Two water-quality laboratories conducting research programs did not meet the quality-assurance criterion because they reported that they did not conduct interlaboratory or intralaboratory testing. Another laboratory reported that no corrective actions were taken for errors found in laboratory data.

## Quality Control

The quality-control criterion consists of the routine application of specific practices during a measurement process to determine data quality. Laboratory quality control is used to determine the replicability of results on the same sample (precision) and the agreement between measurement results and the actual or theoretically true sample value (accuracy). **Control samples** are used to measure precision and accuracy. Control-sample results that are outside acceptable statistical ranges are an indication of significant analytical error. Detailed discussions of methods for determining precision and accuracy in environmental laboratories are available in U.S. Environmental Protection Agency (1979b), Friedman and Erdmann (1982), Kirchmer (1983), and Keith and others (1983).

The quality-control criterion was applied to all the Phase-II properties and constituents except suspended sediment and field measurements of dissolved oxygen, pH, and specific conductance (table 3). The specific procedures that were applied to each constituent can be found in the Laboratory-Practices Questionnaire in the Supplemental Information Section.

The use of quality-control procedures for estimating precision and accuracy, and the application of those procedures to specific analytical methods, were very similar among responding laboratories. Water-quality laboratories responsible for 100 percent of all analyses for Colorado and 99 percent of all analyses for Ohio met the quality-control criterion for the use of control samples to statistically assess data quality for each constituent measured (table 5). Two laboratories reported that no quality-control procedures were used for analysis of microbiological samples. The other laboratories not meeting the quality-control criterion responded that they did not use control samples or, if they did, that no statistical measures were applied to define data quality.

## Analytical Methods

The analytical-methods criterion addresses the use of appropriate methods for determining the concentrations of constituents contained in a water sample. Different analytical methods may be appropriate for different water-quality programs depending on the degree of accuracy required by the goals of the program. Furthermore, different analytical methods used to analyze the same constituent may not provide results that are equivalent. Therefore, when combining data bases, it is important that methods used to analyze a particular constituent yield comparable results.

Specific analytical methods for water analysis are documented in the manuals and handbooks of the American Society for Testing and Materials (1980), American Public Health Association and others (1971, 1976, and 1981), Association of Official Analytical

Chemists (1980), U.S. Geological Survey (Guy, 1969; Fishman and Brown, 1976; Greeson and others, 1977; Thatcher and others, 1977; Skougstad and others, 1979), and U.S. Environmental Protection Agency (1974, 1979a, 1984a, 1984b). Methods appropriate for determining concentrations of constituents at environmentally significant levels, described in these references, were used as the screening criterion for all the selected constituents and properties except those measured in the field (table 3).

To be accepted by the above-listed groups, a laboratory method needs to be rigorously tested and reviewed in inter-laboratory studies. Many of the methods contained in these references are required by regulations for testing conducted under the Clean Water Act by the U.S. Environmental Protection Agency. That agency updates its list of accepted methods periodically, most recently in October 1984 (U.S. Environmental Protection Agency, 1984b). The result of these efforts has been the nationwide recognition of the above references for providing methods of water-quality testing (Carter, 1984).

Nearly all of the analyses performed by laboratories participating in this study met the analytical-methods criterion (94 percent of analyses for Colorado and 93 percent for Ohio; table 5). Most of the analyses were performed using methods cited in four common references: The U.S. Environmental Protection Agency (1974, 1979a), Skougstad and others (1979), American Public Health Association and others (1971, 1976, 1981), and the American Society for Testing and Materials (1980). Methods of the U.S. Environmental Protection Agency and the American Public Health Association and others were the most widely cited.

Most of the analyses that did not meet the analytical-methods criterion were suspended-sediment analyses. The Technical Committee on Water Data has adopted approved methods for sediment analysis adapted from Guy (1969) and the American Society for Testing and Materials (1980). However, only the U.S. Geological Survey and one other Federal program in Colorado reported that they used the approved method. All other programs collecting samples for the analysis of suspended-sediment concentration reported use of the total-nonfilterable-residue method (U.S. Environmental Protection Agency, 1979a; and the American Public Health Association and others, 1971, 1976, 1981). This method has not been accepted by the Technical Committee on Sedimentation because it may yield biased measurements for any sediment sample in which sand-sized materials are present (G. D. Glysson, U.S. Geological Survey, oral commun., 1985).

The method for analysis of total-nonfilterable residue is widely used for analysis of suspended sediment instead of the method approved by the Technical Committee on Sedimentation of the



Interagency Advisory Committee, because the two methods are similar and there is more widespread awareness of the former. Yet, those organizations mentioned above, which publish the nonfilterable-residue method, do not currently endorse or use that method for the analysis of suspended-sediment concentration. No comparability studies to test the equivalency of the two different methods for determining suspended-sediment concentration were found during this study.

Of the other analyses that did not meet the analytical-methods criteria, a few were reported to have been made using methods that are outdated and are no longer considered equivalent to those found in the aforementioned references. In addition, one laboratory reported the use of a nonstandard procedure for determination of total recoverable trace metals.

#### DATA BASE COMPILED FOR THE PHASE-III ASSESSMENT

Phase III of this study will include further evaluation of the 1984 water-quality data that passed the Phase-I and Phase-II screening steps, including the degree to which these data are adequate--in terms of data types, amounts, and areal distribution--for addressing major water-quality questions at the statewide level.

The water analyses and measurements meeting all the screening criteria were compiled into separate data bases for Colorado and Ohio. Relatively few of the analyses and measurements passed all the screening steps of both Phase I and Phase II. For Colorado, about 165,000 surface-water and ground-water analyses and measurements were evaluated in Phase II, and about 26,400 (16 percent) passed the screen (table 6). The number that passed represented only 11 percent of the Colorado analyses and measurements inventoried in Phase I (table 6). For Ohio, about 76,300 surface-water and ground-water analyses and measurements were evaluated in Phase II, and about 34,900 (46 percent) passed the screen (table 7). The number that passed the Phase-II screen amounts to only about 14 percent of the total number of Ohio analyses and measurements inventoried in Phase I (table 7).

It should be noted that the numbers and percentages in tables 6 and 7 exclude analyses from more than 170,000 water samples for Colorado and more than 1 million for Ohio, initially inventoried in Phase I, that were collected for purposes other than to characterize ambient water-quality conditions. (See section on Summary of Phase I; also, Hren and others, 1987.)



Table 6.--Numbers and percentages of surface- and ground-water analyses or measurements entering selected project phases, Colorado

Property or constituent	(1) Number of analyses and measure- ments prior to Phase-I screen <sup>1</sup>	(2) Number of analyses and measure- ments that passed Phase-I screen	(3) Analyses and measure- ments that passed Phase-I screen, percentage of column 1	(4) Number of analyses and measure- ments that passed Phase-II screen	(5) Analyses and measure- ments that passed Phase-II screen, percentage of column 2 (rounded)	(6) Analyses and measurements that passed Phase-I and Phase-II screens, percentage of column 1 (rounded)
Surface-water analyses and measurements						
Dissolved oxygen-----	26,500	20,800	78	2,100	10	8
pH-----	38,800	25,900	67	4,220	16	11
Specific conductance-----	32,200	25,600	80	4,140	16	13
Alkalinity-----	30,900	24,000	78	1,710	7	6
Sulfate-----	13,000	7,990	61	2,000	25	15
Chloride-----	12,500	7,800	62	2,000	26	16
Dissolved solids-----	9,680	5,470	56	1,400	26	14
Total phosphorus-----	18,400	12,800	70	1,140	9	6
Nitrate-----	22,300	15,900	71	2,360	15	11
Lead-----	8,400	5,170	62	1,120	22	13
Polychlorinated biphenyl---	860	180	21	20	11	2
Atrazine-----	0	N/A		N/A		N/A
Suspended sediment-----	4,520	3,120	69	1,650	53	36
Fecal coliform bacteria----	9,480	6,160	65	0	0	0
Totals, surface water (rounded)	228,000	161,000	71	23,900	15	10
Ground-water analyses						
Dissolved solids-----	2,290	890	39	800	90	35
Iron-----	3,680	610	17	250	41	7
Manganese-----	3,680	610	17	250	41	7
Uranium-----	530	230	43	20	9	4
Nitrate-----	1,310	1,220	93	1,130	93	86
Phenol-----	290	40	14	40	100	14
Methylene-blue-active substances-----	30	20	67	20	100	67
Total coliform bacteria----	220	40	18	20	50	9
Totals, ground water (rounded)	12,000	3,660	30	2,530	69	21
Grand totals (rounded)	240,000	165,000	69	26,400	16	11

<sup>1</sup>Numbers include only ambient-water-quality samples; see Summary of Phase I.

Table 7.--Numbers and percentages of surface- and ground-water analyses or measurements entering selected project phases, Ohio

Property or constituent	(1) Number of analyses and measure- ments prior to Phase-I screen <sup>1</sup>	(2) Number of analyses and measure- ments that passed Phase-I screen	(3) Analyses and measure- ments that passed Phase-I screen, percentage of column 1	(4) Number of analyses and measure- ments that passed Phase-II screen	(5) Analyses and measure- ments that passed Phase-II screen, percentage of column 2 (rounded)	(6) Analyses and measurements that passed Phase-I and Phase-II screens, percentage of column 1 (rounded)
Surface-water analyses and measurements						
Dissolved oxygen-----	27,900	11,600	42	8,300	72	30
pH-----	34,500	11,800	34	8,440	72	24
Specific conductance-----	22,000	14,200	64	6,170	43	28
Alkalinity-----	24,200	4,180	17	1,810	43	7
Sulfate-----	16,600	1,060	6	400	38	2
Chloride-----	18,400	1,280	7	340	27	2
Dissolved solids-----	5,150	2,940	57	980	33	19
Total phosphorus-----	14,500	7,090	49	2,250	32	16
Nitrate-----	21,500	8,560	40	2,230	26	10
Lead-----	11,300	4,140	37	220	5	2
Polychlorinated biphenyl--	1,160	600	52	0	0	0
Atrazine-----	750	600	80	0	0	0
Suspended sediment-----	6,340	5,960	94	2,810	47	44
Fecal coliform bacteria---	4,760	1,810	38	430	24	9
Totals, surface water (rounded)	209,000	75,800	36	34,400	45	16
Ground-water analyses						
Dissolved solids-----	800	100	12	100	100	12
Iron-----	9,260	100	1	100	100	1
Manganese-----	9,030	100	1	100	100	1
Uranium-----	0	N/A	N/A	N/A	N/A	N/A
Nitrate-----	1,380	85	6	85	100	6
Phenol-----	780	85	11	85	100	11
Methylene-blue-active substances-----	150	0	0	N/A	N/A	0
Total coliform bacteria---	11,300	0	0	N/A	N/A	0
Totals, ground water (rounded)	32,700	470	1	470	100	1
Grand totals (rounded)	242,000	76,300	32	34,900	46	14

<sup>1</sup> Numbers include only ambient water-quality samples; see Summary of Phase I.

Of the Colorado surface-water analyses and measurements, about 23,900 analyses and measurements (15 percent) evaluated in Phase II passed the Phase-II screen; another 71 percent were provisional (fig. 3A). About one-half (51 percent) of the 23,900 analyses and measurements are of gross characteristics of water quality (dissolved oxygen, pH, alkalinity, or specific conductance). About 34 percent are analyses of inorganic constituents (sulfate, chloride, dissolved solids, lead, and suspended sediment), and about 15 percent are analyses of nutrients (phosphorus and nitrate). Very few organic-compound analyses (20 analyses of polychlorinated biphenyl) passed the screen, and no analyses of atrazine were available for evaluation. Also, no analyses of fecal coliform bacteria passed the Phase-II screen (table 6).

For Colorado ground-water samples, about 2,530 analyses (69 percent) passed the Phase-II screen. Nearly one-half are nitrate analyses and nearly one-third are analyses of dissolved solids. Very few analyses for uranium, methylene-blue-active substances (surfactants, detergents), and total coliform bacteria (20 each) remain after the Phase-I and Phase-II screens (table 6).

Of the Ohio surface-water analyses and measurements, about 34,400 (45 percent) evaluated in Phase II passed the screen; another 23 percent were provisional (fig. 3B). Most of the 34,400 analyses and measurements (72 percent) are of gross characteristics of water quality (dissolved oxygen, pH, specific conductance, or alkalinity). Another 21 percent are analyses of nutrients (phosphorus and nitrate) or of suspended sediment. Few analyses of sulfate, chloride, lead, and fecal coliform bacteria, and no analyses for polychlorinated biphenyl or atrazine, passed the Phase-II screen (table 7).

Of the few Ohio ground-water analyses (about 470) evaluated, all passed the Phase-II screen (table 7). These include about equal numbers of analyses for dissolved solids, iron, manganese, nitrate, and phenol. No Ohio ground-water analyses were reported in Phase II for uranium, methylene-blue-active substances, or total coliform bacteria.

For both States, most of the data that passed both the Phase-I and Phase-II screens were for constituents and properties that broadly characterize water quality; that is, dissolved oxygen, pH, specific conductance, and alkalinity. Therefore, the Colorado and Ohio data bases contain a relatively large number of analyses that are needed to address issues of long-standing concern, such as sanitary quality and salinity (inorganic constituents and physical properties). The fewest analyses that passed the Phase-I and Phase-II screens were for trace constituents; that is, atrazine, polychlorinated biphenyl, and lead. As a result, the data bases for Colorado and Ohio contain relatively few analyses for constituents that are needed to address issues of most recent regional and national concern, such as contamination of waters by potentially toxic organic compounds and trace metals.

There are at least two possible explanations for this uneven distribution. First, the analyses for trace-organic compounds and trace metals reported in 1984 were much fewer than analyses for major inorganic constituents and gross measures of water quality, largely, no doubt, because analyses for the trace constituents are much more expensive. Secondly, analyses for trace-organic compounds and trace metals were less likely to pass the Phase-II screen, because procedures for the collection and analysis of samples for these trace constituents are much more exacting than for common inorganic constituents or for other constituents present in relatively large concentrations.

Data from several programs that met all Phase-I criteria except the criterion requiring that the data be stored in computer files were evaluated in Phase II. These programs were screened out in Phase I only because time constraints precluded transferring all the pertinent data to computer files (Hren and others, 1987). Any of these data that met the Phase-II criteria could be added to the data base if the data were entered into computer files. However, none of these analyses or measurements passed the Phase-II screen. This indicates that at least a preliminary field and laboratory quality-assurance screening needs to be conducted before time and effort are expended to transfer existing water-quality data from paper files to computer files.

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## SUPPLEMENTAL INFORMATION

The following notations have been added to the questionnaires to indicate the criterion to which each question pertains:

### Field-Practices Questionnaire

- S1 Documented sample-collection-techniques criterion;
- S2 Representative-sample criterion;
- S3 Other sample-collection-practices criterion;
- S4 Sample-handling and sample-preservation critrion;
- S5 Field-instrument use and maintenance criterion.

### Laboratory-Practices Questionnaire

- QA Quality assurance criterion;
- QC Quality control criterion;
- AM Analytical methods criterion.

# Field-Practices Questionnaire

## Instructions for Completing the Questionnaire

Check the information listed below and make any necessary corrections (the ID number is a USGS reference number). Please answer the questionnaire only as it pertains to the program listed.

On the second page of the questionnaire, circle the constituents that were analyzed as part of the program. If none of the constituents can be circled, then you need not fill out the rest of the questionnaire.

On page three, list sites that were located to measure ambient water quality, and then list sites that were located to measure water quality downstream of a point source of pollution. If all or none of the sites in the program were selected for one of the above reasons, then write in "all" or "none." If more space is needed, you may attach a list. These questions are intended to give us information about your site-selection strategies; that is, were sites selected randomly or was site selection problem-oriented?

The rest of the questionnaire is in two parts. Questions contained in the first part (pages 4 and 5) should be applied to your program as a whole. These deal with general sampling strategies.

Part two (pages 6 through 11) is grouped by constituent and deals with sample-handling and collection techniques specific to each constituent. Each of the remaining questions can be answered by circling yes or no (Y,N) in the column to the right of each question.

Agency: \_\_\_\_\_ ID Number: \_\_\_\_\_

Address: \_\_\_\_\_

Program name: \_\_\_\_\_

Period of Record: \_\_\_\_\_

Contact Name: \_\_\_\_\_ Phone: \_\_\_\_\_

USGS Contact: \_\_\_\_\_ Phone: \_\_\_\_\_



## 1. GENERAL PROGRAM INFORMATION

1. In the list below, circle the constituents that were analyzed as part of the program.

For surface water:

dissolved oxygen	total phosphorus
pH	total Kjeldahl nitrogen
specific conductance	nitrate-N
alkalinity	nitrite-N
total dissolved solids	ammonia-N
dissolved sulfate	atrazine
dissolved chloride	lead
suspended sediment	fecal coliform bacteria
dissolved orthophosphate	polychlorinated biphenyls (PCB)

For ground water:

iron	total coliform bacteria
manganese	total recoverable phenolics
uranium	methylene-blue-active substances
total dissolved solids	nitrate-N

2. In what computer data base are data from this program stored?  
 \_\_\_\_\_ Who may be contacted  
 about retrieving these data? \_\_\_\_\_

- S1 3. Do you use documented sample-collection and sample-handling techniques, and if so, what is the reference? \_\_\_\_\_

4. List below the laboratories that analyzed samples for this program and the period during which each laboratory was used.

	Laboratory name, address, phone number, and contact person	Period
1.	_____	_____
	_____	
2.	_____	_____
	_____	
3.	_____	_____
	_____	
4.	_____	_____
	_____	
5.	_____	_____
	_____	
6.	_____	_____
	_____	

## 2. GENERAL DATA-COLLECTION STRATEGIES

### A. Site Selection

1. List below any sites that were located to study ambient water quality (that is, were not located specifically to study areas that were previously identified as polluted or were suspected of being polluted). In addition, indicate whether they are ground water (GW) or surface water (SW) sites.

Latitude/longitude

Site name


2. List below any sites that were located downstream or downgradient of a known, nearby point source of pollutants and whether they are ground-water (GW) or surface-water (SW) sites.

Latitude/longitude

Site name


## III. GENERAL FIELD PRACTICES

To answer the following questions, please circle either yes or no (Y,N) to the right of each question. If a question does not apply to your program, then circle not applicable (NA). Please answer all of the questions.

A. Sample Handling

- |    |   |            |
|----|---|------------|
| S4 | 1. Were samples for analysis of dissolved constituents filtered immediately with a membrane filter with pore size 0.45 microns or less? | Y   N   NA |
| S3 | 2. Was filtering equipment rinsed between samples?  | Y   N   NA |
|    | 3. Were filters flushed with native water before the sample container was filled?   | Y   N   NA |

S2   B. Surface-Water Sites

- |    |   |            |
|----|---|------------|
| 1. | Was discharge measured or estimated from a nearby stream gage at the time of sample collection and recorded with the sample analysis?   | Y   N   NA |
| 2. | If collected manually, were samples collected with a depth-integrating sampler at multiple verticals in the cross section?  | Y   N   NA |
| 3. | If collected with an automatic sampler or if grab sampled, were the sample concentrations checked to relate the point sample concentration to that which is representative of the entire cross section and adjusted if necessary? | Y   N   NA |
| 4. | If collected manually, were samples obtained from one point in the stream without integrating sub-samples and without knowledge of mixing conditions?   | Y   N   NA |

C. Ground-Water Sites

1. In general, for your ground-water-quality sampling program, which of the following are known? If known, which are in machine-readable format?

		<u>Known</u>	<u>Machine readable</u>
S2	a. Aquifer names	Y N	Y N
S2	b. Specific lithologic unit within the aquifer	Y N	Y N
	c. Depth interval within which water enters the well	Y N	Y N
S2	d. Well casing type	Y N	Y N
	e. Pump type	Y N	Y N
	f. Well use (public water supply, industrial, and so forth)	Y N	Y N
	g. Method of well construction	Y N	Y N
S2	h. Method of sealing the annulus	Y N	Y N
S2	2. Prior to sample collection, were wells pumped at least three times the casing volume or until the pH or specific conductance stabilized?	Y N NA	
	3. Were anions and cations balanced as a check of analytical results?	Y N NA	

## IV. CONSTITUENT-SPECIFIC DATA-COLLECTION PRACTICES

The following questions are grouped by constituent. The water resource of interest is listed next to the constituent of interest; for example, Dissolved Oxygen (Surface Water). If you do not collect samples for analysis of a constituent listed for the designated water resource, then write "not collected" next to the constituent name. If more than one constituent is listed and not all are measured, circle the constituent that applies to your program and cross out those that do not.

A. Dissolved Oxygen (Surface Water)

- |    |   |   |   |    |
|----|---|---|---|----|
| S3 | 1. Were concurrent temperature measurements made, accurate to 1.0 degree C?   | Y | N | NA |
| S3 | 2. Were sample-collection times recorded and stored with the sample analysis?   | Y | N | NA |
|    | 3. Were measurements made with a membrane electrode either in situ or on site?  | Y | N | NA |
| S5 | .1 If so, were meters calibrated at least once per day when in use (or if using a continuous monitor, at least once every 2 weeks)? | Y | N | NA |
| S4 | 4. If not measured in situ, was the sample bottle filled from the bottom without aeration?  | Y | N | NA |
| S4 | 5. If a membrane electrode was not used, were measurements made by the modified Winkler method and titrated within 8 hours?         | Y | N | NA |

B. pH (Surface Water)

- |    |  |   |   |    |
|----|--|---|---|----|
|    | 1. Was pH measured either on site or in situ?  | Y | N | NA |
| S5 | 2. Was pH measured electrometrically?  | Y | N | NA |
| S5 | .1 If so, were meters calibrated at least daily with at least two different standard solutions when in use (or, if using a continuous monitor, at least once every 2 weeks)? | Y | N | NA |
| S5 | .2 Were measurements temperature-compensated?  | Y | N | NA |



C. Specific Conductance (Surface Water)

	1. Was specific conductance measured either on site or in situ?	Y	N	NA
S5	2. If so, were analyses temperature compensated to 25 degrees C?	Y	N	NA
S5	3. Were meters calibrated with a standard solution at least daily when in use (or, if using a continuous monitor, at least once every 2 weeks)?	Y	N	NA

D. Total and Dissolved Pb (Surface Water)

S3	1. Was a Teflon-coated, epoxy-coated or other nonmetal sampler used to collect samples?	Y	N	NA
S4	2. Were sample bottles polyethylene (or its equivalent) or glass?	Y	N	NA
S4	3. Were sample bottles acid-rinsed then rinsed with deionized water prior to sample collection?	Y	N	NA
S4	4. Were samples preserved with concentrated nitric acid to a pH of 2 or less?	Y	N	NA
	5. Were field blanks (distilled water that is handled identically to regular samples) submitted to the laboratory on a regular basis to determine if any contamination occurred during sample collection and handling?	Y	N	NA

E. Total and Dissolved Fe and Mn (Ground Water)

S4	1. Were sample bottles polyethylene (or its equivalent) or glass?	Y	N	NA
S4	2. Were sample bottles acid-rinsed then rinsed with deionized water prior to sample collection?	Y	N	NA
S4	3. Were samples preserved with concentrated nitric acid to a pH of 2 or less?	Y	N	NA
	4. Were field blanks (distilled water that is handled identically to regular samples) submitted to the laboratory on a regular basis to determine if any contamination occurred during sample collection and handling?	Y	N	NA

F. Total and Dissolved Uranium (Ground Water)

- |    |  |   |   |    |
|----|--|---|---|----|
| S4 | 1. Were sample bottles polyethylene (or its equivalent) or glass?  | Y | N | NA |
| S4 | 2. Were sample bottles acid-rinsed then rinsed with deionized water prior to sample collection?  | Y | N | NA |
| S4 | 3. Were samples preserved with hydrochloric acid to a pH of 2 or less?   | Y | N | NA |
|    | 4. Were field blanks (distilled water that is handled identically to regular samples) submitted to the laboratory on a regular basis to determine if any contamination occurred during sample collection and handling? | Y | N | NA |
|    | 5. Was a minimum of five liters of sample collected for analysis for determination of background concentrations? If not, how much sample was collected? _____  | Y | N | NA |

G. Suspended Sediment (Surface Water)

- |    |  |   |   |    |
|----|--|---|---|----|
| S3 | 1. If sampled manually, were samples collected using a depth-integrating sampler at multiple verticals in the cross-section?   | Y | N | NA |
| S3 | 2. If collected with an auto sampler or if grab sampled, were the sample concentrations adjusted to relate the point-sample concentration to that which is representative of the entire cross section? | Y | N | NA |
| S3 | 3. Were streamflow measurements made or estimated from a nearby stream gage at the time of sample collection?  | Y | N | NA |

H. Alkalinity (Surface Water)

- |    |   |   |   |    |
|----|---|---|---|----|
| S4 | 1. Was alkalinity titrated on site or within 24 hours of sample collection?   | Y | N | NA |
|    | .1 If so, were the samples titrated to an endpoint of 4.5?  | Y | N | NA |
| S4 | .2 If not titrated immediately, were samples stored at 4 degrees C until analysis?  | Y | N | NA |
| S4 | 2. Were sample bottles either polyethylene (or its equivalent) or glass?  | Y | N | NA |
| S4 | 3. If not titrated on site, were sample bottles filled so that sample overflowed when the bottle was capped to prevent entrapment of air? | Y | N | NA |

I. Total Coliform (Ground Water)

S4	1. Were samples collected in sterilized bottles and kept out of sunlight until analysis?	Y	N	NA
S4	2. Were samples either processed and incubated in the field or immediately chilled to 4 degrees C after collection?	Y	N	NA
S4	3. In general, was the time between sample collection and the start of sample processing and incubation no more than 6 hours?	Y	N	NA
S4	4. Were pumps, samplers, and delivery tubes cleaned before sample collection to reduce bacterial contamination?	Y	N	NA
S4	5. If residual chlorine was suspected to be present, were samples pretreated with sodium thiosulfate?	Y	N	NA
	6. If metals were suspected to be present in significant concentrations, were samples pre-treated with a chelating agent?	Y	N	NA

J. Fecal Coliform (Surface Water)

S4	1. Were samples collected from an area where water was well mixed?	Y	N	NA
S4	2. Were samples collected in sterilized bottles and kept out of sunlight until analysis?	Y	N	NA
S4	3. Were samples either processed and incubated in the field or immediately chilled to 4 degrees C after collection?	Y	N	NA
S4	4. In general, was the time between sample collection and the start of sample processing and incubation no more than 6 hours?	Y	N	NA
S4	5. If residual chlorine was suspected to be present, were samples pretreated with sodium thiosulfate?	Y	N	NA
S4	6. If metals were suspected to be present in significant concentrations, were samples pre-treated with a chelating agent?	Y	N	NA

K. Phosphorus Species (Surface Water)

- |    |  |        |
|----|--|--------|
| S4 | 1. Were sample containers either glass or polyethylene (or its equivalent)?  | Y N NA |
| S4 | 2. Were sample containers cleaned with a phosphate-free detergent?   | Y N NA |
| S4 | 3. If the sample was filtered, was the filter thoroughly washed either by soaking in distilled water or by running through several 100-mL portions of distilled water?   | Y N NA |
| S4 | 4. Were total phosphorus samples preserved by one of the following methods:<br>a. Addition of sulfuric acid to a pH of less than 2 and chilled to 4 degrees C;<br>b. Addition of 40 mg mercuric chloride per liter of sample and chilled to 4 degrees C; or<br>c. Chilled to 4 degrees C and analyzed within 24 hours? | Y N NA |
| S4 | 5. Were dissolved orthophosphorus samples preserved by one of the the following methods after immediate filtering:<br>a. Chilled to 4 degrees C and analyzed within 48 hours, or<br>b. Addition of 40 mg mercuric chloride per liter of sample and chilled to 4 degrees C?   | Y N NA |

L. Nitrogen Species (Surface Water and Ground Water)

- |    |  |        |
|----|--|--------|
| S4 | 1. Were sample containers glass or polyethylene (or its equivalent)?   | Y N NA |
| S4 | 2. Were nitrate samples preserved with 40 mg mercuric chloride per liter, or sulfuric acid to pH less than 2, or frozen at or below -20 degrees C? | Y N NA |
| S4 | 3. Were nitrite samples preserved with 40 mg mercuric chloride, or kept at 4 degrees C and analyzed within 48 hours?                               | Y N NA |
| S4 | 4. Were ammonia and total Kjeldahl nitrogen samples preserved with sulfuric acid to a pH less than 2 and stored at 4 degrees C?                    | Y N NA |
| S4 | 5. Were samples stored out of sunlight or in a dark bottle until analysis?   | Y N NA |

M. Total Recoverable Phenolics (Ground Water)

- |    |  |   |   |    |
|----|--|---|---|----|
| S4 | 1. Were sample containers glass with a Teflon-lined cap?   | Y | N | NA |
| S4 | 2. Were samples preserved either to pH 4 with phosphoric, sulfuric, or hydrochloric acid and addition of 1 gram copper sulfate per liter of sample; or to a pH of 2 with sulfuric acid and chilled at 4 degrees C? | Y | N | NA |

N. Methylene-Blue-Active Substances (MBAS) (Ground Water)

- |    |  |   |   |    |
|----|--|---|---|----|
| S4 | 1. Were sample containers glass with a Teflon-lined cap?             | Y | N | NA |
| S4 | 2. Were samples chilled to 4 degrees C or preserved with chloroform? | Y | N | NA |

O. Atrazine and Polychlorinated Biphenyls (PCB) (Surface Water)

- |    |  |   |   |    |
|----|--|---|---|----|
| S3 | 1. Were pumps, samplers, and delivery pipes thoroughly cleaned before use and between sites?   | Y | N | NA |
| S4 | 2. Were sample containers glass with a Teflon-or aluminum-foil-lined cap?  | Y | N | NA |
| S4 | 3. Were sample bottles cleaned, then rinsed with an organic solvent and baked at 300 degrees C?  | Y | N | NA |
| S4 | 4. Were samples for analysis of dissolved constituents filtered immediately through a 0.45-micron silver-membrane filter?  | Y | N | NA |
| S4 | 5. Were samples chilled to 4 degrees C after collection?   | Y | N | NA |
|    | 6. Were field blanks (distilled water that is handled identically to regular samples) submitted to the laboratory on a regular basis to determine if any contamination occurred during sample collection and handling? | Y | N | NA |



Laboratory Practices Questionnaire

## Instructions for Completing the Questionnaire

Check the information listed below and make any necessary corrections. Please answer the questionnaire only as it pertains to the agency and program listed.

The questionnaire consists of two parts. The first (I. Laboratory Quality-Assurance Guidelines) can be completed by circling either yes (Y) or no (N) to the right of each question.

The second part (II. Methods of Analysis) contains a list of analytical methods grouped by constituent. Circle the number corresponding to the method or methods used by your laboratory for the period during which you analyzed samples for this agency. Indicate in the space to the right of the methods circled the time period during which that method was used. Include a reference from the list provided. If a method or reference was used other than one of those listed, then please specify in the space provided for "other."

Laboratory: \_\_\_\_\_

Address: \_\_\_\_\_

\_\_\_\_\_

Phone: \_\_\_\_\_ Contact Name: \_\_\_\_\_

Agency: \_\_\_\_\_ ID Number: \_\_\_\_\_

Program name: \_\_\_\_\_

Period of Record: \_\_\_\_\_

USGS Contact: \_\_\_\_\_ Phone: \_\_\_\_\_

## I. LABORATORY QUALITY-ASSURANCE (QA) GUIDELINES

1. Do you have a quality-assurance plan available for inspection? Y N
- QA 2. Which of the following quality-assurance guidelines does your laboratory follow?
- a. "Quality Assurance Practices for the Chemical and Biological Analyses of Water and Fluvial Sediments," U.S. Geological Survey TWRI Book 5, Chapter A6, by Linda C. Friedman and David E. Erdmann
- b. "Handbook for Analytical Quality Control in Water and Wastewater Laboratories," U.S. Environmental Protection Agency, EPA-600/4-79-019
- c. Other \_\_\_\_\_
3. Which of the following quality-control practices are addressed or formally documented by your laboratory as part of its quality-assurance program;
- |    |  |   |   |
|----|--|---|---|
| QA | .1 Chain-of-custody procedures,  | Y | N |
| QC | .2 Laboratory sample-identification procedures,                            | Y | N |
| QC | .3 Statistical precision controls for each method,                         | Y | N |
| QC | .4 Statistical accuracy controls for each method,                          | Y | N |
| QC | .5 Use of spiked-sample-recoveries for accuracy statements,                | Y | N |
| QC | .6 Use of standard recoveries for accuracy statements,                     | Y | N |
| QC | .7 Method of standard additions,   | Y | N |
| QC | .8 Use of internal standards where required,                               | Y | N |
| QC | .9 Use of surrogate standards where required,                              | Y | N |
| QC | .10 Calibration procedures,  | Y | N |
| QC | .11 Analytical method write-ups,   | Y | N |
|    | .12 Internal laboratory quality-control checks (that is, use of unknowns), | Y | N |
| QA | .13 Independent performance and system audits,                             | Y | N |
| QA | .14 Corrective actions, and  | Y | N |
| QA | .15 Quality-assurance reports to management?                               | Y | N |
- QA 4. Does your laboratory participate in the U.S. Geological Survey Standard Reference Water Sample (SRWS) Program, the U.S. Environmental Protection Agency Performance Evaluation Program, or another audit program? If another audit program, which one? \_\_\_\_\_

## II. METHODS OF ANALYSIS

## Reference list:

USEPA - U. S. Environmental Protection Agency  
 USGS - U. S. Geological Survey  
 APHA - American Public Health Association and others, Standard  
 Methods for the Analysis of Water and Wastewater  
 ASTM - The American Society for Testing and Materials,  
 Annual Book of Standards, Part 31, Water.

## EXAMPLE

23. Total Coliform Bacteria

.1 Most probable number, MPN	June 1970 to Sept 1975	USEPA
.2 Membrane filter	Oct 1975 to present	ASTM
.3 Other _____	Oct 1975 to present	ASTM
.4 Not analyzed		

## INORGANICS AND PHYSICAL PROPERTIES

AM 1. Dissolved Oxygen

.1 Winkler, azide modification \_\_\_\_\_  
 .5 Other \_\_\_\_\_  
 .6 Not analyzed \_\_\_\_\_

AM 2. pH

.1 Electrometric \_\_\_\_\_  
 .2 Other \_\_\_\_\_  
 .3 Not analyzed \_\_\_\_\_

AM 3. Specific Conductance

.1 Wheatstone bridge \_\_\_\_\_  
 .2 Other \_\_\_\_\_  
 .3 Not analyzed \_\_\_\_\_

AM 4. Alkalinity

.1 Methyl orange titration  
     a. Manual \_\_\_\_\_  
     b. Automated \_\_\_\_\_  
 .2 Potentiometric titration to  
     pH 4.5  
     a. Manual \_\_\_\_\_  
     b. Automated \_\_\_\_\_  
 .3 Other \_\_\_\_\_  
 .4 Not analyzed \_\_\_\_\_

- AM 5. Total Dissolved Solids
- .1 Gravimetric, 180 degrees C \_\_\_\_\_
  - .2 Calculated, anions cations \_\_\_\_\_
  - .3 Other \_\_\_\_\_
  - .4 Not analyzed \_\_\_\_\_
- AM 6. Dissolved Sulfate
- .1 Automated methylthymol blue \_\_\_\_\_
  - .2 Gravimetric \_\_\_\_\_
  - .3 Turbidimetric \_\_\_\_\_
  - .4 Titrimetric, thorin \_\_\_\_\_
  - .5 Other \_\_\_\_\_
  - .6 Not analyzed \_\_\_\_\_
- AM 7. Dissolved Chloride
- .1 Titrimetric, silver nitrate \_\_\_\_\_
  - .2 Titrimetric, mercuric nitrate \_\_\_\_\_
  - .3 Colorimetric, ferricyanide \_\_\_\_\_
  - a. Manual \_\_\_\_\_
  - b. Automated \_\_\_\_\_
  - .6 Other \_\_\_\_\_
  - .7 Not analyzed \_\_\_\_\_

#### METALS

Total Recoverable Metals—defined as the concentration of metals in an un-filtered sample following treatment with hot dilute mineral acid (USEPA).

- AM 8. Lead
- .1 Atomic absorption,  
direct aspiration \_\_\_\_\_
  - .2 Atomic absorption,  
graphite furnace \_\_\_\_\_
  - .3 Atomic absorption,  
chelation-extraction;  
methyl isobutyl ketone (MIBK),  
ammonium pyrrolidine  
dithiocarbamate (APDC) \_\_\_\_\_
  - .4 Inductively coupled  
plasma-emission spectrometry \_\_\_\_\_
  - .5 Voltametry \_\_\_\_\_
  - .6 Colorimetric (dithizone) \_\_\_\_\_
  - .7 Other \_\_\_\_\_
  - .8 Not analyzed \_\_\_\_\_

AM 9. Iron

- .1 Atomic absorption,  
direct aspiration \_\_\_\_\_
- .2 Atomic absorption,  
graphite furnace \_\_\_\_\_
- .3 Atomic absorption,  
chelation-extraction (APDC,MIBK) \_\_\_\_\_
- .4 Inductively coupled  
plasma-emission spectrometry \_\_\_\_\_
- .5 Colorimetric, phenanthroline \_\_\_\_\_
- .6 Colorimetric, bipyridine \_\_\_\_\_
- a. Manual \_\_\_\_\_
- b. Automated \_\_\_\_\_
- .7 Other \_\_\_\_\_
- .8 Not analyzed \_\_\_\_\_

AM 10. Manganese

- .1 Atomic absorption,  
direct aspiration \_\_\_\_\_
- .2 Atomic absorption,  
graphite furnace \_\_\_\_\_
- .3 Atomic absorption,  
chelation-extraction (APDC,MIBK) \_\_\_\_\_
- .4 Inductively coupled  
plasma-emission spectrometry \_\_\_\_\_
- .5 Colorimetric, persulfate \_\_\_\_\_
- .6 Other \_\_\_\_\_
- .7 Not analyzed \_\_\_\_\_

AM 11. Uranium

- .1 Fluorimetric method, direct \_\_\_\_\_
- .2 Fluorimetric method, extraction  
procedure \_\_\_\_\_
- .3 Radiochemical method \_\_\_\_\_
- .4 Other \_\_\_\_\_
- .5 Not analyzed \_\_\_\_\_

## PHOSPHORUS SPECIES

AM 12. Total Phosphorus

- .1 Persulfate digestion followed by  
ascorbic acid reduction \_\_\_\_\_
- a. Manual \_\_\_\_\_
- b. Automated \_\_\_\_\_
- .2 Semiautomated block digester,  
ascorbic acid reduction \_\_\_\_\_
- .3 Other \_\_\_\_\_
- .4 Not analyzed \_\_\_\_\_



AM 13. Dissolved Orthophosphate

- .1 Ascorbic acid reduction
  - a. Automated \_\_\_\_\_
  - b. Manual, single reagent \_\_\_\_\_
  - c. Manual, two reagent \_\_\_\_\_
- .2 Other \_\_\_\_\_
- .3 Not analyzed \_\_\_\_\_

## NITROGEN SPECIES

AM 14. Total Kjeldahl Nitrogen

Digestion and distillation  
followed by:

- .1 Titration--sulfuric acid \_\_\_\_\_
- .2 Nesslerization \_\_\_\_\_
- .3 Ion-selective electrode \_\_\_\_\_
- .4 Automated phenate \_\_\_\_\_
- .5 Semiauto block digester  
salicylate colorimetric \_\_\_\_\_
- .6 Other \_\_\_\_\_
- .7 Not analyzed \_\_\_\_\_

AM 15. nitrate-N

- .1 Brucine sulfate \_\_\_\_\_
- .2 Nitrate nitrite-N minus  
nitrite-N \_\_\_\_\_
- .3 Other \_\_\_\_\_
- .4 Not analyzed \_\_\_\_\_

AM 16. Nitrate Nitrite-N

- .1 Cadmium reduction
  - a. Manual \_\_\_\_\_
  - b. Automated \_\_\_\_\_
- .2 Automated hydrazine \_\_\_\_\_
- .3 Other \_\_\_\_\_
- .4 Not analyzed \_\_\_\_\_

AM 17. Nitrite-N

- .1 Spectrophotometric (diazotization)
  - a. Manual \_\_\_\_\_
  - b. Automated \_\_\_\_\_
- .2 Other \_\_\_\_\_
- .3 Not analyzed \_\_\_\_\_

AM 18. Ammonia-N

Manual distillation at pH 9.5  
followed by:

Y N

- .1 Nesslerization
- .2 Titration
- .3 Ion-selective electrode
- .4 Automated phenate
- .5 Other \_\_\_\_\_
- .6 Not analyzed

## ORGANICS

AM 19. Total Recoverable Phenolics

Chloroform extraction performed

Y N

Distillation followed by:

- .1 Manual colorimetric,  
4-aminoantipyrene
- .2 Automated colorimetric,  
4-aminoantipyrene
- .3 Other \_\_\_\_\_
- .4 Not analyzed

AM 20. Methylene-Blue-Active Substances

- .1 Colorimetric, methylene-blue
- .2 Other \_\_\_\_\_
- .3 Not analyzed

AM 21. Atrazine

- .1 Gas-chromatographic method;
  - a. Methylene chloride extraction  
with alkali flame ionization  
(N/P) detector
  - b. Methylene chloride extraction  
with electrolytic conductivity  
detector (ECD) or a nitrogen-  
specific thermionic detector
- .2 Other \_\_\_\_\_
- .3 Not analyzed

AM 22. Polychlorinated Biphenyls (PCB)

- .1 Gas-chromatographic method;  
hexane extraction with electron-  
capture detector
- .2 Other \_\_\_\_\_
- .3 Not analyzed

## BIOLOGICAL CONSTITUENTS

AM 23. Total Coliform Bacteria

- .1 Most probable number, MPN
- .2 Membrane filter
- .3 Other \_\_\_\_\_
- .4 Not analyzed

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AM 24. Fecal Coliform Bacteria

- .1 Most probable number, MPN
- .2 Membrane filter
- .3 Other \_\_\_\_\_
- .4 Not analyzed

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## SEDIMENT

AM 25. Suspended Sediment

- .1 Evaporation and drying at 110 degrees C.
- .2 Filtration (glass fiber filter) and drying at 110 degrees C.
- .3 Other
- .4 Not analyzed

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Table 8.--Numbers of surface-water analyses and measurements pertaining to each screening criterion and percentages meeting each criterion, by organizational category, Colorado

Organizational category	Field practices										Laboratory practices								All field- and laboratory practices criteria
	Documented sample-collection techniques		Collection of representative samples		Other sample-collection practices		Sample handling and preservation		Field instrument use and maintenance		Quality assurance		Quality control		Analytical methods				
	Num-	Per-	Num-	Per-	Num-	Per-	Num-	Per-	Num-	Per-	Num-	Per-	Num-	Per-	Num-	Per-			
	ber	cent	ber	cent	ber	cent	ber	cent	ber	cent	ber	cent	ber	cent	ber	cent			
Federal agencies:																			
U.S. Geological Survey-----	19,300	100	19,300	100	2,580	100	7,260	94	6,910	100	10,600	100	10,600	100	12,200	100	98		
Other-----	24,200	100	24,200	3	1,690	100	8,250	98	5,930	98	16,400	95	16,400	99	16,500	99	.0		
Regional agencies----	5,690	100	5,690	0	830	75	3,090	67	1,030	100	4,130	68	4,130	100	4,130	90	0		
State agencies-----	102,000	100	102,000	0	19,900	100	61,800	92	49,000	100	35,800	100	35,800	100	36,700	91	0		
Local agencies-----	7,320	100	7,320	43	810	100	3,570	93	900	100	5,740	100	5,740	100	6,170	93	39		
Academic institutions	2,520	100	2,520	100	360	100	1,080	33	0	--	2,160	100	2,160	100	2,160	100	71		
Totals (rounded)	161,000	100	161,000	16	26,200	99	85,000	91	63,800	100	74,800	97	74,800	100	77,900	94	15		

<sup>1</sup> Criterion was applied only to analyses for dissolved oxygen, lead, atrazine, polychlorinated biphenyl, sulfate, chloride, dissolved solids, and suspended sediment.

<sup>2</sup> Criterion was applied only to analyses for dissolved oxygen, lead, alkalinity, sulfate, chloride, fecal coliform, total phosphorus, nitrate, atrazine, and polychlorinated biphenyl.

<sup>3</sup> Criterion was applied only to dissolved oxygen, pH, and specific conductance measured on site or in situ.

<sup>4</sup> Criterion was applied to all analyses and measurements except dissolved oxygen, pH, and specific conductance measured on site or in situ, and suspended sediment.

Table 9.--Numbers of surface-water analyses and measurements pertaining to each screening criterion, and percentages meeting each criterion, by organizational category, Ohio

Organizational category	Field practices										Laboratory practices						All field- and laboratory practices criteria
	Documented sample-collection techniques		Collection of representative samples		Other sample-collection practices		Sample handling and preservation		Field instrument use and maintenance		Quality assurance		Quality control		Analytical methods		
	Num-	Per-	Num-	Per-	Num-	Per-	Num-	Per-	Num-	Per-	Num-	Per-	Num-	Per-	Num-	Per-	
	ber	cent	ber <sup>1</sup>	cent	ber <sup>2</sup>	cent	ber <sup>3</sup>	cent	ber <sup>4</sup>	cent	ber <sup>4</sup>	cent	ber	cent	ber	cent	
Federal agencies:																	
U.S. Geological Survey-----	15,500	100	15,500	100	7,280	100	4,800	92	11,300	100	1,250	100	1,250	94	4,060	100	97
Other-----	3,810	100	3,810	43	1,500	90	2,620	50	977	37	2,540	72	2,540	91	2,830	90	22
Regional agencies----	7,670	100	7,670	100	2,500	93	3,030	100	6,830	100	836	100	836	100	836	100	98
State agencies-----	34,700	100	34,700	44	12,500	97	22,000	84	13,800	67	20,200	100	20,200	100	20,600	98	32
Local agencies-----	3,330	0	3,330	0	832	100	2,500	83	416	100	2,910	100	2,910	100	2,910	100	0
Academic institutions	10,800	100	10,800	100	3,600	33	6,000	0	0	--	8,400	0	8,400	100	10,800	78	0
Totals, (rounded)	75,800	96	75,800	67	28,200	89	41,000	72	33,300	84	36,100	75	36,100	99	42,000	93	45

<sup>1</sup> Criterion was applied only to analyses for dissolved oxygen, lead, atrazine, polychlorinated biphenyl, sulfate, chloride, dissolved solids, and suspended sediment.

<sup>2</sup> Criterion was applied only to analyses for dissolved oxygen, lead, alkalinity, sulfate, chloride, fecal coliform, total phosphorus, nitrate, atrazine, and Polychlorinated biphenyl.

<sup>3</sup> Criterion was applied only to dissolved oxygen, pH, and specific conductance measured on site or in situ.

<sup>4</sup> Criterion was applied to all analyses and measurements except dissolved oxygen, pH, and specific conductance measured on site or in situ, and suspended sediment.



Table 10.--Numbers of ground-water analyses pertaining to each screening criterion, and percentages meeting each criterion, by organizational category, Colorado and Ohio

[Dash indicates no data available; N/A indicates criterion or percentage not applicable. The criterion for instrument use and maintenance is not applicable to ground-water constituents selected.]

Organizational category	Field practices								Laboratory practices						All field- and lab- oratory- practices criteria
	Documented sample- collection techniques		Collection of repre- sentative samples		Other sample- collection practices		Sample handling and preser- vation		Quality assurance		Quality control		Analyt- ical methods		
	Num- ber	Per- cent	Num <sub>1</sub> ber	Per- cent	Num <sub>2</sub> ber	Per- cent	Num <sub>3</sub> ber	Per- cent	Num <sub>4</sub> ber	Per- cent	Num- ber	Per- cent	Num- ber	Per- cent	
Federal agencies:															
U.S. Geological Survey, Colorado--	1,150	100	1,150	100	0	N/A	600	100	1,150	100	1,150	100	1,150	100	100
Ohio-----	470	100	470	100	0	N/A	370	100	470	100	470	100	470	100	100
Other, Colorado---	2,510	100	2,510	100	40	100	1,510	100	2,510	83	2,510	94	2,510	80	55
Ohio-----	--	N/A	--	N/A	--	N/A	--	N/A	--	N/A	--	N/A	--	N/A	N/A
Regional agencies-----															
State agencies-----															
Local agencies-----															
Academic institutions---															
-----No ground-water analyses available-----															
Totals, Colorado-----	3,660	100	3,660	100	40	100	2,100	100	3,660	88	3,660	96	3,660	86	69
Totals, Ohio-----	470	100	470	100	--	N/A	370	100	470	100	470	100	470	100	100

<sup>1</sup> Criterion applied only to total coliform analyses.

<sup>2</sup> Criterion was applied only to iron, manganese, uranium, total coliform, nitrate, phenols, and methylene-blue-active substances.



