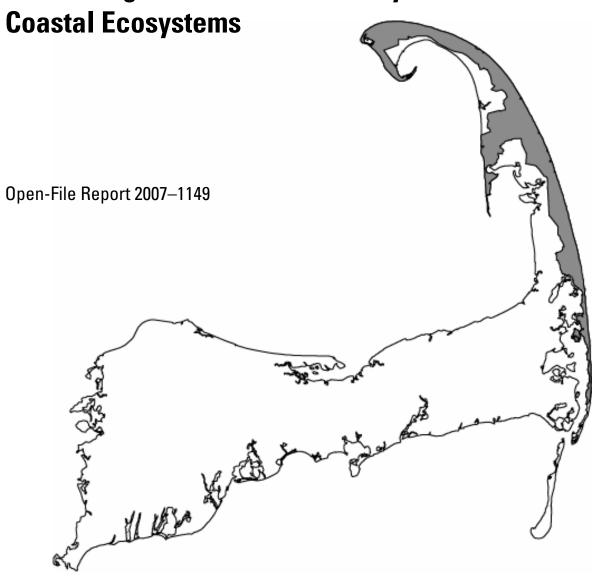


**Long-Term Coastal Ecosystem Program at Cape Cod National Seashore** 

**Monitoring Ground-Water Quality in** 



Prepared in cooperation with the NATIONAL PARK SERVICE

U.S. Department of the Interior U.S. Geological Survey

# Monitoring Ground-Water Quality in Coastal Ecosystems

By John A. Colman and John P. Masterson

Open-File Report 2007-1149

Prepared in cooperation with the NATIONAL PARK SERVICE

As part of a series of monitoring protocols for the LONG-TERM COASTAL ECOSYSTEM MONITORING PROGRAM AT CAPE COD NATIONAL SEASHORE

USGS Patuxent Wildlife Research Center Coastal Research Field Station University of Rhode Island Narragansett, Rhode Island

# **U.S. Department of the Interior**

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#### **PREFACE**

# **Overview of Long-Term Monitoring Program**

The Cape Cod National Seashore serves as a National Park Service prototype monitoring park for the Atlantic and Gulf Coast biogeographic region. The U.S. Geological Survey, in cooperation with the National Park Service, is charged with designing and testing monitoring protocols for implementation at Cape Cod National Seashore. It is expected that many of the protocols will have direct application at other coastal park units, as well as U.S. Fish and Wildlife Service coastal refuges within the biogeographic region.

The Long-Term Coastal Ecosystem Monitoring Program at Cape Cod National Seashore will rely upon numerous protocols that are relevant to the major ecosystem types (Estuaries and Salt Marshes, Barrier Islands/Spits/Dunes, Ponds and Freshwater Wetlands, Coastal Uplands). The ground-water-quality protocol is associated with all of these ecosystem types. The overall monitoring program is designed so that all of the protocols are interrelated. Roman and Barrett (1999) present a conceptual description of the entire monitoring program.

# **Protocol Organization**

To maintain consistency among the various monitoring protocols, each protocol is organized as follows: PART ONE of the protocol details the objectives of the monitoring protocol and provides justification for the recommended sampling program. The relevant literature and data collected during the protocol-development phase of the project are used to illustrate a particular sampling design, sampling method, or data-analysis technique. For example, PART ONE describes the objectives of a ground-water-quality monitoring program, the types of solute constituents addressed, and justification as to why certain monitoring wells and measurement schedules were selected.

PART TWO is a step-by-step description of the field, data-analysis, and data-management aspects of the protocol. For example, PART TWO states the recommended frequency and step-by-step procedures for collecting water samples for analysis of nitrogen chemical species at a monitoring well.

### **EXECUTIVE SUMMARY**

Long-term monitoring of ground-water quality by means of a standard data-collection protocol is essential for the effective management of terrestrial, aquatic, and estuarine ecosystems in the coastal park environment. This study develops a consistent protocol for monitoring changes in water-quality constituents in ground water, including plant nutrients, toxic compounds, and physical and chemical field parameters (alkalinity, conductance, pH, and temperature) by using methods and techniques established by the U.S. Geological Survey for use in the Long-Term Coastal Monitoring Program at Cape Cod National Seashore. The protocol establishes a ground-water-quality sampling network in the five ground-water-flow cells in the National Seashore area, and provides justification for the sampling method, water-quality constituents, and spatial and temporal sampling frequencies selected. Data collected during the first year of network observations are included in this report, as are maps indicating ground-water-flow direction and contributing areas to surface-water features. Long-term water-quality monitoring at the Seashore will aid in interpretation of the findings of other monitoring programs, especially those monitoring productivity of lakes and estuaries. Developing and initiating long-term ground-water-quality monitoring programs will provide a better understanding of the effects of natural and human-induced change at both the local and global scales on coastal water resources in park units.

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# CONVERSION FACTORS, CONCENTRATION UNITS, AND HORIZONTAL AND VERTICAL DATUMS

Multiply	Ву	To obtain
	Length	
centimeter (cm)	0.3937	inch (in.)
millimeter (mm)	0.03937	inch (in.)
meter (m)	3.281	foot (ft)
kilometer (km)	0.6215	mile (mi)
micrometer (µm)	0.0000394	inch (in.)
	Area	
square meter (m <sup>2</sup> )	0.0002471	acre
hectare (ha)	2.471	acre

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:  $^{\circ}F=(1.8\times^{\circ}C)+32$ 

Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius (°C) as follows:  $^{\circ}C=(^{\circ}F-32)/1.8$ 

#### **CONCENTRATION UNITS**

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius ( $\mu$ S/cm at 25°C). Concentrations of chemical constituents in water are given in milligrams per liter (mg/L), micrograms per liter ( $\mu$ g/L), nanograms per liter ( $\mu$ g/L), or parts per million ( $\mu$ g).

#### HORIZONTAL AND VERTICAL DATUMS

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83). Vertical coordinate information is referenced to the National Geodetic Vertical Datum of 1929 (NGVD 29). Altitude, as used in this report, refers to distance above or below the NGVD 29.

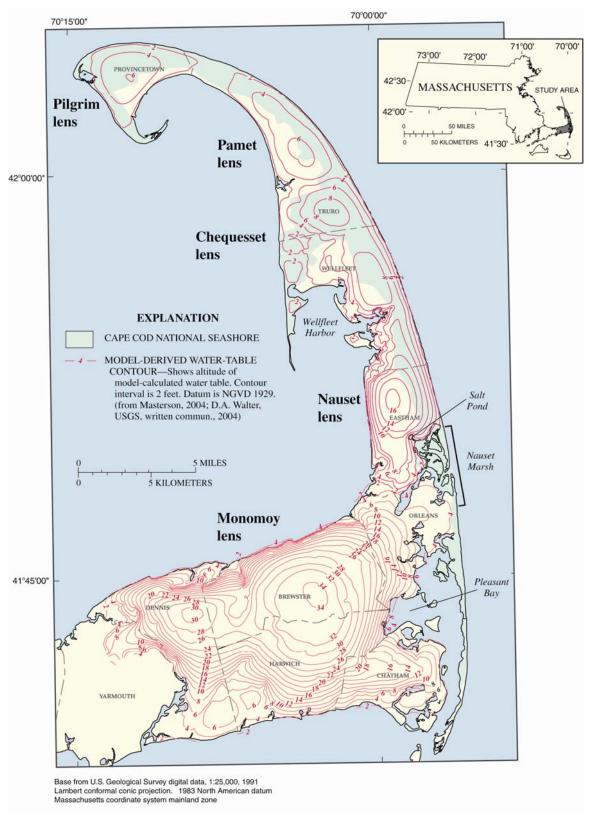
# Monitoring Ground-Water Quality in Coastal Ecosystems

By John A. Colman and John P. Masterson

# PART ONE Protocol Background and Justification

#### INTRODUCTION

The Cape Cod National Seashore (CACO) extends along more than 70 km of Atlantic Ocean open-beach coastline and includes three large saltwater bays—Wellfleet Harbor, Nauset Marsh, and Pleasant Bay (fig. 1). CACO encompasses about 18,000 ha of uplands, lakes, wetlands, and tidal lands (Godfrey and others, 1999) including most habitats typical of the sandy coast in National seashores and parks extending southward from Massachusetts to Florida. In 1995, CACO was selected by the National Park Service (NPS) as a prototype park typifying the Atlantic and Gulf Coast biogeographic region for long-term coastal ecosystem monitoring. The U.S. Geological Survey (USGS) is currently (2007) assisting the NPS in the development of protocols for a Long-Term Coastal Ecosystem Monitoring Program at the CACO in Massachusetts. The overall purpose of the monitoring program is to characterize both natural and human-induced change in the biological resources of the CACO, over a time scale of decades, in the context of a changing global ecosystem.



**Figure 1.** Cape Cod National Seashore, Massachusetts, with ground-water contours indicating the five ground-water-flow lenses beneath or adjacent to the Seashore lands.

This protocol, for long-term ground-water-quality monitoring, developed in cooperation with the NPS for CACO, will help define baseline conditions and trends in ground-water quality. The ground-water hydrologic system of the lower Cape Cod consists of five distinct ground-water lenses, or flow cells, which receive recharge through precipitation. These lenses are separated by tidal bays, freshwater streams, marshes, and glacial outwash valleys, which receive discharge from the ground-water system (fig. 1). The protocol for monitoring ground water addresses the strategy and methodology for characterizing chemical constituents and properties of the ground water as it moves from recharge sources to discharge sinks, and builds on the earlier hydrologic-monitoring protocol (McCobb and Weiskel, 2003) and the findings of current field and modeling studies that the USGS is conducting at CACO (Masterson, 2004). The ground-water-quality monitoring protocol excludes consideration of seawater intrusion, which is covered in the hydrologic-monitoring protocol (McCobb and Weiskel, 2003).

The conceptual framework for developing the long-term monitoring protocols relates (1) agents of change; (2) ecosystem stresses, which occur when the agents of change operate outside the range of natural variability; and (3) ecosystem responses, which are "detectable changes or trends in any measurable value of the coastal ecosystem's structure" (Roman and Barrett, 1999). Altered ground-water quality is classified mainly as an ecosystem stress resulting from agents of change such as sea-level rise, erosion, climate change, and probably most importantly, from urbanization. Urban sources of contamination of ground water in the CACO include the visitor and personnel facilities, which, like many private and commercial facilities on Cape Cod, dispose of wastewater to the ground. Ground-water movement from private inholdings in the CACO and upgradient town development also can transport contaminated water to CACO land. Five town landfills on the lower Cape may affect or are on CACO lands. The CACO aquifer also is affected by airborne constituents such as acid precipitation and atmospheric deposition of mercury, sulfate, and nitrate.

The ground-water ecosystem stresses cause ecosystem change in surface waters receiving ground water. These surface-water bodies include kettle lakes, which are in close hydraulic connection with the Cape Cod aquifer; wetlands or seasonally flooded vernal ponds; and coastal wetlands, embayments, and tidal-creek systems. The water and nutrient budgets of many of these sensitive resources are dominated by ground water. (The ecosystem of the aquifer, in which bacteria are the most investigated life form (Chapelle, 1993), is considered in the protocol only in relation to biogeochemical alteration of solute-transport processes.)

Drinking water is an important water-management issue for the CACO. Certain constituents in ground water degrade drinking-water quality as well as coastal ecosystem health. Nitrate from wastewater disposal, for example, is a toxin in drinking water, as well as a nutrient that contributes to eutrophication in marine waters. The CACO has water-supply requirements for its own infrastructure and may also, at some time in the future, be requested to allow development of water supplies on CACO land for use in adjacent towns. Thus, this protocol is concerned with effects on existing or potential drinking-water supplies as well as on ecosystems.

In a program of assessing long-term coastal ecosystem change, adherence to the procedures and quality-assurance methods for ground water as outlined in this protocol is particularly important. Because ground water moves slowly and transported solutes are buffered by chemical interaction with the large surface area of aquifer solids, changes in the concentrations of some ground-water constituents are slow and difficult to detect. The methodological integrity of the data set will determine whether changes detected over time can be attributed conclusively to changes in the environment, rather than to the effects of methodological differences that have inadvertently become incorporated into the data.

# MONITORING QUESTIONS: Specific Ground-Water-Quality Trends and Issues to Address

Long-term ground-water-quality monitoring is essential for evaluating the ecosystem stresses resulting from agents of change such as coastal erosion, sea-level rise, climate change, and urbanization; and for evaluating the effects of such stresses on the aquatic and estuarine ecosystems of the CACO. Characteristics of the agents of change determine the temporal and spatial monitoring requirements necessary to quantify the effects of these agents on ground-water quality.

Baseline water-quality conditions must be assessed to provide a basis for measuring any changes in those conditions. Baseline conditions may reflect the effects of anthropogenic influences that occurred before the time of the assessment. Evaluation of changes that may have occurred prior to the baseline assessment requires comparison with background conditions, which do not include anthropogenic influences. For example, determination of whether metal contamination has occurred in the ground water at a firing range could be approached by comparing the concentrations of the metals in ground water at the firing range with concentration of the metal in ground water at a background location, where sources of metal contamination are not present locally and are not present in locations upgradient in the ground-water flow field.

# **Climate Change**

Climate change has multiple effects on ground-water quality. Sea-level rise changes the way ground water flows in the aquifer, and temperature fluctuations affect rates of reaction.

#### Sea-Level Rise and Erosion

Sea level has been rising at the Boston Harbor tidal gage at the rate of about 2.65 mm/yr (±0.1 mm/yr) or about 0.265 m/100 years (Masterson, 2004). This rate, which has been confirmed in nearshore wells on Cape Cod (Masterson, 2004), is estimated to double, on average, over the next 100 years (Intergovernmental Panel on Climate Change, 2001). Likely effects of sea-level rise include alteration of ground-water-flow paths through the erosion of the eastern shore of Cape Cod (fig. 1) and increased ground-water discharge to stream runoff because of a rising water table (Masterson, 2004). Although the rate of change of these effects is increasing, the cumulative difference over the past 1,000 years of sea-level rise has already accounted for substantial erosion of the seaward side of the lower Cape. Coastal erosion has decreased the lateral extent of the lower Cape and likely shifted the locations of the freshwater lenses.

A shift in recharge location can shift ground-water-flow paths and thus alter aquifer geochemistry. Because of the slow geochemical weathering of the aquifer sediments of Cape Cod, water quality in a given location in the aquifer is determined largely by natural and anthropogenic chemical conditions at the recharge area, and to a lesser extent, by ground-water-flow paths that extend from the recharge area to deep locations in the aquifer. For example, leaching of organic carbon from wetlands can cause alterations in the solid phase of aquifers, for example, reductive dissolution of iron hydroxides. Along flow paths downgradient from wetlands, aquifer sediments can be stripped of iron, which could alter their ability to sorb phosphate. If flow paths change over time, geochemical conditions in the aquifer would logically change as well in accordance with conditions present at the new recharge area.

The tops of the flow-cell mounds on the lower Cape are generally halfway between the coastlines; however, erosion of the beach escarpment on the eastern shore would, over a long time, shift the top of the flow cells westward. Evidence for westward movement of the seaward side of the lower Cape is given by the changing relative position of a historic shipwreck. The *Sparrow Hawk*, which was wrecked on the

inner shore of Nauset Beach in Pleasant Bay in 1626, was discovered 237 years later on the outer shore because the beach had moved west about 300 m (Wood, 2002). Escarpment erosion at the rate of 1 m per year accounts for the loss of a coastal strip of land 1 km wide during the last 1,000 years, when sea level has been sufficiently high to cause erosion of the land surface (Leatherman and Zaremba, 1986).

#### Temperature Change

Ground-water temperature generally reflects the average air temperature of the region; therefore ground-water temperature would be expected to change if global warming changes the air temperature. The temperature-change effects on ground-water geochemistry have not been investigated widely, although temperature change has been hypothesized to influence some geochemical reactions, for example, the precipitation of travertine (Dramis and others, 1999). Temperature change can shift chemical equilibrium (changes are reaction-specific) and rates of both biological and chemical reactions (roughly a doubling in rate for every 10°C increase in temperature).

#### **Baseline and Trends**

Monitoring sea-level rise and erosion is covered by the hydrologic protocol written by McCobb and Weiskel (2003). Data about baseline conditions and trends in the temperature of aquifer water could be used to determine how climate warming might alter ground-water chemistry. Temperature could be monitored by recording ground-water temperature with a thermistor in a deep borehole. These data could be used for correlation with average air-temperature trends and for interpreting changes in chemical data.

#### **Urbanization**

Urbanization (and suburban development) is one of the biggest environmental stresses on the Cape. The effects of urbanization on ground water can include eutrophication of discharge areas (from ground-water transport of nutrients), which can happen in both freshwater and saltwater bodies; altered chemical constituents in precipitation, which can change ground-water chemistry; and introduction of toxic elements and compounds to ground water from point sources such as municipal landfills.

#### Eutrophication

Eutrophication of both freshwater and coastal saltwater is a big concern in developing areas, because increased waste generation, lawn-fertilizer use, and runoff from impervious surfaces increases the loads of plant nutrients (primarily phosphorus and nitrogen) delivered to surface water. In a recent survey of water quality in Massachusetts lakes and ponds, more than 75 percent of the surveyed water acreage did not support its designated use (U.S. Environmental Protection Agency, 1998). The reason for unsupported use was usually excessive plant growth. Introduction of nonnative species plays a role, but overall, growth of both native and nonnative plants can continue only to the extent that plant nutrients, such as phosphorus, are available. Disposal of wastewater can result in significant eutrophication of receiving freshwater because of the phosphorus contained in the effluents (Moore and others, 2003). Eutrophication of coastal waters is a global problem, caused by intense development of coastal areas. A recent analysis of population distribution has concluded that nearly 75 percent of the United States population resides within 80 km of coastal waters (National Research Council, 2000). Eutrophication as a consequence of the activities of an increasing population is of particular concern on Cape Cod, where data from the U.S. Census Bureau indicate that the population has increased by more than 130 percent during the past 30 years. Coastal embayments are adversely affected by increased delivery of nutrients, which cause nuisance blooms of algae (fig. 2), loss of eelgrass habitat, and depletion of oxygen from deep water (Hauxwell and others, 2001; Hauxwell and others, 2003). The development of lower Cape Cod in areas outside of the CACO borders is clearly shown in a land-use map (fig. 3).



**Figure 2.** Algae, mostly *Cladophora* and *Ulva*, festooning Salt Pond salt marsh grass, June 12, 2001, in a northward view toward the Cape Cod National Seashore Visitor Center. Photo by Barbara Dougan, National Park Service.

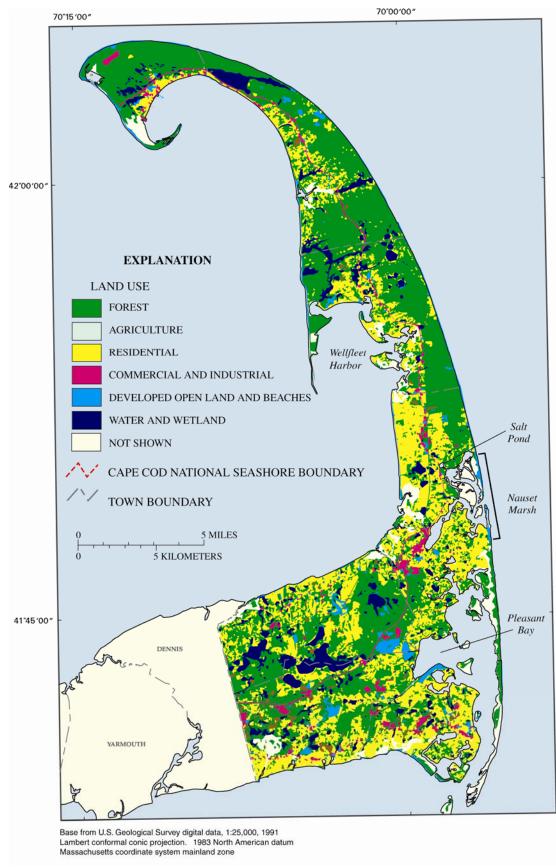


Figure 3. Land use on lower Cape Cod, Massachusetts, 1999 data layer (MassGIS, 2001).

#### **Phosphorus Sources and Transport**

The principal sources of nutrients in ground water are fertilizer, atmospheric deposition, septic systems, (Valiela and Bowen, 2002), and landfills (Christensen and others, 1994). These sources contain substantial amounts of phosphorus, but investigation of phosphorus transport in sandy, noncalcareous, aerobic aquifer sediments indicates that phosphorus does not move readily because of sorption to sediment surfaces and precipitation of iron- and aluminum-phosphate minerals (Robertson, 2003; Colman, 2005); large phosphorus loads, such as originate from disposal of wastewater at municipal treatment plants, may, however, overcome attenuation in the subsurface (Parkhurst and others, 2003).

High concentrations of phosphorus would be expected in landfill leachate, but phosphorus concentrations measured in plumes downgradient of landfills have not been high (Stollenwerk and Colman, 2002). Phosphate is unlikely to be transported in landfill plumes because of the potential for precipitation with calcium, iron, and aluminum.

Because phosphorus movement is attenuated in aerobic aquifers, surface-water bodies that receive ground-water discharge may not be appreciably affected by phosphorus that enters the aquifers from contamination sources upgradient of the surface-water bodies. Transport of phosphorus under natural anaerobic conditions, such as those that may be present downgradient from a wetland, has been less well investigated, although phosphorus sorption and precipitation processes should also apply there. A current area of research pertains to whether a long-term natural phosphorus release associated with a long period of reductive dissolution of iron hydroxide on the sediments could fill all of the sorption sites in the aquifer solids, so that any additional phosphorus loads from a contamination source would progress downgradient undiminished.

Surface water also may be affected by ground-water transport of phosphorus associated with altered aquifer geochemistry such as changes in pH resulting from acidic atmospheric deposition. If the increase in pH were transmitted to the aquifer by infiltrating precipitation, phosphorus would have been released from sorption sites on the aquifer sediments. Even a small shift in the background load of phosphorus in ground water could affect the ecosystem of the relatively oligotrophic CACO lakes. Long-term lakemonitoring records indicate that some of the kettle-hole lakes of the CACO are becoming more eutrophic (Portnoy and others, 2001). Although aesthetic degradation of the lakes is not yet manifest (nuisance growths of algae are not present), the causes of eutrophication should be identified so that the future conditions of the lakes can be anticipated and management decisions can be informed. Algal growth in these now (2006) relatively oligotrophic lakes may be limited by phosphorus; if so, their progression toward a more eutrophic state implies that annual loads of phosphorus are increasing.

Possible sources of increasing phosphorus include swimmers and atmospheric deposition, but the possible source of greatest importance in the development of this protocol is the aquifer. Changes in phosphorus load to CACO lakes from on-site sewage disposal (septic systems) is a possibility, even though no additional disposal installations have been allowed since the establishment of CACO in 1961. Although phosphorus is greatly attenuated during transport through noncalcareous sediments such as those on the Cape (Colman, 2005; Weiskel and Howes, 1992), upgradient phosphorus plumes would, in theory, continue to move forward from source to discharge into surface water as long as disposal of wastewater continues at the source. Thus, phosphorus could be discharging to lakes from phosphorus plumes advancing from on-site disposal sources constructed before 1961.

Duck Pond, which has only one private cottage inholding, and that on the downgradient shore, has a 20-year Secchi-disc record of decreasing depth (Portnoy and others, 2001); this record indicates an increase in planktonic algae. (Secchi-disc depth, the depth at which a white disc can no longer be seen from the surface, is a measure of water clarity.) Increased phosphorus loading from the aquifer could be the cause of increasing planktonic algae, but this area has no septic-system sources of phosphorus. Another ground-water-based mechanism for kettle-lake eutrophication that might account for increased phosphorus loading is large amounts of phosphorus on sediment surfaces of the aquifer in equilibrium

with the low concentrations of dissolved phosphorus. Small changes in aquifer geochemistry, such as a small change in pH, could shift the equilibrium, change the concentrations of dissolved phosphorus, and thus change the phosphorus load to a lake.

Precipitation monitoring at the National Atmospheric Deposition site operated by the National Seashore in Truro, Massachusetts, indicates that the pH of precipitation has increased from 4.4 to 4.6 during the period 1989–2001, in concert with decreases in sulfate in precipitation during the same period. Monitoring of phosphorus and pH in background locations of the CACO aquifer (away from the influence of any development) would indicate whether this potential source of increased phosphorus load is important.

#### Nitrogen Sources and Transport

Ground-water sources of nitrogen have been investigated on Cape Cod, especially at Waquoit Bay in the town of Falmouth (Valiela and others, 1997; Valiela and Bowen, 2002), and in Nauset Marsh in the towns of Eastham and Orleans (Portnoy and others, 1998). Similar to Pleasant Bay and Nauset Marsh in the National Seashore, Waquoit Bay receives little surface-water input and has become increasingly eutrophic as a result of recent development in its ground-water contributing area. Septic-system, fertilizer, and atmospheric deposition accounted for 48, 15, and 30 percent, respectively, of the estimated total ground-water nitrogen loading to Waquoit Bay (23,100 kg/yr) (Valiela and Bowen, 2002). High concentrations of nitrogen also have been measured in ground water discharging to the subembayments of Nauset Marsh (Portnoy and others, 1998).

Landfills are an additional nitrogen source for CACO embayments, but are not present in the contributing area of Waquoit Bay. The National Seashore has six town landfills either inside the park boundary or near enough to affect the ecosystem of CACO lands (Cape Cod National Seashore, 2000). Nitrogen loading from even one landfill could be large enough to cause eutrophication of a coastal embayment. Nitrogen in landfill leachate derives from decomposition of the organic wastes in disposed fill materials (Christensen and others, 1994).

In small sources like septic systems, nitrogen is converted to nitrate in the unsaturated zone before reaching the water table, and is transported in the ground water as nitrate (Colman and Friesz, 2001). In large discharges of nitrogen, such as that from the sewage-disposal site at the Massachusetts Military Reservation on the lower Cape (LeBlanc, 1984), the Tritown septage-treatment facility in Orleans (DeSimone and Howes, 1998), and from landfills (Christensen and others, 1994), some or all of the nitrogen gets transported in the reduced form, as ammonia. Reducing conditions develop in the aquifer because not all of the organic carbon discharged from the larger sources is oxidized in the unsaturated zone (DeSimone and Howes, 1998; Parkhurst and others, 2003). Whereas nitrate travels at approximately the same velocity as ground water (about 0.3 m per day), ammonia is transported at about one half that velocity. At the pH values typically found in ground water, ammonia occurs primarily in the cation form (ammonium ion) and is slowed by cation exchange with the solids.

Nitrogen from fertilizer likely is transported in the aquifer in the nitrate form. Little organic carbon would be expected to leach from the soil zone through the unsaturated zone beneath lawns or agricultural fields. Conditions in the aquifer in these areas would likely be aerobic so that the nitrate form of nitrogen would persist.

#### **Limiting Nutrients**

Phosphorus is commonly the limiting nutrient for plant growth in freshwater, and thus its supply to surface water can control eutrophication (Scheffer, 1998). In noncalcareous rock areas such as Cape Cod, most phosphorus that enters lakes is sequestered in iron compounds in the bed sediments (Colman and Friesz, 2001). The CACO kettle lakes may be phosphorus-limited even in the presence of ground-water contamination, because although nitrogen from inputs would be transported with the ground water, phosphorus would not.

In calcareous rock areas and in marine systems, sulfur is more abundant (than in non-calcareous areas) and combines with iron as FeS, so that phosphorus brought to the sediment-water interface by settling algae can be released (remineralized) and used in primary production (Rozan and others, 2002). With recycling of phosphorus, marine and calcareous systems are less likely to be phosphorus limited and more likely to become nitrogen limited. In addition, atmospheric nitrogen may be fixed more slowly in marine water than in freshwater (Paulsen and others, 1991), thereby contributing to nitrogen limitation in marine water.

#### **Computing Nutrient Loads**

Because the ecosystem at risk is in surface water rather than ground water, loads of chemical constituents that may discharge from ground water into surface water are important to determine, in addition to the concentrations of these constituents in the aquifer. Distances along flow lines from the top of the Nauset flow cell in Eastham to locations on the CACO coast range from 2.8 km to the east to 4.5 km to the south (near Salt Pond), with the longest travel times in excess of 100 years. Along most of the CACO coast, the nitrogen load associated with the last 20 years of development will not yet have arrived. The monitoring of ground-water nitrogen concentrations at the coast and at upgradient boundaries of the CACO would allow determination of nitrogen concentrations in ground water moving toward the coast. The monitoring data also could be used to calibrate and verify reactive solute-transport models of nitrogen flux to the coast. Fluxes from models that simulate real-time loads would be useful for determining the effect of nutrient loading on aquatic ecosystems and for anticipating future loads.

#### **Baseline and Trends**

Baseline concentrations of nutrients could be determined by monitoring their concentrations in ground water; such information could be used in evaluating the role of ground water in eutrophication. In addition, increased transport of nutrients to the marine margin may be predicted and tracked through use of reactive-solute-transport models that incorporate sources and reactions kinetics. Monitoring in strategic places would provide data to calibrate the models. If nutrient remediation measures are taken, continued collection of monitoring data will be needed to determine if management actions are having their intended effect.

#### Ground-Water Transport of Toxins, Mutagens and Endocrine Disruptors

Many potentially toxic or ecosystem-affecting constituents, in addition to nutrients, may be present in ground water on or near CACO. Through on-site disposal of wastewater, spills or leaks from tanks, or leaching of land-surface applications, these constituents can be introduced to the aquifer. In addition to contaminating ground water, these materials may be transported through the subsurface to surface-water ecosystems.

#### Types of Contaminants

More than 100 toxic contaminants may be present in ground water on the lower Cape; these include volatile organic compounds (VOCs), including solvents and gasoline hydrocarbons, as well as pesticides, trace elements, and organic compounds used for cosmetic and medicinal purposes. Potential sources of VOCs and pesticides include commercial and residential septic tanks, landfills, leaking underground or above-ground storage tanks, spills, runoff from lawns and other places where pesticides are applied, and atmospheric deposition (Fetter, 1999). Trace elements occur naturally in ground water although their distribution may be related to variations in subsurface geology and geochemistry. Organic compounds used for cosmetic and medicinal purposes enter ground water through the disposal of wastewater (nationally—Kolpin and others, 2002; Cape Cod—Zimmerman, 2005).

The Massachusetts Department of Environmental Protection maintains a list of reported releases of oil and hazardous materials from point sources. There are about 30 known hazardous-materials-release sites and 5 landfills upgradient of CACO land or coastal interests or on CACO property (table 1, fig. 4). Nonpoint sources, by contrast, are ubiquitous, including atmospheric deposition and domestic wastewater disposal through septic systems.

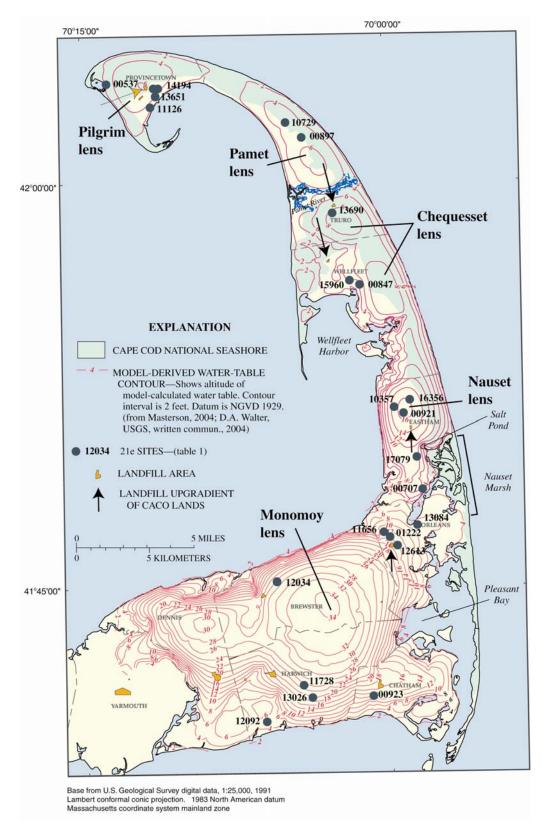
**Table 1.** Selected solid-waste-disposal sites (landfills) and Massachusetts General Law Chapter 21E sites, as of July 2005, in Massachusetts Department of Environment

Protection Region 4, near Cape Cod National Seashore, Massachusetts.

Trotection negion 4, near cape cou National Seasmore, Massachusetts.				
Release tracking number	Name	Address	Town	Status
4-0013321	CAPE COD OIL BULK FAC	30 WINTHROP ST	PROVINCETOWN	TIER 2
4-0011126	NO LOCATION AID	150 COMMERCIAL ST	PROVINCETOWN	DEF TIER 1B
4-0013651	DUARTES BRADFORD ST MALL	132 BRADFORD ST	PROVINCETOWN	TIER 2
4-0000537	RODS SERVICE STATION INC	CONWELL ST PO BOX 625	PROVINCETOWN	TIER 2
4-0014194	BREWSTER ST	HARRY KEMP WAY	PROVINCETOWN	TIER 2
4-0000897	S HIGHLAND RD LANDFILL	HIGHLAND RD	TRURO	TIER 2
4-0013753	NO LOCATION AID	7 PROFESSIONAL HEIGHTS RD	TRURO	DEF TIER 1B
4-0013690	JACKS GAS	100 RTE 6	TRURO	TIER 1C
4-0010729	OFF RTE 6	6 HIGHLAND RD	TRURO	DEF TIER 1B
4-0000847	MOBIL STATION 01-N3T	2665 U.S. ROUTE 6	WELLFLEET	TIER 1B
4-0000895	WELLFLEET TEXACO STATION	ROUTE 6 RURAL ROUTE 2	WELLFLEET	TIER 1B
4-0013524	ROCKWELL HOUSE	95 OCEAN VIEW DR	WELLFLEET	TIER 2
4-0015960	UNITED METHODIST CHURCH	241 MAIN ST	WELLFLEET	DEF TIER 1B
4-0010357	LOT ORV II	135 OAK RIDGE RD	EASTHAM	DEF TIER 1B
4-0013463	NO LOCATION AID	200 SUMMIT AVE	EASTHAM	DEF TIER 1B
4-0011959	NATL SEASHORE RANGER STATION	1050 NAUSET RD	EASTHAM	TIER 2
4-0000707	NEIGHBORHOOD SERVICE CTR	RTE 6	EASTHAM	TIER 1A
4-0000921	EASTHAM SUNOCO STATION	4565 STATE HWY	EASTHAM	TIER 1C
4-0016246	CAPE COD CITGO	4565 STATE HWY	EASTHAM	DEF TIER 1B
4-0001222	CHRIS BULLOCK TOYOTA	6 WEST RD	ORLEANS	TIER 2
4-0013084	NO LOCATION AID	100 TONSET RD	ORLEANS	TIER 2
4-0011656	NO LOCATION AID	21 SALTY RIDGE RD	ORLEANS	DEF TIER 1B

**Table 1.** Locations of solid-waste-disposal sites (landfills) and Massachusetts General Law Chapter 21E sites, as of July 2005, in Massachusetts Department of Environment Protection Region 4, near Cape Cod National Seashore, Massachusetts.—Continued

Release tracking number	Name	Address	Town	Status
4-0012613	NO LOCATION AID	26 GIDDIAH HILL RD	ORLEANS	DEF TIER 1B
4-0012092	RTE 28 & GREY NECK RD	219 MAIN ST	HARWICH	DEF TIER 1B
4-0011728	CANTO RESIDENCE	21 PLEASANT PARK RD	HARWICH	TIER 2
4-0013026	NO LOCATION AID	11 CRANBERRY LN	HARWICH	DEF TIER 1B
4-0013191	NO LOCATION AID	120 FOREST ST	HARWICH	TIER 2
4-0000518	RESIDENCE	622 DEPOT ST	HARWICH	TIER 1B
4-0001200	HARWICHPORT TEXACO STATION	570 MAIN ST	HARWICH	TIER 2
4-0006015	PROPERTY	321 OAK ST EXTENSION	HARWICH	TIER 2
4-0000406	ACME LAUNDRY CO	497 ORLEANS RD	CHATHAM	TIER 2
4-0000923	CLARKS AUTO SERVICE	2345 MAIN ST	CHATHAM	TIER 2
4-0014517	OYSTER RIVER BOATYARD	END OF BARN HILL LN EXT	CHATHAM	TIER 2



**Figure 4.** Landfills and selected Massachusetts General Law, Chapter 21E, sites (table 1) near Cape Cod National Seashore.

Toxic contaminants differ considerably in their transport characteristics in the subsurface and in their attenuation through interaction with aquifer sediments, or for organic compounds, through biodegradation. Solubility and density characteristics cause some toxic organic contaminants to float on top of the water table, and others to sink through the saturated zone. The variability in concentrations of trace elements in water may be controlled by subsurface pH or redox conditions; dissolved oxygen concentrations also may affect the transport of organic compounds by favoring or inhibiting specific biodegradation reactions.

Landfill-leachate plumes are potential concentrated sources of multiple toxins such as VOCs and semivolatile organic compounds, such as polychlorinated biphenyls (PCBs). Landfills as sources of toxins are of particular concern to the CACO, because five landfills on the lower Cape are upgradient of CACO water resources (fig. 4). Uncertainty regarding the presence and probable concentrations of toxic constituents flowing from landfills stems from lack of knowledge regarding the deposited waste as well as the potential for attenuation of toxic constituents. All of the landfills on the lower Cape are closed or in the process of being closed and are monitored onsite and near the sites in accordance with State requirements. Contaminants detected in these investigations may be transported downgradient and are candidates for additional monitoring. However, the only way to assess downgradient contaminants in landfill plumes is to locate the plume and determine analytically what materials are present in it. Plumes of landfill leachate tend to sink because of density effects but still move downgradient in the direction of ambient ground-water flow. For the CACO, discharge of landfill-leachate plumes to surface water is the principal concern, as none of the landfills are within the ground-water contributing areas of public or CACO drinking-water supplies.

#### Background, Baseline, and Trends

Determining both background and baseline concentrations of toxic compounds is necessary for monitoring ground-water quality in the CACO. For trace metals, which occur naturally at low concentrations in aquifer materials, and even for synthetic organic constituents that could be transported through the atmosphere, detectable concentrations of compounds are possible in background locations. One task of investigators of toxic materials in plumes from point sources or in suspected affected areas is to determine whether measured concentrations are significantly different from those in background areas.

Determination of baseline conditions is part of the investigation of trends. Baseline conditions are determined by monitoring of wells installed wherever a trend analysis is to be conducted. Initial sampling provides the data that constitute the baseline. Subsequent sampling could be periodic or a one-time event to determine trends or change.

# Ground-Water Transport of Materials Deposited From the Atmosphere— Major Ions, Nitrogen, Acidity, and Mercury

Although atmospheric deposition is the topic of another protocol in the series for Long-Term Coastal Ecosystem Monitoring, discussion of atmospheric deposition is included here because it is an important source of some constituents in ground water. Atmospheric-deposition monitoring programs, such as the National Atmospheric Deposition Program/National Trends Network (NADP/NTN) (National Atmospheric Deposition Program, 2005), monitor only wet deposition, which does not account for the other substantial deposition component, dry atmospheric deposition. Monitoring of ground water, which is affected by wet and dry atmospheric deposition, however, can be used to determine total atmospheric deposition of some constituents.

#### Types of Contaminants

Constituents of atmospheric deposition become part of ground water after infiltration through the soil and unsaturated zones and are subject to the effects of evapotranspiration and chemical alteration during passage. Whereas the ground water will always include the constituents from atmospheric deposition, ground-water composition may not be dominated by them. The effects of atmospheric deposition on ground-water chemistry may be overcome for those constituents that are released or removed in soils or aquifer solids in large amounts.

Nitrogen loading to the landscape and directly to surface water from atmospheric deposition contributes to the eutrophication of coastal water, which is discussed under the first topic in this section. Sources of nitrates in atmospheric deposition (NO compounds) include anthropogenic sources such as combustion of gasoline in automobiles. In the northeastern United States, atmospheric deposition has been identified as a dominant source of nitrogen to estuaries and their associated watersheds (Jaworski and others, 1997). For the Waquoit Bay system investigated on the Cape, however, nitrogen from atmospheric deposition constituted only 30 percent of the total nitrogen loading (Valiela and Bowen, 2002). The atmosphere contributes nitrogen to embayments on the Cape, but is not likely to be a dominant source, and the nitrogen loading rate from the atmosphere during the past 20 years appears to have remained fairly constant. Nitrate concentrations in precipitation in the U.S. may have leveled off during the 1980s. Statistically significant downward trends in wet deposition of nitrate were found at 3 of 33 NADP stations (Baier and Cohn, 1993); visual inspection of the NADP/NTN nitrate data collected during 1981–2002 from the lower Cape (station MA01), which were not included in the Baier and Cohn analysis, indicated no trend. Deposition of ammonia also is affected by anthropogenic activity, but the source is mostly in agricultural areas in the Midwest (NADP/NTN); visual inspection of the NADP/NTN MA01 ammonia deposition data collected during 1981–2002 indicated no trend.

Nitrogen loading from atmospheric sources to embayments through the aquifer may be better quantified by measurements of nitrogen in background locations in the aquifer rather than by estimates based on wetfall, the data available from the NADP/NTN network. Processes such as dryfall and plant uptake cause the amount of nitrogen from atmospheric deposition delivered to the aquifer to differ from the amount deposited by wetfall. Nitrogen load from atmospheric deposition can be determined as the product of recharge and nitrogen concentration in the aquifer at the water table in a background location.

Another plant nutrient, phosphorus, is also present in atmospheric deposition. Phosphorus from atmospheric deposition may be important to ground-water chemistry, but little is known about total deposition rates of phosphorus or about the leaching of deposited phosphorus from the soil zone to ground water. There are measurable concentrations of phosphorus in ground water at background locations, but unlike nitrogen, which is not present in crystalline rock, the source of phosphorus could be either dissolution (weathering) of aquifer solids or leaching from the surface.

Acid rain also needs to be considered in ground-water-quality monitoring. Changes in the acidity of deposition can alter the surface chemistry of the aquifer solids, resulting in the leaching of calcium and other base cations from soil and aquifer solids. Changes in the pH of water-solid systems can also change the sorption of oxyanions such as phosphate. Changes in ground-water pH are likely to be small because of buffering in the soil and aquifer and because pH changes in precipitation are not large. Because even small changes in aquifer pH could substantially affect phosphorus movement, however, careful monitoring of ground-water pH should be a part of the ground-water-monitoring protocol.

In surface-water systems dominated by ground water (kettle-hole lakes), ground-water transport of atmospherically deposited trace materials may be important. For instance, part of the mercury load to kettle lakes in amounts that cause high levels of mercury in fish may originate from atmospheric deposition (Krabbenhoft and Babiarz, 1992; Krabbenhoft and others, 1998).

#### **Baseline and Trends**

Ground-water-monitoring baseline and trends for atmospherically deposited materials may be especially useful. Monitoring for trends can be done by repeated samplings at a fixed point in the aquifer (monitoring well) or, for some constituents, by sampling at one time at multiple levels within the aquifer (multilevel sampler). Changes in concentrations of conservative constituents with depth can be interpreted as changes in the atmospheric-deposition rate over time, because older water on longer flow paths is collected in progressively deeper samples in the aquifer (Robertson and others, 1989).

# **Munitions and Discharge from Firearms**

Firing ranges and hunting areas can be sources of contamination by trace elements, which are associated with bullets, casings, and unconsumed explosives (Peddicord and LaKind, 2000). Organic contaminants have been detected in ground water beneath firing ranges (Ogden Environmental and Energy Services, 1999). Distinguishing between background concentrations of inorganic constituents in ground water and concentrations resulting from munitions at firing ranges is a topic of current investigation at the Massachusetts Military Reservation on upper Cape Cod.

### Types of Contaminants

An investigation of trace metals in the streambed sediments of the 67 tributaries of Lake Champlain in Vermont, New York, and Quebec (Colman and Clark, 1994) identified highest concentrations for some elements at three sites that were apparently affected by munitions—two in a National Wildlife Area where duck hunting was common, and one at a State Police firing range, where guns on one side of a stream were aimed at targets on the other side. Concentrations of several inorganic constituents—antimony, cadmium, lead, and tin—were higher at these sites than at the 95 other sites in the Lake Champlain Basin. The concentrations of several additional constituents—arsenic, iron, manganese, molybdenum, and zinc—were second highest at these sites, and the concentration of chromium was fifth highest. Because the elements were measured in sediment samples, their effects on water quality are not known. Firing ranges and hunting areas should be considered, however, in establishing a network for determination of background concentrations for these constituents.

Residues of explosives have been measured in the ground water beneath the impact area at Camp Edwards in the Massachusetts Military Reservation (AMEC, 2001). Compounds detected that are of concern because of environmental risk are perchlorate, 2A-DNT, 4A-DNT, and RDX.

# Background, Baseline, and Trends

Many of the contaminants that might be expected from a firing range are metals and could be present at low concentrations in ground water even under natural conditions. Background measurements for a firing range could be made by using a well network for assessing the effects of atmospheric deposition, described previously under Ground-Water Transport of Materials Deposited From the Atmosphere—Major Ions, Nitrogen, Acidity, and Mercury. The background data could be compared to that in samples from wells in the firing range or hydraulically downgradient from the range.

Baseline data for ground-water quality beneath a firing range could be obtained by a well network in the range or downgradient from the range. Monitored over time, the network would indicate any trends in contaminant concentrations.

### DESIGN OF A GROUND-WATER-MONITORING NETWORK

Criteria considered for establishing a water-quality-sampling network have been reviewed by past investigators (Roman and Barrett, 1999; DeSimone and others, 2001). Monitoring objectives must be established. Monitoring objectives, discussed in detail previously, are to (1) establish baseline and background conditions and (2) determine changes in ground-water quality resulting from agents of change in a way that would be useful in determining ecosystem response. In addition, monitoring approaches to achieve the objectives must be determined. According to DeSimone and others (2001), five criteria need to be considered in developing these approaches: (1) type of water resource, (2) use of the collected information, (3) type of measurement, (4) monitoring-site selection (targeted or probability based), and (5) sampling frequency and duration of the program.

In addition, for this protocol for long-term monitoring, sufficient documentation about quality assurance, data storage, and methods of sample collection, preservation, and chemical analysis must be kept so that any changes in water quality caused by changes in methodology can be distinguished from those caused by changes in the environment.

# Type of Water Resource and Use of the Information

This protocol is concerned with monitoring the quality of ground water at the CACO. The intended use of the monitoring data is the evaluation of ecosystem stresses and the interpretation of ecosystem changes observed in surface water. The community of organisms in ground water is not considered except in relation to how microorganisms might alter ground-water quality.

# **Types of Measurements**

The types of measurements required in this monitoring protocol are dictated by current and future environmental agents of change and resulting stresses. The measurements are of chemical characteristics and physical properties of ground water, which are affected by environmental agents of change and which may stress ecosystems after discharge to surface water. These measurements are discussed under the subtopics Types of Contaminants for each environmental agent of change. For example, under the section Munitions and Discharge from Firearms, the inorganic contaminant list includes antimony, arsenic, cadmium, chromium, iron, lead, manganese, molybdenum, perchlorate, tin, and zinc. The organic contaminant list includes 2A-DNT, 4A-DNT, and RDX. Ancillary monitoring data are required as well for interpretation of the stresses resulting from changed ground-water quality. Ancillary data include information on ground water, hydrology, and flow covered in the Hydrologic Protocol (McCobb and Weiskel, 2003); chemical constituents such as major ions, iron, manganese, and dissolved organic carbon; and physical and chemical properties, such as pH, alkalinity, temperature, ionic strength, redox state, and specific conductance. Ancillary data requirements are described in the Part Two step-by-step sampling approach.

# **Monitoring-Site Selection**

The issues for site selection include the general question of random sampling versus targeted sampling. After determination of the appropriate type of sampling, a sampling design must be adjusted for the particular contaminant source that is being investigated.

# Site-Selection Approaches

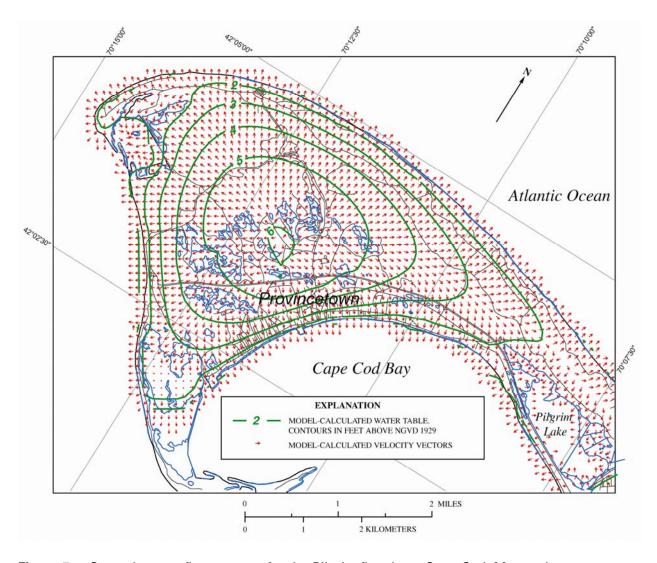
There are several possible approaches for site selection for ground-water monitoring. The approaches recommended in this protocol are those best suited to the monitoring objective of establishing baseline ground-water quality conditions and determining changes associated with the identified agents of change—sea level rise, urbanization, and firearms discharge.

An important criterion for the recommended site-selection approach is that it is appropriate for long-term monitoring, because the changes associated with the identified agents of change occur over decades. The need for long-term monitoring, along with logistic and resource considerations, indicate that fixed-station monitoring of a limited number of sites selected by using a targeted approach is appropriate. In fixed-station site selection, specific sites are chosen for monitoring on the basis of prior knowledge about important factors affecting ground-water quality, such as the locations of contaminant sources and ground-water flow direction.

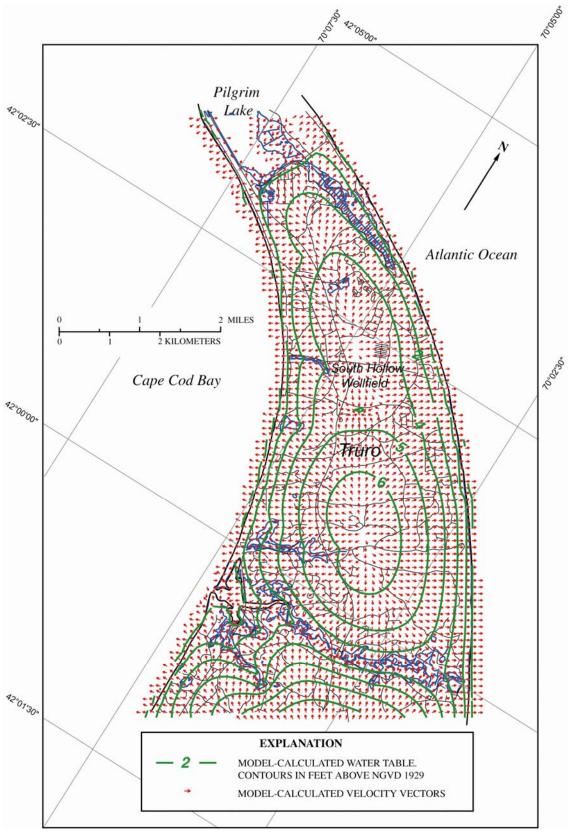
Wells installed for fixed-station monitoring have known construction and are available for repeated sampling. The alternative—short-term surveys either of private wells or randomly placed wells—could be difficult to arrange (for private wells outside the CACO), costly to install (random coverage requiring many wells), and difficult to use in assessing trends. The area of CACO is large, so monitoring would likely proceed by quantifying data for each type of source rather than for every source.

Choosing monitoring sites to best represent the water-quality conditions of interest depends on knowledge of (1) ground-water-flow paths, which determine whether a given site is in the flow path from a contamination source (agent of change) and (2) what environmental resource the resulting stress might affect. Ground-water flow is also a consideration in the placement of monitoring wells intended to detect the effects of atmospheric deposition and background conditions, that is, monitoring in areas protected from development or upgradient from human activities. This is also true of wells for monitoring the effects of nonpoint sources such as agricultural practices.

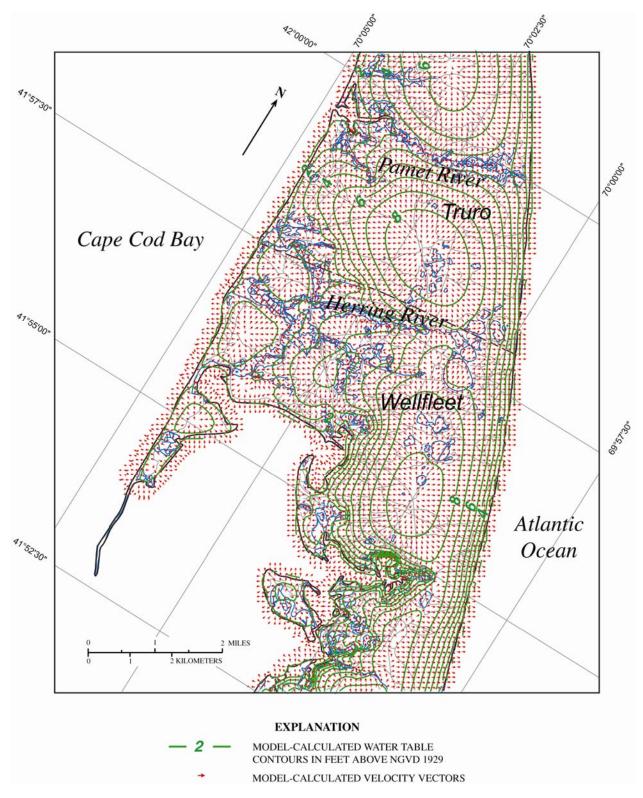
Subsurface flow, especially in unconsolidated materials common in sandy coastal areas, is predictable by numerical ground-water modeling. For the CACO, results from simulations of ground-water models show the contours of the ground-water table and vectors of flow at the water table (figs. 5–8). The vectors could be used to determine the best placement of monitoring wells between contamination sources and surface-water bodies receiving ground-water discharge. Ground-water-flow vectors also could be used to define ground-water contributing areas for surface-water features such as lakes and embayments (fig. 9). The contributing areas must be determined to identify source areas for ground water that eventually discharges to a surface-water body.



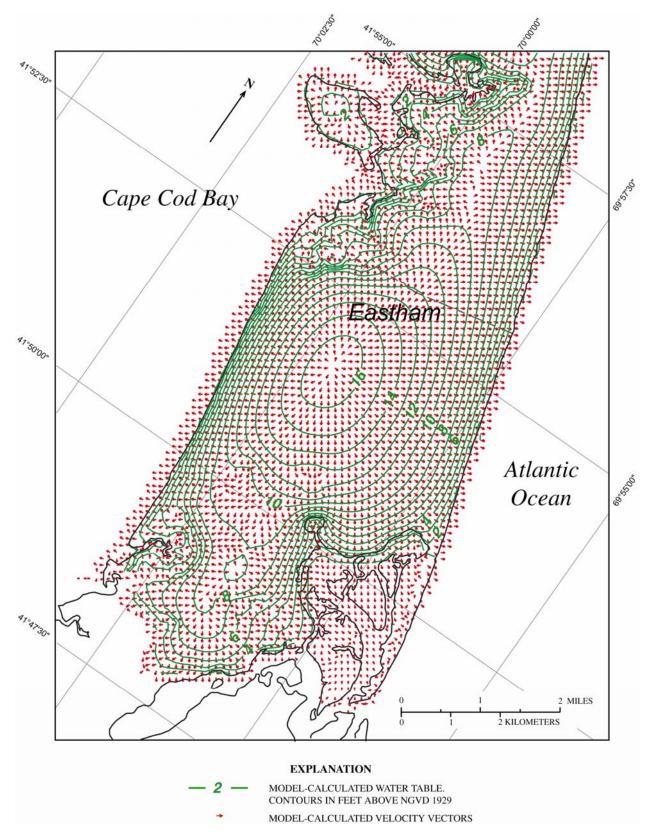
**Figure 5.** Ground-water-flow vectors for the Pilgrim flow lens, Cape Cod, Massachusetts. Modified from Masterson (2004).



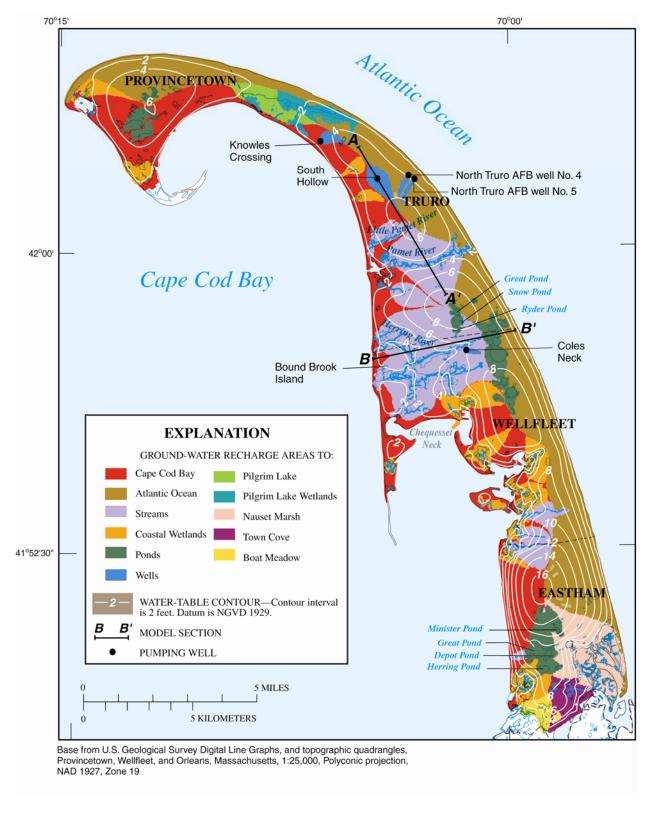
**Figure 6.** Ground-water-flow vectors for the Pamet flow lens, Cape Cod, Massachusetts. Modified from Masterson (2004).



**Figure 7.** Ground-water-flow vectors for the Chequesset flow lens, Cape Cod, Massachusetts. Modified from Masterson (2004).



**Figure 8.** Ground-water-flow vectors for the Nauset flow lens, Cape Cod, Massachusetts. Modified from Masterson (2004).



**Figure 9.** Ground-water-contributing areas for embayments of the Cape Cod National Seashore, Massachusetts. Modified from Masterson (2004).

# Monitoring Networks

Separate monitoring networks are needed to define conditions associated with atmospheric deposition and background conditions, and to assess the effects of nonpoint and point sources of contamination.

#### Atmospheric Deposition and Background

Background and atmospheric deposition effects cannot be distinguished from the effects of point sources of contamination on the basis of data from wells downgradient of such sources. Their combined effects can be separated from point-source effects, however, by choosing monitoring sites without upgradient point sources. The main requirement for investigation of atmospheric deposition and background in ground water is that no point or nonpoint source (other than atmospheric deposition) be present upgradient on the flow paths to the monitoring wells.

In the northern Chequesset flow cell, long flow paths that are entirely within the present-day protected CACO lands are minimally affected by point sources of contamination (figs. 1, 3, 4, and 7). Model-simulated traveltimes along flow paths in this cell range up to 150 years in the top 50 m of aquifer sand sediments. The chemical reactivity of many constituents with the sands during this time frame is negligible. Therefore, chemical analysis of the ground water along a flow path would result in a time-series record of atmospheric deposition. The early parts of these records would indicate atmospheric deposition before many anthropogenic influences were in effect.

#### Septic-System and Other Nonpoint Sources Associated with Development

Septic systems are used in large areas of residential and commercial development outside of the CACO boundary, and in isolated inholdings and CACO facilities inside the boundary. Practical considerations indicate that the hundreds of private septic systems outside the boundary that may affect CACO lands cannot be monitored individually. The nutrient plumes of many individual disposal sites become indistinguishable in the water of the downgradient aquifer and thus can be treated as nonpoint sources. Monitoring of several leachfields within CACO that are close enough to CACO surface water for possible individual effects could be done with separate networks and is addressed in the next section of this protocol.

A monitoring network to characterize the effects of septic tanks outside the CACO must take into account the direction of ground-water flow. The tops of three of the five ground-water flow cells that influence CACO lands are within the park boundaries (fig. 1). The CACO aquifer and CACO coast are generally protected from ground-water contamination originating in the three cells because the direction of subsurface flow of water is from the CACO lands to the developed areas rather than the reverse. Thus, monitoring ground-water quality is low priority in those areas. The tops of the Nauset and Monomoy flow cells, however, are outside the CACO boundary. The ground-water flow from these cells affects the principal embayments of CACO, Nauset Bay and Pleasant Bay, so that monitoring water quality in the flow from these is a priority for the ground-water-quality monitoring protocol. In addition, ground water from the Nauset, Chequesset, and Pilgrim lenses flows to Wellfleet Harbor and Provincetown Harbor on the west side of the Cape. The CACO lands of Long Point in Provincetown and Great Island in Wellfleet border these harbors. Thus the quality of ground water flowing from these developed areas is also a concern.

Likely tools and locations for intercepting the nutrient loads from the developed portion of the Cape include multilevel samplers (MLS) installed near the receiving water. These samplers are operated by peristaltic pump, and thus the water must be within suction depth of the water table, a maximum of about 7.5 m (25 ft). The depth to water near locations of ground-water discharge to surface-water bodies generally is shallow enough for efficient use of MLS. Also, ground-water flow begins to converge as flow lines get close to discharge at the surface; as a result, an MLS depth of 45 m (150 ft), which is the approximate maximum depth of installation possible by hollow-stem auger, may be able to intercept most of the flow paths along which nutrients would be transported to the overlying surface-water body.

Monitoring water quality at locations near discharge points cannot provide data to characterize conditions that exist upgradient, however. Thus, water-quality monitoring adjacent to surface water should be in conjunction with the use of a 3-D reactive solute-transport model. In areas for which such a model is available, ground-water-quality monitoring data are used for model calibration and verification. After verification, the model could be used to compute the ground-water loads of nonpoint-source contamination to a surface-water body, likely conditions upgradient, and simulations of loads that will discharge to the surface water in the future.

#### Septic Systems at CACO Facilities

Leachfields associated with facilities within the CACO contribute more directly to CACO ground-water quality than those outside of the boundary. Investigation of individual plumes is warranted because of their proximity to CACO surface-water bodies and because, in some cases, their remediation is under the control of the CACO. Results of investigations of individual septic systems elsewhere that were monitored for downgradient water quality have been published (Robertson, 2003; Colman and Friesz, 2001), and instrumentation of a few such systems on CACO lands to characterize the plumes could indicate similarities between the CACO plumes and the published examples.

The plume from the leachfield for the CACO Visitor Center is being investigated by using the USGS automatic well-sampling system (Granato and Smith, 2005). In 2002, the leachfield that had been servicing the Visitor Center was decommissioned and replaced with a new system that was capable of removing nitrogen from the wastewater. The investigation has measured the effect of the old system on ground-water quality and the decrease in nutrient concentrations during the decommission period. The investigation is also intended to collect data on the effect of the new system on ground-water quality. Wells upgradient from the leachfield provide data needed for a background determination, and a "fence" of wells downgradient intercepts the plume from the leachfield.

A second leachfield that has been investigated is that serving a bathhouse facility at Gull Pond in the town of Wellfleet. Again, wells have been installed upgradient and in a fence downgradient to determine the effect of the leachfield on the ground water. Both the investigation and the wells are described in detail in Part Two of this report on the GROUND-WATER-QUALITY WELL NETWORK.

#### Landfills and Other Hazardous Waste Sites

Determination of the full extent of a landfill plume is very costly, partly because a large number of toxic constituents may be involved in addition to nutrients that cause eutrophication. However, the potential effect of the leachate discharging to a coastal embayment makes landfill-plume monitoring essential. Leachate from several of the landfills—in Provincetown, Truro, and Wellfleet—likely is already discharging to adjacent coastal water. The nitrogen loads associated with these expected current discharges could be investigated to determine effects that may be observed eventually in other coastal areas where the nitrogen loading apparently is still upgradient (for example, at the Eastham landfill).

At several of the landfills, only the near-landfill part of the plume is well defined. But defining a plume at a distance from the source may be difficult because the plume may be narrow and of unknown depth below the surface. Before monitoring wells are drilled, the likely location of the plume should be defined by means of flow-vector diagrams, particle tracking, or other output from existing ground-water-flow and solute-transport models, and surface and downhole electromagnetic-induction surveys. Ionic constituents of landfill leachate greatly increase the conductance of leachate-contaminated ground water over that of ambient water. Periodic electromagnetic logging of deep wells (45 m) installed in the expected path of a landfill plume can indicate the depth and progress of the plume. Also the "footprint" of leachate discharge can be determined by using pushpoint sampling on the shore of the receiving water (McCobb and others, 2003). After the flow path of the plume is defined, wells may be drilled (1) near the source, to enable sampling for analyses of a broad spectrum of contaminants, which would include some that move slowly in ground water; and (2) downgradient, to enable sampling for analysis of nitrogen, which may move more rapidly. This approach would characterize those compounds that are or may become concerns for a

given landfill (near-landfill sampling) as well as characterize the transport of nitrogen, which will almost certainly be present and moving downgradient (downgradient sampling). More constituents may be included in the analyses of downgradient samples as those constituents are detected (at the near-landfill wells) and determined to be a potential stress to the environment. The data from these investigations would be used to determine whether more elaborate investigations were necessary, to maintain databases on toxic constituents, and to evaluate the transport of nitrogen, an ecologically important constituent in landfill leachate. The downgradient concentrations and time trends could be used to calibrate the solute-transport model of nitrogen loading.

Under Massachusetts General Law, Chapter 21E, the Massachusetts Department of Environmental Protection (MDEP) maintains a database of sites where oil or hazardous materials have been discharged into the environment (fig. 4). These sites, such as leaking underground storage tanks at gas stations, are generally monitored by MDEP. Additional monitoring of such sites within CACO would depend on review of the MDEP monitoring measures already in place, which is beyond the scope of this protocol.

#### Firing Ranges

The ground-water contamination that may occur on firing ranges can be assessed by the collection and analysis of water samples from wells installed within, downgradient, and upgradient of the ranges. Special precautions must be observed for drilling within ranges where unexploded ordnance may be present. At some military firing ranges, drill rigs have been operated remotely to prevent injury in case ordnance is encountered and detonated.

Wells constructed of polyvinyl chloride (PVC) are appropriate for monitoring of explosives and trace metals. Careful sampling and analytical methods are necessary for detection of trace metals. These may be present at low, parts-per-billion concentrations in affected wells and below-detection concentrations in wells that are not affected, even when very sensitive analytical methods are used. Because contaminants from munitions may move very slowly through the soil to the water table and in the aquifer, long-term monitoring at wells is usually warranted.

# **Sampling Frequency and Duration of Program**

The frequency of sampling required in a ground-water-quality monitoring program is dictated by the expected rate of change in the concentrations of chemical constituents in and the physiochemical properties of the water being measured. Ground water moves slowly, perhaps only a few centimeters to a few decimeters per day, so that day-to-day fluctuations in concentrations of constituents and in properties at a point (or well) commonly are too small to be detected. For monitoring concentrations of major ions and nutrients, and values of physical properties of ground water, twice yearly sampling should be sufficient, and by varying the season selected for sampling, conditions during all four seasons could be documented over a 2-year cycle. A second group of constituents, trace inorganic and organic compounds, could be adequately monitored by collecting samples once every 2 years from wells in background areas (those areas unaffected by human activities), but more frequent sampling should be considered if the types and conditions of any upgradient sources of these compounds are changing.

Consideration of several factors suggests that monitoring of ground-water quality should be a long-term activity. Not only does the structure of the program described herein mandate long-term monitoring, but the scales over which ground-water quality is likely to fluctuate also are long. Because of the slow rate of ground-water movement, any changes in factors that affect the quality of the water in recharge areas can take a long time to be reflected in surface-water bodies that are discharge areas for the ground water. Where ground-water-flow paths are relatively short, such as those within local ground-water cells near the coasts of Cape Cod, the water may move from recharge to discharge areas within a few years to a few decades. Flow paths between the tops of the five principal flow cells that constitute the ground-water system of lower Cape Cod and the coastlines of the Cape, however, are much longer, and represent traveltimes of perhaps 100 to 200 years. Even longer flow paths that extend through the deep lacustrine

clay beneath some of the flow cells may exist, but the effects of these impermeable deposits on the quality of ground water discharging to the surface-water ecosystems is unknown.

The duration of a ground-water-quality monitoring program also is affected by the time scale of changes in the source area for the chemical constituents of interest. Water quality can be affected by land-use activities associated with ongoing development, but also by long-term changes in climate and sea-level rise. In summary, planning for 100 years of monitoring ground-water quality in an area should not be considered unreasonable.

# **Quality Assurance**

Quality-assurance (QA) procedures help the investigator determine whether data collected are accurate and precise. Especially when measurements of trace constituents are involved, the potential for contamination of samples is a common problem. Quality-assurance procedures, a required part of any ground-water-quality investigation, are especially important for long-term monitoring projects. Data from these projects should be examined for time trends and changes. It is important to determine whether a measured change is a result of changes in methods or reflects real environmental changes. Quality-assurance data are needed to determine the answer.

Chain of custody, a component of quality-assurance procedures required in U.S. Environmental Protection Agency (USEPA) investigations, legally ensures that samples were not tampered with before analysis. This is not required for investigations with primarily scientific rather than legal objectives.

Quality-assurance procedures should be described for each water-quality investigation in a quality-assurance plan, which also is required in USEPA investigations. A quality-assurance plan contains (1) data-quality objectives, which describe the required precision and accuracy for the data to be collected so that scientific inferences from the data will be reliable, (2) verification procedures that ensure that the data collected are meeting the required levels of precision, and (3) a laboratory quality-assurance plan that applies to analytical laboratory procedures.

In ground-water-quality monitoring, the analytical methods selected should have detection limits low enough for quantification of data that are environmentally significant. Appropriate levels by constituent are given in table 2.

**Table 2.** Methods and detection limits for chemical constituents included in the ground-water-quality monitoring protocol, Cape Cod National Seashore, Massachusetts.

[Methods listed are suggestions rather than required specifications. Methods in parentheses are currently used at the North Atlantic Coastal Laboratory of the Cape Cod National Seashore. mg/L, milligrams per liter;  $\mu$ g/L, micrograms per liter;  $\mu$ g/L, nanograms per liter]

Water-quality parameter or property	Analytical method	Desired reporting level to meet data-quality objectives
Field measurements: pH, conductance, temperature, dissolved oxygen	See discussion Part 2	See discussion Part 2
Field alkalinity	See discussion Part 2	See discussion Part 2
Dissolved organic carbon	UV-promoted persulfate oxidation and infrared spectrometry	0.1 mg/L
Dissolved nitrate	Spectrophotometry (Lachat QuikChem Method 31-107-04-1-A)	1 μg/L
Dissolved ammonia	Spectrophotometry (Lachat QuikChem Method 10-107-06-1-C)	1 μg/L
Total nitrogen	Persulfate digestion and spectrophotometry	1 μg/L
Dissolved phosphorus	Spectrophotometry (Lachat QuikChem Method 31-115-01-1-G)	1 μg/L
Total phosphorus	Persulfate digestion and spectrophotometry	1 μg/L
Dissolved iron and manganese	Atomic absorption spectroscopy	10 μg/L
Dissolved major ions— Ca, Mg, Na, K, Cal, SO <sub>4</sub>	Atomic absorption spectroscopy	0.1 mg/L
Trace inorganic contaminants	Inductively coupled plasma-mass spectrometry	0.1 μg/L
Volatile organic compounds	Purge and trap gas chromatography mass spectrometry	0.1 μg/L
Trace organic contaminants	Gas chromatography mass spectrometry	1 μg/L
Endocrine disruptors	High pressure liquid chromatography	1 μg/L
Mercury	Oxidation, purge and trap, and cold vapor atomic fluorescence spectrometry	0.1 ng/L

Several kinds of quality-assurance samples and standards are available to verify that data-quality objectives are being met. These include blank samples, equipment blanks, duplicate samples, spike samples, and standard reference materials. The quality-assurance samples address potential data problems of systemic contamination, random contamination, sample-matrix problems and analyte loss. Systemic contamination can be determined by analyses of sample blanks, which indicate whether sampling materials, such as sample bottles, pumps, pump tubing, and preservation acids, contain analyte or are leaching analyte into the sample. Blank water is pumped through the system, collected in a sample bottle, and preserved and analyzed in the usual way to indicate whether any of these sources is a problem.

Random contamination, such as might occur from airborne contaminants falling into a sample, can be checked by using sample duplicates. A small particle of metal oxide dissolved in a sample with acid preservation may cause a large change in sample trace-metal concentrations. Sample replicates can help in these cases to identify random contamination. Analyses of two ground-water samples obtained sequentially at the same location should result in the same concentration; otherwise, contamination from a random source is suspected.

Sample spikes are used to determine whether the sample matrix can alter the sensitivity of the analytical method used to quantify analyte concentration. Duplicate samples are taken and a known amount of analyte is added (spiked) to one sample. Recovery of the spike is computed by comparison of analytical results from the spiked and unspiked samples. Spikes are useful, for example, during PCB sampling and extraction to determine whether all of the PCBs in a sample have been extracted. The requirement for two samples can be avoided by spiking analyte with a different isotope, such as C-13 labeled PCBS.

Standard reference materials are samples that have a known concentration and are prepared in laboratories. Standard reference materials are used to evaluate the accuracy of the measurement procedure in the analytical laboratory and are generally are not used in field quality-assurance procedures.

#### **Data Reduction and Database**

Equally important as collecting data correctly is the processing and storage of data after collection. Trends analysis and baseline comparisons for long-term monitoring can be accomplished only if all data collected over the years can be retrieved with appropriate ancillary information sufficient to determine how the data were collected and what the accuracy and precision of the data were.

As a result of its experience in assessing data-documentation requirements and storage, the USGS has confronted the problems of changes in methods, database platform, and software. The ideal system consists of dual record keeping—on paper and in computer files. The computer files are necessary for ease of data retrieval and analyses by the individual investigator and for public use through the internet. The paper files are necessary because long-term storage by paper is more reliable and because the database updates lag program changes, so that not all of the data collected can be stored electronically. The record-keeping system must be clearly defined, used systematically, and offer a means of checking data entry.

# PART TWO Specific Protocols

# **OVERVIEW OF DATA-COLLECTION PROCEDURES**

This part of the protocol includes descriptions of existing well networks and step-by-step instructions for the installation of additional wells and for water-quality sampling. After an initial reading, these descriptions may be skipped by many protocol users. That is because the ground-water-sampling personnel will collect data after the sampling network has been established and the monitoring wells drilled. The steps for data-collection preparation and sampling follow:

- 1. Identify the wells to sample. Use table 3 to determine which network and how many wells or multilevel sampler (MLS) ports are to be sampled.
- 2. Determine the number of samples required for analysis of each water-quality property and constituent. Use table 4 to determine properties and constituents for each sampled well, and add the required QA samples as described in the QA section.
- 3. Prepare samples bottles. Use table 5 to calculate the required number of each type of sample bottle and the types of preservation acids needed. Print out bottle labels, referring to the section Labeling Sample Bottles.
- 4. Prepare field forms. Collect the field forms required for MLS and wells to be sampled, referring to the section Logbook and Field Forms.
- 5. Sample wells. Follow the steps in the sampling protocol under GROUND-WATER QUALITY SAMPLING.

Sample count	Local name	Station name	USGS number	Latitude	Longi- tude	Port altitude or (depth BLS), in m
		ATMOSPHERIC D	EPOSITION NETWO	RK		
1	Near NADP site	MA-TSW-256	415821069591601	41 58 22	69 57 16	(58.71– 60.71)
2	Lombard Hollow Rd	MA-TSW-257	415808070024301	41 58 08	70 02 43	(32.55– 34.55)
NA	Proposed MLS	NA	NA	41 57 54.8	79 03 53.2	NA
	Prince Valley Rd water-table well	MA-TSW 266	415808070034516	41 58 08.6	70 03 45.9	(5.64– 6.25)
3	Prince Valley Road MLS	MA-TSW 265-01PT	415808070034501	41 58 08.6	70 03 45.9	0.67
4	Prince Valley Road MLS	MA-TSW 265- 02GNT	415808070034502	41 58 08.6	70 03 45.9	-3.60
5	Prince Valley Road MLS	MA-TSW 265-03RT	415808070034503	41 58 08.6	70 03 45.9	-6.65
6	Prince Valley Road MLS	MA-TSW 265- 04BUT	415808070034504	41 58 08.6	70 03 45.9	-9.71
7	Prince Valley Road MLS	MA-TSW 265- 05BKT	415808070034505	41 58 08.6	70 03 45.9	-12.77
8	Prince Valley Road MLS	MA-TSW 265-06WT	415808070034506	41 58 08.6	70 03 45.9	-15.83
10	Prince Valley Road MLS	MA-TSW 265-07O	415808070034507	41 58 08.6	70 03 45.9	-18.89
11	Prince Valley Road MLS	MA-TSW 265-08GY	415808070034508	41 58 08.6	70 03 45.9	-21.94
12	Prince Valley Road MLS	MA-TSW 265-09Y	415808070034509	41 58 08.6	70 03 45.9	-25.00
13	Prince Valley Road MLS	MA-TSW 265-10P	415808070034510	41 58 08.6	70 03 45.9	-28.06
14	Prince Valley Road MLS	MA-TSW 265-11GN	415808070034511	41 58 08.6	70 03 45.9	-31.10
15	Prince Valley Road MLS	MA-TSW 265-12R	415808070034512	41 58 08.6	70 03 45.9	-34.16
16	Prince Valley Road MLS	MA-TSW 265-13BU	415808070034513	41 58 08.6	70 03 45.9	-37.22
17	Prince Valley Road MLS	MA-TSW 265-14BK	415808070034514	41 58 08.6	70 03 45.9	-40.27
18	Prince Valley Road MLS	MA-TSW 265-15W	415808070034515	41 58 08.6	70 03 45.9	-43.31
		NONPOINT-SO	OURCE NETWORK			
	Kennedy water table	MA-EGW 57	415019069574816	41 50 19.1	69 57 48.5	(13.02– 13.62)
1	Kennedy MLS	MA-EGW 54-01PT	415019069574801	41 50 19.1	69 57 48.5	4.83
2	Kennedy MLS	MA-EGW 54- 02GNT	415019069574802	41 50 19.1	69 57 48.5	3.92
3	Kennedy MLS	MA-EGW 54-03RT	415019069574803	41 50 19.1	69 57 48.5	3.01
4	Kennedy MLS	MA-EGW 54-04BUT	415019069574804	41 50 19.1	69 57 48.5	1.92

Sample count	Local name	Station name	USGS number	Latitude	Longi- tude	Port altitude or (depth BLS), in m
		NONPOINT-SOURC	E NETWORKConti	nued		
5	Kennedy MLS	MA-EGW 54-05BKT	415019069574805	41 50 19.1	69 57 48.5	1.16
6	Kennedy MLS	MA-EGW 54-06WT	415019069574806	41 50 19.1	69 57 48.5	0.25
7	Kennedy MLS	MA-EGW 54-07O	415019069574807	41 50 19.1	69 57 48.5	-0.67
8	Kennedy MLS	MA-EGW 54-08GY	415019069574808	41 50 19.1	69 57 48.5	-1.59
9	Kennedy MLS	MA-EGW 54-09Y	415019069574809	41 50 19.1	69 57 48.5	-2.51
10	Kennedy MLS	MA-EGW 54-10P	415019069574810	41 50 19.1	69 57 48.5	-3.42
11	Kennedy MLS	MA-EGW 54-11GN	415019069574811	41 50 19.1	69 57 48.5	-5.87
12	Kennedy MLS	MA-EGW 54-12R	415019069574812	41 50 19.1	69 57 48.5	-8.93
13	Kennedy MLS	MA-EGW 54-13BU	415019069574813	41 50 19.1	69 57 48.5	-12.61
14	Kennedy MLS	MA-EGW 54-14BK	415019069574814	41 50 19.1	69 57 48.5	-16.28
15	Kennedy MLS	MA-EGW 54-15W	415019069574815	41 50 19.1	69 57 48.5	-19.94
	Grist Mill	MA-EGW 56	414941069581416	41 49 41.5	69 58 14.0	(5.57–
16	water-table Grist Mill MLS	MA-EGW 55-01PT	414941069581401	41 49 41.5	69 58 14.0	6.18) 1.88
17	Grist Mill MLS	MA-EGW 55-	414941069581402	41 49 41.5	69 58 14.0	0.97
18	Grist Mill MLS	02GNT MA-EGW 55-03RT	414941069581403	41 49 41.5	69 58 14.0	0.05
19	Grist Mill MLS	MA-EGW 55-04BUT	414941069581404	41 49 41.5	69 58 14.0	-1.02
20	Grist Mill MLS	MA-EGW 55-05BKT	414941069581405	41 49 41.5	69 58 14.0	-1.79
21	Grist Mill MLS	MA-EGW 55-06WT	414941069581406	41 49 41.5	69 58 14.0	-2.70
22	Grist Mill MLS	MA-EGW 55-07O	414941069581407	41 49 41.5	69 58 14.0	-3.61
23	Grist Mill MLS	MA-EGW 55-08GY	414941069581408	41 49 41.5	69 58 14.0	-4.54
24	Grist Mill MLS	MA-EGW 55-09Y	414941069581409	41 49 41.5	69 58 14.0	-5.45
25	Grist Mill MLS	MA-EGW 55-10P	414941069581410	41 49 41.5	69 58 14.0	-6.36
26	Grist Mill MLS	MA-EGW 55-11GN	414941069581411	41 49 41.5	69 58 14.0	-9.12
27	Grist Mill MLS	MA-EGW 55-12R	414941069581412	41 49 41.5	69 58 14.0	-12.79
28	Grist Mill MLS	MA-EGW 55-13BU	414941069581413	41 49 41.5	69 58 14.0	-16.48
29	Grist Mill MLS	MA-EGW 55-14BK	414941069581414	41 49 41.5	69 58 14.0	-20.14
30	Grist Mill MLS	MA-EGW 55-15W	414941069581415	41 49 41.5	69 58 14.0	-23.81

Sample count	Local name	Station name	USGS number	Latitude	Longi- tude	Port altitude or (depth BLS), in m
		NONPOINT-SOUR	CE NETWORKCont	inued		
31	Minister Pond MLS	MA-EGW 58-01PT	415024069583001	41 50 24	69 58 30	(2.97)
32	Minister Pond MLS	MA-EGW 58- 02GNT	415024069583002	41 50 24	69 58 30	(6.00)
33	Minister Pond MLS	MA-EGW 58-03RT	415024069583003	41 50 24	69 58 30	(9.08)
34	Minister Pond MLS	MA-EGW 58-04BUT	415024069583004	41 50 24	69 58 30	(12.13)
35	Minister Pond MLS	MA-EGW 58-05BKT	415024069583005	41 50 24	69 58 30	(15.18)
36	Minister Pond MLS	MA-EGW 58-06WT	415024069583006	41 50 24	69 58 30	(18.23)
37	Minister Pond MLS	MA-EGW 58-07O	415024069583007	41 50 24	69 58 30	(21.28)
38	Minister Pond MLS	MA-EGW 58-08GY	415024069583008	41 50 24	69 58 30	(24.32)
39	Minister Pond MLS	MA-EGW 58-09Y	415024069583009	41 50 24	69 58 30	(27.37)
40	Minister Pond MLS	MA-EGW 58-10P	415024069583010	41 50 24	69 58 30	(30.42)
41	Minister Pond MLS	MA-EGW 58-11GN	415024069583011	41 50 24	69 58 30	(33.47)
42	Minister Pond MLS	MA-EGW 58-12R	415024069583012	41 50 24	69 58 30	(36.52)
43	Minister Pond MLS	MA-EGW 58-13BU	415024069583013	41 50 24	69 58 30	(39.56)
44	Minister Pond MLS	MA-EGW 58-14BK	415024069583014	41 50 24	69 58 30	(42.61)
45	Minister Pond MLS	MA-EGW 58-15W	415024069583015	41 50 24	69 58 30	(45.66)
		POINT-SOURCE N	ETWORK—GULL P	OND		
	Bee well water table	MA-WNW 131	415719070004631	41 57 18.8	70 00 46.5	(7.79– 8.43)
	Hill well water table	MA-WNW 132	415718070004701	41 57 17.7	70 00 46.9	(6.49– 7.09)
1	Gull Pond MLS- #1	MA-WNW 125- 01BKT	415718070004601	41 57 18.5	70 00 46.5	(4.05)
2	Gull Pond MLS- #1	MA-WNW 125- 02WT	415718070004602	41 57 18.5	70 00 46.5	(4.36)
3	Gull Pond MLS- #1	MA-WNW 125-03O	415718070004603	41 57 18.5	70 00 46.5	(4.66)
4	Gull Pond MLS- #1	MA-WNW 125- 04GY	415718070004604	41 57 18.5	70 00 46.5	(4.97)
5	Gull Pond MLS- #1	MA-WNW 125-05Y	415718070004605	41 57 18.5	70 00 46.5	(5.27)
6	Gull Pond MLS- #1	MA-WNW 125-06P	415718070004606	41 57 18.5	70 00 46.5	(5.88)
7	Gull Pond MLS- #1	MA-WNW 125- 07GN	415718070004607	41 57 18.5	70 00 46.5	(6.49)

Sample count	Local name	Station name	USGS number	Latitude	Longi- tude	Port altitude or (depth BLS), in m
-	Pe	OINT-SOURCE NETW	ORK—GULL POND-	-Continued		
8	Gull Pond MLS- #1	MA-WNW 125-08R	415718070004608	41 57 18.5	70 00 46.5	(7.10)
9	Gull Pond MLS- #1	MA-WNW 125- 09BU	415718070004609	41 57 18.5	70 00 46.5	(7.71)
10	Gull Pond MLS- #1	MA-WNW 125- 10BK	415718070004610	41 57 18.5	70 00 46.5	(8.32)
11	Gull Pond MLS-	MA-WNW 125-11W	415718070004611	41 57 18.5	70 00 46.5	(8.93)
12	Gull Pond MLS- #2	MA-WNW 126- 12BKT	415718070004610	41 57 18.3	70 00 47.7	(4.13)
13	Gull Pond MLS- #2	MA-WNW 126- 13WT	415718070004611	41 57 18.3	70 00 47.7	(4.44)
14	Gull Pond MLS- #2	MA-WNW 126-14O	415718070004612	41 57 18.3	70 00 47.7	(4.74)
15	Gull Pond MLS- #2	MA-WNW 126- 15GY	415718070004613	41 57 18.3	70 00 47.7	(5.05)
16	Gull Pond MLS- #2	MA-WNW 126-16Y	415718070004614	41 57 18.3	70 00 47.7	(5.35)
17	Gull Pond MLS- #2	MA-WNW 126-17P	415718070004615	41 57 18.3	70 00 47.7	(5.96)
18	Gull Pond MLS- #2	MA-WNW 126- 18GN	415718070004616	41 57 18.3	70 00 47.7	(6.57)
19	Gull Pond MLS- #2	MA-WNW 126-19R	415718070004617	41 57 18.3	70 00 47.7	(7.18)
20	Gull Pond MLS- #2	MA-WNW 126- 20BU	415718070004618	41 57 18.3	70 00 47.7	(7.79)
21	Gull Pond MLS- #2	MA-WNW 126- 21BK	415718070004619	41 57 18.3	70 00 47.7	(8.40)
22	Gull Pond MLS- #2	MA-WNW 126-22W	415718070004620	41 57 18.3	70 00 47.7	(9.01)
23	Gull Pond MLS- #3	MA-WNW 127- 01BKT	415718070004801	41 57 18.9	70 00 45.9	(4.05)
24	Gull Pond MLS- #3	MA-WNW 127- 02WT	415718070004802	41 57 18.9	70 00 45.9	(4.36)
25	Gull Pond MLS- #3	MA-WNW 127-03O	415718070004803	41 57 18.9	70 00 45.9	(4.66)
26	Gull Pond MLS- #3	MA-WNW 127- 04GY	415718070004804	41 57 18.9	70 00 45.9	(4.97)
27	Gull Pond MLS- #3	MA-WNW 127-05Y	415718070004805	41 57 18.9	70 00 45.9	(5.27)
28	Gull Pond MLS- #3	MA-WNW 127-06P	415718070004806	41 57 18.9	70 00 45.9	(5.88)
29	Gull Pond MLS- #3	MA-WNW 127- 07GN	415718070004807	41 57 18.9	70 00 45.9	(6.49)
30	Gull Pond MLS- #3	MA-WNW 127-08R	415718070004808	41 57 18.9	70 00 45.9	(7.10)
31	Gull Pond MLS- #3	MA-WNW 127- 09BU	415718070004809	41 57 18.9	70 00 45.9	(7.71)

Sample count	Local name	Station name	USGS number	Latitude	Longi- tude	Port altitude or (depth BLS), in m
		OINT-SOURCE NETW				
32	Gull Pond MLS- #3	MA-WNW 127- 10BK	415718070004810	41 57 18.9	70 00 45.9	(8.32)
33	Gull Pond MLS- #3	MA-WNW 127-11W	415718070004811	41 57 18.9	70 00 45.9	(8.93)
34	Gull Pond MLS- #4	MA-WNW 128- 01BKT	415719070004601	41 57 18.8	70 00 45.8	(3.90)
35	Gull Pond MLS- #4	MA-WNW 128- 02WT	415719070004602	41 57 18.8	70 00 45.8	(4.21)
36	Gull Pond MLS- #4	MA-WNW 128-03O	415719070004603	41 57 18.8	70 00 45.8	(4.51)
37	Gull Pond MLS- #4	MA-WNW 128- 04GY	415719070004604	41 57 18.8	70 00 45.8	(4.82)
38	Gull Pond MLS- #4	MA-WNW 128-05Y	415719070004605	41 57 18.8	70 00 45.8	(5.12)
39	Gull Pond MLS- #4	MA-WNW 128-06P	415719070004606	41 57 18.8	70 00 45.8	(5.73)
40	Gull Pond MLS- #4	MA-WNW 128- 07GN	415719070004607	41 57 18.8	70 00 45.8	(6.34)
41	Gull Pond MLS- #4	MA-WNW 128-08R	415719070004608	41 57 18.8	70 00 45.8	(6.95)
42	Gull Pond MLS- #4	MA-WNW 128- 09BU	415719070004609	41 57 18.8	70 00 45.8	(7.56)
43	Gull Pond MLS- #4	MA-WNW 128- 10BK	415719070004610	41 57 18.8	70 00 45.8	(8.17)
44	Gull Pond MLS- #4	MA-WNW 128-11W	415719070004611	41 57 18.8	70 00 45.8	(8.78)
45	Gull Pond MLS- #5	MA-WNW 129- 12BKT	415719070004612	41 57 18.5	70 00 45.5	(4.05)
46	Gull Pond MLS- #5	MA-WNW 129- 13WT	415719070004613	41 57 18.5	70 00 45.5	(4.36)
47	Gull Pond MLS- #5	MA-WNW 129-14O	415719070004614	41 57 18.5	70 00 45.5	(4.66)
48	Gull Pond MLS- #5	MA-WNW 129- 15GY	415719070004615	41 57 18.5	70 00 45.5	(4.97)
49	Gull Pond MLS- #5	MA-WNW 129-16Y	415719070004616	41 57 18.5	70 00 45.5	(5.27)
50	Gull Pond MLS- #5	MA-WNW 129-17P	415719070004617	41 57 18.5	70 00 45.5	(5.88)
51	Gull Pond MLS- #5	MA-WNW 129- 18GN	415719070004618	41 57 18.5	70 00 45.5	(6.49)
52	Gull Pond MLS- #5	MA-WNW 129-19R	415719070004619	41 57 18.5	70 00 45.5	(7.10)
53	Gull Pond MLS- #5	MA-WNW 129- 20BU	415719070004620	41 57 18.5	70 00 45.5	(7.71)
54	Gull Pond MLS- #5	MA-WNW 129- 21BK	415719070004621	41 57 18.5	70 00 45.5	(8.32)
55	Gull Pond MLS- #5	MA-WNW 129-22W	415719070004622	41 57 18.5	70 00 45.5	(8.93)

Sample count	Local name	Station name	USGS number	Latitude	Longi- tude	Port altitude or (depth BLS), in m
	P	OINT-SOURCE NETW	ORK—GULL POND-	Continued		
56	Gull Pond MLS-	MA-WNW 130-	415718070004501	41 57 18.4	70 00 45.6	(3.99)
	#6	01BKT				
57	Gull Pond MLS- #6	MA-WNW 130- 02WT	415718070004502	41 57 18.4	70 00 45.6	(4.30)
58	Gull Pond MLS- #6	MA-WNW 130-03O	415718070004503	41 57 18.4	70 00 45.6	(4.60)
59	Gull Pond MLS- #6	MA-WNW 130- 04GY	415718070004504	41 57 18.4	70 00 45.6	(4.91)
60	Gull Pond MLS- #6	MA-WNW 130-05Y	415718070004505	41 57 18.4	70 00 45.6	(5.21)
61	Gull Pond MLS- #6	MA-WNW 130-06P	415718070004506	41 57 18.4	70 00 45.6	(5.82)
62	Gull Pond MLS- #6	MA-WNW 130- 07GN	415718070004507	41 57 18.4	70 00 45.6	(6.43)
63	Gull Pond MLS- #6	MA-WNW 130-08R	415718070004508	41 57 18.4	70 00 45.6	(7.04)
64	Gull Pond MLS- #6	MA-WNW 130- 09BU	415718070004509	41 57 18.4	70 00 45.6	(7.65)
65	Gull Pond MLS- #6	MA-WNW 130- 10BK	415718070004510	41 57 18.4	70 00 45.6	(8.26)
66	Gull Pond MLS- #6	MA-WNW 130-11W	415718070004511	41 57 18.4	70 00 45.6	(8.87)
	POINT-SOURC	E NETWORK—VISITO	RS CENTER SEPTIC	S-SYSTEM LE	EACHFIELD	
1	A1	MA-EGW-62	415012069582201	41 50 12.0	69 58 22.2	(5.94–7.47)
2	A1a	MA-EGW-63	415012069582202	41 50 12.0	69 58 22.2	(5.94–7.47)
3	A2	MA-EGW-64	415012069582203	41 50 12.0	69 58 22.2	(7.47–8.99)
4	A3	MA-EGW-65	415012069582204	41 50 12.0	69 58 22.2	(8.99– 10.52)
5	A4	MA-EGW-66	415012069582205	41 50 12.0	69 58 22.2	(10.52– 12.04)
6	A5	MA-EGW-67	415012069582206	41 50 12.0	69 58 22.2	(12.04– 13.56)
7	A6	MA-EGW-68	415012069582207	41 50 12.0	69 58 22.2	(13.56– 15.09)
8	B2	MA-EGW-69	415012069582101	41 50 12.2	69 58 21.8	(7.42–8.99)
9	B4	MA-EGW-70	415012069582102	41 50 12.2	69 58 21.8	(10.52–
						12.04)
10	B5	MA-EGW-71	415012069582103	41 50 12.2	69 58 21.8	(12.04– 13.56)

Sample count	Local name	Station name	USGS number	Latitude	Longi- tude	Port altitude or (depth BLS), in m
POI	NT-SOURCE NET	WORK—VISITORS	CENTER SEPTIC-SYST	EM LEACHF	IELDConti	nued
11	C3	NR	NR	41 50 12.3	69 58 21.2	(10.52– 12.04)
12	C4	NR	NR	41 50 12.3	69 58 21.2	(12.04– 13.56)
13	Y4	NR	NR	41 50 11.8	69 58 23.1	(10.52– 12.04)
14	Z2	MA-EGW-72	415011069582201	41 50 11.9	69 58 22.7	(7.47– 8.99)
15	Z4	MA-EGW-73	415011069582202	41 50 11.9	69 58 22.7	(10.46– 11.98)
16	Z5	MA-EGW-74	415011069582203	41 50 11.9	69 58 22.7	(12.04– 13.56)
17	ROBO-BG1	MA-EGW-61	415016069582503	41 50 16.1	69 58 26.0	(8.42– 11.16)
	JOINT VI	SITOR CENTER LEA	ACHFIELD AND EASTI	HAM LANDF	ILL	
18	Upgradient PVC well	MA-EGW-60	415016069582502	41 50 16.2	69 58 25.9	(34.7– 39.7)
	Upgradient geophysical logging well	MA-EGW-59	415016069582501	41 50 16.2	69 58 25.7	(43.59– 45.11)

**Table 4.** Water-quality properties, constituents, and sampling-frequency interval in years, by network, Cape Cod National Seashore, Massachusetts. [NS, no sampling]

------WELL NETWORK-----

Water-quality parameter or property	Back- ground/ atmos- pheric deposition	Nonpoint- source nutrients	Point source: Gull Pond	Point source: Visitors Center	Point source: Landfill	Point source: Under- ground storage tanks	Point source Firing range
Frequency per year Field measurements: pH, conductance, temperature, dissolved oxygen	0.5 0.5	0.5 0.5	0.5 0.5	0.5 0.5	0.5 0.5	1 1	1
Field alkalinity	0.5	0.5	0.5	0.5	0.5	NS	NS
Dissolved organic carbon	2	2	2	2	2	NS	NS
Dissolved nitrate	0.5	0.5	0.5	0.5	0.5	NS	1
Dissolved ammonia	0.5	0.5	0.5	0.5	0.5	NS	NS
Dissolved total nitrogen	0.5	0.5	0.5	0.5	0.5	NS	NS
Dissolved phosphorus	0.5	0.5	0.5	0.5	0.5	NS	NS
Dissolved total phosphorus	0.5	0.5	0.5	0.5	0.5	NS	NS
Dissolved iron and manganese	0.5	0.5	0.5	0.5	0.5	NS	
Dissolved major ions— Ca, Mg, Na, K, SO <sub>4</sub>	2	NS	NS	NS	0.5	NS	NS
Trace inorganic contaminants	2	2	2	2	0.5	1	-
Mercury <sup>1</sup>	2	2	NS	NS	2	NS	2
VOCs	NS	NS	NS	NS	0.5	1	NS
Trace organic contaminants	2	2	NS	NS	0.5	1	:
Endocrine disruptors, pharmaceuticals, and antibacterial compounds <sup>2</sup>	2	2	2	2	2	NS	NS

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<sup>&</sup>lt;sup>1</sup> Requires installation of wells with Teflon casing.

<sup>&</sup>lt;sup>2</sup> Requires installation of wells with Teflon or stainless-steel casing.

**Table 5.** Sample-bottle types, preservation, shipping, and holding requirements for monitoring ground water, Cape Cod National Seashore, Massachusetts.

[FC, filtered brown polyethylene bottle; DOC, baked amber glass bottle; FA, 250-mL acid rinsed polyethylene bottle; d, days; mL, milliliter]

Water-quality constituents	Bottle type	Preservation	Shipping requirements	Holding requirements
Dissolved organic carbon	125 mL DOC	$H_2SO_4$ to pH < 2	On ice 20 hours	15 d refrigerated
Dissolved nitrate	125 mL FC	HCl to pH < 1.5	On ice 20 hours	30 d refrigerated
Dissolved ammonia	125 mL FC	HCl to pH < 1.5	On ice 20 hours	30 d refrigerated
Dissolved phosphorus	125 mL FC	HCl to pH < 1.5	On ice 20 hours	30 d refrigerated
Dissolved total nitrogen	125 mL FC	Freezing	On ice 20 hours	30 d frozen
Dissolved total phosphorus	125 mL FC	Freezing	On ice 20 hours	30 d frozen
Dissolved iron and manganese	125 mL FA	$HNO_3$ to pH < 1.5	No chilling or time requirements	6 months
Dissolved major ions— Ca, Mg, Na, K, Cl, SO <sub>4</sub>	125 mL FA	$HNO_3$ to pH < 1.5	No chilling or time requirements	6 months
Trace inorganic contaminants	125 mL FA	$HNO_3$ to pH < 1.5	No chilling or time requirements	6 months
Trace organic contaminants	Baked glass	Variable	Variable	Variable

# **GROUND-WATER-QUALITY WELL NETWORK**

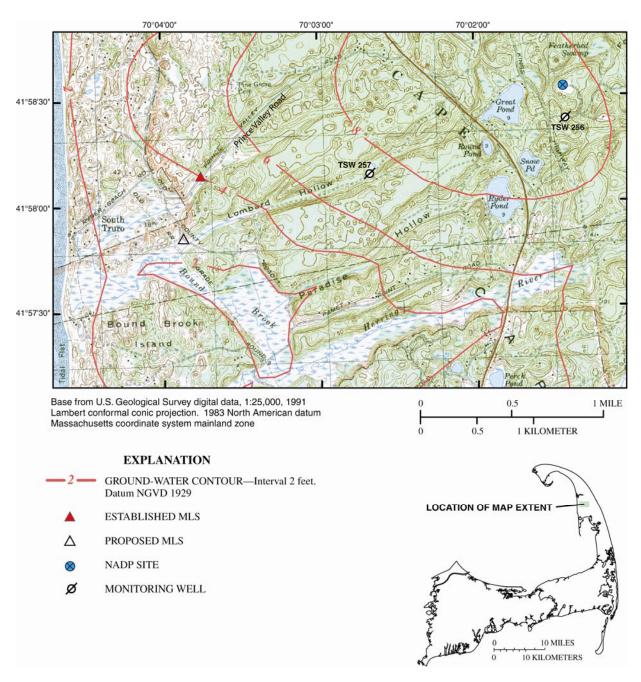
The design of the ground-water-quality network was covered in Part One. The design descriptions included types of networks and water-quality constituents and properties to be included in each network, which is summarized here in Part Two in tables 3 and 4, respectively. Part Two also includes descriptions of the wells that have been installed and their uses for each network. A part of the intended ground-water-quality network for the Cape Cod National Seashore (CACO) is not yet installed. The network description below includes suggestions for expanding the networks and procedures for monitoring-well installation.

# **Nonpoint Sources**

The nonpoint sources are atmospheric deposition, which contributes everywhere to background, and the cumulative effects of waste disposal by septic systems. Separate networks are described to monitor these two types of sources.

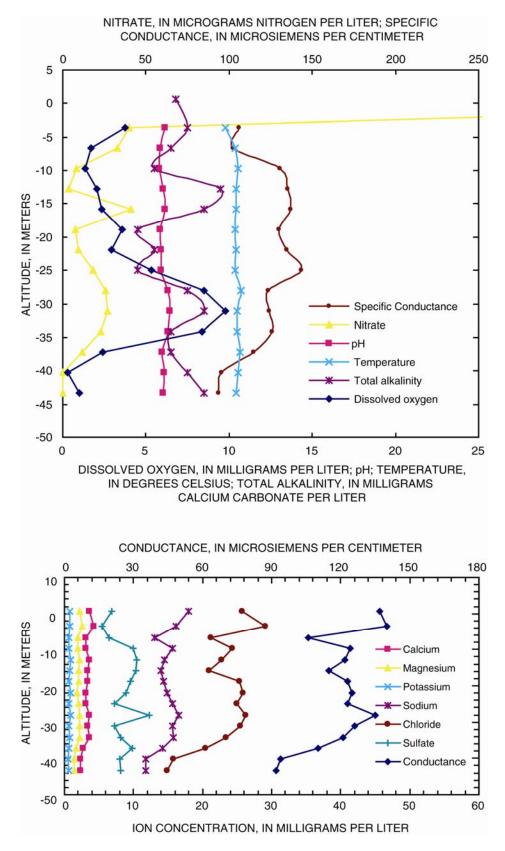
# Atmospheric Deposition and Background

The atmospheric deposition and background network is located in the Chequesset flow cell (fig. 10, table 3) in Truro. This flow cell was chosen for monitoring because it is within protected CACO lands, so that recharge for all the flow paths intercepted by a downgradient MLS could be assumed to be uncontaminated, and because of proximity to the NADP atmospheric-deposition collector at Truro. The network consists of the MLS at Prince Valley Road, several water-table wells, and a proposed second MLS near the Prince Valley site (fig. 10) as discussed below.

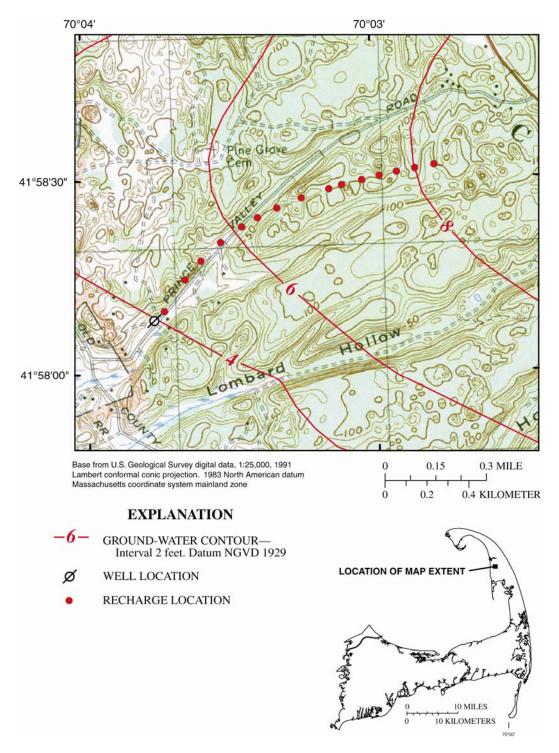


**Figure 10.** Ground-water-quality well network for atmospheric deposition and background investigation, Cape Cod, Massachusetts. MLS, multilevel sampler.

The network has been monitored since 2000. Analyses of ground water from the Prince Valley Road MLS show consistent zones of high and low dissolved oxygen (fig. 11). The variation in oxygen likely is caused by a variation in the amounts of organic-carbon leakage from the soil layer (Pabich and others, 2001) at the points of recharge (fig. 12). The concentration of dissolved oxygen, in turn, affects the concentrations of other constituents such as iron and nitrate. Simulation of traveltimes by the regional flow model (Masterson, 2004) indicates that the age of the water increases with depth, ranging from several years at the most shallow port to 150 years at the deepest port. Variability in the concentrations of solutes measured in samples obtained from the MLS ports reflect, in part, variability in concentrations recharged over time. For example, the sulfate record may be interpreted in this way if oxic conditions are assumed to apply to the travel path (Robertson and others, 1989). To obtain a more complete record of the ground-water chemistry under completely oxic conditions, a second background MLS could be installed (fig. 10). The proposed site, downgradient from areas of recharge through a thick unsaturated zone, would likely yield data that reflects the effect of atmospheric deposition and background recharge for a completely aerobic flow path.



**Figure 11.** Concentration profiles for the background multilevel sampler along Prince Valley Road, Truro, Massachusetts.



**Figure 12.** Simulated recharge locations (red dots) for Prince Valley Road multilevel sampler, Cape Cod, Massachusetts.

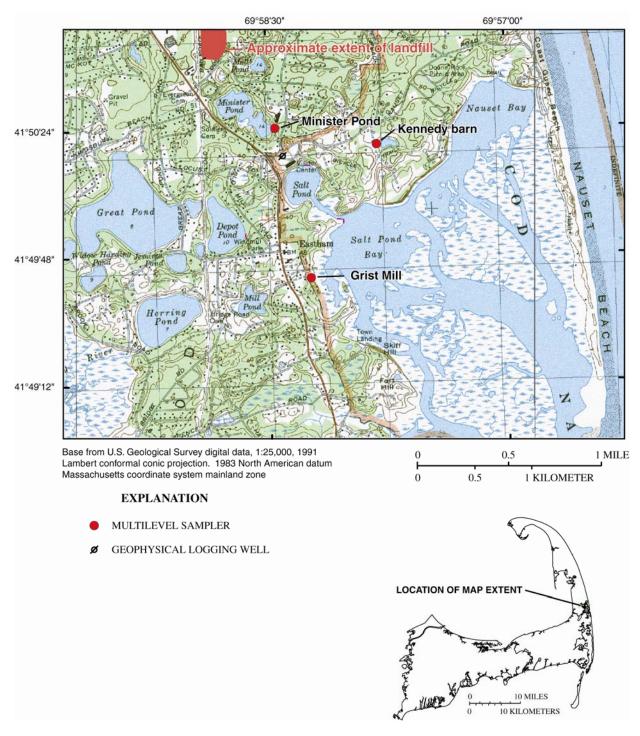
The design for the atmospheric deposition and background network, described in Part One and summarized in table 4, includes sampling for trace metals and trace-organic compounds in addition to the water-quality constituents and properties just discussed (table 4). Sampling for most metals could be done with the existing well network; sampling for trace organic compounds would require installation of additional monitoring wells constructed of stainless steel or Teflon. Sampling for mercury would require monitoring wells constructed of Teflon.

The network wells were sampled twice per year during 2001–2003. The frequency of measurement specified in the design is twice per year and is varied among seasons so that all four seasons are sampled in a 2-year period (table 4).

# Septic Systems and Other Nonpoint Sources Associated with Development

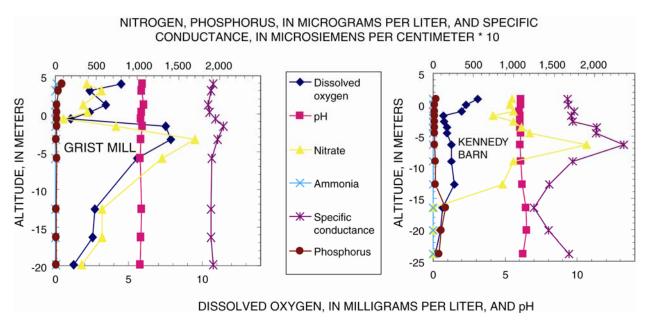
Three MLS have been installed in the ground-water monitoring network for nonpoint sources associated with development (fig. 13, table 3). These include the Kennedy Barn MLS, which is sited to intercept ground-water plumes to Nauset Bay from septic systems associated with housing that was recently constructed (1991–1999) east of the landfill; the Grist Mill MLS, which is sited to intercept plumes in ground water from development along Route 6; and the Minister Pond MLS, which is sited to intercept water exiting Minister Pond and a possible underflow plume from the Eastham landfill.

The MLS that are already installed may intercept ground-water plumes from the principal types of nonpoint sources that affect CACO lands or coastal water that borders CACO land. Determination of water-quality baseline conditions and trends can be conducted at these sites. These MLS sites do not, however, intercept flow affected by the area of most intense land use that contribute to CACO coastal embayments waters, which are the urban centers of Provincetown, Wellfleet, Orleans, and Chatham, and there are not a sufficient number of MLS installed to characterize spatial variability of water quality from nonpoint sources in the CACO. Additional installations of MLS would be required to characterize plumes from the urban sites and to characterize spatial variability of ground-water quality in the CACO.

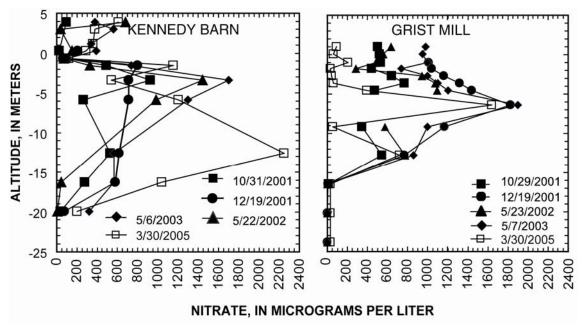


**Figure 13.** Ground-water-quality well network for nutrient loading to coastal embayments. The Minister Pond multilevel sampler and the geophysical logging well may be affected by the plume from the Eastham landfill, Cape Cod, Massachusetts.

Ground-water quality has been monitored at two of the nonpoint source MLS during 2000–2003. Water-quality measurements indicate that ammonia and phosphorus concentrations were low in all of the samples obtained (fig. 14). Concentrations of nitrate in samples from the Kennedy Barn MLS have been increasing, and nitrate concentrations in samples from the Grist Mill MLS have been variable (fig. 15). Trends are not yet known for the Minister Pond MLS, which was installed in 2003 and has been sampled only once. Frequency for sampling of the MLS in the network design is twice per year for measurements of most water-quality constituents and properties (table 4).



**Figure 14.** Water-quality profiles from multilevel samplers near Nauset Marsh Estuary, Cape Cod, Massachusetts.



**Figure 15.** Nitrogen profiles from 2001 to 2005 from the MLS near Nauset Marsh Estuary, Cape Cod, Massachusetts.

## **Point Sources**

Well networks have been installed at the CACO to monitor the ground-water plumes from individual point sources to characterize types of point sources. The types of point sources considered in this protocol are septic systems and landfills.

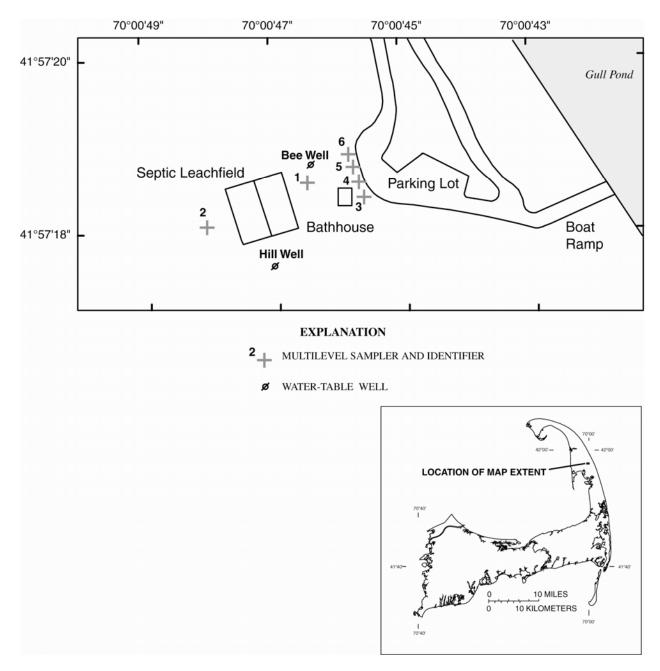
# Septic Systems as Point Sources

Monitoring wells have been installed around the leachfields of two septic systems on CACO lands. The plume from one septic system, at the bathhouse at Gull Pond landing, discharges to a freshwater site, Gull Pond. The plume from the other septic system, at the CACO Visitor Center, discharges to a saltwater site, Salt Pond. Both installations include wells with PVC casing or plastic tubing, which can be used to collect samples for analysis of nitrogen, phosphorus, major elements, iron, and manganese. The installation at the CACO Visitor Center includes stainless-steel wells, which can be used to collect samples for analysis of emerging contaminants such as endocrine disruptors and pharmaceuticals that may be present in disposed sewage.

#### **Gull Pond**

MLS and water-table wells have been installed in the leachfield of the septic system at the Gull Pond bathhouse. Five MLS were installed downgradient from the leachfield to intercept the ground-water plume as it moves from the disposal site towards Gull Pond; one MLS was installed upgradient from the leachfield site to determine background conditions (fig. 16). The direction of ground-water flow around the leachfield was determined by triangulation (McCobb and Weiskel, 2003) by using measurements of water level of the lake and in the water-table wells (fig. 16). Phosphorus and nitrogen are constituents of principal concern in septic system leachate at Gull Pond because aquatic plant growth in the lake may be controlled by the supply of one or both of these elements. In the data resulting from the MLS sampling during 2001 to 2003, concentrations of phosphorus have been very low, even in zones where high specific

conductance and concentrations of nitrate indicate that septic-system leachate is passing through. Apparently the transport of phosphorus is attenuated compared to that of nitrogen during the movement of ground water from the leachfield to the positions of the MLS.



**Figure 16.** Well network for the point-source leachfield for the bathhouse at Gull Pond, Cape Cod National Seashore, Massachusetts.

Although the twice-yearly sampling is listed in the design (table 4) for the Gull Pond MLS, more frequent sampling, four times per year, may be appropriate until a consistent pattern emerges. The bathhouse is used only in the summer months, and the associated seasonal discharge of wastewater to the leachfield may result in fluctuations in water-quality data measured in the MLS.

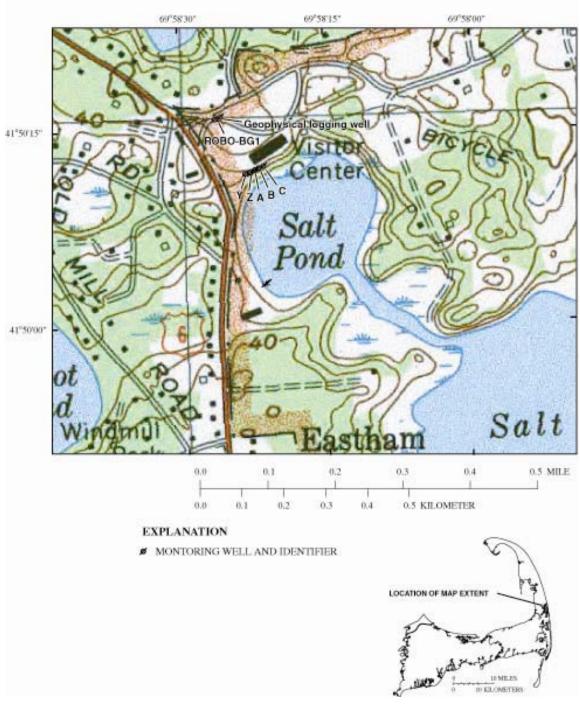
#### Salt Pond

Seventeen drive-point stainless-steel wells, a PVC water-table well, and a geophysical logging well have been installed around the leachfield that receives wastewater from the Visitor Center (Granato, 2002) (fig. 17, table 3). The stainless-steel wells have an inside diameter of 1.6 cm (5/8 inch)—too small for submersible pumps to be used—so they are sampled by suction applied to tubing that is inserted from the surface. The PVC water-table well and the logging well are upgradient from the leachfield, and the stainless-steel wells are aligned in a well "fence" across the estimated path of the leachfield plume.

Geophysical logs have been completed for the logging well in each fall during 2003 to 2005. The logs were analyzed to determine whether a landfill plume from the Eastham landfill was present. Interpretation of results from the downgradient wells would be more complex if two plumes, from a landfill and the Visitor Center, were present in the same location. There is no indication from the three logs that landfill leachate is intercepted by the well.

High concentrations of nitrogen were measured in samples from downgradient wells in 2003. 2003 was the year that discharge to the leachfield was discontinued because of temporary closing of the Visitor Center for reconstruction. Concentrations measured in samples from downgradient wells in 2004 were substantially lower than they had been in 2003. When leachfield construction is complete, discharge will resume with a system designed to remove more nitrogen. Nitrogen is the principal nutrient of concern because of the proximity of Salt Pond, where nitrogen may control aquatic plant growth. Phosphorus should also be monitored, because nitrogen input to Salt Pond may have increased so much that the limiting nutrient has changed to phosphorus.

The stainless-steel well installations would be appropriate for sampling trace organic contaminants (emerging contaminants) as well as nitrogen and phosphorus. The network should be sampled four times per year until a consistent pattern emerges, at which time the 0.5-year interval (table 4) should be used.



**Figure 17.** Well network for the septic-system leachfield at the Cape Cod National Seashore Visitor Center, Massachusetts. Information about the wells A, B, C, Y, and Z is given in table 3.

#### Landfills and Other Hazardous-Waste Sites

Of the five municipal landfills on or near CACO lands, two are discussed in this protocol in the context of designing networks of water-quality monitoring wells. These are the Eastham landfill, from which ground water likely discharges to Minister Pond (freshwater) and to Salt Pond (saltwater) (fig. 4, 13, and 18) and the Truro landfill, which has produced a leachate plume moving toward freshwater. No CACO project has yet (2007) been established to include monitoring of the landfill plumes. Several wells installed during the investigations of plumes from nonpoint sources and the Visitor Center are downgradient from the Eastham landfill and may be useful for investigation of the landfill plume.

#### Eastham Landfill

The direction of the ground-water flow in the area of the Eastham landfill (fig. 13) may be inferred from computer simulations of ground-water flow in the area (fig. 8). The local ground-water flow would likely cause a plume from the Eastham landfill to discharge into Minister Pond. The expected heavy nitrogen loading of Minister Pond, however, may saturate removal processes, so that some nitrogen may exit Minister Pond and move downgradient to Salt Pond. Plume water from the Eastham landfill that is not intercepted by Minister Pond would also enter Salt Pond.



**Figure 18.** Aerial photograph of Eastham landfill (above white wing), Molls Pond (bottom left), and Minister Pond (left above Molls Pond), Cape Cod Massachusetts. Photograph by Barbara Dougan, National Park Service.

One geophysical logging well (MA-EGW-59) between the landfill and Salt Pond has been installed in the inferred landfill plume path (figs. 13 and 17, and table 3). Gamma radiation and electromagnetic inductance can be logged in the well. Assuming that the well has been correctly placed and the plume is shallower than the 45-m well depth, annual logging of the well would record changes in the conductance of the saturated zone and thus would show the advance of the landfill plume.

MLS EGW58 (fig. 13) would also likely intercept plume water from the landfill. Shallow ports of the MLS may receive water that has exited from the lake to the aquifer. Deep ports may receive water that includes landfill leachate transported under the lake; however, no systematic sampling of this MLS has been initiated to date. Additional wells may have to be installed to monitor nitrogen concentrations in ground water entering Salt Pond once evidence of the plume has been detected in upgradient wells.

Downgradient portions of the landfill plume would not be expected to change quickly, so that sampling of this MLS once or twice per year for nutrients should be adequate. Trace metals and organic contaminants possibly present in landfill leachate would be monitored once every 2 years in locations where groundwater analyses have confirmed the presence of the plume. The MLS (MA-EGW58) was installed near Minister Pond in 2003 to a depth of 30 m.

#### Truro Landfill

Access to this landfill may be easier than access to landfills on the lower Cape because of its location within the CACO boundary. The simple hydrogeology of the area (no intervening lakes between landfill and discharge area) and short distance from the landfill source to the discharge area (the Pamet River) should enable an accurate delineation of the boundaries of the landfill plume, the chemical characteristics of the plume, and the discharge areas. Surface geophysical conductance measurements could be used to mark the center of the plume, and downhole geophysical logging of wells installed along the center line of the plume could indicate the depth of the plume. Installation of wells with well screens at the depth of maximum of aquifer conductance, as determined from the well logs, could make possible the collection of samples of concentrated leachate.

Data from monitoring wells used in previous studies (Cape Cod Commission, 1989) facilitate plume mapping and characterization. Data from analyses of water samples collected from wells installed between the landfill and the Pamet River indicate that the landfill plume is moving toward the river. Ground-water-flow simulations also indicate that flow would be toward the river (fig. 7). The long period of plume formation relative to the likely short traveltime between the landfill and to the hypothesized discharge area in the river means that the plume may already discharge there. If so, a distinct discharge footprint of the plume could be mapped in the Pamet River using pushpoint samplers to extract ground water from the river sediments.

Similar to the approach used for the Eastham landfill, monitoring at the Truro landfill should be planned on the basis of the results from ground-water modeling investigations and water-quality measurements. Nitrogen loads can be estimated from nitrogen concentrations measured in water samples taken under the landfill and the output from solute-transport models. Following the method used at the Massachusetts Military Reservation for the mapping of a nutrient plume entering surface water (McCobb and others, 2003), a fence of MLSs could be installed on the shore of the Pamet River to intercept the existing plume. On the basis of the plume boundary delineated from analysis of water samples collected from the MLS fence, the footprint of discharge into the river could be determined by installing temporary or permanent drive points in the river sediments. The loading of nitrogen into the Pamet River could be determined by multiplying the cross-sectional concentration field determined at MLS fence by the velocities determined by the ground-water-flow model.

The monitoring approaches outlined above would characterize nutrients and trace contaminants in the landfill plume, but currently (2007) only the Cape Cod Commission study wells have been installed. A full investigation of either the Eastham or the Truro landfill plumes would likely require additional funding.

#### Other Landfills

Because landfills are potential major sources of nitrogen and trace contaminants, their effects on CACO land may be large. Landfill investigations require large amounts of funding, however, for the installation and monitoring of additional sites. Until additional funding becomes available, the data collected in previous and ongoing investigations (Provincetown Landfill, Urish and others, 1993; Truro, Cape Cod Commission, 1989) should be maintained as part of the CACO long-term-monitoring database.

## Firing Ranges

No specific monitoring network for firing ranges is included in this protocol. If monitoring at or near firing ranges become a priority, however, information presented in the section Munitions and Discharge from Firearms in Part One of in this protocol could be used to design a network.

# WELL INSTALLATION

This section can be used as a guide for installing new wells to expand the monitoring network. It can also help inform well users about the characteristics, uses, and limitations of wells that are already in the network.

# **Monitoring-Well Installation**

Well installation has been covered in the companion protocol on hydrologic monitoring (McCobb and Weiskel, 2003). The installation of monitoring wells for water-quality monitoring is the same process as the installation of wells for determination of ground-water levels. Many wells are used to provide both water-level and water-quality information. Well materials and diameter requirements may be more restrictive for water-quality sampling, however (non-contaminating materials and a 5.08-cm (2-in.) well diameter for pump insertion), than for water-level measurements.

# Multilevel-Sampler (MLS) Installation

The construction of an MLS according to the sample design and tubing-color conventions described by Rudolph and others (1996) facilitates their use by sampling personnel. Planning and careful construction of parts are key to the successful installation of an MLS. The samplers consist of joined 3.048-m (10-ft) lengths of PVC pipe with color-coded 0.635-cm (1/4-in.) tubing that extends from the ground surface to the sampling depth.

Two forms of the MLS have been used at CACO: the conventional form, with sampling tubes on the inside of a 3.18-cm (1 ¼-in.) PVC pipe (internal-tube MLS), from which the tubes emerge for sampling the water in the aquifer; and a new form, installed at the Gull Pond bathhouse leachfield, with the tubes on the outside of a 1.91-cm (¾-in.) PVC pipe (external-tube MLS). The internal-tube MLS is installed with a drill rig and hollow-stem auger. The external-tube MLS is installed inside a schedule-40 plastic well casing (subsequently removed) by portable drilling equipment. The PVC pipe in the external-tube MLS can be used to obtain a water level in the aquifer because the sampling tubes are on the outside. No water-level measurements are possible with the internal-tube MLS because there is no extra space inside the MLS for a water-level recorder.

Typically 15 or fewer ports have been used in the conventional internal-tube MLS. The practical limit for the number of ports for the internal-tube MLS is determined by the number of sampling tubes that will fit inside the diameter of the PVC pipe. The number of ports in the external-tube MLS is limited by the number of sampling tubes that will fit between the outside of the PVC pipe and the inside of the schedule-40 casing.

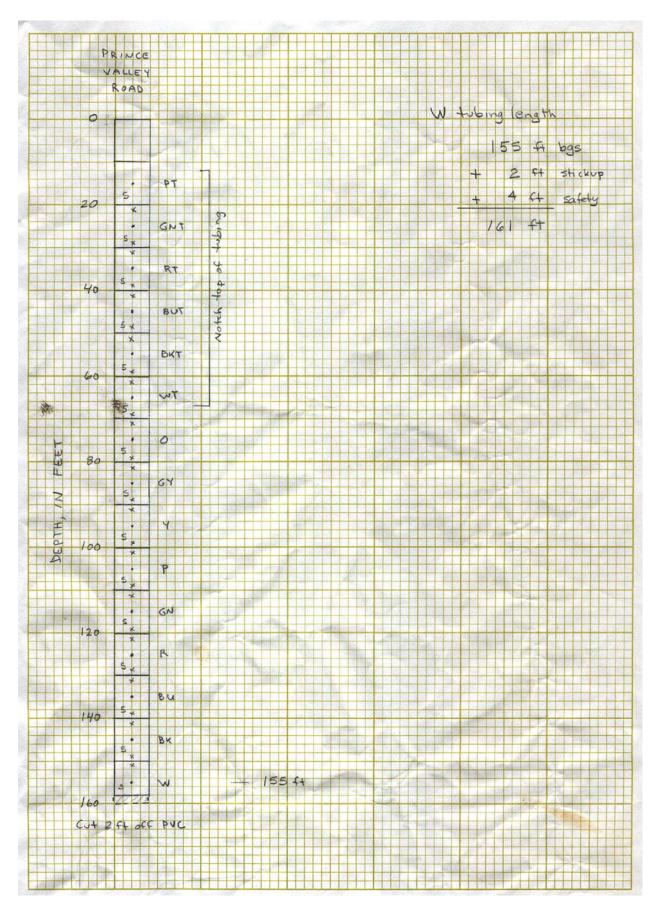
Sampling tubes are color-coded according to depth; the same color code (table 6) has been used for the nearly 100 MLS that have been installed by the USGS on Cape Cod. Only 8 colors are available for the 15 ports. The duplicate colors have a distinguishing tape mark and are designated WT, BKT, for white tape, black tape, and so on. The colors listed in table 6 are assigned from the bottom up, so that the color corresponding to the greatest depth is always white, the next is black, and so on. When fewer than 15 ports are used, the upper rather than lower colors are not used.

**Table 6.** Assignment of colors to multilevel-sampler ports for monitoring at Cape Cod National Seashore, Massachusetts. Because colors are assigned from the bottom up, samplers with fewer than 15 ports lack one or more of the taped colors.

Port color	Color abbreviation
Purple tape	PT
Green tape	GNT
Red tape	RT
Blue tape	BUT
Black tape	BKT
White tape	WT
Orange	O
Gray	GY
Yellow	Y
Purple	P
Green	GN
Red	R
Blue	BU
Black	BK
White	W

#### Internal-Tube Construction

First, diagrams are drawn indicating all sampler dimensions and locations of the sampling ports (fig. 19). Second, the materials are assembled (fig. 20). Lengths of PVC pipe are measured (and discrepancies from 3.048-m (10-ft) lengths noted), numbered from deepest to shallowest, and the following items marked on the pipes: (1) locations of all sampling ports, (2) tubing color at each port, and (3) the points 0.3048 m (1ft) from the ends of the pipes for use in determining the length of the pipe joint at MSL installation. Third, 0.63 cm (¼-in.) holes are drilled in the PCV pipes at the locations of sampling ports with the drill pulled down so that tubing will fit through the hole without crimping. Before tubing is attached, couplings should be attached with PVC solvent cement only on the upper end of each pipe. The tubing of the correct color is threaded through each port and the ends are attached with nylon-mesh covering (stocking) to the PVC pipe using stainless-steel wire. The tubing is cut to lengths long enough to reach the surface and made ready for stringing by being stretched out on the ground from the PVC pipes to the tubing ends.



**Figure 19.** Diagram of multilevel sampler used to plan required lengths of PVC pipe and to guide drilling of ports for tubing.

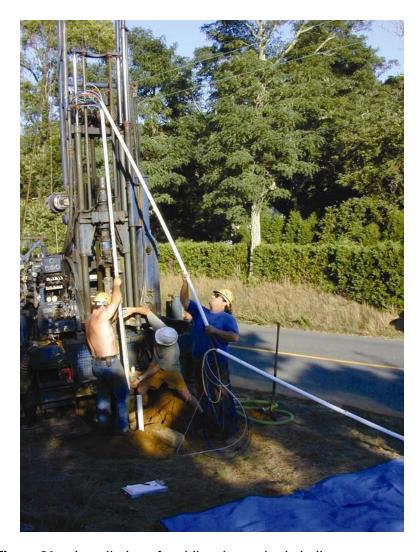


**Figure 20.** Multilevel sampler before installation at Prince Valley Road. Each pipe segment is nominally 10 feet long. Internal tubing emerges through the PVC segments at their midsections.

Stringing the MLS—threading the tubes through the inside of the pipes—is accomplished sequentially, beginning with the second deepest pipe, with its tubing attached at ports, by threading through the tubes from the deeper pipe. When the stringing is finished for all the pipes, the pipe segments can be folded against each other so that the bundled MLS assembly is only about 3 m long, the length of one pipe segment (fig. 20).

# **Drilling and Installation**

The internal-tube MLS is installed with a hollow-stem drill rig. After augering down to the desired depth, the auger toe plate is knocked out and the depth is checked. Once the correct depth has been reached inside the auger, the pipes can be lowered, their joints cemented, and the distances between joints recorded (fig. 21). (Each glue joint may have a different vertical dimension, which would affect the final port depths.) After the complete MLS is inside the drill hole, the sampling tube ends are taped up so that they will not be damaged by removing the auger. While the PVC pipe is initially held down, the auger is spun out. Sand can be shoveled down the hole and the well finished either with a flush mount or stickup (fig. 22).



**Figure 21.** Installation of multilevel sampler in hollow-stem auger at Prince Valley Road, Truro, Massachusetts. The distance between marked sections of two pipes is being measured to determine length of the joint.



**Figure 22.** Finished flush-mount multilevel sampler well. Repeat colors are marked with yellow tape.

#### **External-Tube Construction**

External-tube MLS construction is similar to that for internal tubes, except that drilling holes for the ports is not necessary because the tubes are on the outside of the PVC pipe, and stringing is not required. The tubes may be taped on a PVC pipe in the position required for the sampling port and higher on the pipe, but the remainder of the tube is gathered with the other tube remainders and bundled in a coil for transportation to the drill site.

At the drill site, schedule-40 pipe is installed in the ground as for a monitoring well (McCobb and Weiskel, 2003). At Gull Pond, 9.1-m (30-ft) MLSs were installed with a portable non-hollow auger. The hole was augered to a depth of 9.1 m and the auger spun in place to clean out the hole. Then the auger was removed and the hole collapsed below the water table at a depth of about 3 m, but the sediments were loose enough to allow the schedule-40 casing to be pushed to the correct installation depth. The casing was filled with water to help force it down. The MLS was installed inside the casing and used to push out an end cap on the casing. Finally, the casing was removed and the sediment allowed to collapse around the MLS.

# **Installations For Monitoring Trace Contaminants**

Wells that will be used for monitoring trace contaminants in samples of ground water must be constructed of materials that will not contribute to the concentrations of the trace contaminants in the well water. In general, appropriate materials for well construction differ according to whether inorganic or organic contaminants are being sampled.

# **Trace Inorganic Contaminants**

Most trace inorganic contaminants that are measured in water-quality-monitoring programs are trace metals, for example, copper, lead, or zinc. Prevention of contamination of well water with trace metals from the well casing requires monitoring wells to be constructed of plastic or Teflon. Because metal compounds are components of some plastic dyes, well materials that are made of colored plastic must be tested for potential contamination of well water before they are used. Teflon, which generally does not contaminate well water, may be a necessary material to use for well construction if samples from the wells are to be analyzed for low-concentration constituents such as mercury or cadmium.

# Trace Organic Contaminants

Plastics generally should be avoided as well construction materials if water samples are intended for the analysis of trace organic contaminants, because plasticizers in these materials may leach into the well water. Plasticizers such as phthalate esters can interfere with the analysis of other trace materials, and may themselves be of interest as water contaminants. Stainless steel or Teflon is appropriate for the casings of wells that will be for monitoring trace organic contaminants in well water.

# **GROUND-WATER-QUALITY SAMPLING**

A detailed description of water-quality sampling of ground water is available in the National Field Manual (NFM) for the Collection of Water Quality Data, which is available through the internet (http://pubs.water.usgs.gov/twri9A). References to the appropriate chapter of the NFM will be included in the sections below as: U.S. Geological Survey, variously dated, chapter number. The NFM descriptions can be consulted for more detailed accounts of ground-water-quality sampling and for procedures for constituents that are not included here.

The ground-water-quality sampling methods described here apply to the monitoring networks discussed above and to the constituents and water properties listed in table 4. The methods generally are compatible with the methods described in the NFM; some procedures (for example, the clean sampling technique) are derived from additional references.

# **Equipment**

Specialized equipment for pumping the wells, making measurements of water-quality properties in the field, and processing water samples that will be analyzed subsequently in a laboratory is required to prevent contamination of samples during the sampling procedure. Any equipment touching a water sample, or in some cases, being close to a sample, could change constituent concentrations from those that are present in the ground water. Exhaust from gas motors, airborne copper from electric motors, or metal oxides from corroding equipment could contaminate a sample through transport of fumes or small particles in the air.

## **Pumps**

Pumps (U.S. Geological Survey, variously dated, chapter 2.1.2.A) are used to transport water from the subsurface to the land surface either by suction lift (such as by peristaltic pumps on the land surface) or by positive pressure (such as by inertial submersible and centrifugal pumps placed below the water table). Sampling of the MLS used in the CACO network requires peristaltic pumps because of the small diameter (¼ in.) of the sampling tubes. Samples may be collected from the conventional wells either by submersible pumps, or by peristaltic pumps if the water table is within suction depth of the land surface.

The depth to the water table, the possible exposure of samples to air, and degassing are important considerations for choosing a pump. Peristaltic pumps are convenient because they are light, can be run with power from a small battery, and are less likely than other types of pumps to contaminate the sample because the water contacts only the inside of the pump tubing. Peristaltic pumps with a robust reversing switch and variable-speed motor, like the GeoPump, are useful for developing the sampling ports of an MLS because they keep the sampling lines clear of clay and silt. Limitations of peristaltic pumps include low pumping rates (1 to 2 L/min); the maximum height of suction, about 9 m, and an operational lift as little as 6 m (20 ft); degassing from the water sample; and exposure of the sample water to air. Because of decreased pressure on the water when suction is applied, gases that were dissolved in the ground water may come out of solution (degas). Dissolved gases can also increase in a water sample. Atmospheric gases (oxygen) can diffuse through the tubing during the pumping process, especially in the pump head, where rollers deform the tubing. Diffusion of oxygen into the water sample can be minimized by selecting low-permeability tubing for the pump head.

Submersible downhole pumps are useful for sampling conventional monitoring wells. As compared to perastaltic pumps, submersible pumps have higher pumping rates, can lift water higher, can make use of noncontaminating, nonpermeable pump tubing, and do not create a vacuum in the lift portions of the tube. Downhole pumps can also be equipped with packers. Packers close off the well bore above the pump. They can be used to obtain water samples from deep wells without the need to flush full casing volumes to obtain a representative sample. They also prevent oxygen from contacting the sample, which otherwise mixes in from the well-water surface. Packer pumps can be used to obtain samples for measurement of

accurate concentrations of redox-sensitive ground-water constituents (Colman and Friesz, 2001). An inexpensive nonpacker model (such as the Purge Pump) will lift water to a height of 18 m (60 ft). Grundfos and Keck pumps can pump at variable rates and to a greater height above the water table.

## Tubing, Gloves, and Filters

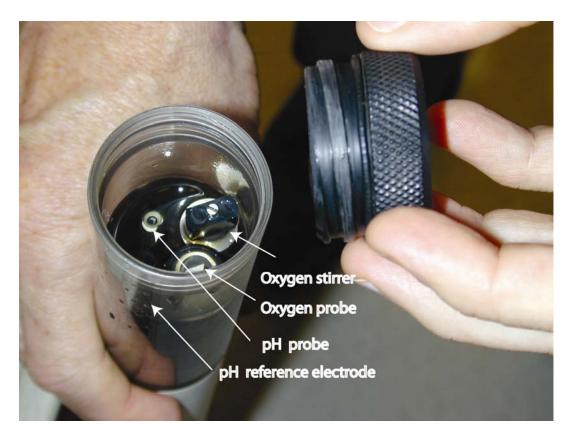
The tubing selected (U.S. Geological Survey, variously dated, chapter 2.2.4) for use with peristaltic pumps should keep water samples from being contaminated by constituents that may leach from the tubing and keep constituents in the water from sorbing to the tubing. The tubing used for pumping an MLS is short, so that the effect of the tubing on the constituents usually sampled will be minimal. For the monitoring of trace contaminant work, however, the noncontaminating properties of the tubing, even tubing used in an MLS, must be verified through analysis of equipment blanks. Pump tubing for submersible pumps are typically 30 m long. Usually submersible pump tubing is permanently attached to the pump and reused from well to well. Thus, the tubing would need to reach to the bottom of the deepest well that is sampled with a given pump. Teflon tubing generally is used in these situations so that the pump can be used for all types of network-well sampling without concern about contamination from the tubing.

Disposable gloves (U.S. Geological Survey, variously dated, chapter 2.0.2) should be worn during sampling and changed when contaminated. Although disposable gloves are appropriate for sampling, care should be taken that sample water does not touch the gloves.

Capsule, rather than membrane, filters (U.S. Geological Survey, variously dated, chapter 2.2.3) generally are most useful for ground-water sampling. The filter pore size should be 0.45  $\mu$ m. Capsule filters, such as AquaPrep 600 Capsules, can be inserted into the sample tubing and will prevent the well water sample from exposure to air. Samples filtered before exposure to air will not be subject to changes in redox-sensitive species, such as oxidation and precipitation of iron. AquaPrep 600 capsules were used in the network sampling through 2003. Smaller, less expensive filters are available, such as the Millipore Milex–HV, hydrophylic PVDF filters. These plug more easily than the bigger filters, but often work for ground water, which may be clear of particulate material.

### Temperature, Dissolved Oxygen, pH, and Electrical-Conductance Meters

Meters used to make field water-quality measurements can be equipped either with multiple probes or individual probes. Meters and probes for all of the measurements of water quality that are completed in the field—temperature, dissolved oxygen (DO), pH, and electrical conductance—are reviewed in the NFM (U.S. Geological Survey, variously dated, chapter 6.3.1). A multiple probe meter (fig. 23) with flow-through cell (fig. 24) (U.S. Geological Survey, variously dated, chapter 6.0.3B) produces data that are accurate enough for most purposes, although the most accurate electrical conductance and pH values can be obtained with separate meters, such as the Orion 115A conductance meter and a separate pH meter with a Ross Electrode pH probe. Meters such as the Orion 115A measure temperature and conductance and can be run in a mode to display conductance results corrected to 25°C. The Ross pH electrode responds quickly and accurately in water of low conductance, such as the ground water on Cape Cod.



**Figure 23.** Filling the Hydrolab multimeter calibration chamber to just below the level of the dissolved oxygen membrane. After the cap is screwed on, and 100 percent humidity has developed in the chamber, calibration can proceed.



Figure 24. Flow-through cell for field measurements of water quality.

### Field-Meter Calibration and Measurement

Whether or not a multiple probe meter is used, field meters must be calibrated before use. In small field areas such as the CACO, where overnight field trips are not necessary, calibrations can be completed at the laboratory, and with the exception of temperature, at the beginning of each day of sampling. Temperature probes should be calibrated twice per year.

### Logbook and Field Forms

Calibration data for field equipment should be stored in two places: with the primary water-quality records in the project office (on calibration field forms, appendix 1) and in a logbook kept with the field meter. Logbooks for field meters should identify the meter by manufacturer, model description, and serial or property number and contain records of calibration and any adjustments or repairs made to the meter. When more than one field site is sampled on the same day, the calibration field form should be duplicated so that a copy can be attached to the data sheets that are filed for each site.

### **Temperature**

Usually, thermistors rather than liquid-in-glass thermometers are used to measure temperature, and must be calibrated in each instrument that includes the thermistors—the multiple probe instrument, the conductance meter, and the pH meter. Detailed temperature-calibration instructions are in U.S. Geological Survey, variously dated, chapter 6.1.2.

### Calibration

- 1. The frequency of calibration is once every 6 months.
- 2. Calibration should be against a National Institute of Standards and Technology traceable thermometer in a beaker of stirred water that is insulated against heating from the stirring plate by a Styrofoam pad.
- 3. The calibration checks should include the range of temperatures anticipated in the field, such as from ice water to room temperature.
- 4. For routine ground-water work, temperature sensors should be accurate to within 0.1°C.

### Measurement

- 1. For the true temperature of the water in an aquifer, measure the temperature of water downhole in a well, as described by Lapham (1989), or
- 2. Measure the temperature of well water in a flow-through cell at the surface to give a result close to the temperature of the water in the aquifer. The accuracy of the measurement depends on whether flow through the pump tubing alters the water temperature before the water reaches the temperature probe.
- 3. Record the temperature of the water at the surface in association with measurements of conductance, dissolved oxygen, and pH.
- 4. Record temperature to the nearest 0.1°C.

### **Electrical Conductance**

Electrical conductance (U.S. Geological Survey, variously dated, chapter 6.2.1) is a measure of the capacity of water to conduct an electrical current. Electrical conductance is a function of the types and concentrations of dissolved ions in water. Specific conductance, which is the conductance measure usually reported, is electrical conductance adjusted to 25°C. The purpose of the calibration procedure is to verify that the cell constant and temperature correction are set correctly. Procedures for calibrating conductance meters vary (U.S. Geological Survey, variously dated, chapter 6.3.2). Meters may or may not be adjustable and may or may not have built-in temperature compensation. Calibration procedures are:

#### Calibration

- 1. The frequency of calibration is once during each day of use.
- 2. Use two KCl calibration standards that bracket the range of conductance expected.
- 3. Rinse the conductance probe and container with three rinse aliquots of standard before filling the container a fourth time for a reading.
- 4. Immerse the probe and dislodge any bubbles that may be adhered to the conductance probe.

Record the temperature, conductance, and cell constant for each standard, adjusted to 25°C, both before and after any meter adjustments in microsiemens per centimeter at 25 degrees Celsius (μS/cm at 25°C).

#### Measurement

- 1. Rinse the probe and measuring container with sample water three times to ensure that no solution remains from the last sample.
- 2. Immerse the probe in the sample and dislodge any bubbles that be adhered to the probe.
- 3. Record sample temperature and specific conductance (conductance corrected to 25°C) on the field forms.
- 4. The probe should be cleaned for storage soon after use by rinsing in distilled water and wiping dry with a lab paper tissue.

### pН

Details of pH measurement and calibrations are in the U.S. Geological Survey, variously dated, chapter 6.4. Standardization of pH electrodes requires two pH buffer standards—one of pH 7 and another which, with the pH-7 buffer, brackets the expected pH range. For Cape Cod ground water, appropriate standards are pH 7 and pH 4.

### Calibration

- 1. The frequency of calibration is once during each day of use.
- 2. Determine if pH filling solution is needed. For the Ross pH electrode, filling solution should be supplied through the hole in the side of the electrode to a level higher than that in the sample when the probe is immersed in the sample (fig. 25). Filling solution should be flowing out through the liquid junction in the bottom of the probe driven by the difference in height between the levels of fluid inside the probe and outside the probe in the sample. (The flow is too small to be visible.) Also the filling hole must be left open during measurement to facilitate the flow of solution; if air cannot move in to replace the solution, it will stop flowing. When the probe is not in use, the filling hole can be closed to keep solution from running out if the probe is stored horizontally.
- 3. The reference electrode (fig. 23) of the Hydrolab needs to be supplied with KCl filling solution every 2 weeks.
- 4. Start the calibration with the buffer of pH 7. Rinse the pH and temperature electrodes in three aliquots of buffer before filling the beaker for the calibration and recording the pH and temperature.
- 5. Using the zero adjust, calibrate the meter to the actual pH of the buffer at that temperature. (A complication is that the standard buffers change pH slightly as a function of temperature.)
- 6. Rinse the beaker and electrodes with distilled water and blot them dry with a lab tissue.
- 7. Rinse the electrodes and beaker with three aliquots of the second buffer. Record the initial pH, and then adjust the slope control to read the actual pH of the buffer at the measured temperature.
- 8. Record the calibration slope of the relation between pH and the potential difference between electrodes.



**Figure 25.** Filling the Ross pH probe with KCl filling solution. The level of the filling solution should be above the level of the surface of the sample during measurement.

#### Measurement

pH can be measured by multiple probe in a flow-through cell or in a separate sample drawn just for pH measurement. Because the dissolved carbon dioxide concentration in the water can affect pH, measurement by use of a flow-through cell might be preferable if degassing of carbon dioxide from a sample is likely; the flow-through cell minimizes the time during which carbon dioxide could leave the sample. Measurement of low conductance ground water like that on Cape Cod is more accurate by Ross electrode, however, which responds more quickly than other pH probes in low conductance water.

- 1. Rinse the electrodes and beaker with three aliquots of the sample solution.
- 2. Immerse the electrodes in the sample and record the pH to hundredths of a unit.
- 3. Record the temperature of the sample when measuring pH, but do not correct pH to a standard temperature.

# Dissolved Oxygen

The concentration of dissolved oxygen (DO) can be measured by an electrode method, the Winkler-titration method, or by spectrophotometric methods. The electrode method is accurate to 0.1 mg/L oxygen at concentrations above 1.0 mg/L, if the temperature of the electrode during calibration has been at or near the temperature of the sample water. The Winkler titration method is more cumbersome but more accurate than the electrode, especially at low DO concentrations at which precise electrode-method results are not possible. The Winkler and spectrophotometric methods are described in the NFM (U.S. Geological Survey, variously dated, chapter 6.2).

#### Calibration

A DO probe can be calibrated in water-vapor-saturated air, which has a constant proportion of oxygen (U.S. Geological Survey, variously dated, chapter 6.2). A calibration chamber with 100-percent humidity is used.

- 1. Check for bubbles beneath the DO electrode membrane (fig. 23), which indicate damage or loss of electrolyte filling solution. Change the membrane immediately if damaged and otherwise once per month. Record membrane changes in the record book.
- 2. Turn the multiple probe meter so that the DO membrane faces up (fig. 23). Pour water into the calibration chamber to a water level that approaches but does not cover the membrane.
- 3. Cap the chamber and wait 5 minutes for the humidity to build up to 100 percent in the chamber.
- 4. Read and record on the calibration field form and in the instrument logbook the atmospheric pressure from a barometer and the temperature of the probe in the calibration chamber.
- 5. Look up and record the value of the DO concentration at saturation for the measured pressure and temperature (table 7).
- 6. After the 5-minute wait, record the reading of the DO sensor in the chamber. Finally, adjust the meter to the value for 100-percent DO saturation determined in the table. The DO meter should not drift more than 1 mg/L per day; a drift larger than this indicates that the meter or probe needs to be serviced or replaced.
- 7. Store the DO probe with water in the chamber so that the membrane does not dry out.

**Table 7**. Solubility of oxygen in water as a function of temperature and pressure. [mmHg, millimeters of mercury; °C, degrees Celsius]

Tem-	1g, IIIII	<u> </u>	9 01 1110	icary,	<u> </u>	Atmos		pressi	ıre, in	mmHg					
ature in °C	790	785	780	775	770	765	760	755	750	745	740	735	730	725	720
0	15.2	15.1	15.0	14.9	14.8	14.7	14.6	14.5	14.4	14.3	14.2	14.1	14.0	13.9	13.8
1	14.7	14.7	14.6	14.5	14.4	14.3	14.2	14.1	14.0	13.9	13.8	13.7	13.6	13.5	13.4
2	14.3	14.3	14.2	14.1	14.0	13.9	13.8	13.7	13.6	13.5	13.4	13.3	13.3	13.2	13.1
3	14.0	13.9	13.8	13.7	13.6	13.5	13.4	13.3	13.3	13.2	13.1	13.0	12.9	12.8	12.7
4	13.6	13.5	13.4	13.3	13.3	13.2	13.1	13.0	12.9	12.8	12.7	12.6	12.6	12.5	12.4
5	13.3	13.2	13.1	13	12.9	12.8	12.7	12.7	12.6	12.5	12.4	12.3	12.2	12.2	12.1
6	12.9	12.8	12.8	12.7	12.6	12.5	12.4	12.3	12.3	12.2	12.1	12.0	11.9	11.8	11.8
7	12.6	12.5	12.4	12.4	12.3	12.2	12.1	12.0	12.0	11.9	11.8	11.7	11.6	11.6	11.5
8	12.3	12.2	12.1	12.1	12.0	11.9	11.8	11.7	11.7	11.6	11.5	11.4	11.3	11.3	11.2
9	12.0	11.9	11.8	11.8	11.7	11.6	11.5	11.5	11.4	11.3	11.2	11.2	11.1	11.0	10.9
10	11.7	11.6	11.6	11.5	11.4	11.3	11.3	11.2	11.1	11.0	11.0	10.9	10.8	10.7	10.7
11	11.4	11.4	11.3	11.2	11.2	11.1	11.0	10.9	10.9	10.8	10.7	10.6	10.6	10.5	10.4
12	11.2	11.1	11.0	11.0	10.9	10.8	10.8	10.7	10.6	10.5	10.5	10.4	10.3	10.3	10.2
13	10.9	10.9	10.8	10.7	10.7	10.6	10.5	10.4	10.4	10.3	10.2	10.2	10.1	10.0	10.0
14	10.7	10.6	10.6	10.5	10.4	10.4	10.3	10.2	10.1	10.1	10.0	9.9	9.9	9.8	9.7
15	10.5	10.4	10.3	10.3	10.2	10.1	10.1	10.0	9.9	9.9	9.8	9.7	9.7	9.6	9.5
16	10.2	10.2	10.1	10.0	10.0	9.9	9.8	9.8	9.7	9.6	9.6	9.5	9.5	9.4	9.3
17	10.0	10.0	9.9	9.8	9.8	9.7	9.6	9.6	9.5	9.4	9.4	9.3	9.3	9.2	9.1
18	9.8	9.8	9.7	9.6	9.6	9.5	9.4	9.4	9.3	9.3	9.2	9.1	9.1	9.0	8.9
19	9.6	9.6	9.5	9.4	9.4	9.3	9.3	9.2	9.1	9.1	9.0	8.9	8.9	8.8	8.8
20	9.4	9.4	9.3	9.3	9.2	9.1	9.1	9.0	8.9	8.9	8.8	8.8	8.7	8.6	8.6
21	9.2	9.2	9.1	9.1	9.0	8.9	8.9	8.8	8.8	8.7	8.6	8.6	8.5	8.5	8.4
22	9.1	9.0	9.0	8.9	8.8	8.8	8.7	8.7	8.6	8.5	8.5	8.4	8.4	8.3	8.2
23	8.9	8.8	8.8	8.7	8.7	8.6	8.6	8.5	8.4	8.4	8.3	8.3	8.2	8.1	8.1
24	8.7	8.7	8.6	8.6	8.5	8.4	8.4	8.3	8.3	8.2	8.2	8.1	8.0	8.0	7.9
25	8.6	8.5	8.5	8.4	8.3	8.3	8.2	8.2	8.1	8.1	8.0	8.0	7.9	7.8	7.8
26	8.4	8.4	8.3	8.3	8.2	8.1	8.1	8.0	8.0	7.9	7.9	7.8	7.8	7.7	7.6
27	8.3	8.2	8.2	8.1	8.0	8.0	7.9	7.9	7.8	7.8	7.7	7.7	7.6	7.6	7.5
28	8.1	8.1	8.0	8.0	7.9	7.9	7.8	7.7	7.7	7.6	7.6	7.5	7.5	7.4	7.4
29	8.0	7.9	7.9	7.8	7.8	7.7	7.7	7.6	7.6	7.5	7.5	7.4	7.3	7.3	7.2
30	7.8	7.8	7.7	7.7	7.6	7.6	7.5	7.5	7.4	7.4	7.3	7.3	7.2	7.2	7.1

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### Measurement

- 1. Turn on the stirring device in the multiple probe meter.
- 2. Immerse the DO probe in the water sample.
- 3. Record the DO concentration, temperature, and percent saturation.

## Alkalinity and Acid-Neutralizing Capacity

Alkalinity and acid-neutralizing capacity (ANC) are measures of the ability of a sample to neutralize strong acid (U.S. Geological Survey, variously dated, chapter 6.6). These quantities are determined by acid titration of a sample to either the inflection point of the titration curve or fixed pH value designated as the endpoint of the titration. The difference between the procedures for measuring alkalinity and ANC is that the alkalinity sample is filtered, whereas the ANC sample is not filtered. Particulate concentrations, which cause the difference between alkalinity and ANC, are difficult to measure in ground water because pumping of well water stirs up particulates in the well resulting in particulate concentrations that are not necessarily the same as particulate concentrations of ground water in the aquifer. Therefore alkalinity measurements of filtered samples, rather than ANC measurements, are recommended for most groundwater investigations.

### **Determination of Alkalinity**

Alkalinity in most natural waters is attributable to the presence of bicarbonate and carbonate ions, in proportions determined by the pH of the sample. The fact that the pH of most ground water is less than 8.3, the pH of equal concentrations of carbonate and bicarbonate ions, indicates that most ground water contains more bicarbonate ions than carbonate ions. Alkalinity may also include contributions from borates, phosphates, silicates, or other bases, including hydroxide, which would combine with acid during the titration.

Alkalinity determination should be completed as soon as possible after sample collection. Although not as strongly affected by air contact as a dissolved oxygen measurement would be, alkalinity should be measured in the field to minimize the period of exposure to air before titration. Exposure to air can affect alkalinity through degassing or chemical precipitation. Gain or loss of CO<sub>2</sub> does not affect the total alkalinity of a sample, although it does affect proportions of bicarbonate to carbonate. Introduction of oxygen may cause oxidation of reduced iron, which releases acid and would change the alkalinity. Immediate titration is most important for anaerobic samples that have dissolved iron concentrations greater than 1 ppm. If a sample must be stored, it must be kept in a stoppered glass biological oxygen demand (BOD) bottle in the cold (4°C) and in the dark, but for not longer than 24 hours before titration.

The USGS commonly obtains alkalinity titration acid, of 0.16 or 1.6 normality, from the Hach company. Most CACO samples can be titrated successfully by adding 0.16 normal acid to a 100-mL sample. Some ground-water samples that contain appreciable concentrations of organic carbon (such as downgradient from wetlands or landfills) will have much larger alkalinities. For these samples, higher concentrations of acid (1.6 normal) and smaller sample volumes (50 mL) can be used. The object is to use enough titrant so that its volume can be accurately measured.

### Measurement

- 1. Filter the alkalinity samples with the 0.45-µm flow-through disposable filter capsule. Collect a sample for alkalinity by directing the outflow from the capsule filter to the bottom of the sample container. Allow three volumes of overflow to flush away sample water that has contacted air.
- 2. Set up a beaker, magnetic stirring plate, titrant dispenser, and the calibrated pH meter for a titration (figs. 26 and 27).
- 3. Use three rinses of the beaker and probes that will touch the sample to remove any acid from the previous sample. Because titrations end at pH 3.0, a small amount carried over from the previous sample will decrease the initial pH of the next sample.
- 4. After the rinses, the beaker and electrodes should be dried with a lab tissue.
- 5. Measure out the sample (usually 50 mL) with a cleaned plastic 100-mL graduated cylinder. Pour the sample into a beaker with magnetic stirring bar.
- 6. Insert the pH electrodes into the sample, wait for equilibration, and record the pH of the unstirred sample.
- 7. Start the magnetic stirring at a slow but constant rate. Use a Hach titrator to deliver the acid to the titration sample (fig. 27). Use a constant time interval between additions of acid, and, after every addition, write down the pH and volume of acid added. Continue the titration to pH 3.0.
- 8. Analyze the titration curve to determine the titration endpoint and alkalinity. Alkalinity determined by fixed endpoint, inflection point, and Gran plot methods can all be determined quickly by computer program (U.S. Geological Survey, 2003). Alternatively, alkalinity can be determined by using the formula on the alkalinity field forms (appendix 2).



**Figure 26.** pH meter for alkalinity measurements.



Figure 27. Addition of acid during titration.

# **Well Purging and Field Measurements of Water Quality**

Water in the well casing must be removed and replaced, prior to sample collection, with water drawn in through the well screen from the aquifer. The well is pumped, or purged, to exchange the water. Purging is necessary so that the composition of the water sample collected is as close to the composition of the aquifer as is possible. For a conventional well, three well-casing volumes must be purged before sampling. The well-casing volume equals the well cross section times the distance from the water table to the bottom of the well. For wells with a packer pump, only three times the volume of the casing below the packer needs to be purged. Purging can stir up more sediment into the water from the bottom of the well than would be representative of the water in the aquifer. Low-flow purging and sampling has been proposed to overcome this problem (Sevee and others, 2000). Low-flow sampling, however, takes a long time and may still not produce completely representative samples; for instance, oxygen may be entrained from the water-column surface. This protocol recommends conventional purging, sampling, and inline filtration of samples to remove particulates.

Casing volume in the sampling tubes of an MLS is small, about 560 mL for 45 m of tubing. Also, because water mixing in an MLS is less than in a conventional well casing, purging 1 L before collection of water samples is sufficient for any MLS sampling port.

Measurements of temperature, electrical conductance, pH, and alkalinity must be completed during or close to the time of sampling. Except for alkalinity, which is determined by titration, these measurements can be used to monitor the process of well purging. The effectiveness of purging can be checked by determining whether measurements of each quantity have reached a constant value. A constant value would indicate that the original water in the well casing had been completely replaced with water from the aquifer.

The usual device for monitoring water quality during purging is the multiple probe meter with a flow-through cell (fig. 24). Operation of the multiple probe meter probe with a flow-through cell involves the following steps:

- 1. After the probes have been calibrated, turn on the pump (fig. 28); all or part of the pumped water will be routed through the flow-through cell. Although flow is continuous through the cell, the oxygen-probe stirrer must be turned on for accurate oxygen measurements.
- 2. Periodically record water-quality measurement from the multiple probe meter on a well purge log data sheet (appendix 3).
- 3. When the measurements have stabilized, record the final readings and the time of sampling on the field form (conventional well appendix 4 or MLS, appendix 5). The station number, date, and time constitute a unique sample designation, which is used to identify the final values of each water-quality measurement completed in the field as well as for the samples collected for any additional analyses in the laboratory.
- 4. After the well is purged, collect water for determination of alkalinity by disconnecting the flow-through cell and inserting a capsule filter on the pump tubing.



Figure 28. Geopump set up for pumping multilevel sampler ports.

# **Collection of Water Samples**

After calibration of instruments, purging of the well, and determination of field water-quality properties, water samples intended for analysis in a laboratory are collected. Determination of which bottle materials, handling procedures, and preservation methods are appropriate depends on constituent and concentration range of interest (table 5).

# Preventing Sample Contamination and Cross Contamination

Keeping sample equipment and bottles clean is an important part of any ground-water-quality monitoring program. For ultra-low-level constituents like mercury, whose range in concentrations is at the low nanogram-per-liter level, extraordinary measures must be taken during sampling to prevent sample contamination. Even for constituents such as nitrogen and phosphorus with concentrations in the low microgram-per-liter levels, care must be taken to keep sampling equipment and bottles clean. For analyses of dissolved phosphorus, small amounts of dust (phosphate is in many cleaners, detergents, and in pH buffer) can alter sample concentrations.

Measures that help prevent contamination during sampling include:

- 1. Keeping sample bottles in new plastic bags before and after sampling;
- 2. During sampling, not allowing bottles to touch surfaces that might be contaminated;
- 3. Keeping bottles on a clean surface and using a clean bottle-holder rack (carry it around in a plastic bag) to keep bottles upright, even under windy conditions;
- 4. Wearing plastic gloves during bottle handling and changing them after touching contaminated surfaces. For example, gloves protect samples from lotions applied to skin to prevent sunburn, which have been found to contaminate samples with zinc; and
- 5. Preventing contamination of samples during sample preservation. Preservatives contain high concentrations of chemicals. Care must be taken that fumes from preservative acids, HNO<sub>3</sub> or HCl, for example, do not contact samples intended for analysis of the acid anion constituent, NO<sub>3</sub> or Cl<sup>-</sup>.

In collecting water samples for analyses of constituents present at very low concentrations (nanograms per liter), the protocol designated "clean hands-dirty hands" is used (U.S. Geological Survey, variously dated, chapter 4.0.1). The collection of samples for mercury analysis, for example, involves two people, one designated "clean hands" and the other "dirty hands," and specially cleaned bottles that are double bagged (usually plastic Ziploc bags are used). Contamination is prevented by allowing only clean hands to manipulate the inner bag and bottle contained therein. The steps are:

- 1. The gloved dirty-hands person opens the outer bag and presents the inner bag with sample bottle to the gloved clean-hands person.
- 2. The inner bag is extracted and opened by clean hands only.
- 3. The clean-hands person removes the bottle from the inner bag and fills it with sample water.
- 4. After the sample is in the bottle, the clean-hands person puts the bottle back in the inner bag and stuffs it into the outer bag, which is held open by the dirty-hands person.
- 5. Finally, the dirty-hands person puts the doubled bagged bottle away in a plastic bag that carries all the samples.

# Labeling Sample Bottles

Labeling sample bottles includes the following steps:

- 1. Create labels for all sample bottles with lines or spaces for station, date, time, and intended analyses.
- 2. Print the labels on waterproof paper with adhesive back (for example, Avery labels). Microsoft Word/tools/letters and mailings/mail merge wizard/ can be used to set up the template and merge the data to create the labels.
- 3. Apply the labels to the bottles before filling the bottles. This will ensure that no bottle is mislabeled and that the labels stick to the bottles.

# Filling Sample Bottles

- 1. Generally, bottles are rinsed three times by shaking at least 30 mL of sample water in the bottle with the cap on and discarding the water before the final filling with sample.
- 2. For filtered samples, a capsule filter with 0.45-µm pore size is attached to the pump line to filter samples inline before collection into bottles.
- 3. For whole-water samples, the filter is removed and samples pumped directly to bottles.

## Prevention of Degassing and Maintenance of Anaerobic Conditions

Degassing and contamination of ground-water samples by oxygen are potential problems in ground-water sampling. Water in deep wells is under multiple atmospheres of pressure (one atmosphere is about 10 m of water), and, as a result of bacterial decomposition of organic matter, may contain large amounts of dissolved gases (such as CO<sub>2</sub> and CH<sub>4</sub>). Concentrations of gases in excess of equilibrium with one atmosphere of pressure will degas when brought to the surface. Loss of carbon dioxide would cause pH to decrease and the proportions of the components of alkalinity (carbonate and bicarbonate) to change, but would not affect the total alkalinity. Most ground-water samples, however, contain only bicarbonate alkalinity so that altered proportions of bicarbonate and carbonate alkalinity are not a concern. Degassing can be minimized by using submersible pumps to obtain samples rather than suction pumps.

Ground water is typically either low in oxygen concentration (below atmospheric equilibrium) or, occasionally completely anaerobic. When anaerobic samples contact air, concentrations of oxygen and reduced species (for example, NH<sub>3</sub>, As (III), Fe (II), and Mn (II)) can change dramatically. When iron oxidizes, it precipitates as iron hydroxide and can substantially change dissolved concentrations of other species, such as arsenic and phosphate, that coprecipitate with it. Commonly the sample is filtered inline, and then the sample is acidified to keep iron and other constituents in solution.

# Sample Preservation

Samples often need to be preserved with chemicals (acids are used in this protocol) or kept cold so that water-quality constituents do not change before analysis (table 5). Because sample bottles are to be rinsed with sample water, preservation acids must be added in the field after the sample is collected. Acid can be conveniently applied in the field by counting drops from a Teflon dropping bottle (fig. 29). Teflon does not degrade, even in contact with strong acids. The number of drops required to bring the sample to a given preservation pH can be determined by titration of the sample with the acid. The possibility of sample contamination is high during preservation because most preservatives are concentrated chemicals (fig. 30). Samples should be acidified outside in the field or in a fume hood in the laboratory to prevent personnel from breathing in acid fumes and to prevent sample contamination. Storing preserved samples in separate plastic bags for each preservative added is also good practice.



Figure 29. Preservation of samples by using concentrated acid from a Teflon dropping bottle.



**Figure 30.** Potential contamination problems are associated with samples that are opened in a laboratory, for example, during preservation by acid addition.

# **QUALITY-ASSURANCE PROCEDURES**

Quality of data can be verified by use of QA sample blanks, analyte-spike solutions, and sample duplicates. So that QA data can reflect the effects of those processes and problems that occur in field work, most QA samples in a sampling program are generated in the field. Sampling equipment and bottles must be cleaned and protected during transportation in a standard way so that a minimal number of QA samples will be sufficient to describe and document sampling error. Because the ground-water-quality monitoring program at the CACO is designed to continue for a long period, a small fraction of the total number of samples—for example between 5 and 10 percent—is required to be duplicates and blanks. The QA samples can be pooled from several sampling rounds to calculate QA statistics. Thus, one duplicate sample for each constituent at one port of a 15-port MLS is appropriate, or one blank sample for each MLS. A greater percentage of duplicates and blanks is needed to define QA for the conventional monitoring wells (20 percent) because fewer samples will be generated during each round of sampling at a monitoring well.

Field spikes of analyte into samples are appropriate QA procedures for investigations of metals, VOCs, or trace organics. Recovery investigations of spikes are recommended to determine if the particular water matrix is affecting results or if analyte is being lost on equipment, such as bottles and filters in contact with the sample.

# **DATA MANAGEMENT**

Data management is as important as data collection for the success of a long-term monitoring program. Management includes both computations and storage of the data.

# **Data Computations**

Two types of data analysis can be defined: the analysis of QA data, and analysis of data from the field. For QA data analysis, variance should be computed on duplicate samples from each constituent analyzed and compared to the variance computed from laboratory splits. This computation is described for mercury data by Colman and Breault (2000). The variances reflect variability of the data caused by random error associated with sampling and analysis. If the variance associated with field duplicates is not greater than that of laboratory splits, then the random contamination of samples during sampling (such as from dust or oxide coatings on sampling equipment) is not a problem. Blank samples and equipment blank samples should be compared to determine the extent of any systemic contamination associated with the leaching of constituents into samples from sampling equipment or from preservation chemicals. Finally, spike recoveries should be computed to determine if the sample matrix is causing an incomplete response from known additions of spiked analyte.

Water-quality data from the ground-water protocol should be analyzed first for time trends. Statistical methods for analysis of time trends in water-quality data are covered by Helsel and Hirsch (1992) and for data including "less than" values by Helsel (2005). Other more complex analyses beyond the scope of this protocol may also be warranted. In particular, solute-transport modeling based on calibration data collected through the ground-water-quality protocol might be needed to simulate nutrient loading to estuaries.

# **Maintenance of Project Files and Records**

In a long-term monitoring program, records must be clearly understood so that data can be used and interpreted years after collection. In addition to computer databases, paper records are still used by the USGS and archived to store data.

## **Primary-Record Files**

Today, record keeping is more commonly done by computer rather than paper files. The convenience and reliability of paper files used in the field, however, mean that paper records of field notes and field-instrument calibrations are still in common use. Recently, more of these "original" records are actually generated by computer, such as analytical results from a laboratory-information management system. For each well sampled, the field forms with results of measurements completed in the field, instrument calibrations, analytical request forms, and paper results from the lab should be kept in primary-record files sorted according to station ID number. For MLS, however, all data from one MLS is kept in one file, even though each port of every MLS has a different station ID number.

Water-quality measurements made in the field and the purging data for each monitoring well sampled are recorded on a field-data form. Example forms are in appendixes 3 and 4. Field forms for MLS are similar, except that data from all levels of sampling ports can be recorded on one sheet (appendix 5). For each field alkalinity measurement, an alkalinity-titration sheet (appendix 2) should be completed and filed in the sample primary record.

The analytical-services request form, also included in the primary record file, records the analyses requested of the laboratory and the bottle types and preservatives used in the samples that were sent to the laboratory (appendix 6). Finally a paper copy of the analytical results that are returned from the laboratory should be kept in the primary record file (appendix 7).

### Field Notebook

Use a bound notebook with numbered pages. The first 3 pages should be reserved for a table of contents to be compiled as the notebook is filled. Photocopies of new sections of the book should be made periodically and kept in the office as a backup in case the field notebook is lost. Record general notes about the sites, dates, times, and samples collected. The notebook serves as a chronological record of what was sampled. The same information is in the primary record files, but is not a chronological record of the field work.

## Meter-Calibration Logbook

Equipment calibration information for the field meters is recorded in bound notebooks kept with the meters. These records are used to keep track of the accuracy of the instruments and to prove that the field-measured properties are accurate. The calibration data for each meter for each day should be photocopied from the meter book and kept as part of the primary record file for sampling of a well or MLS.

### **Database**

Electronic data storage is an important component of long-term monitoring programs. Databases should contain sufficient ancillary and QA data that results can be fully interpreted when retrieved. The database must be maintained and moved without error from one computer platform to the next and possibly from one software data-management system to the next, because platforms and systems become obsolete and are periodically replaced. The USGS database for water quality, QWDATA, meets these requirements. The use of this database for CACO data is now under review.

# **Archiving Procedures**

Typically data records are kept in file cabinets in the office of the project chief. Records need to be kept up to date and available for reference during project report writing and for project reviews.

When the volume of files for long-term projects becomes very large, the files may need to be put in a permanent storage facility. Archiving space is available in Federal storage facilities and is an appropriate location for primary records and other project materials when space in the office becomes inadequate.

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	ad by:						STN	NO
Dale:		Tin	18:				Laca	dion:
			na	ETER CALIBI	RATION6/FI	ELD MEASUR	REMENTS	
TEMPER	RATURE Mete	r make/mod	el		3/N	п	hermister SAN	Thermometer ID
Calibrati	ion cuiteria: ±1 g	rescent or ± 0.5	i CC for liquid-fil	led themsmeters	± 0.2 (C for	thormistors		
Lab Test	ted against NIS	ST Thermon	etar/Thermi	ster? Y	N C	ete:		±°C
bleasure	sment Location	: FLOW-TH	IRIJ CHAMBER	SINGLE P	CARNT AT	th blav LSI	D VERTICAL AN	G. OF POINTS
Field Re	actings # 1_	#2		3	#4	_ #5	MEDIAN:	^C RemarkQualifier
aH Mei	er make/mode			SAN		Electrode No	<u>.</u>	Type: GEL LIQUID OTHER
								MERCTICAL ASAS, OF POINTS
oH Buffer	Buffer Temp	Theoretical pH from	pH Before Adj	pH j. After Adj.	Slope	Millivolts	Temperature con	rection factors for buffers applied? Y N
417		table	-	_		1	BUFFER LOT BUNBERS	
#17 ****				+		<u> </u>		pH;
#17 ~				1			CHECK	рн;
H7	$\vdash$		┞	$\downarrow$		ļ	BUFFER EXP.	pH 7:
#I			<u> </u>				DATES:	pH:
#			<u> </u>				CHECK	pH;
#1								
HECK							Galilasatian Galisais	c ± 9.2 pH units
Field Ra	eadings # 1	#2	# 3	5 64		5 131	EDIAN:	
THE RESERVE OF	THE SECTION AND THE	ANCE Met	er makelmod	tel		SIN_	ა	ensorType: Dip Flow-thru Other
							. of points	enserType: Dip Flow-thru Other s
	ue Std	SC Before	Single point  SC  After		it blev lad	Vertical avg.	Std Exp. Date	
Sample:	ue Std	SC	Single point	sat1	it blev lad	Vertical avg.	Std Exp. Date	Calibration Criteria: the greater of 5 Stom or 3%
Sample:	ue Std	SC Before	Single point  SC  After	sat1	it blev lad	Vertical avg.	Std Exp. Date	Calibration Criteria: the greater of 5 Ston or 3% of measured value
Sample:	ue Std	SC Before	Single point  SC  After	sat1	it blev lad	Vertical avg.	Std Exp. Date	Calibration Criteria: the guestier of 5 Stom or 3% of measured value  AUTO TEMP COMPENSATED METER  MANUAL TEMP COMPENSATED METER
Sample:	ue Std	SC Before	Single point  SC  After	sat1	it blev lad	Vertical avg.	Std Exp. Date	Calibration Criteria: the guestier of 5 Stom or 3% of measured value  AUTO TEMP COMPENSATED METER  MANUAL TEMP COMPENSATED METER
Sample: Std Val µS/cm	: Floer-thru.cl	SC Before Adj.	Single point SC After Adj.	Stot 1	It laker laid	Vertical avg. Std type (KCI; NaCI)	ofpoint	Calibration Criteria: the greater of 5 Stom or 3% of measured value  Auto Temp Compensated Meter  Manual Temp Compensated Meter  Consection Factor Applied? Y M
Sample: Std Vali µS/cm	tue Std Temp	SC Before Adj.	Single point SC After Adj.	Stot 1	it blev lad	Verilical avig. Std type (KCI; NaCI)	ofpoint	Calibration Differior the greater of 5 Scienter 3% of measured value  AUTO TEMP COMPENSATED METER  MANUAL TEMP COMPENSATED METER  CORRECTION FACTOR=  Safcan Remark Qualifier
Sample: Std Vali µS/cm	: Floer-thru.cl	SC Before Adj.	Single point SC After Adj. #3	Stot 1	It blev lad	Verilical avig. Std type (KCI; NaCI)	ofpoint	Calibration Criterio: the greater of 5 Storn or 3% of measured value  AUTO TEMP COMPENSATED METER  MANUAL TEMP COMPENSATED METER  CORRECTION FACTOR=  Safcan Remark Qualifier
Sample: Std Vali µS/cm Fileld Re DISSOLI Sensor T Sample:	E Floer-thru d  Lee Std Temp  Readings #1  LEED OXYGEN Type: Polarog Floer-thru che	SC Before Adj. #2_ Meter ma prephic Lun annber Sin	Single point SC After Adj.  #3  ive/model innescent gle point at_	Stot 1 Stot Lot N Probe No 11 blar	it blev lad	Std type (KCI; NaCI)  5ME	Std Exp. Date  Std Exp. Date  DIAN:  points BOD bo	Calibration Criteria: the greater of 5 Stom or 3% of measured value  AUTO TEMP COMPENSATED METER  MANUAL TEMP COMPENSATED METER  CORRECTION FACTOR=  Safcan Remark Cualifier  #Ille Stirrer Used? Y N
Sample: Std Vali µS/cm Fleid Re DISSOL! Sensor T Sample:	eadings #1_ WED OXYGEN Polarog Flore-flore dusated Air A	SC Before Adj.	Single point SC After Adj.  #3 ke/model ninescent gle point et_	Stot Lot N  Probe No	it blw lad	Std type (KCI; NaCI)  5ME SiN al ang. of afer Air Calib	Std Exp. Date  Std Exp. Date  EDIAN:	Calibration Criteria: the greater of 5 Stom or 3% of measured volue  AUTO TEMP COMPENSATED METER MANUAL TEMP COMPENSATED METER CONFRECTION FACTOR=  SIGN Remark Qualifier  Mile Stirrer Used? Y N  Air Winkler Titration Other
Stamplex Std Vali	E Flow-thru of Temp  Barometric Pressure  Plow-thru chromaturated Air A	#2_ #42_ Meter main prophic Lun amber Sin Uir-Saturated  DO Table Reading	Single point SC After Adj.  #3  keemodel Ilmescent gle point at I Water Air Salinity Correc-	Stot Lot N  Stot Lot N  Probe No	It blev lad	Std type (KCI; NaCI)  5ME SN all ang. of after Air Calibo	Std Exp. Date  Std Exp. Date  DIAN:  points BCD by ration Chamber in	Calibration Criterio: the guestier of 5 Storn or 3% of measured volue  AUTO TEMP COMPENSATED METER  MANUAL TEMP COMPENSATED METER  CONRECTION FACTOR =  SIGN Remark Questifier  Mile Stirrer Used? Y N  Air Winkier Titration Other  ongfl. Date:
Sample: Std Vali  µS/cm  Fileld Re  DISSOL  Sensor T  Sample: Water-Se	tue Std Temp  sadings #1_  WED OXYGEN Type: Polarog Flow-flux che abusated Air A	#2_ # Meter ma miner Sin  Nir-Saturated  DO Table	Single point SC After Adj.  #3  kermodel ninescent gle point et Salinity	Stot Lot N  Stot Lot N  Probe No	it blev lad	Std type (KCI; NaCI)  SiN	Std Exp. Date  Std Exp. Date  EDIAN:	Calibration Criteria: the greater of 5 Schmor 3% of measured value  AUTO TEMP COMPENSATED METER  MANUAL TEMP COMPENSATED METER  CORRECTION FACTOR=  SECON Remark CAUSTION  Mile Stirrer Used? Y N  Air Winkler Titration Other  sentider Check? Y N Date  sentider Check? Y N Date
Samplex Std Vali    µS/cm  Fileld Re  DISSOL  Sensor T  Samplac  Water-Se  Callibratio  Temp	E Flow-thru of Temp  Barometric Pressure  Plow-thru chromaturated Air A	#2_ #42_ Meter main prophic Lun amber Sin Uir-Saturated  DO Table Reading	#3  #6  #6  #6  #6  #6  #6  #6  #6  #6	Stot Lot N  Stot Lot N  Probe No	lad Vartic hamber in W  DO After djust- ment Ma	Std type (KCI; NaCI)  5ME SN all avg. of ster_Air Calib DO Check e DD Solution D mbrane Change	Std Exp. Date  Std Exp. Date  DIAN:  points BOD to ration Chamber in mall. Asj. I hale.  The dr. N. V. Nill.	Calibration Criteria: the guester of 5 Scienter 3% of measured value  AUTO TEMP COMPENSATED METER  MANUAL TEMP COMPENSATED METER  CORRECTION FACTOR=  SACIN Remark Cualifier  SILEN Stimer Used? Y N  Air Winkler Titration Other  complicitles: Y N Date  contribler Check? Y N Date  Consider  Calibration Check  Contribler Check? Y N Date  Consider  Consider Check? Y N Date  Consider  Consider Check? Y N Date
Stamplex Std Vali	E Flow-thru of Temp  Barometric Pressure  Plow-thru chromaturated Air A	#2_ #42_ Meter main prophic Lun amber Sin Uir-Saturated  DO Table Reading	#3  #6  #6  #6  #6  #6  #6  #6  #6  #6	Stot Lot N  Stot Lot N  Probe No	t blev lad  i No.  lisel Vertic hamber in W  DO After djust- ment Me	Std type (KCI; NaCI)  SiN	Std Exp. Date  Std Exp. Date  EDIAN:  points BIOD by radion Chamber in  mg/L Asj;  finale  Their? N Y Nah	Calibration Criteria: the guester of 5 Scienter 3% of measured value  AUTO TEMP COMPENSATED METER  MANUAL TEMP COMPENSATED METER  CORRECTION FACTOR=  SACIN Remark Cualifier  SILEN Stimer Used? Y N  Air Winkler Titration Other  complicitles: Y N Date  contribler Check? Y N Date  Consider  Calibration Check  Contribler Check? Y N Date  Consider  Consider Check? Y N Date  Consider  Consider Check? Y N Date
Std Vali µS/cm Fileld Re DISSOL' Sensor T Sample: Calibratio Temp °C	E Flow-thru of Temp  Barometric Pressure  Plow-thru chromaturated Air A	#2_ #Meter main raphic Lun amber Sin Ur-Saturated  DO Table Reading mg/L	#3  #6  #6  #6  #6  #6  #6  #6  #6  #6	Stot Lot N  Stot Lot N  Probe No	t blev lad  i No.  lisel Vertic hamber in W  DO After djust- ment Me	Std type (KCI; NaCI)  5ME  SW all awg. of after Air Calibo to DO Cheek to DO Solution D mbrane Change smeler Calibrate	Std Exp. Date  Std Exp. Date  EDIAN:  points BIOD by radion Chamber in  mg/L Asj;  finale  Their? N Y Nah	Calibration Criteria: the guester of 5 Scienter 3% of measured value  AUTO TEMP COMPENSATED METER  MANUAL TEMP COMPENSATED METER  CORRECTION FACTOR=  SACIN Remark Cualifier  SILEN Stimer Used? Y N  Air Winkler Titration Other  complicitles: Y N Date  contribler Check? Y N Date  Consider  Calibration Check  Contribler Check? Y N Date  Consider  Consider Check? Y N Date  Consider  Consider Check? Y N Date

GW form ver. 7.0

**Appendix 1.** Example of a field-meter-calibration form.

										STN NO
			AL	KALINITY/	ANC CAL	CULATION	S			
BEGINN	ING H <sub>2</sub> O T	TEMP	°c							CALCULATIONS
pН	PН	VOL ACID	VOL ACID	pН	pН	pН	VOL ACID	VOL ACID	PH	ALKALINITY or ANC (meq/L) = 1000 (B) (Ca) (CF) / $V_s$
		DC or mL	DC/mL	VOL ACID			DC or mL	DC/mL	VOL	ALKALINITY (mg/L as CaCO <sub>3</sub> ) = 50044 (B) (C <sub>a</sub> ) (CF) / V <sub>s</sub>
				710.0					710.0	where:
					$\vdash$			$\overline{}$		B = volume of acid titrant added from the initial pH to the bicarbonate equivalence point (near pH 4.5), in
					┢					milliliters. To convert from digital counts to milliliters,
					$\vdash$			$\leftarrow$		divide by 800 (1.00 mL = 800 counts)  C <sub>3</sub> = concentration of acid titrant, in milliequivalents
					$\vdash$			$\overline{}$		per milliliter (same as equivalents per liter, or N)
					├			$\leftarrow$		CF = correction factor (obtain from OWQRL for Hach
					├			$\leftarrow$		acid cartridges of certain lot numbers — default value is 1.00)
		_			⊢			$\leftarrow$		V <sub>s</sub> = volume of sample, in milliliters
			$\langle \cdot \rangle$		$\vdash$			$\leftarrow$		For samples with pH 9.2:
								<		
								$\leq$		BICARBONATE (meq/L) = 1000 (B-2A) (C <sub>a</sub> ) (CF) / V <sub>s</sub>
								$\angle$		BICARBONATE (mg/L) = 61017 (B-2A) (C <sub>a</sub> ) (CF) / V <sub>s</sub>
								<		CARBONATE (meq/L) = 2000 (A) (Ca) (CF) / Vs
					L			<		CARBONATE (mg/L) = 60009 (A) (C <sub>a</sub> ) (CF) / V <sub>s</sub>
								$\leq$		where:
								$\angle$		A = volume of acid titrant added from the initial pH to
								$\angle$		the carbonate equivalence point (near pH 8.3), in milliliters. To convert from digital counts to milliliters,
								$\leq$		divide by 800 (1.00 mL = 800 counts)
								$\angle$		NOTE: For samples with pH > 9.2, these equations for bicarbonate and carbonate will fail to give accurate results.
								$\angle$		Use the Alkalinity Calculator at http://oregon.usgs.gov/alk
										HACH CARTRIDGE CORRECTION FACTOR
										[SEE OWQRL WEB PAGE (NEWS) FOR INFO]
	FIRST	TITRATION	RESULTS			SECON	TITRATION	RESULTS		http://owqrl.er.usgs.gov/owqrlnews.shtml
DATE_	/_	_/			DATE_	/_				COMMENTS/CALCULATIONS:
ı				-	1				.	
			meq/L							
l			mg/L As		1			mg/L AS		
ı			meq/L A					meq/L A		
ı		mg/L SN 0.01639	meq /L A	S CO 32-	1		mg/L N 0.016391		IS CO 34-	
							0.010001			
ı				_					_	
l			<i>J</i>		1			//		
l			mL		1		:			
I—		UNFILT					UNFILTE			
	AN METHO	POINT TITRA D	AT ION			ECTION F AN METHO	POINT TITRA D	IION		
STIRRIN	NG METHO	D: MAG	SNETICN	MANUAL	STIRRIN	IG METHO	D:MAG	NETICN	MANUAL	

**Appendix 2.** Example of an alkalinity-calculation field form.

					WEL	L PURGE LOC	3	5	STN NO		
Purge m	nethod: STAN	DARD _		LOW-FLOW	ОТН	ER		_			
TIME	WATER LEVEL BLW MP LSD ft	DRAW f		WELL YIELD gpm	PUMPING RATE gpm	WATER TEMP <sup>®</sup> C	conductivity µs/cm	pH units	DISSOLVED OXYGEN mg/L	TURBIDITY NTU Or FTU	COMMENTS [CLARITY, ETC.]
											MEDIAN VALUES
											QUIESCENT PH
											FINAL FIELD MEASUREMENTS
				l				l		_	
			PAR	AMETER		STA	BILITY CRITERIA*				
		-	PH		± 0.1 UNITS (		INSTRUMENT DISE		CIMAL)		
			TEMP	PERATURE	± 0.2° C (TF	HERMISTOR)					
		-		CIFIC ELECTRICAL		C 100 µS/cm C > 100 µS/cn	n n				
			Disso	OLVED OXYGEN	(DO)	± 0.3 mg/L					
		-	TURB	IDITY (TU)	± 10%, FOR	TU< 100 NTU: A	MBIENT TU IS < 5 YSTEMS (VISIBLE	NTU TU > 5 NTU)			
		L	*ALLOV	NABLE VARIATION BETW	VEEN <b>5</b> OR MORE SEQUE	ENTIAL FIELD-MEASUR	EMENT VALUES				
						Notes, Calo	ulations				

**Appendix 3.** Example of a well-purge log.

### U. S. GEOLOGICAL SURVEY GROUND-WATER QUALITY NOTES

NWIS RECORD NO \_\_\_\_\_

Station No Stati	on Name	Field ID
Sample Date Mean S	ample Time (watch)	_ Time Datum (eg. EST, EDT, UTC)
Sample Medium Sample Type Samp	le Purpose (71999) Purpos	se of Site Visit (50280)
Project No Proj Name	Project No	Proj Name
Sampling Team	Team Lead Signature	Date
Sample Set ID LA		
Samples Collected: NUTRIENTS MAJOR IONS TRACE	BORATORY INFORMATION  ELEMENTS: filtered unfiltered ME	PCLIPV: filtered unfiltered MICPORIOLOGY
ORGANICS: filtered unfiltered PEST VOC		
ISOTOPES DOC TPC(vol filteredmL) PIC		
Lab Schedule:		
Lab Codes:ADD/DELETEADD/DELETE	ADD/DELETEADD/DELETE	ADD/DELETEADD/DELETE
COMMENTS		Date Shipped
**Notify the NWQL in advance of shipment of potential	y hazardous samples—phone 1-866-	ASK-NWQL or email LabLogin@usgs.gov
F	ELD MEASUREMENTS	
STATIC WATER LEVEL (72019)ft TEMP,	WATER (00010) °C	ANC ( )mg/L
FLOW RATE (00059) gpm pH (0	0400) units	ALKALINITY ( ) mg/L
SAMPLING DEPTH (78890) ft blw MSL COND	(00095) µS/cm@25 °C	BICARBONATE ( )mg/L
TOP OF INTERVAL (72015) ft blw LSD DIS. O	XYGEN (00300)mg/L	CARBONATE ( )mg/L
BTM OF INTERVAL (72016)ft blw LSD DO SA	т. (00301)%	HYDROXIDE ( )mg/L
· · · · ·		HYD. SULFIDE ODOR? (71875) Yes No
TEMP, AIR (00020) °C eH (0	0090) mvolts	DIS. SULFIDE, MEAS. ( 99119)mg/L
TURBIDITY ( ) METHOD CODE		
UNITS: FNU NTRU FNMU FBU OTHER	E	OTHER:
SAN	PLING INFORMATION	
Sampler Type (84164) Sampler/Pump Type (make	/model)	Pump/Sampler ID
Sampling Method (82398) Sampling Cor	ndition (72006)	
Sampler Material: STAINLESS STEEL PVC TEFLON OTHER	Tubing Material: TEFLON	N PLASTIC TYGON COPPER OTHER
Aquifer name	Depth pump	set at:ft blw LSD MSL
Sampling point description		
GW Color GW Clarity GW Odor	Sample in contact with: ATM	OSPHERE OXYGEN NITROGEN OTHER
Weather: SKY- CLEAR PARTLY CLOUDY CLOUDY PRE	CIPITATION- NONE LIGHT MEDIUM H	HEAVY SNOW SLEET RAIN MIST
WIND- CALM LIGHT BREEZE GUSTY WINDY EST. WIND SPEED	MPH TEMPERATURE- VI	ERY COLD COOL WARM HOT
OBSERVATIONS:		
COMPILED BY : DATE CHECKED BY	/: DATE LOG	GGED INTO NWIS BY: DATE

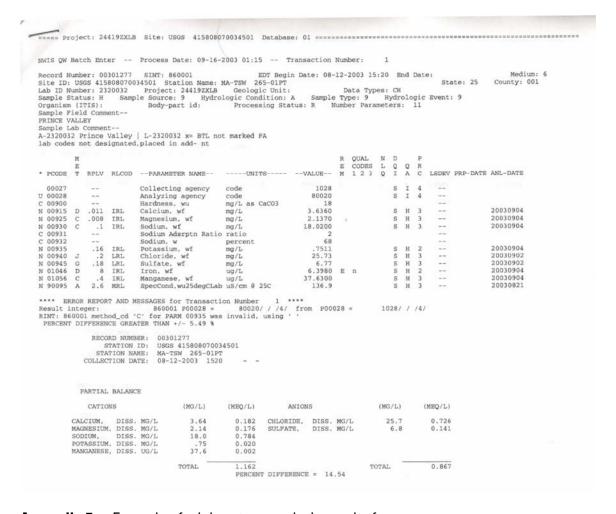
**Appendix 4.** Example of a conventional-well field form.

MULTI	MULTILEVEL SAMPLERS	MPLERS	_										
Sampler					Sampling event					BOTTLES COLLECTED:	LLECTED:		
Date					Crew Weather Conditions	rions							
SpC Meter					VVR Photometer								
pH Meter					Turbidity Mete								1
remp Metnod	Dou				pri probe Filter Type:	☐ Gelman ☐ Millex	Millex						
Port	Time	pH (#1)	pH (#2)	Temp	SpC (#1)	SpC (#2)	Turbidity	Oxy 1 (#1)	Oxy 1 (#2)	Oxy 3 (#1)	Oxy 3 (#2)	BOD	YSI D.O.
PT				(2)			(3.1.)		(28	( A	(2,8,0,0)		
GNT													
RT													
BUT													
BK													
2													
3													
<b>&gt;</b>													
4													
3													
×													
PE													
¥ ≥													
Dup													
Dup													
Port	Pump Rate (sec/100mL)	Fe (0-6 mg/L)	PO4 (0-6 mg/L)	1:1 PO4 dilution	(1:1 PO4 dilution) x 2 =	Alkalinity	pH Standard Temp (oC)	Calibrate pH=7	Calibrate Meter to: pH=7 pH=4	Slope	Buffer Check	Check pH=4	
PT													
GNT													
E E													
100												Ī	
TW TW													
0													
C.													
>													
Ь													
NS													
ĸ													
BU													
BK													
W													
Dup													
Dup													
						NOTES ON BACK	BACK			Field data enter	and by:		
					]				][	Field data checked by:	had hv.		
									]	Field data chees	ken oy.		

**Appendix 5.** Example of a multilevel-sampler field form.

					LAB USE ONLY	SAMPLE
SMS CONTROL NO	NWIS REC	ORD NO	LABORA	TORY ID		SET
		*1_				
STATION NAM	Œ		STA	TION ID OR	UNIQUE NO.	
FIELD OFFICE	*PHONE NO.	*PROJ	ECT CHIEF	FIELD	SAMPLE ID	SITE
						TYPE
* _ _  * _ STATE DIST	RICT/USER	CNTY	*1_	PROJECT	ACCOUNT	_
*BEGIN DA	ATE:  1 9	_ _	1_1_1	1_1_1	1_1_1_1	_1
END DA	TE:  1 9					_
	YEAF		MONTH	DAY	TIME	
	SCHEDULE					-
CHEDULE 1:					SAMPLE TYPE:	
CHEDULE 2:			NIT:		HYDRO EVENT:	
CHEDULE 3:			CE:			
CHEDULE 5:		RO CONDITI				
A/D		A/D		A/D		A/D
DDE:	CODE:		CODE:		CODE:	_
DDE:	CODE:				CODE:	
DDE:	CODE:		CODE:		CODE:	
		TITLE	D VALUES =			
AB/P CODE VALUE RMK				LAB	/P CODE   VALUE	E RMK
21/00095		51/00400			2/39086	
171/00452	111	70/00453				
COMMENTS (Limit to	138 characte	rs):	4-			
OGIN COMMENTS:						
HIPPED BY:		PHON	E NO.:		DATE: _	I
	BOTTLE TYPES					OII.
	U FAM			FCC		CU VOA
	NRCB		PHENO	The second second second second		OTHER
USTOM/SPECIAL SAMPL					AL NO	
ROGRAM/PROJECT:N	PDESNA	WQAI	RINKING WA	TER FIL	L IN OTHER	

**Appendix 6.** Example of an analytical-services request form.



**Appendix 7.** Example of a laboratory-analysis results form.

Prepared by Publications Service Centers 1 and 2

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