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**Long Term Resource Monitoring Program Procedures:**  
**Water Quality Monitoring**



March 2004

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# **Long Term Resource Monitoring Program Procedures: Water Quality Monitoring**

by

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## Preface

The Long Term Resource Monitoring Program (LTRMP) was authorized under the Water Resources Development Act of 1986 (Public Law 99-662) as an element of the U.S. Army Corps of Engineers' Environmental Management Program. The LTRMP is being implemented by the Upper Midwest Environmental Sciences Center, a U.S. Geological Survey science center, in cooperation with the five Upper Mississippi River System (UMRS) States of Illinois, Iowa, Minnesota, Missouri, and Wisconsin. The U.S. Army Corps of Engineers provides guidance and has overall Program responsibility. The mode of operation and respective roles of the agencies are outlined in a 1988 Memorandum of Agreement.

The UMRS encompasses the commercially navigable reaches of the Upper Mississippi River, as well as the Illinois River and navigable portions of the Kaskaskia, Black, St. Croix, and Minnesota Rivers. Congress has declared the UMRS to be both a nationally significant ecosystem and a nationally significant commercial navigation system. The mission of the LTRMP is to provide decision makers with information for maintaining the UMRS as a sustainable large river ecosystem given its multiple-use character. The long-term goals of the Program are to understand the system, determine resource trends and effects, develop management alternatives, manage information, and develop useful products.

This report was prepared under Strategy 2.2.3, *Monitor and Evaluate Water Quality*, of the Operating Plan (U.S. Fish and Wildlife Service 1993). This report was developed with funding provided by the LTRMP.



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## 1. Rationale and Strategy for Monitoring Water Quality

The Long Term Resource Monitoring Program (LTRMP) monitors only selected aspects of water quality in the Upper Mississippi River System (UMRS). Study areas in the UMRS on the Mississippi River main stem are Lake Pepin and Navigation Pool 4 near Lake City, Minnesota; Navigation Pool 8 near Onalaska, Wisconsin; Navigation Pool 9, near Lansing, Iowa; Navigation Pool 13, near Bellevue, Iowa; Navigation Pool 26 near Alton, Illinois; and the Open River reach (sometimes called the Middle Mississippi River) near Cape Girardeau, Missouri. Sampling of the UMRS on the Illinois River is conducted on the La Grange Pool near Havana, Illinois (Figure 1).

Water quality monitoring in the LTRMP emphasizes basic limnological characteristics that pertain to the suitability of habitat for aquatic organisms and the movement of sediment and materials within the system (cf. Hynes 1970). Because of logistic limitations, monitoring in the LTRMP includes only a small subset of important limnological variables; parameters of importance primarily for human consumptive uses are not measured. Standard methods are used in all data collection efforts and because the Program strives to document long-term trends, long-term consistency is maintained to the extent possible.

General techniques and procedures for routine water quality monitoring and analysis are well established and published elsewhere (USEPA 1974; Lind 1979; Wetzel and Likens 1991; APHA 1992; U.S. Geological Survey 1999). The LTRMP uses these published procedures where applicable, and unless specific guidance in this document indicates otherwise, LTRMP

water quality monitoring activities follow the guidelines in *Standard Methods* (APHA 1992). Likewise, the LTRMP follows the manufacturer's published instructions for the operation and maintenance of monitoring instruments and equipment unless indicated otherwise by specific guidance in this document.

The LTRMP trend monitoring network for water quality has a mixed-model sampling design (see Section 1.1 for additional discussion). In this design, a relatively small number of fixed sites are monitored every 14 to 28 days, and a larger number



**Figure 1.** Long Term Resource Monitoring Program field stations. Each field station team conducts water quality monitoring in nearby reaches of the Mississippi or Illinois Rivers and major tributaries.

of randomly selected locations are sampled at seasonal intervals (quarterly).

Before 1993, all water quality monitoring was done at regular intervals at fixed sampling locations. In this pre-1993 design, statistical inferences were possible only for the specific locations selected for sampling. Replication of site types (habitat classes) was inadequate, there was no statistical capability to extrapolate to larger areas or to area types, and points of unique or special significance (i.e., tributary inflows) were not adequately represented. Consequently, the LTRMP scientific staff revised the design in 1992–93. This new design combined fixed-site sampling (FSS) with stratified random sampling (SRS) to allow valid statistical inferences about sampled strata and across entire pools over time while also tracking locations of special interest, such as tributary inflows and unique habitats. Further details of this design, implemented in 1993, are in Sections 1.1.1 and 1.1.2.

### *1.1 General Sampling Approach*

Water quality monitoring is conducted by the staffs of six field stations that collect samples and information from the Mississippi River and Illinois River main stem and adjoining tributaries. Each field station conducts monitoring operations on reaches within an 80 km (50 mile) radius of their base station and field teams are familiar with the sampled areas. The reaches covered by each field station are as follows from north to south: Lake City (field station 1, Lake City, Minnesota), Pools 4 and 5, including Lake Pepin; Onalaska (field station 2, Onalaska, Wisconsin), Pools 7 through 9; Bellevue (field station 3, Bellevue, Iowa), Pools 12 through 14; Great Rivers (field station 4, Brighton, Illinois), Pool 26, Illinois River mouth, Missouri River mouth, and immediately below the Mississippi–Missouri confluence; Havana (field station 6, Havana, Illinois), La Grange Pool of the Illinois River; Open River (field station 5, Jackson Missouri), from the Ohio River to about 100 mi upstream of the confluence.

The timing and location of water quality monitoring is guided by the spatial and temporal patterns of variance in the parameters being

measured and by the information desired. The limited resources of the LTRMP and the large spatial expanse of the study area prohibit routine measurements at high frequencies (i.e., daily or hourly) or close spatial intervals (i.e., <50 m between sampling points). However, measurements must be at intervals of time and space that allow the detection of large-scale habitat changes and biotic responses among adjacent years and over long periods (i.e., 5 to 10 years). Consequently, the routine monitoring is designed to detect patterns at spatial scales on the order of kilometers and temporal scales of months or seasons.

Because the LTRMP is attempting to detect resource differences and similarities among the study reaches, as well as changes over time, the sampling regime in all reaches must be consistent and adhere closely to established protocols. Without this consistency, apparent differences in physical and chemical characteristics can result from differences in methodology rather than actual temporal or geographic variation.

Routine water quality monitoring in the LTRMP is performed in two phases, FSS and SRS.

#### **1.1.1 Fixed-Site Sampling Design**

The FSS is conducted by field teams at approximately constant intervals (e.g., 2 or 4 weeks) at permanently designated locations. If the point of sampling for an FSS location is to be moved significantly, then a new site designator must be registered in the LTRMP database, and this is only done with the approval of the LTRMP water quality coordinator. In selected locations where distinct and persistent cross-channel gradients in water quality have been documented, multiple (3–4) fixed-sampling sites are arrayed as a linear transect across the channel. Compositing has not been used to date to reduce sample load as the additional complications in the field and in data management, combined with the reduction in information seem to outweigh the costs of analyzing these few additional samples for the LTRMP parameters.

The purpose of FSS is to track conditions at specific locations over time (seasonal time

scale and longer). Because the fixed sites were subjectively chosen (often to monitor unique conditions), they cannot be assumed to represent other locations of the same general type.

### 1.1.2 Stratified Random Sampling Design

The SRS is used in the LTRMP for fish, water quality, invertebrate, and vegetation monitoring in the six LTRMP study reaches. This approach is designed to give unbiased estimates that can be extrapolated to entire strata, pools, and reaches and for making comparisons among strata, among pools, and over time. Random selection of sites eliminates many sources of sampling bias and produces results that can be extrapolated with known confidence. The use of defined strata allows the sampling effort to be adjusted to variability or ecological importance of targeted areas. The SRS tracks conditions at spatial scales corresponding to sampling strata or larger (i.e., whole pool or sampling reach) and seasonal-annual time scales or longer. Quarterly SRS episodes are intended to encompass major seasonal events (Table 1), but their scheduling is not changed from year to year. The allocation of sampling locations among the strata is not proportional to stratum surface area, so a weighting method (e.g., area based) must be

used to extrapolate SRS means to an entire study reach.

The sample collection methods used in SRS are identical to FSS. However, there are important design differences: (a) the sampling locations are selected with statistical randomization to represent specific strata (aquatic area types; Wilcox 1993); (b) the suitability of the site and its precise location must be determined in the field at the time of sampling; (c) a specific location is unlikely to be sampled repeatedly over time except in reaches where certain strata are rare; (d) SRS is conducted quarterly; in late January to early February, in late April to early May, in late July to early August, and in early to mid-October; and (e) the full suite of chemical analyses are not performed at SRS sites. An important concept of the SRS design in LTRMP water quality is that the measurement at an individual sampling location is considered a random observation from a population (stratum of sampling points) during a sampling episode (about 10 days). When pooled together, this set of random measurements provides an accurate estimate of conditions within the entire stratum, even though an individual site measurement may not be a good representation of typical (i.e., average) conditions at the specific point of sampling or across the whole stratum during the episode.

**Table 1.** Calendar used for stratified random sampling (SRS) in the Long Term Resource Monitoring Program. The primary sampling period begins on a Monday and extends over the next 14 days exclusive of weekends. A third week may be used if necessitated by urgent circumstances, safety considerations, or equipment failure. The SRS sampling schedule takes second priority if it conflicts with fixed-site sampling.

Sampling period	Start date	Rationale
Spring	Monday of last full work week in April	Period of maximum discharge in the Upper Mississippi River
Summer	Monday of last full work week in July	Late summer conditions, typically low-flow period of maximal water temperature, minimal oxygen
Fall	Monday of second full work week in October	Low-flow period after aquatic vegetation die-back and before ice formation. Period of maximum waterfowl migration. Moved forward a week in 1996 and 1997 to avoid conflict with waterfowl hunters.
Winter	Monday of last full work week in January	Period of maximal ice and snow cover, lowest water temperatures, and minimal oxygen concentration.

### *1.1.2.1 Definition of Sampling Strata*

The primary function of the sampling strata is statistical, and they are based on the aquatic areas of Wilcox (1993) as implemented by Owens and Ruhser (1996). Although the LTRMP sampling strata reflect differing habitat types, they are not habitat classes, and a precise correspondence between strata and habitat is not intended. The statistical validity and utility of the strata does not require a perfect match between mapped strata and habitat or aquatic areas. However, it is essential that the strata be defined and mapped quantitatively. In the LTRMP, this means the sampling strata are defined in a geographic information system (GIS).

The LTRMP sampling strata are areas on a map defined by major, enduring geomorphic and physical features as described by Wilcox (1993) and quantified from 1989 aerial photography using a GIS. Some minor modifications were made using bathymetric and land cover data, as suggested by Wilcox (1993). Additional changes were requested by field personnel on the basis of field observations during the first 2 years of stratified random sampling.

### *1.1.2.2 Changes in Stratum Boundaries*

To facilitate analysis of the LTRMP data, the boundaries of the sampling strata are intended to be relatively static over several years. These boundaries are clearly defined and reproducible within a GIS framework. Field teams can report apparent changes in strata boundaries, but redefining the sampling strata requires more extensive information. Subjective interpretations, or reinterpretations, of strata boundaries (i.e., by field teams) are not consistent or reproducible over time, and inconsistent changes in the strata boundaries would make long-term data interpretation difficult or impossible. Subjective interpretations differ among individuals, and modifications based on transient properties (e.g., river stage or flow velocities) are not appropriate. The collection of ancillary data during sampling, combined with appropriate sample comments, is extremely important to detect and interpret unusual or “nonrepresentative” conditions within

a stratum and can provide the basis for initiating a quantitative remapping of the strata boundaries.

### *1.1.2.3 Atypical Conditions within Strata*

Sampling strata are not expected to be uniform, and each individual site is not expected to be typical of the average physical, chemical, or biological conditions within the stratum. Each stratum is expected to contain a broad mosaic of habitat types, with the distribution of habitats differing among the strata. Unlike habitats, strata do not have a set of physical, chemical, or biotic attributes (i.e., depth, velocity, substrate type, vegetation) that uniquely define them. Habitat conditions and classifications can change on a scale of minutes to hours in response to discharge. In contrast, changes in the mapping of LTRMP sampling strata are done to reflect relatively permanent changes in the river and floodplain geometry.

### *1.1.2.4 Changes in the River Over Time*

Two fundamentally different approaches can be taken to assess spatial changes within a stratified sampling framework. One method is to frequently remap the strata on the basis of field observations and then attempt to track or quantify the mapped changes. This approach is impractical because of the enormous difficulties inherent in remapping at frequent intervals in a defined, quantitative, and consistent manner. Further, the routine field sampling in the LTRMP does not provide the level of spatial information needed to perform this remapping, so a separate, intensive effort would be required to support this approach. An alternative is to have the sampling strata permanently fixed in space, and then quantify changes in conditions within the permanently fixed strata based on the sampling data. This approach is workable and consistent with the LTRMP design, but over time the correspondence between strata and aquatic areas slowly degrades so that conditions within aquatic areas are not well tracked, even though information at the pool and reach scale is maintained. The LTRMP has implemented a compromise approach. Strata are relatively permanent, intended to be

revised only at infrequent intervals (i.e., 5 to 10 years) in response to major changes in system morphometry. Changes in conditions within the strata (and at the pool or reach level), rather than changes in the strata boundaries, are used to indicate short-term changes in the system.

#### *1.1.2.5 Remapping of Sampling Strata*

Remapping of strata requires detailed, objective information in the form of GIS coverages and cannot be based on a few observations. Therefore, only large, extreme errors have been corrected in the strata maps on an ad hoc basis. Smaller errors are few (typically less than 5% of total sites sampled) and are not generally corrected as they are encountered over short periods. However, consistent mapping errors are scheduled to be addressed in a major remap (originally planned for the year 2000). Data from routine SRS sampling is not adequate to remap the strata in the short term, but SRS data should be used to help guide the major remapping effort when eventually performed.

#### *1.1.2.6 Spatial-Temporal Scales and Cross-Component Consistency*

The explicit focus of SRS within the LTRMP is the pool or reach and annual scale, and the sampling strata are statistical tools that allow valid, unbiased estimates at this scale of time and space. Secondly, the strata allow inferences about the strata themselves and, to a lesser degree, about habitats or aquatic areas. Patterns at the subannual scale can sometimes be addressed with the SRS data, and interpretation of SRS data in terms of specific habitats are sometimes possible. However, this must be done with care because the strata are geographic areas on a map, not habitats. To understand the ecological significance of patterns within strata and differences among the strata usually requires the use of ancillary information (e.g., water depth, sampling location, current velocity, number of sites, etc.).

Because the primary target of SRS is the pool (or reach) and annual scale, this is also the intended scale for cross-component synthesis

or integration using the SRS data. For example, the water quality data from SRS is not intended to explain why a certain netting effort produced a certain result (ancillary data collected while netting might serve this purpose), but rather why catches or year classes of some species may be declining in a pool over several years. The strata used for each component need not be identical across components because the design is not intended for cross-component inferences at the stratum scale. Further, to make valid cross-component inferences at the pool and annual scale, the strata must differ among components. If, for example, the water quality sampling was limited to the times and locations (e.g., strata) used for fish sampling, conditions at times and places unsuited to fishing (e.g., ice cover in shallow backwaters), but critical to fish success or failure, would not be sampled. The same holds for vegetation and invertebrates.

Cross-component analysis or synthesis at time scales shorter than years and space scales less than a whole pool are not prohibited by the SRS design, but it requires a customized approach to the data, and some analyses at the stratum or substratum level may not be fully supported. Appropriate ancillary information must be collected if small-scale, short-term processes are of interest and, in the LTRMP design, this finer scale of time and space is considered the realm of focused, specialized studies, rather than routine, long-term monitoring.

### **1.1.3 Other Sampling Approaches**

In addition to routine monitoring, focused water quality investigations within the LTRMP have used continuous monitoring devices (e.g., at 15-min intervals) placed *in situ* to document the time course of significant phenomena (e.g., diurnal or seasonal anoxia in specific areas). However, these studies are not part of routine monitoring, and the protocols used are not listed in this manual. Likewise, Lagrangian methods (i.e., sampling from a mass of water as it moves downstream) are not part of routine water quality monitoring by the LTRMP and are not described here.

## *1.2 Sampling Schedule*

Field team leaders are ultimately responsible for maintaining sampling schedules and have the authority to postpone sampling during unsafe weather periods. However, sampling is never rescheduled simply to take advantage of good weather or to avoid unpleasant conditions as this introduces statistical bias and can invalidate LTRMP results.

To the extent possible, a single sampling schedule is used for water quality monitoring by all the LTRMP field stations. This schedule has undergone modifications with a major redesign of the Program in 1993 (Section 1, introduction) and less dramatic changes in other years (Appendix A). The daily sampling schedule used for water quality monitoring in the LTRMP is described in Section 1.3; the calendar used for SRS sampling is described in Table 1. Note that the SRS calendar takes second priority behind the FSS schedule. In many instances, both SRS and FSS can be conducted simultaneously.

### *1.3 Standardization and Randomization of Sampling Time*

Without randomization of the sampling route and consistency among sampling teams in scheduling of the workday, the short-term effects of time (i.e., daily cycles) are confounded with the effects of stratum or sampling location.

In SRS, the differing strata should be sampled evenly across an entire sampling episode. For example, all the “side channels” cannot be sampled on day 1 and all the “backwaters” on day 2, nor can the main channel sites be sampled primarily in the morning and backwaters in the afternoon. Because of logistical constraints, one longitudinal section of the river may be sampled on one day and another the next, but to the extent possible, sampling of strata within the workday and across the entire sampling episode must be randomized. Sometimes, this is accomplished by randomly selecting a map panel (e.g., 5 to 10 km<sup>2</sup> of study area) for each day or half-day of work and then sampling all sites on the panel, but in

other situations a more sophisticated approach is used.

Randomization of sampling times or site order must be closely observed. Sampling order for SRS is randomized by panels, workdays, or other suitable methods in advance of sampling. This randomized order must be adhered to and is not modified to adjust for field conditions. In FSS, the sampling route is varied randomly within logistic constraints so that (1) sites are not sampled in the same sequence during each sampling day and (2) differences among study reaches are not confounded by differences in work schedule. At a minimum, the sampling route is reversed at random (i.e., by coin toss before leaving the field station). This keeps cyclic, diel variation from contaminating the long-term results of SRS and FSS.

Sampling times for FSS and SRS are standardized among all field stations and remain unchanged over the course of the year. Beginning in April 1994, a standard workday for sampling was established for SRS and FSS water quality monitoring. This workday is based on central standard time and is unaffected by changes in the clock because of daylight savings. The schedule for each workday is centered on noon, such that the mean of sampling times during a day is as close as practical to 1200 hours, and sampling should not be conducted before 0800 hours or after 1600 hours. The need for this standardization is clearly evident in the LTRMP water quality data collected before 1994 (FSS only). In these data, the effect of daylight savings time on the work schedule confounds the effects of diel variations with the effects of season. Likewise, before 1994, consistent differences in the work schedule among field stations confounds diel variation with geographic location.

### *1.4 Geographic Coordinates*

Geographical positions in the LTRMP are identified using Universal Transverse Mercator (UTM) grid coordinates. This rectangular coordinate system identifies a location by its

distance (in meters) east (easting) and north (northing) of reference lines on a transverse mercator chart. The reference lines for the easting and northing distances are defined by the UTM zone.

In LTRMP water quality monitoring, the geographic coordinates of all sampling locations are defined by reference to a base map. The geographic location (UTM coordinates) of each LTRMP water quality sampling location is registered in the LTRMP central database. These coordinates may be corrected or verified by additional field measurements, but the physical location of a sampling site does not change over time. Whenever a new location is sampled, this is registered as a new, unique site in the LTRMP database. A site cannot be moved. Changing a sampling location is accomplished by establishing a new site and discontinuing monitoring activity at the previous location. Various techniques are used to locate sampling locations in the field, including global positioning system (GPS) equipment and visual landmarks. The UTM coordinates of FSS locations are determined when the site is first established and the coordinates for SRS sampling are published in advance. Consequently, UTM coordinates are not recorded on the data sheet (Section 8.3) except during special project monitoring and then only at sites that have not been registered in the LTRMP database.

### *1.5 Fixed-site Sampling Locations*

The LTRMP sampling of fixed sites is intended to provide a relatively continuous record of limnological conditions and constituent concentrations at (1) major inflow and outflow points of the LTRMP study reaches and (2) locations of special long-term interest. The locations selected for FSS are used only to represent the sampling point and, for tributaries, the contributions from the watershed upstream of the sampling site. See Appendix B for a list of location codes and descriptions of fixed-site water quality sampling locations.

### **1.5.1 Main Stem Location Codes**

Main stem location codes are used to designate routine FSS sites in the Mississippi and Illinois Rivers and associated backwaters. This system was established in 1988 at the start of the Program and was not changed in the redesign of 1993. The codes are based on the distance upstream (river miles) from the river mouth or major confluence and on the relative left to right (facing upstream) location of the site between the river bluffs. Main river site codes for FSS have the form:

Axxx.xB

where

- A is a one-letter designator for the river (I = Illinois River; M = Mississippi River),
- xxx.x is the distance in stream miles (with tenths) upstream from the confluence with the main river (padded with leading zeros as needed to result in four digits), and
- B is a suffix (A–Z) that indicates the relative distance from the left ascending bluff (i.e., on the left looking upstream; A is the left bluff, Z is the right bluff, M is midway between bluffs). For example, site M245.1M is a site on the Mississippi River, at River Mile 245.1 (245.1 mi upstream from the Ohio River confluence), midway between the left and right bluffs. This suffix assignment is done by reference to an appropriate topographic map or navigation chart, but is only a rough indicator of site location that is defined more precisely by geographic coordinates.

See Appendix B for a list of main stem location codes.

### **1.5.2 Tributary Location Codes**

Tributary location codes are used to designate routine FSS sites only when the sampling is done in the tributary itself, upstream from its confluence with the main river. Otherwise, the main river nomenclature applies. Tributary

location codes for FSS are similar to main stem locations and have the form:

AAxx.xM

where

- AA represents a one- or two-letter abbreviation of the tributary name,
- xx.x is the distance in stream miles (with tenths) upstream from the confluence with the main river, and
- M is a suffix (A–Z) that indicates the distance from the left bank of the tributary looking upstream at main river sites (i.e., A is the left bank, Z is the right bank). The letter M is used to designate midtributary sampling. For example, AP01.1M indicates a midchannel site on the Apple River, 1.1 mi upstream from its mouth. As with main stem sites, the site coordinates define the location more precisely.

The distance in stream miles is padded with leading zeros as needed to bring the entire location code to a length of seven characters (including the decimal point). See Appendix B for a list of tributary location codes.

### 1.6 Stratified Random Sampling Locations

The SRS for water quality is based on six aquatic area strata (Wilcox 1993; Table 2). From 1993 through January 1995, the sampling strata were divided into rectangular north–south, east–west grids with 200 m between grid lines in all strata. Beginning with spring 1995 SRS, this was changed to 50 m between grid lines in the contiguous backwater and side channel strata. All other strata remained at 200-m grid spacing. The higher density grid is appropriate here because the data have shown greater spatial variability within these strata. The sampling grid is used for selecting sites, but the geographic coordinates (UTM) of each site are used to locate the site in the field and the site identifier (described later) makes no reference to this grid.

The number of sampling strata, total number of sampling sites, and the allocation of sampling sites among the sampling strata was based on several factors: (1) analysis of 1988-92 sampling that showed the number of sites that could be sampled in about 2 weeks (10 workdays) and the relative levels of variance to be expected in the differing strata, (2) consultation with the field

**Table 2.** Relation of Long Term Resource Monitoring Program aquatic area codes and sampling stratum used in stratified random sampling for water quality monitoring. Aquatic areas are based on Wilcox (1993).

Aquatic area codes	Stratum	
	Code	Description
1501	1	Main channel (MC)
1504	2	Side channel (SC)
1510	3	Backwater area contiguous to the main channel at low water conditions (BWC)
1513	4	Lake Pepin or Swan Lake (Lake)
1520	5	Open water area above the dam influenced directly by impoundment (IMP)
1530	6	Isolated, no surface connection to the main channel (BWI)
N/A	7	Aquatic areas that have been dewatered for extended periods so that terrestrial vegetation has become established. This includes areas that have become terrestrial at normal water elevations.

teams to verify the results of the data analysis, (3) a desire to detect differences in single variable and multivariable means at about the 10% level among strata or sampling episodes with good statistical reliability ( $P < 0.10$ ), and (4) extensive monitoring experience and professional best judgment. The allocation of sampling locations among the strata is not proportional to strata surface areas or volumes, so weighting is required to extrapolate stratum means to broader areas (e.g., an entire study reach).

For each study reach (field station) and SRS sampling episode, three sets of sampling locations are drawn at random and without replacement from the list of available sites within the study reach. The sites selected within each of these three groups are then numbered consecutively within strata in north to south (top to bottom) columns that progress from west to east. The numbering sequence by strata is BWC (backwaters, contiguous), BWI (backwaters, isolated), IMP (impounded areas), Lake (Pepin or Swan Lake), MC (main channel), and SC (side channels). The first group of selected sites are the primary sampling locations that are monitored for a full suite of parameters. The second group is drawn randomly and without replacement from locations that were not selected in the first drawing. This second group of sampling locations is monitored for a reduced or partial suite of parameters, including all *in situ* measurements, plus chlorophyll-*a* and suspended solids (see parameter list in Appendix A). Site numbering of this second series continues the numbering sequence of the first series and a “P” suffix (partial) is added to the site number. Finally, a third group of sites is randomly selected from those not chosen in the first two drawings. This third group is used as alternate sampling locations that substitute for sites in the first two series that are unusable (see Section 1.8 for more details on alternate site use). Site numbering of this third series continues the numbering sequence of the second series and an “A” suffix (alternate) is added to the site number. Site numbers are, therefore, a single continuous series, and the actual stratum associated with a sampling site and the UTM coordinates of the

site are recorded as separate fields in the LTRMP database.

In the initial summer and fall SRS sampling episodes conducted from July through September 1993, the site numbering system differed from all subsequent episodes. In just these first two episodes, site numbering within each of the three site categories (primary, partial, and alternate) was consecutive, starting at site number 1. The sequence numbers in each category were converted to a unique value by adding an offset of 100 to “P” (partial parameter) sites and an offset of 200 to “A” (alternate) sites. This approach was extremely vulnerable to errors and was confusing for field teams. It was replaced by the system described above in all subsequent SRS sampling episodes.

Within a sampling episode and study reach (field station), each SRS site identifier is unique, but the same site identifiers are reused in other episodes and in other study reaches. Additional identification is thus required to uniquely identify an SRS location in the LTRMP database; this is provided by the data sheet serial number (sheet bar code) and a permanent location code.

Site identifiers used in the field (and on data sheets) for stratified random sampling have the form:

$$NNNx$$

where

NNN is the sequential site number within the episode and

x is a suffix that indicates site category as follows: no suffix = full parameter, primary sampling site; suffix A = alternate site (may be used for full or partial parameter); suffix P = partial parameter site.

In addition to the temporary field identifier, each SRS location is assigned a unique seven-digit location code of the form:

$$YYFENNN$$

where

YY is the calendar year (e.g., 01 for 2001, this system must be revised before 2093),

F is the field station identifier (1 = Lake City, 2 = Onalaska, etc.),

E is the seasonal episode (1 = spring, 2 = summer, 3 = fall, 4 = winter), and

NNN is the field identifier with any suffix omitted.

Stratum type and UTM coordinates (in meters) for each site are permanently registered in the LTRMP database. The strata codes (Table 2) are used in the registered site descriptions and were chosen to be consistent with the aquatic areas/land use spatial data coverages maintained in the ARC/INFO software environment at the Upper Midwest Environmental Sciences Center (UMESC).

### *1.7 Locating Stratified Random Sampling Locations in the Field*

In SRS, sites are located by reference to a base map. The SRS sites are not defined as points, but circular areas with either a 25 or 100 m radius. The smaller radius circle is used in side channels and backwaters, the larger radius applies to all other sampling strata. The SRS samples are taken to represent the general habitat stratum, not the exact sampling point. Although it is critical that the sampling site be suitable and randomly selected, it is not necessarily at the exact preselected coordinates (center of the sampling circle), although field teams make a concerted effort to sample from the center point of the predefined sampling circle if possible and appropriate.

If the center of the sampling circle (see previous paragraph) is unsuitable (e.g., dry land or other obstruction), the field team can use the appropriate procedure (described later) to select another point within the sampling circle. Although close positional accuracy (e.g., less than half the radius of the sampling circle) is not required, field teams exercise care and professional judgment to ensure that the actual point of measurement is randomly chosen and that personal bias (e.g., preference for shady areas, absence of aquatic vegetation, calm, or deeper water) does not influence the selection process. If a suitable sampling point cannot be found or accessed within this sampling circle, then an alternate site is used (Section 1.8.2).

When the central position of a predefined sampling location is unsuitable or inaccessible, but suitable sampling can be performed within

the site radius (25 or 100 m), the field team uses the following procedure to select another location:

- a. Use the suitable location that is nearest to the center of the sampling circle.
- b. If several nearby sites are suitable and approximately equidistant from the center, the more upstream of the available choices is used.
- c. If proximity and upstream-downstream priority cannot be clearly established, then the nearest site to the right (looking upstream) of the center is selected.

A simple mnemonic (memory helping) phrase may be helpful; e.g., “**C**lose **U**p is **R**ight where you want to be.”

Prior to the fall 1998 SRS episode, whenever possible, the field crews were required to sample within one-half of the sampling radius (i.e., one-half of 25 m in BWC and SC = 12.5 m, and one-half of 100 m in other strata = 50 m). When those criteria could be met, a site type of 0 (Primary) and a Position Method of 1 (Base map) were assigned. In the event that close positioning could not be obtained, but a suitable sampling location existed within the sampling radius (see previous discussion in this section), then a Site Type 3 (other) was assigned, GPS coordinates were recorded, and the Positioning Method was recorded as 2 (GPS). Beginning in fall 1998, positioning requirements were changed to those discussed previously. For all practical purposes, positioning requirements were not affected, as the crews still must sample within the sampling radius and as close to the center of the circle as possible; however this did result in a change to the recording methods.

### *1.8 Use of Alternate Sites in Stratified Random Sampling*

#### **1.8.1 Requirement to Sample an Alternate Site**

If water depth ( $Z_{\max}$ ; Section 3.1) of a sampling location is  $<0.2$  m (but the site is inundated at normal water levels) or the site cannot be sampled because of intervening dry land or other impassible conditions, then the use of an alternate site is strongly encouraged

due to the difficulty associated with obtaining a clean sample. However, alternate site sampling must be performed within the limits of the daily sampling window and if extensive areas are dewatered or inaccessible, then field teams must consider the upper limit on use of alternate sites (Section 1.8.3). Field teams should not exclude a site (and use an alternate) because the site does not appear representative of the designated stratum. If a site can be sampled, then sampling should be performed. Special characteristics of the site should be recorded as site comments and flagged by the use of appropriate site summary codes and field-derived stratum codes.

### 1.8.2 Picking an Alternate Site

If a suitable sampling location does not exist within the 25- or 100-m sampling radius appropriate to the stratum, then a site from the alternate site list is used. This site is chosen by examining the available alternate sites and picking the one that is closest to the rejected site and within the same sampling stratum. If two or more sites are approximately equidistant from the rejected site, the procedure to select one of these is the same as that used to select a sampling point within the sampling circle (“**Close Up is Right** where you want to be,” Section 1.7).

If the alternate site is distant, it should be sampled when it is efficient to do so (e.g., other sites are in the same vicinity). All sampling scheduled for the original site (i.e., collection of samples for chemical analysis) is performed at the alternate site. If the original site was designated for quality assurance and quality control (QA/QC) sampling, then the alternate site should be used in this capacity if it is sampled by the same field team and on the same day. Otherwise, another QA/QC site must be randomly selected from those that remain on the day’s sampling plan. A datasheet header for the original site must be filled out, bar coded, and appropriate site comments recorded (e.g., “site replaced by alternate site number 151a”).

Sampling order for SRS is randomized by panels, workdays, or other suitable method in advance of sampling. This randomized order

must be closely adhered to and is not modified to adjust for river conditions.

### 1.8.3 Limits on the Replacement of Primary Sites with Alternates

Alternate sampling sites for SRS have been used infrequently in Pools 4, 8, and 13; mostly in winter when ice extends to the substrate. In the lower reaches of the system (Pool 26, La Grange Pool of the Illinois River, and Open River), water level fluctuations are more extreme, and the use of alternate sites is more common. In these study reaches, the entire backwater or side channel stratum may be dewatered or rendered inaccessible and this requires creative approaches to the use of alternate sites.

*Case 1. A small portion of the stratum cannot be sampled.* The free substitution of an alternate location within the sampling circle (Section 1.7) is often adequate for these situations. The nearest site on the alternate list can also be used.

*Case 2. A large portion of the stratum cannot be sampled.* The sampling effort should be redistributed across the portion of the stratum that remains usable. This situation requires prior knowledge of the sampling conditions and the extent of suitable sites; advanced scouting of the stratum is probably needed. Conditions must remain stable for a few days if this strategy is to be successful. The inaccessible areas are determined in advance, the sampling sites affected are counted, and replacement sites are then chosen at random from the alternate list. Site selection can be accomplished by randomizing the list of alternates for the stratum, and then picking the sites in order until a full set of replacements has been chosen. Randomization of the alternate list is required in this situation because the site list is generated in a geographic (north-south, west-east) sequence. Alternate sites in the inaccessible areas are excluded from this reselection. If the list of alternate sites is exhausted before all the inaccessible sites are replaced, additional sites can be generated in consultation with the component coordinator. The need for advanced notice is clear, but may not be possible in many instances. This approach is not appropriate when the usable portion of

the stratum is already heavily sampled (i.e., sampling exceeds about 3% of the total available sites within side channels or backwaters or about 15% of the total sites in the main channel). The sampling grid is 16 times more dense in off-channel areas than in the main channel, so a larger percentage of the total sites in the main channel can be sampled without reaching the same number of samples or percentage of area as in the off-channel strata. Using a rough estimate of the area rendered inaccessible and the information in Table 3, the increase in sampling intensity that will result from reallocation of sites to the remaining area can be estimated.

To illustrate Case 2, an example from La Grange Pool can be used. Suppose that only 48 of the 80 selected backwater sites (60%) in the study area remain usable or accessible (32 have become inaccessible). Because the sites are randomly selected, this implies that only about 60% of the total stratum is still available. Table 3 indicates that there are 4,197 sites in the full stratum, so about 2,518 (60% of 4,197) should be usable. Because the upper limit on backwater sampling is 3% of the available sites, the maximum number of sites required is now about 76 (3% of 2,518). Because 48 original sites remain available, 28 alternate sites ( $48 + 28 = 76$ ) now need to be selected.

*Case 3. No sites are usable within the stratum or the usable, primary sites exceed the suggested sampling percentage for the area that remains.* In this instance, no alternate sites are used. However, data sheets are completed for the missed sites to the extent appropriate and the comment section on each data sheet indicates that the site was inaccessible. Additional details are provided in the comments as appropriate.

### 1.9 Site Location Maps

For SRS, each field station is provided with electronic files (ASCII text format) that list the site identifiers, geographic coordinates, and stratum codes for primary, partial, and alternate sites. In these files, partial parameter sites (*in situ*, plus fluorometric chlorophyll-*a* and suspended solids; Appendix A) are listed with a

“P” suffix; alternate sites are listed with an “A” suffix. For each field station, there are 120 to 150 sites. Of these, 35 to 80 are full-parameter sites, and the remainder are partial parameter sites (Appendix A). Approximately 150 alternate sites are also provided. The field teams use suitable GIS software (e.g., ArcView™) to plot these sampling locations on a map of the sampling area.

## 2. Quality Assurance and Quality Control (QA/QC)

The LTRMP QA/QC procedures are designed to quantify the reliability of the water quality data and allow identification of specific sources of error or variance. Various recommendations or requirements for QA/QC have been published, especially with regard to sample frequency, and these should be consulted for additional background and specific details (USEPA 1974; APHA 1992, 1998). The approach to QA/QC used in LTRMP water quality monitoring corresponds generally to the recommendations of *Standard Methods* (APHA 1998) with minor modifications.

### 2.1 QA/QC Samples for Chemical Constituents

*Standard Methods* (APHA 1992, 1998) recommends that a minimum of 5% of each type of chemical measurement should be accompanied by QA/QC measurements. In LTRMP water quality monitoring, each field team attempts to perform QA/QC measurements at about 5% (1 in 20) of all sites sampled during each sampling day. To gauge team performance in the LTRMP water quality component, each separate sampling team or laboratory team performs at least one full QA/QC series during each day of operation or field sampling. Because a field team rarely samples more than 20 sites in a single day, the daily team requirement exceeds the 5% recommendation in almost every instance and results in QA/QC measures being performed at about 15% of all sites. In the event that a field team visits more than 29 sites in a single day, a second QA/QC sample is required to comply

**Table 3.** Water quality sampling strata and sampling allocations in the six Long Term Resource Monitoring Program (LTRMP) study areas.

Study areas	Sampling stratum	Fraction of study area within the stratum (%)	Number of potential sampling sites in the stratum <sup>a</sup>	Number of sites assigned	Fraction of sites sampled (%)	Fraction of total effort (%)
Lake City (Pool 4)	Main channel	8	310	25	8.1	19
	Side channel	5	2,887	30	1.0	22
	Backwater	16	9,203	50	0.5	37
	Lake Pepin	66	2,441	30	1.2	22
	Impounded	0	–	–	0.0	0
	Isolated	4	165	–	0.0	0
	Total <sup>b</sup>	99	15,006	135	0.9	100
Onalaska (Pool 8)	Main channel	14	314	25	8.0	17
	Side channel	16	5,522	30	0.5	20
	Backwater	20	7,067	60	0.8	40
	Impounded	40	869	25	2.9	17
	Isolated	1	31	10	32.3	7
	Total <sup>b</sup>	92	13,803	150	1.1	100
Bellevue (Pool 13)	Main channel	24	675	30	4.4	20
	Side channel	7	3,219	30	0.9	20
	Backwater	25	11,242	60	0.5	40
	Impounded	32	890	30	3.4	20
	Isolated	1	29	0	0.0	0
	Total <sup>b</sup>	89	16,055	150	9.3	100
Brighton (Pool 26)	Main channel	52	1,215	20	1.6	17
	Side channel	16	5,983	42	0.7	35
	Backwater	4	1,658	29	1.7	24
	Swan Lake	0	237	15	6.3	12
	Impounded	2	44	15	34.1	12
	Isolated	6	145	0	0.0	0
	Total <sup>b</sup>	81	9,282	121	1.3	100

**Table 3.** Continued.

Study areas	Sampling stratum	Fraction of study area within the stratum (%)	Number of potential sampling sites in the stratum <sup>a</sup>	Number of sites assigned	Fraction of sites sampled (%)	Fraction of total effort (%)
Jackson (Open River)	Main channel	90	1,298	75	2.7	50
	Side channel	7	1,689	75	3.8	50
	Total <sup>b</sup>	98	2,987	150	3.3	100
Havana (La Grange Pool)	Main channel	22	623	35	5.6	26
	Side channel	1	558	20	3.6	15
	Backwater	9	4,197	80	1.9	59
	Impounded	0	0	0	0.0	0
	Isolated	0	0	0	0.0	0
	Total <sup>b</sup>	32	5,378	135	2.5	100

<sup>a</sup>Total potential sites reflect a 200-m grid in most strata but a 50-m grid in side channels and backwaters.

with the 5% requirement (i.e., 5% of 30–49 sites rounds to 2). There is no carryover of QA/QC from day to day. For example, if a field team performs two QA/QC samplings in one day, this does not eliminate the requirement for a QA/QC site on the following day. Likewise, the number of sites sampled on one day does not influence the number of QA/QC sites required for the same field team on the following day (at least one QA/QC site is required).

### 2.1.1 QA/QC Sampling Types

In LTRMP water quality monitoring, six types of QA/QC samples are defined for field use (Table 4). These sample types are intended to evaluate the effects of natural variability and sample collection and processing on field measurement precision (repeatability) and accuracy. These checks are separate, but similar to, QA/QC measures performed daily in the LTRMP water quality laboratory to evaluate analytical performance. As of the date of publication, LTRMP water quality monitoring did not use field additions of known constituents (spikes) to evaluate accuracy.

### 2.1.2 Selection of Sampling Sites for QA/QC Measurements

Because SRS and FSS are considered separate efforts with differing site types and collection requirements, the 5% QA/QC requirements for these two portions of the sampling design are met separately. However, the daily QA/QC check on each deployed sampling team can be performed in association with either SRS or FSS sampling.

For SRS, the team or crew leader uses past experience and best professional judgment to estimate how many days it will take to complete the SRS episode. The team or crew leader then calculates how many sites will have QA/QC measurements added to obtain QA/QC sampling at 5% of the total sites in the episode. Rarely, sites in excess of the one/crew/day requirement must have QA/QC measures added to meet the overall 5% requirement; this can only occur when an SRS event is completed rapidly (less than 4–7 days, dependent on the number of sites allocated to the study reach). If additional sites must have QA/QC performed, then they should be randomly selected from the entire

**Table 4.** Description of six quality assurance and quality control (QA/QC) sample types used in Long Term Resource Monitoring Program water quality monitoring.

Sample type	Description
Routine	A sample or measurement collected in the usual way at the sampling site. This is not a separate QA/QC sample, but is included here because a routine sample is required along with the following sample types to complete the QA/QC evaluation at a site.
Split	A sample that is as identical as possible to the routine sample. This sample is used to evaluate laboratory precision and the variability introduced by field handling or processing. To obtain a suitable split, the routine and split samples are both taken from a single, fully mixed container of processed (e.g., filtered) water.
Split plus spike	A split sample to which a precisely defined quantity of analyte has been added. This sample is used to determine laboratory accuracy, practical detection limits, and to detect problems in analytical technique, field handling, or preservation of samples. The routine sample, split, and split plus spike are all taken from a single, mixed container of processed (e.g., filtered) water.
Blank	A sample processed in the same manner as a routine sample, but with reagent grade water (Section 7.11) used instead of ambient water as the initial sample. The blank is used to check for contamination in the analytical water supply or sample containers, or contamination and losses during handling and storage. It is also used to evaluate accuracy and precision near the detection limits of the laboratory. Water used for blanks must be reagent grade or better (Section 7.11).
Blank plus spike	A blank sample to which a precisely defined quantity of analyte has been added. A blank plus spike sample tests for laboratory accuracy in the absence of any interfering materials or organisms. It gives a second verification of the spike quantity and the background “blank” value of laboratory grade water. It also provides verification of the effects of sample handling and storage.
Replicate	A second, separately collected sample taken in the same manner as the routine sample but separated by a short interval (2–5 min). This sample provides information on the natural random background variability in the system.

group of SRS sites before the episode begins. However, to greatly increase efficiency, QA/QC sites should also correspond to a chlorophyll-calibration/phytoplankton-collection site. The spectrophotometric chlorophyll (CHLS) samples are collected for fluorometric chlorophyll (CHLF) calibration at approximately 10% of the CHLF sampling sites (phytoplankton samples are also collected at these locations). Because more CHLS sites than QA/QC sites are required (10% vs. 5%), a subset of the CHLS sites should be used for QA/QC. Specific guidelines for selecting these two types of sites together are provided in Section 7.7.

In FSS, as in SRS, each field team randomly selects a daily QA/QC site from the day’s schedule of sites. This single site will exceed the 5% requirement unless more than 29 fixed sites are sampled in a single day (this has never occurred in LTRMP and is almost impossible under the present design).

When one field team participates in both FSS and SRS on a single day, the procedure for QA/QC site selection is modified slightly. The daily team QA/QC check may be done with the QA/QC site selected for FSS (because the FSS site will include all routine sampling parameters). However, QA/QC measurements are still required at those SRS sites (if any) that were originally designated as additional QA/QC sites in excess of the daily crew requirement needed to meet the 5% requirement for the SRS episode. If multiple teams are in the field, it does not matter which team performs QA/QC checks at these additional SRS sites, as long as each field team performs its daily QA/QC check.

The advantage of performing both SRS and FSS sampling on the same day with a single team is that an additional field team (with its own daily QA/QC requirement) need not be deployed to sample a small number of fixed sites (e.g., less than five). The one site used for the daily team

QA/QC check cannot satisfy the 5% overall requirement for both the SRS and FSS, but normal operations (less than 29 sites per day per team) will still exceed the 5% requirement, and this approach can thus save significant time and reduce analytical sample load.

### 2.1.3 Incomplete QA/QC

When a QA/QC site is inaccessible in SRS, routine procedures are used for site replacement (Section 1.8). When a site scheduled for QA/QC under FSS cannot be sampled, QA/QC is performed at a site picked at random from those remaining on the daily schedule. In the event that no additional sites are scheduled for that day or continued sampling is not possible, then one acceptable approach is to designate the final sampling site of the day as the QA/QC site. However, samples for this alternate site may be available only if water is being returned to the field station for processing, and no immediate action in the field is required in this instance. When QA/QC sites are missed because of inaccessibility or transportation problems, the team leader should ensure that the overall 5% QA/QC requirement is still met for the sampling episode (SRS) or the week (FSS).

If the QA/QC site may be reached and is suitable for sampling, but other equipment failure prevents completion of the full suite of QA/QC measurements, then a partial completion of the QA/QC is acceptable, but must be explained in the site comments. In the event of equipment failure or other event that halts sampling for the day, the field team leader must, to the extent possible, ensure that all requirements for sample holding and storage are met and that deviations are documented in the site and sample comments.

### 2.1.4 Collection and Processing of QA/QC Samples and Measurements

On each field sampling day, each field team collects QA/QC samples and measurements at each site designated for QA/QC (Section 2.1.2). The following measures and parameter groups are included in field QA/QC measurements: water temperature, dissolved

oxygen, pH, specific conductivity, turbidity, dissolved inorganic nitrogen (DIN), dissolved metal ions (MET bottle), soluble reactive phosphorus and chloride (SRP bottle), suspended solids, spectrophotometric chlorophyll-*a* (CHLS planchet), fluorometric chlorophyll-*a* (CHLF tube), and total nitrogen and phosphorus (TNP bottle). Because they are inherently imprecise or difficult to control or replicate, the following measurements are excluded from QA/QC: current velocity, current direction, maximum water depth, phytoplankton, Secchi disk transparency, substrate, vegetation, wave height, and all measurements of snow and ice cover. All QA/QC samples are collected and processed in a manner compatible with the descriptions in Table 4. Except for travel, a QA/QC site requires the sample collection and processing time of approximately five routine sites.

Samples for QA/QC (Table 4) are collected and handled exactly as routine samples (Section 7) with the following modifications and special considerations:

- a. *Split sample.* A split sample must resemble the original, routine sample as closely as possible and is part of the routine sample until it is finally poured into its own sample bottle for shipment or addition of spike. All filtration and preservation (e.g., addition of acid) is performed before the split is separated from the routine sample. Because the original sample volume required to prepare the routine, split, and spiked samples may sometimes exceed the volume of a single grab, the necessary volume can be obtained by combining (compositing) multiple grab samples into a single container before proceeding with sample processing (e.g., filtering and preservation). For samples that are filtered, filtration is done into a single, common pool of filtrate, also derived from the single, original sample. The routine and split containers are filled from this single pool of filtrate only after the total volume of filtrate required to fill all necessary containers has been generated. When parameters with differing preservation requirements are taken from the common

pool of filtrate, the parameters requiring addition of a common preservative (e.g., nitric acid) are separated into a subpool and preserved before further splitting into individual sample containers. The original sample must be kept well agitated during subsampling and filtration.

Routine and split samples for sensor readings (temperature, dissolved oxygen, pH, and conductivity) are obtained from two sequential measurements from the sonde, separated by the usual 3–5-sec interval between readings after the instrument has stabilized. These readings are taken *in situ* and are not “split samples” in the strictest sense, as differences in the readings may reflect either ambient changes or instrument fluctuations. However, they do give an indication of the fundamental variability in the readings.

- b. *Spiked sample.* Spiked samples are obtained by adding a precise defined volume of known composition (spike) to split samples (either routine or blank splits). The addition of spike is done at the same time as the original and split samples are processed (e.g., placed into their final shipping container). Spikes (1.00 mL) are provided to the field teams by the analytical laboratory in labeled, 50-mL volumetric flasks (polycarbonate, same as sample bottle). The analytical laboratory provides spikes for four chemical sample types (DIN, MET, SRP, and TNP). Spikes for suspended solids, chlorophyll-*a*, and phytoplankton are not used. The field team generates the spiked sample by adding completely processed sample water (filtered and preserved as appropriate) to the volumetric flask, making up a total volume of exactly 50.0 mL (bottom of meniscus). The sealed volumetric flask is then labeled, logged, and shipped to the analytical laboratory in the same manner as all other samples (Section 7). Sample depth and sonde readings are not recorded for spiked samples.

- c. *Blank sample.* The blank sample for QA/QC is processed exactly as any other sample (including filtration, acidification, and splitting), except that analytical grade water (Section 7.11) is used as the sample source. Sample depth and sonde measurements are not recorded for sample blanks, but a turbidity measurement is required. Note that the analytical water taken into the field for preparation of blanks must be kept tightly sealed when not in use and care must be taken to ensure that contaminants are not introduced into the container while it is opened. The analytical water should be discarded at the first sign of contamination, or if contamination is suspected, or at the end of the sampling day.
- d. *Replicate sample.* Replicate samples are obtained from a completely independent grab and a separate set of sonde measurements, usually taken 2–5 min after the routine grab sample. Readings for temperature, dissolved oxygen, pH, and conductivity should be taken as closely as possible to the same time as the replicate grab sample.

## 2.2 Equipment Calibration

The performance of all measuring equipment must be verified at regular intervals to ensure accurate (i.e., unbiased and precise) results. In LTRMP water quality monitoring, most monitoring instruments are calibrated at the start and end of each sampling day and whenever unusual or questionable behavior is noted. For some sensors (e.g., temperature), less frequent calibration is required unless operation appears abnormal. The results of calibrations are recorded and control charts are maintained on all instruments. The serial number of the multiparameter instrument used to collect field readings is recorded on the data sheet. To document the performance of individual instruments or sensors during the sampling day, quality factor (QF) codes are assigned to each instrument reading (Sections 2.3 and 8.4).

Guidelines for assigning these codes are in Appendix C.

### 2.3 Quality Factor Codes

Field or laboratory conditions and equipment performance can strongly influence sample quality and the accuracy and precision of field measurements. Likewise, the storage and processing of samples may, on occasion, depart from standard procedures because of unusual circumstances. These situations must be carefully documented to properly analyze, interpret, and evaluate the water quality data that result. To this end, almost all water quality measurements in LTRMP have an associated QF code to indicate abnormalities or deviation from standard procedure (Section 8.4).

## 3. Sampling Site Characteristics and Conditions

The features of the sampling site and conditions at the time of sampling are important for interpreting the collected measurements. In stratified random sampling, the physical configuration and prevailing conditions at the randomly sampled sites can also be aggregated across sites within the stratum to characterize the sampling stratum or the entire sampling area. Sampling site characteristics that are measured in LTRMP water quality monitoring include water depth, water velocity (speed and direction), levels of wave action (sea state), ice and snow characteristics, substrate composition, and aquatic vegetation (type, density, and coverage). Quantitative measures of air temperature, sky cover, or wind speed are not collected, but site comments are used to note general ambient conditions and record unusual circumstances.

### 3.1 Water Depth

Vertical position, the third spatial dimension of an aquatic system after length (y) and width (x), is denoted by the symbol “Z” in limnological usage and is measured downward from the water

surface ( $Z_0$ ). The vertical extent of the water or maximum water depth ( $Z_{\max}$ ) is an important feature that affects a host of environmental factors, including water velocity, vertical mixing, temperature, ice cover, and the distribution and abundance of river biota. In the UMRS,  $Z_{\max}$  is influenced by deposition of sediment, scouring, and water level fluctuations. Sediment movement during high flow can produce major changes in substrate elevation and resultant  $Z_{\max}$ . Construction or alteration of channel training structures and dredging can also change water depth. In the UMRS, the greatest values for  $Z_{\max}$  (up to 20 m) are usually found in the main river channel.

Precise determination of water depth in backwaters and sloughs is often complicated by soft, flocculent bottom sediments that are easily disturbed and are not distinct from the overlying water.

#### 3.1.1 Definition

Water depth ( $Z_{\max}$ ) is the vertical distance between the substrate and the free-water surface. This differs from bathymetry (as defined in the LTRMP) that measures the absolute elevation of the substrate above some vertical reference (usually mean sea level). The first published version of the LTRMP Procedures Manual (Lubinski and Rasmussen 1988) defined a measurement called water depth (WDP) that is the vertical thickness of the liquid layer of water between the substrate and the bottom of any overlying ice cover. The measurement associated with this definition has been renamed available water depth (AWD; Section 3.2).

For ice-cover periods before 1993, WDP (now AWD) was calculated in the field by subtracting ice thickness from a measure of maximum water depth. The maximum water depth (i.e., what is now called  $Z_{\max}$ ) was not recorded in the field, but has since been estimated in the database by adding 90% of the reported ice depth to the reported WDP (now AWD). Since July 1, 1993, AWD is no longer calculated in the field, but is now calculated in the database by subtracting submerged ice thickness ( $Z_{\text{sice}}$ ) from  $Z_{\max}$ .

### 3.1.2 Method

Water depth ( $Z_{\max}$ ) at a sampling site is measured using a marked sounding pole, nonstretch sounding line, or a calibrated acoustic depth finder. The  $Z_{\max}$  is recorded in meters with two significant figures (e.g., 3.1 m, 0.12 m). However, three significant figures may be reported for water >1.0 m deep if such precise measurements are possible (i.e., through the ice) and necessary (e.g., to accurately calculate AWD). If measurements or samples are to be taken at a site, these are done before the substrate is disturbed by mechanical depth sounding. Precise measurement of water depth in rough water can be difficult, but comparison with a relatively fixed reference (i.e., average boat waterline) rather than the moving water surface can help, and best professional judgment must be used. Problems are reported with site comments and appropriate QF codes.

In aquatic habitats deeper than 1 m,  $Z_{\max}$  can also be measured using a calibrated acoustic depth finder or a weighted line. If an acoustic sensor is mounted on the boat hull, then the depth from the water surface to the mounted sensor must be considered (note that this can change significantly depending on the weight distribution, loading, or operation of the boat). A sounding line (nonstretch material) marked at 10-cm intervals can be used if current velocity is low enough to permit sounding with this approach and the substrate is firm enough to give unambiguous readings. If a sounding weight is used, the weight must be of sufficient mass to keep the cable vertical. Firmness of the substrate can be determined by gently bouncing the sounding weight up and down on the substrate.

#### *3.2 Water Depth—Available*

When ice is present, the fraction of the water column available to biota beneath the ice can be substantially less than the distance from the free-water surface to the substrate. Generally, this is significant when ice completely covers the water surface, but is also applicable to other forms of ice cover (e.g., large blocks). In LTRMP water quality monitoring, information is collected when

appropriate and possible to evaluate the vertical extent of the water column below the ice.

### 3.2.1 Definition

This measurement, now abbreviated AWD, was called water depth (WDP) in the first published version of the LTRMP Procedures Manual (Lubinski and Rasmussen 1988). It indicates the thickness of the liquid vertical water column available for aquatic organisms. When ice is present, this is the vertical thickness of the water layer between the substrate and the bottom of the ice. Because ice in the river is not always free-floating, but may be grounded or subjected to various buoyant or hydraulic pressures, it is not possible to calculate precisely the AWD from measurements of total ice thickness ( $Z_{\text{ice}}$ ) and water depth ( $Z_{\max}$ ) alone.

### 3.2.2 Method

The AWD and water depth ( $Z_{\max}$ ) are identical when ice is not present. When ice is present, AWD is determined in three steps:

- Water depth ( $Z_{\max}$ ) is determined as described earlier.
- Submerged ice thickness ( $Z_{\text{sice}}$ ), the distance from the bottom of the ice to the free-water surface (in the auger hole), is measured (Section 3.8.3). This should not be confused with total ice thickness ( $Z_{\text{ice}}$ ).
- The AWD is calculated (to the nearest centimeter) in the database (not in the field) by subtracting the submerged ice thickness ( $Z_{\text{sice}}$ ) from the water depth ( $Z_{\max}$ ).

#### *3.3 Water Elevation*

Water elevation data are collected in the bathymetric survey of LTRMP, but not routinely as part of water quality monitoring (Wlosinski et al. 1995). Basic information on LTRMP bathymetry is provided here for reference.

Water elevation is the height of the water surface above the National Geodetic Vertical Datum. It is not the same as water depth ( $Z_{\max}$ ), which is the vertical thickness of the water

layer. Water elevation in pooled reaches of the UMRS is controlled by dam operations when river discharges are low to moderate. The relation between water elevation and discharge is strongest in upper pool reaches. Water elevations at navigation control points may not fluctuate in response to changes in discharge under low or moderate flow conditions. Immediately above the navigation dams on the UMRS, water elevations may actually decrease as discharge increases and more gates are opened. At high discharges, all gates in the dams are opened completely, and water elevations are a function of discharge volume and river topography. Water elevations typically rise in springtime because of snow melt and high seasonal rains, decline during the summer, rise moderately again during fall rains, and drop in the winter.

### 3.4 Wave Height

Wind- or vessel-generated waves induce shear stress that can cause erosion, sediment resuspension, and mixing of the water column. These effects can influence water quality and aquatic biota (e.g., vegetation). Wave height is one index of the energy associated with wave action. Maximum wave height can be limited by water depth, because when wavelength (the distance between wave crests) exceeds about half the water depth, the wave begins to drag against the bottom and the wave rolls over on itself. The height of wind-generated waves is determined by wind energy input (velocity and duration), fetch (open water distance), and water depth.

#### 3.4.1 Definition

Wave height is the vertical distance (amplitude) between the highest (crest) and lowest (trough) point on the wave form. In LTRMP water quality monitoring, wave height is measured with a variety of equipment for differing purposes. It has been conclusively demonstrated that wave height cannot be precisely and consistently estimated by simple visual observations, even by skilled observers (U.S. Naval Oceanographic Office 1966). Consequently, wave categories from the Beaufort

Scale (Table 5) are used to report wave heights encountered during routine monitoring.

**Table 5.** Beaufort wind/sea-state scale.

Beaufort number	Wind speed		Description
	m/sec	MPH	
0	0.0–0.2	<1	Calm, like glass
1	0.3–1.5	1–3	Light air, ripples w/o crests
2	1.6–3.3	4–7	Light breeze, wavelets w/o breaking crests
3	3.4–5.4	8–12	Gentle breeze, wavelets w/breaking crests, scattered whitecaps
4	5.5–7.9	13–18	Moderate breeze, waves w/numerous whitecaps
5	8.0–10.7	19–24	Fresh breeze, whitecaps w/spray. Too rough for small open boats

#### 3.4.2 Method

Wave heights observed during LTRMP water quality monitoring are reported using the Beaufort wind/sea-state scale.

Although Beaufort Scale conditions above 4 should be encountered rarely by monitoring teams (especially when samples are being collected), the Beaufort scale extends to Force 17 (four levels above hurricane). This method of reporting wave heights in LTRMP was implemented on May 19, 1993.

### 3.5 Water Current Velocity

The speed of horizontal water movement is a primary feature of riverine habitat and strongly influences the presence and absence of many aquatic species. It influences material transport, sedimentation, erosion, the degree of turbulent mixing, and the level of abrasion and shear stress experienced by aquatic biota. In LTRMP water quality monitoring, water current measurements

are used to generally assess aquatic conditions and to explain or confirm other measurements at the sampling site. This measurement suggests the general level of turbulent mixing that might be expected at the sampling site and the connection between the sampling site and nearby areas (e.g., tributaries, main channel flows, and upstream areas). The routine current measurements made in LTRMP water quality monitoring are made near the water surface and usually from a boat that is not rigidly fixed to the substrate. They are not intended to be used in flow volume (discharge) calculations.

In a flowing channel without obstructions, current velocity generally decreases in a logarithmic fashion from just below the water surface to the bottom of the channel. The mean velocity for the entire water column is closely approximated by the velocity observed at a depth equal to about 0.6 of the maximum depth. In deep channels moving at high velocity, special equipment is needed to accurately (and safely) gage velocity at depth. Further, current velocity can vary dramatically both spatially (horizontal and vertical) and temporally (over time). Consequently, spot measurements of current velocity at routine sampling sites provide only a coarse indication of water movement in the vicinity of the site at the time of sampling.

Because a general indicator of water velocity is generally sufficient for the purposes of routine LTRMP water quality monitoring, water velocity measurements may be reported in velocity categories (Section 3.6) when more precise measuring equipment is not available.

### 3.5.1 Definition

Velocity is a measurement of both speed and direction (a vector). However, the terms “speed” and “velocity” are commonly (if incorrectly) used interchangeably. The LTRMP water quality monitoring includes both scalar components of horizontal water movement (speed and direction), and in this manual the scalar speed of horizontal water movement is referred to as current velocity. Current velocity spans a wide range, (0–3 m/sec) and is recorded in meters per second using

two significant figures. Measurement of flow direction is described in Section 3.7.

### 3.5.2 Method

Velocity can be measured using a float, venturi tube, rotating-element, or electromagnetic (Faraday effect) device. Floats are not used routinely in the LTRMP and can give only a rough estimate of surface water velocity. They cannot be used if velocity at depth must be measured. However, as a backup or emergency measure, a float can be any object with slight positive buoyancy (a whiffle ball or an orange are reliable and inexpensive floats). The float is placed in the river so that the middle of its flow path is at the point being described. The time it takes for the float to traverse a known distance (minimum distance = 3 m) is recorded. Times from three trials are used to calculate a mean time. Surface velocity is calculated from the travel time and the distance traversed. Care is taken to use trials that are uninterrupted by wind, debris, or other surface disturbances.

Routine current velocity measurements are made with an electromagnetic device following the manufacturer’s instructions (Appendix D). Velocity is recorded from stable readings (no significant change over 10 sec) or, in turbulent conditions with unstable readings, is calculated as the mean of six consecutive readings of 5 sec each. Built-in averaging capabilities within the instrument are used as appropriate.

Velocity measurements are taken at the same depth as the corresponding water quality sample. However, velocity measurements below 0.2 m are not taken routinely as part of water quality monitoring.

The orientation of the sensor is critical when using a directional sensor (venturi or uni-directional electromagnetic current meter). If the sensor is not oriented correctly (i.e., facing directly into the current or direction of maximum velocity), the reading will be incorrect. In turbulent waters, negative velocities may be indicated, but this problem can often be corrected by increasing the period of averaging (time constant).

Electromagnetic velocity meters generally do not require any field calibration. The zero point should be checked regularly (each day of use), and the meter should be recalibrated once per year. Care must be taken to ensure that the sensor surfaces on an electromagnetic device are kept clean (follow manufacturer’s guidelines) and are not scratched.

Maintenance is performed on the velocity meter according to the manufacturer’s instructions and is noted in the maintenance log book.

### 3.6 Water Current Velocity Category

The LTRMP field teams can report flow velocities using a categorical scale (Table 6) when precision equipment is unavailable or inoperative. Flow velocity category measurements can be made using any suitable floating object. Flow velocity category corresponds to one of a series of seven logarithmically increasing classes. When this is done, a QF code of “C” (category measure) must be recorded.

**Table 6.** Flow velocity classes used in the Long Term Resource Monitoring Program.

Flow velocity (m/sec)	Category	Visual indication
0.00–0.02	0	No detectable water movement
0.02–0.06	1	Water movement just detectable
0.07–0.14	2	Perceptible surface wakes
0.15–0.30	3	Estimated from object transit time
0.31–0.62	4	Estimated from object transit time
0.63–1.26	5	Estimated from object transit time
>1.26	6	Estimated from object transit time

### 3.7 Water Current Direction

Flow direction is the second component of flow velocity (speed is the first). Information on the direction of flow has limited use in routine monitoring but may be helpful in detecting anomalous conditions (i.e., backflows or subsurface currents) or dramatic changes in system geometry.

#### 3.7.1 Definition

Flow direction is the magnetic compass direction from which the flow is moving at the sampling point. This is the same system as that commonly used to report wind velocity. The direction of current flow is estimated to the nearest 10°.

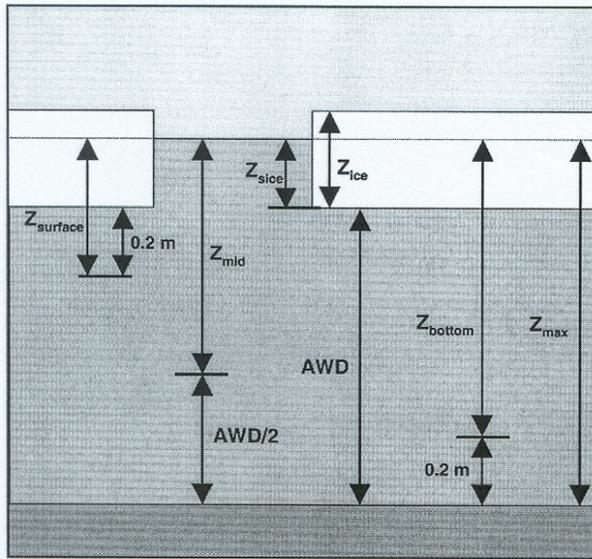
#### 3.7.2 Method

A magnetic compass is properly aligned with the predominant direction of flow, and the heading is noted and recorded to the nearest 10°. The direction of flow is not determined at current speeds ≤0.02 m/sec.

### 3.8 Ice and Snow

When ice is present, the underwater light climate is strongly influenced by the characteristics of the ice (thickness, clarity), the horizontal extent of ice cover, and the amount of snow covering the ice. Ice cover isolates the underlying water from gas exchange and the effects of wind resuspension. In the absence of resuspension, unusually clear water may develop under the ice. If the ice itself is transparent and lacks thick or complete snow cover, then light penetration is often adequate to support massive under-ice algal blooms. Dissolved oxygen levels of 200% to 300% of saturation may occur directly under the ice in such conditions. Likewise, a thick and complete snow cover can eliminate light penetration, prevent photosynthesis, and result in under-ice anoxia with subsequent winter kill.

The presence of ice complicates sampling and alters the definition of some depth-related measurements (Figure 2). Additional information and specific details on under-ice sampling are provided in Section 7.5.



**Figure 2.** Diagram of various depth ( $Z$ ) definitions associated with ice cover and under-ice sampling. The AWD is available water depth,  $Z_{\text{bottom}}$  is the depth of the near-bottom sample,  $Z_{\text{ice}}$  is the total vertical extent of ice,  $Z_{\text{max}}$  is the vertical extent of water between the substrate and the free surface of the water,  $Z_{\text{mid}}$  is the depth of the mid-depth sample (if required),  $Z_{\text{sice}}$  is the vertical extent of ice below the water surface, and  $Z_{\text{surface}}$  is the depth of the near-surface sample.  $Z_{\text{surface}}$  is always recorded as 0.2 m, regardless of ice presence. Thus, in all instances, the actual depth of  $Z_{\text{surface}}$  below the level of the free-water surface is 0.2 m plus  $Z_{\text{sice}}$ .

### 3.8.1 Ice—Percent Cover

The fraction of the water surface that is covered by ice will influence light availability, gas exchange (e.g., oxygen, ammonia, carbon dioxide), wind mixing, thermal regime, and suitability of habitat for aquatic biota. Ice cover also affects recreational boating and commercial navigation.

#### 3.8.1.1 Definition

Percent ice cover is a semiquantitative estimate of the fraction of water surface covered by ice in the vicinity of the sampling point. Ice cover in the upstream direction (the source of water that flows by the sampling point) is

of primary interest in this estimate. The ice coverage is estimated in increments of 10%.

#### 3.8.1.2 Method

Percent ice cover is estimated by visual observation around the sampling site. The area considered in this assessment corresponds to half the grid spacing (i.e., the sampling circle, Section 1.7) in stratified random sampling. Thus at side channel and contiguous backwater sites, ice conditions within a radius of 25 m are considered. At all other sites, a radius of 100 m is applied. If water does not extend to the assessment radius in all directions, then the water surface within the radius is considered. Exposed land and ice that is beached (i.e., laying on land that would be exposed at the prevailing water level) in the vicinity is not considered. The presence of ice in any amount less than 10% is reported as 1%.

### 3.8.2 Ice—Total Thickness

Total ice thickness ( $Z_{\text{ice}}$ ) influences light penetration, the potential for ice breakup and movement, the extent and chemical composition of the underlying water (in isolated backwaters), and the suitability of under-ice habitat for aquatic organisms.

#### 3.8.2.1 Definition

Total ice thickness ( $Z_{\text{ice}}$ ) is the vertical thickness of ice at a defined point. When ice extends to or into the underlying substrate, only the portion of the frozen block that represents the water column is measured and reported. The measurement of total ice thickness excludes the depth of any water above the ice surface.

#### 3.8.2.2 Method

The  $Z_{\text{ice}}$  is measured through a hole in the ice. A rod or stick marked at centimeter intervals and tipped with a right-angle crosspiece (e.g., a Secchi disk or 12-cm rod) is used for the measurement. The crosspiece is pulled up

against the bottom of the ice, while the rod is held vertically and the vertical distance from the crosspiece to the upper surface of consolidated ice (exclusive of slush, snow cover, or overlying water) is noted. Three measurements, separated by about 120° in the horizontal, are made to reduce errors when irregular ice surfaces or artifacts are produced by making the hole. The mean of the three measurements is reported in centimeters.

### 3.8.3 Ice—Submerged Thickness

When ice is present, the vertical distance between the substrate and the free surface of the water ( $Z_{\text{max}}$ ) does not accurately reflect the vertical thickness of the water column available for aquatic organisms. To accurately calculate AWD, a measurement of submerged ice thickness ( $Z_{\text{ice}}$ ) is subtracted from total water depth ( $Z_{\text{max}}$ ). When the surface of the ice is submerged, whether naturally or by weight of sampling equipment, etc.,  $Z_{\text{ice}}$  is measured to the water surface. This is necessary to get a proper calculation of AWD and sample depth ( $Z$ ).

#### 3.8.3.1 Definition

When ice is present, the thickness of the submerged portion ( $Z_{\text{ice}}$ ) is determined to the nearest centimeter by measuring the vertical distance between the bottom of the ice and the free surface of the water (usually within the auger hole, but see below). If the ice cover is perched so that the free surface of the water is below the bottom of the ice, then submerged ice thickness is reported as zero. If the ice cover is submerged so that free water is above the ice surface, then the thickness of the overlying water layer is included in the submerged ice thickness ( $Z_{\text{ice}}$ ).

#### 3.8.3.2 Method

The technique is identical to that used for ice thickness (see above) except that the upper point of measurement is the free surface of the water rather than the upper vertical extent of the ice.

### 3.8.4 Snow Depth

The depth of snow on top of the ice influences light penetration to the surface of the ice and the light available to aquatic biota below the ice. Because of its insulating properties, accumulation of snow over the ice can significantly retard ice formation and prevent the water column from freezing completely in shallow locations.

#### 3.8.4.1 Definition

Snow depth is the vertical thickness of snow on the ice in the vicinity of the sampling location measured to the nearest centimeter.

#### 3.8.4.2 Method

Snow depth is measured by pushing a graduated staff vertically into the snow until an abrupt increase in resistance is encountered. The end of the staff should have a 6.4-cm<sup>2</sup> (1-inch<sup>2</sup>) surface area. Three measurements are made within 1 m<sup>2</sup> to reduce errors from irregular snow and ice surfaces. The mean of the three measurements is reported in centimeters.

### 3.8.5 Snow—Percent Cover

The discussion of snow depth (Section 3.8.4) also applies to percent snow cover.

#### 3.8.5.1 Definition

Percent snow cover is a semiquantitative estimate of the fraction of the total horizontal surface (water and ice) covered by snow in the vicinity of the sampling site. It cannot exceed the percent ice cover (i.e., the fraction of the water surface covered by ice).

#### 3.8.5.2 Method

Percent snow cover is estimated in a manner similar to that used for percent ice (i.e., visual observation around the sampling site). The percent ice cover can be multiplied by the

fraction of ice covered by snow to estimate the snow fraction. For example, if percent ice cover equals 50% and 70% of the ice is covered by snow, then percent snow cover equals  $0.5 \times 0.70 = 0.35$  or 40% (rounded to the nearest 10%). Percent snow cover is reported in increments of 10%. If the percent snow cover is less than 10% but greater than zero, it is reported as 1%.

### 3.9 Substrate Characteristics

Sediment dynamics (resuspension, transport, deposition, modification) and sediment characteristics are central to the functioning of the UMRS ecosystem. In addition, the effects of human activities (e.g., navigation, recreational boating, dredging, agriculture) are tied to (and reflected by) the spatial distribution of sediment types. Water quality monitoring in the LTRMP emphasizes parameters that are related to suspended sediment (e.g., turbidity, suspended solids, Secchi disk transparency, total phosphorus), but detailed information on substrate sediment characteristics and the spatial distribution of sediments in the UMRS is not addressed in water quality monitoring. As part of routine water quality monitoring, general information on substrate type is collected to suggest (1) the prevailing flow regime at the sampling site, (2) the nature and extent of the bottom sediment influence on water quality in the overlying water, and (3) the type and amount of biota that might be expected at a specific location.

#### 3.9.1 Substrate Particle Size

Substrate particle size is not measured as part of routine water quality monitoring. The following information is provided for reference only. These categories are modified from Wentworth's classification (Welch 1948) to include particles common to UMRS aquatic habitats.

#### 3.9.1.1 Method

The previous version of this manual outlined the following methodology: Substrate is collected using a sampler appropriate to the situation. Variability in substrate types, water depth, and current velocity in the UMRS has prevented standardization on a single sampler. Either a corer or a Ponar sampler is appropriate for most situations. In high velocity areas characterized by mussels, hard clay, bedrock, or boulders, diving may be necessary to adequately identify the true substrate particles present. The upper 10 cm of the substrate sample is visually inspected by a technician trained in the identification of substrate particle categories. Table 7 describes one method for classifying substrate particles.

**Table 7.** Substrate particle categories based on Wentworth's classification (Welch 1948).

Category	Description or particle diameter (mm)
Bedrock	None
Boulder	>256
Cobble	255–64
Gravel	63–2
Coarse sand	1–0.25
Fine sand	0.24–0.062
Silt	0.061–0.004
Clay	<0.004
Detritus	Dead plant parts, any size (with the exception of woody debris, which will be quantified later under "fish cover")
Mussel shells	Either live or dead

#### 3.9.2 Substrate Hardness

Substrate hardness is not measured in routine water quality monitoring, but the following information is included for reference. Substrate

hardness is widely variable in the UMRS and is not a direct function of substrate particle size. For example, backwater sediments composed primarily of silt can vary considerably in hardness depending on their past history of exposure to air, the presence of anaerobic conditions, aquatic vegetation, and general turbulence. Firm silt substrates are likely to support more diverse and abundant epibenthic and macrobenthic communities than do extremely flocculent silts.

### 3.9.2.1 Method

Standard methods for determining substrate hardness in the LTRMP have not been developed. The first published version of the LTRMP Procedures Manual (Lubinski and Rasmussen 1988) called for measurement with a 9.1-kg (20-lb) weight attached to a disk 20 cm in diameter. The disk is suspended at the surface of the substrate by a cable graduated in centimeters. The disk is released and allowed to penetrate the substrate. The depth of the disk is recorded at 15-sec intervals until no change in depth is observed. The distance in centimeters between the final resting depth of the disk and the water depth is reported as substrate hardness. Using this technique, substrate hardness can only be measured in silt-dominated sediments. Other methods have been investigated, but none adopted for routine use.

### 3.9.3 Predominant Substrate

Water quality monitoring in the LTRMP uses five categories to record predominant substrate type (Table 8).

Any suitable device for obtaining a surficial sample of bottom material can be used to make the determination. This measurement is required in backwaters only, but at the discretion of the field team these measurements can also be made in channels. In FSS, measurements of predominant substrate are made at least once per quarter; they are required in backwaters during all SRS episodes.

**Table 8.** Predominant substrate categories used in the Long Term Resource Monitoring Program.

<b>Numeric code</b>	<b>Category</b>	<b>Description</b>
0	Clay	Hard, without sand or organic material
1	Silt	Soft, flocculent
2	Silt/clay/sand	Any mixture of two or more of these materials
3	Sand	May contain small amounts of other material
4	Hard	Concrete, rock, gravel, riprap, etc.
9	Not obtainable	Cannot obtain sample

### 3.10 Aquatic Vegetation

A separate component of the LTRMP addresses the spatial and temporal distribution and abundance of aquatic plants in the UMRS and this is described elsewhere (Rogers and Owens 1995). Water quality teams in the LTRMP only collect rudimentary information on aquatic vegetation in the immediate vicinity of the sampling site as needed to help interpret measurements from the site.

#### 3.10.1 Percent Aquatic Plant Coverage

Four general categories are used to report the approximate extent of aquatic plant coverage (submergent, emergent, and floating) around the sampling site. The area considered in this assessment corresponds to half the grid spacing (i.e., the sampling circle, Section 1.7) in SRS. Thus, at backwater and side channel sites, coverage within a radius of 25 m are considered. At all other sites, a radius of 100 m is applied.

- 0 = No aquatic vegetation visible at the site
- 1 = 1–19% coverage of the sampling site with aquatic vegetation
- 2 = 20–49% coverage
- 3 = Greater than 50% coverage

### 3.10.2 Vegetation Density

Vegetation density is reported in two categories, sparse or dense. This subjective measure gives an approximate characterization of stem or leaf density within the plant bed.

### 3.10.3 Vegetation Type

The LTRMP uses the following five categories to record the predominant vegetation growth form(s) at a sampling site:

- S = Submergent
- E = Emergent
- F = Floating
- B = Two of the above categories
- C = Combination of S, E, and F

## 4. Physical and Aggregate Properties of Water

The physical and aggregate properties of water are of major importance to the aquatic biota but are not gaged directly by the concentrations of distinct chemical or biological species. This category of measurement includes acidity, alkalinity, conductivity, hardness, light extinction, density stratification, temperature, turbidity, transparency, pH, and suspended solids. Of these, routine LTRMP water quality monitoring includes conductivity, Secchi disk transparency, suspended solids, temperature, turbidity, and pH. Photosynthetically active radiation (PAR) is not monitored routinely at present in LTRMP water quality, but may be added in the future. Vertical water density differences (stratification) are not measured in the field, but evaluated from vertical measurements of temperature and conductivity.

Although turbidity, Secchi disk transparency, and suspended solids are interrelated, all three continue to be monitored in the LTRMP water quality component. The data collected from 1993–2001 show that the relations among these variables are not precise and can change over space and time. With the exception of suspended solids (a high priority measure in the LTRMP), these measures are quick and easy to obtain and

provide cross-check and back up if a result is in question or missing.

The instruments used to measure physical and aggregate properties of water in the LTRMP have evolved over the course of the Program. Care has been taken to compare the performance of new equipment to existing instruments to ensure that artifacts are not introduced into the long-term record by instrument replacements. Sometimes (e.g., turbidity) the need for long-term consistency has prevented the LTRMP from using all the capabilities of newer instruments. The equipment used in LTRMP for *in situ* water quality monitoring as of the date of this manual's publication are listed in Appendix E.

### 4.1 Conductivity

Conductivity (the ability of water to conduct an electric current) is an aggregate property that reflects the total amount of ionic material dissolved in the water. Conductivity is useful for determining the source and movement of water, for gaging the impact of precipitation events, for cross-checking the validity of correlated measurements, and (sometimes) for estimating chemical characteristics that are more difficult to measure directly. It is also a major consideration in electrofishing efficiency.

#### 4.1.1 Definition

Conductivity is the ability of a cubic centimeter of water (1 cm<sup>2</sup> in cross section and 1 cm in length) to transmit an electric current. It is the reciprocal of resistance (ohms) and is reported in microseimens per centimeter (μS/cm). This unit is exactly equivalent to the micromho per centimeter (μmho/cm). Conductivity (also called specific conductance) is defined at 25°C and measurements made at other temperatures must be corrected accordingly. The exact correction is dependent upon the precise ionic composition of the water, but an approximate correction can be made that will bring the result within 1–2% of the actual value under most circumstances. This approximation is acceptable for LTRMP purposes and is performed

automatically by all conductivity devices used in the LTRMP.

#### 4.1.2 Method

Conductivity measurements are usually made *in situ* as part of a multisensor array, but grab samples can be collected and measured when measurements *in situ* are not feasible. Grab samples are collected using a suitable depth-specific sampler (Section 7.3). Grab sample conductivity measurements should be made immediately and samples should not be stored. The calibration of conductivity instruments must be checked at the start and end of each day according to the instrument manual (Appendix D) by comparison to standards that bracket ambient conditions (i.e., 0.002 M and 0.005 M potassium chloride solutions; APHA 1992).

### 4.2 pH

Measurement of pH is one of the most important and frequently used measurements in water chemistry (APHA 1992). Chemical equilibria, biotic processes, and toxicity of various constituents (e.g., ammonia) are all pH-dependent. Natural waters generally have pH values in the range of 4 to 9. The UMRS, which is well-buffered, has pH values generally above 7 and usually between 6.5 and 8.5. Photosynthesis will strongly influence pH, and higher pH values can be expected in the afternoon, on sunny days, or beneath clear ice in association with aquatic vegetation beds or algal blooms. See *Standard Methods* (APHA 1992) for additional information. Remember that pH is a logarithmic measurement and that each pH unit indicates a 10-fold difference in hydrogen ion activity. For this reason, pH values should not be “averaged” in the same fashion as nonlogarithmic measurements.

#### 4.2.1 Definition

The pH of a solution is the negative logarithm (base 10) of hydrogen ion activity (approximately

the hydrogen ion concentration). Thus, the hydrogen ion activity in a pH 7.0 sample is 10 times greater than in a pH 8.0 sample. The LTRMP measures pH potentiometrically with a glass electrode and records it to the nearest 0.1 unit.

#### 4.2.2 Method

In LTRMP water quality monitoring, pH is generally measured *in situ* as part of a multisensor array (Appendix D). *In situ* measurements are required because a pH sample cannot be preserved and pH can change rapidly and dramatically because of degassing, aeration, photosynthesis, or respiration.

### 4.3 Photosynthetically Active Radiation

The PAR is not routinely measured in LTRMP water quality monitoring, but the following information is provided for reference.

The photosynthetic activity of plants is related to incident radiation between the wavelengths of 400 and 700 nm. The penetration of light into the water column can be a major factor in the presence or absence of aquatic macrophyte species, the quantity and composition of phytoplankton, and the rate of carbon fixation (primary production).

The PAR is only a fraction of the total light that strikes the water surface. Seasonal weather patterns (particularly clouds) influence this measurement. During low precipitation years (less cloud cover), incident PAR may be above average and may also be accompanied by lower turbidity (greater light penetration).

#### 4.3.1 Definition

The PAR is a measure of incident light intensity (number of photons per unit time per unit area) between the wavelengths of 400 and 700 nm (it is sometimes called photosynthetic photon flux density). The PAR is typically measured in units of micromoles of photons per second per square meter ( $\mu\text{mol s}^{-1} \text{m}^{-2}$ ). It assesses the light available for plant growth. The

PAR measurements taken at discrete depths are used to estimate the extinction coefficient in the following equation:

$$I_z/I_0 = \exp(-\text{extinction coefficient} * z)$$

where  $I_z$  and  $I_0$  are the PAR measurements at depth ( $z$ ) and the surface, respectively, and  $\exp$  is the exponential function.

### 4.3.2 Method

At defined locations, PAR is measured above the water surface (1 m) and at logarithmic increments (e.g., 10, 20, 40, 80, 160, and 320 cm) below the water surface until the PAR is  $<10 \mu\text{mol s}^{-1} \text{m}^{-2}$  or the bottom is encountered. It is critical that reflections or shadows from the boat and equipment, the field team, and the sensor cables themselves do not influence measurement. Measurements should be taken on the sunny side of the boat. Keep in mind that the boat's shadow, although perhaps not visible on the water surface, projects downward at an angle below the boat (dependent on the position of the sun), and that the sensors can be inadvertently lowered into this shadow, if care is not taken. Likewise, reflections from the boat hull and equipment can influence the readings—particularly surface or deck cell measurements. If a deck cell is used, it should be positioned above the boat and equipment. Submerged measurements should be taken away from the boat as much as practicable (a polyvinyl chloride plastic pipe is useful for this purpose).

The simultaneous use of two sensors (deck and submersed cells or two submersed cells) is strongly recommended and allows for an estimate of light extinction in the water, even when sky conditions are variable. Under clear sky conditions and for short intervals, dual cells are not necessary. Specific LTRMP methods for measurement of PAR are not established. The LTRMP is using quantum light sensors (LI-COR, Inc., Lincoln, NE [previously LAMBA Instruments Corporation]) connected to various data loggers and the manufacturer's operating and maintenance procedures are followed.

## 4.4 Secchi Disk Transparency

Secchi disk transparency is an established and convenient limnological index for measuring water clarity. It correlates reasonably well with turbidity, suspended solids, visual light extinction, and light availability for plant growth (Cole 1979). When multiplied by a value between 2.7 and 3.0, Secchi disk transparency roughly indicates the depth at which 1% of the surface incident light remains and this depth is commonly accepted as the lower boundary of the euphotic zone (Cole 1979). Secchi disk transparency can be measured easily and quickly, can be compared to historical data, and can provide a check on other measurements such as PAR, turbidity, suspended solids, and chlorophyll-*a* related to water clarity. Disadvantages of this method are that it requires suitable midday illumination, only surface measurements are possible, it is unusable in clear, shallow water where the disk is in view while resting on the bottom, and it can be difficult or impossible to obtain readings in water that is rough or moving at velocities greater than a few centimeters per second.

### 4.4.1 Definition

Secchi disk transparency is the vertical distance below the water surface at which a Secchi disk disappears from the view of a person located directly above the disk. In the LTRMP database, Secchi disk transparency is recorded in centimeters. The measurement depends on the ambient light at the water surface, the light attenuation characteristics of the water between the disk and the water surface, the roughness of the water surface, and the visual acuity of the observer.

### 4.4.2 Method

Secchi disk values are made with a flat, circular plate with alternating black and white quadrants. A Secchi disk attached to a cable or rigid rod marked at centimeter intervals is lowered into the water in the shade of either the

boat or the observer to avoid glare off the water surface. Sunglasses are not worn while making this measurement. The distance at which the disk disappears is noted, the disk is raised, and the depth at which it reappears is noted. The mean of these two depths in centimeters is recorded as Secchi disk transparency. Various sizes of Secchi disk are in common use; the LTRMP generally uses a disk with a 20 cm diameter. If necessary, any white object that can be raised and lowered in a controlled fashion and that has a reasonably flat upper surface can be used for Secchi disk measurements. If a nonstandard device is used, this is so noted using a QF code of "A" (nonstandard method used) and an explanation provided in the site comments field of the data sheet.

In flowing water, Secchi disk transparency measurements require a heavily weighted or rigidly mounted disk. Alternatively, the boat may be allowed to drift with the moving water to ensure that the disk hangs vertically. In situations where the Secchi disk can be seen even after it comes to rest on the substrate, the depth at which the disk comes to rest is recorded and an appropriate QF code of "2" (reading off-scale, high) is recorded. Before June 12, 1993, when the Secchi disk transparency could not be directly measured (e.g., disk was visible on the bottom), a Secchi disk transparency of -9 was recorded. In rough water, accurate Secchi disk transparency readings can be nearly impossible and best professional judgment must be used to estimate the average depths of disappearance and appearance of the Secchi disk.

#### **4.4.3 Calibration**

Secchi disk transparency is an individualized measurement and cannot be easily calibrated for precise measurement. Observers who are accustomed to turbid water will usually report greater Secchi disk transparencies under turbid conditions than observers who work primarily in clear water. The Secchi disk equipment itself is calibrated by remeasuring the rope or cable once a month to check for shrinkage or stretching. The graduated markings are renewed as needed to

correct for fading, and the Secchi disk itself can be repainted.

#### *4.5 Suspended Solids*

As in most large rivers, sediment dynamics are a central feature of the ecological structure and functioning of the Upper Mississippi River. The movement of suspended material (seston) is the main determinant of turbidity in the system and is the process involved in both erosion and sedimentation. The deposition of suspended (and bed load) material in backwaters of the Upper Mississippi River is considered by many to be the most serious threat to habitat and recreation in the river, and the processes that affect suspended solids concentrations are a major concern in evaluating the effects of navigational traffic on the UMRS. High levels of suspended solids increase the cost of treatment for municipal and industrial water supply uses and are aesthetically undesirable.

Because suspended sediment has been identified as a high priority measurement for the LTRMP, this variable is collected at all sampling locations in FSS and SRS.

Suspended solids (wash load) concentrations are generally determined as total dry mass per liter (total suspended solids, TSS) and as two fractions of the total: (1) nonvolatile (inorganic) solids (NVSS), and (2) volatile (organic) solids (VSS). The concentration in these two fractions is useful in determining or estimating the source of the material and other important characteristics.

The nomenclature for material suspended in the water has varied with time and across disciplines. In limnology, the total of all suspended particulate material is called seston (Wetzel 2001). In water treatment and engineering practice, this same material has been called nonfilterable residue, although the term suspended solids is now standard (APHA 1992). Suspended solids, or seston, includes organic detritus, phytoplankton, and inorganic particulates (e.g., clay, silt, sand).

Rivers transport variable amounts of high-density or large-particle sediment along their

beds (bed load) and, thus, the concentration of suspended solids taken near the surface may not represent the total mass of material transported downstream. Nonetheless, suspended solids concentration is an accurate measure of the fine particulate carried by the channel and is appropriate to LTRMP that emphasizes the biological effects of transported material and relative changes in transport over time, rather than total mass. It is also significant that the bulk of particle-associated contaminants (including phosphorus) in the water are associated with the smaller particles that are represented well by suspended solids. Further, these finer particles near the surface (which includes suspended algae) are the primary contributors to turbidity that impacts light penetration and water clarity.

#### 4.5.1 Definition

Suspended solids and the fractions thereof (total, inorganic, or fixed, and organic or volatile) are defined by the methods used in their determination. In LTRMP, the methods described in *Standard Methods* (APHA 1992, 1998) are used in these determinations. Note that in some earlier editions of *Standard Methods*, suspended solids were called nonfilterable residue. The LTRMP follows the practices of the 18th edition of *Standard Methods* (APHA 1992), and total particulate material that is trapped by a glass-fiber filter (type A/E) disk and dried at 105°C is called TSS. This material is then ignited (combusted) at 500°C and the residue (ash) that remains is called NVSS. This is considered the inorganic or mineral fraction of the suspended material. Finally, the weight lost during the combustion process is called VSS, considered to be the organic fraction of the suspended material. Particles >2 mm are excluded from suspended solids measurements in LTRMP water quality monitoring.

#### 4.5.2 Method

The methods for filter preparation and final analyses are detailed in *Standard Methods* (APHA 1992). Only the methods for sample filtration and handling are addressed here.

The filtration apparatus is assembled with the 47-mm glass-fiber filter (type A/E) positioned with wrinkled side up. Suction is started and the filter is wetted with a small volume of reagent-grade water to seat it. There is no restriction specified for the level of vacuum used in this suction procedure, but the suction equipment used in the LTRMP will generally not produce more than 20 inches (65 kPa) of vacuum. Sensible limits must always be observed to avoid rupturing of the filter or causing other equipment failure. In preparation for filtering, the sample is agitated in its container vigorously to resuspend any material that may have settled. The graduated cylinder used to measure the sample volume is rinsed first with a small volume of sample water before the measurement. After rinsing the cylinder, the capped water sample is agitated vigorously once more and a suitable volume (roughly 50–1,000 mL depending on location, season, etc.) of sample is immediately poured into the graduated cylinder (type TD). See below for guidelines on highly concentrated samples. The measured volume is then poured from the graduated cylinder onto the seated filter and the sample is suctioned to dryness (at least 30 sec after filtration looks complete). The funnel is then rinsed with at least three small volumes of reagent-grade water to move any particles clinging to the walls. The filtered sample volume (excluding the reagent water used for rinsing) is recorded. The damp filter is carefully removed from the apparatus and transferred to the storage planchet. The filter is positioned in the planchet so that the residue on the filter surface does not contact the planchet. An appropriate label (bar code) is attached to the planchet and it is then stored in darkness and frozen until ready for shipment to the LTRMP laboratory.

Several trade-offs must be made in this procedure. To maximize analytical accuracy, it is important to filter the maximum practicable volume, while keeping the total residue considerably under 200 mg (a lot!) to avoid forming a water-impermeable crust on the filter surface. Once the filter has become clogged with material, the filtration rate drops abruptly and the time required to complete the filtration becomes impractical. When dealing with small

filtration volumes (i.e., 50–100 mL) having high concentrations of suspended solids, a precision ( $\pm 1\%$ ) pipette (i.e., 25–50 mL) should be used to measure out the sample volume instead of a graduated cylinder. Care must be taken to ensure the sample is vigorously agitated immediately before drawing off the sample and that the sample is taken from middepth in the container. Adding repeated small volumes of sample (i.e., 20-mL increments) to the filter is generally unacceptable because measurement errors accumulate with each increment added (this is particularly true with graduated cylinders) and settling of material in the sample is increasingly likely. When repeated volumes must be used, precise and accurate ( $\pm 1\%$ ) measuring equipment is essential and the number of incremental additions should be kept to four or less. Further, the sample container **MUST** be agitated vigorously before each subsample is withdrawn. If a graduated cylinder is used to deliver a single increment of sample and filtration time is prolonged (several minutes), then special care must be taken to ensure that no material settles to the bottom of the graduated cylinder or clings to the wall. If TC glassware is used, then a small volume of reagent-grade water should be used to rinse any material that clings to the cylinder walls onto the filter (this volume is not included in the reported filtration volume).

Large particles (>2 mm) are not included in suspended solids measurements made by the LTRMP water quality teams. This practice may exclude some large algal colonies, but these large colonial aggregates are not uniformly distributed in the water column at the scale of LTRMP measurements, they do not arrive at the laboratory intact (easily damaged by shipping and handling), and they create aberrant, nonreproducible results. The LTRMP near-surface samples (0.2 m) are specifically intended to exclude material floating on the water surface and field teams can avoid many of these large particulates (e.g., duckweed and vegetation fragments) by proper sampling. Several methods can also be used to remove large pieces of vegetation and other debris from

the whole water sample before measurement and filtration for suspended solids. Passing the water through a #10 sieve (2 mm, 0.0787 inch, USA standard testing sieve) or equivalent is appropriate. Large pieces of vegetation and other debris can also be individually plucked from the sample container using clean forceps or other suitable and clean device, but in most instances another sample should be collected. The surface of the filter media should be visually examined when filtration is complete. If large particulate is present, the filter must be discarded. It is not acceptable to manually remove particulate from the filter surface or from the filtration volume after it has been measured. If not enough sample volume remains to repeat the filtration and replacement sample cannot be obtained (i.e., filtration is conducted in the laboratory), then the sample is lost and should be appropriately flagged (QF code of “5”).

#### *4.6 Temperature—Water*

Temperature is perhaps the most commonly measured water quality parameter. It is used to correct conductivity, pH, and dissolved oxygen measurements in multiparameter field instruments and is a critical chemical–biological factor that affects a wide range of phenomena, such as the presence or absence of species, growth rates, the rates of chemical–biological reactions, chemical equilibria, and organism tolerance to disturbance or stress. Water temperature has additional importance as the primary contributor to density stratification. Water temperature and thermal stratification in the UMRS are influenced by solar radiation, precipitation, tributary and groundwater inflow, and thermal discharges (i.e., from generating plants). In general, river temperatures increase downstream (north to south) on both the Illinois and Mississippi Rivers. Backwaters tend to warm more rapidly in the spring and cool more rapidly in the fall than do open channels. Shallow backwaters also tend to exhibit greater diurnal temperature fluctuations and more frequent thermal stratification than the main channel.

#### 4.6.1 Definition

Water temperature in LTRMP is defined as the *in situ* reading obtained with a properly calibrated thermistor probe and reported in degrees Celsius (°C) to the nearest tenth of a degree. Thermometers and thermistors are checked quarterly against a precision thermometer readable to 0.1°C. Calibration is checked against two temperature points once a year, or whenever a deviation >0.2°C from the reference thermometer is observed. Temperature sensing instruments used for field measurement of water temperature in LTRMP water quality monitoring should have a maximum error of ±0.2°C in the range of 0–40°C and a response time of <1 min. For calibration, the thermistor reading is compared to a certified temperature of a precision thermometer traceable to the National Institute of Standards (NIST, formerly the National Bureau of Standards). Note the checks must be performed at one of the certified temperatures provided on the certification chart for the reference thermometer because the accuracy of intermediate marks on a certified thermometer is not guaranteed. Quarterly checks of thermistors should include a reference point in the 0–5°C range during winter.

#### 4.6.2 Method

Temperature measurements in LTRMP are generally made with a thermistor probe as part of a multisensor array (Appendix D). Although any laboratory grade thermometer can suffice for surface measurements, a thermistor probe is required for temperature measurements at depth. Vertical profiles of temperature (0.2 m below the surface and 0.2 m above the bottom at minimum) are required in areas >0.60 m deep with current velocity <0.10 m/sec. If a thermometer is used for surface temperature measurements, it should have a scale marked for every 0.1°C, with markings etched on the capillary glass and it should have a metal case to prevent breakage. The thermometer or thermistor should have a minimal thermal capacity to permit rapid equilibration (response time <1 min). A mercury thermometer should never be used for

field measurements. It is strongly recommended that mercury thermometers, if used, be limited to backup and cross-checking of thermistor readings and that a calibrated thermistor be used as the primary method for measuring water temperatures in the field.

Good quality thermistors are stable and calibration by the operator is not required for general field work. However, before such equipment is used for the first time in the field, the linearity (accuracy) and response time of the thermistor is verified by comparison to a certified (NIST) thermometer as described on pages 7–9 of the Hydrolab Performance Manual (Hydrolab Corporation 1991b).

#### 4.7 Turbidity

Turbidity is a measurement of those light-scattering characteristics of water that reduce clarity and, thus, affect the light or visual regime for aquatic plants and animals (e.g., visual predators). Turbidity is caused, or influenced, by suspended matter such as clay, silt, finely divided organic material, soluble colored organic compounds, and plankton and other microscopic organisms. Correlation of turbidity with the weight concentration of suspended matter is often difficult because the light-scattering properties of the suspension are influenced by the size, shape, and refractive index of the particulates in suspension.

Older (visual) methods of measuring turbidity based on the Jackson candle turbidimeter (JTU) have been supplanted almost entirely by nephelometric techniques that produce measurements of nephelometric turbidity units (NTU). These two methods are fundamentally different, and interconversion between NTU and JTU is highly approximate.

The advantages of using nephelometric turbidity in addition to Secchi disk transparency as a measure of water clarity are that turbidity measurements can be made on samples taken from discrete depths, NTU measurements are not influenced by ambient light levels, and measurement is less dependent on the individual observer or operator. Further, Secchi disk transparency cannot be measured when

transparency exceeds the depth of the water column.

From 1988 to 1996, the LTRMP used Hach Model 16800 portable nephelometers (Hach Company, Loveland, CO) in the field for turbidity measurements. This method has advantages but also serious drawbacks. The primary advantages are that (1) sample storage is eliminated, (2) field teams have a real-time indication of conditions, and (3) sample processing can be done during travel among stations rather than after return to the laboratory. The major disadvantages are that (1) repeated field calibrations are necessary, which require time and cause equipment wear, even if done properly; (2) additional hardware is being carried into the field (space limitations, increased risk of loss, increased wear of equipment); (3) analyses are being performed in a marginal environment; and (4) the Hach Model 16800 is now obsolete. For routine field measurements, the LTRMP replaced the Hach Model 16800 with the Hach Model 2100P in September 1994. Substantial testing was performed to verify that readings with the new instrument are consistent with the older method in the 0–100 NTU range. Turbidity measurements made after September 1, 1996, using the Hach Model 16800 are indicated with a QF code of “A” (Section 8.4, nonstandard method used).

#### 4.7.1 Definition

Turbidity is measured in the LTRMP using the nephelometric method (APHA 1992). This technique measures turbidity by the amount of light from an incandescent lamp scattered at 90° to an incident beam. Turbidity is recorded as NTU to the nearest whole unit. Turbidity measurements made after September 1, 1996, using the Hach Model 16800 are indicated with a QF code of “A” (Section 8.4, nonstandard method used).

#### 4.7.2 Method

Nephelometric turbidity can be measured by processing grab samples of water, by an *in situ* probe, or with a flow-through instrument.

The LTRMP has not identified a suitable *in situ* device, and so relies on processing of grab samples. Grab samples for turbidity are collected using the appropriate depth-specific sampler (Section 7.3). The LTRMP does not require that turbidity measurements be made in the field, but turbidity should be measured at the time of collection or as soon as practicable to avoid changes in sample characteristics that might result from particle precipitation, flocculation, dissolution, growth, or decomposition. If the measurement is delayed, samples are kept from freezing, held in the dark at about 4°C, and measured within 24 hours of collection. The steps for measuring turbidity on a grab sample are as follows (consult the manufacturer's user's guide for more specific information on use and function of the instrument):

- a. A grab sample is collected (Section 7) and inspected to ensure that it has not been contaminated with bottom sediment or contains large debris or vegetation fragments. If the bottom sediment has been disturbed or the sample is otherwise contaminated, then another sample is collected, either in an undisturbed section of the site or after the water current has cleared the disturbance.
- b. The sample should be **gently** inverted several times immediately before measurement. This resuspends any settled particulates without introducing air bubbles into the sample.
- c. The cuvette is rinsed with sample water, and then an appropriate volume of sample is carefully poured into the clean cuvette. **Avoid creating air bubbles while pouring the sample, and do not handle the cuvette in the optical area as oils from the skin will cause an erroneous reading.**
- d. Carefully wipe the cuvette dry with a piece of cheesecloth or other soft material (laboratory wipes may scratch the glass). Periodically apply a thin film of silicone oil and wipe with a soft cloth to cover glass imperfections. Place cuvette into the nephelometer (Hach Model 2100P). Maintain a consistent orientation of the

- cuvette (i.e., one surface always facing forward).
- e. Record the turbidity measurement. If the reading is unstable (i.e., fluctuates more than  $\pm 5\%$  because of settling of material or movement of large particles), use signal averaging mode.
  - f. Sample dilution is required whenever the raw turbidity reading is greater than 100 NTU. Although the nephelometer (Hach Model 2100P) presently used in LTRMP can read values higher than 100 NTU, previous equipment could not. Thus, dilution is required to maintain consistency with the earlier data. Nephelometer readings are recorded before (raw instrument reading) and after dilution. When samples are returned from the field for turbidity measurement, it is possible to use precision equipment to produce the minimum dilution required by the ambient turbidity (Table 9). However, when measurements are made in the field and a large number of samples require dilution, containers with premeasured dilution volumes can be prepared up to 24 hours in advance of sampling. Typically, the same premeasured dilution volume (e.g., 25 mL) of analytical grade water is dispensed precisely into each dilution container. The containers are then sealed for transport to the field. In the field, a preset sample volume (5.00 mL) is precisely dispensed into a preloaded

dilution container and the sample gently mixed. The resultant NTU is determined as quickly as possible. The dilution factor is determined as in equation (1). For example, a premeasured volume of 25.00 mL of dilution water and 5 mL of grab sample results in a dilution factor of 6.

$$\text{Dilution factor} = (\text{sample vol.} + \text{premeasured dilution vol.}) / (\text{sample vol.}) \quad (1)$$

Knowledge of field conditions should be used whenever possible to guide the selection of premeasured dilution volumes. The goal of field dilution is to produce a sample in the 30–50 NTU range, but clearly this goal will not be achieved with premeasured dilution volumes if field conditions vary widely or differ greatly from expectation.

Whenever practical, dilution of turbidity samples is performed using a precision pipette (e.g., 1–10 mL) for measuring the sample and a volumetric flask (20–100 mL) for preparing the final dilution. After the sample is added to the volumetric flask, reagent grade water is added (swirled when about half the water is added and then again when three-fourths has been added) up to the full volume mark (bottom of meniscus). The diluted sample is then poured into a separate clean container to ensure good mixing and finally is dispensed (poured) into the cuvette for measurement. Care is taken when transferring samples to avoid the introduction of air bubbles. The diluted sample is read in the nephelometer as usual, with the dilution factor applied to calculate the NTU (e.g., 30 NTU in a diluted sample with a dilution factor of 6 is reported as 180 NTU). The dilution factor is calculated and applied automatically to the diluted sample reading when using the electronic data sheet software (Section 8.5).

Each diluted sample is read immediately after it is prepared. A batch of diluted samples should not be prepared and then read in sequence.

Repeated dilution or spiking of a diluted sample is not permitted. If turbidity is outside the desired range after dilution, the diluted sample

**Table 9.** Recommended dilution volumes for turbidity samples greater than 100 nephelometric turbidity units (NTU). The objective of dilution is to bring the instrument reading into the 30–50 NTU range.

NTU	Sample (mL) volume per 100 mL total volume	Dilution factor
100–200	25	4
201–500	10	10
501–1,000	5	20
1,001–2,500	2	50
2,501–5,000	1	100

is discarded and a completely new dilution is prepared.

The sample and dilution volumes (i.e., 5 + 25) are recorded in the sample comment (done automatically by ScanLog32). Keep in mind that dilution can alter the particles in the sample (e.g., by dissolution or precipitation), so dilution should be kept to a minimum.

When dilution is used to produce a final turbidity reading, a QF code of “8” (sample diluted) is applied to the final turbidity reading, but not to the raw instrument reading. A QF code of “8” assigned to a raw instrument reading indicates that the raw value was off-scale high (i.e., >1,000 NTU) and could not be read without dilution. The QF code of “8” takes priority over a QF code of “4” (sample returned to laboratory) that is not required for turbidity samples because these are routinely returned to the laboratory for analysis.

Near-surface (0.2-m) nephelometric turbidity measurements are made at all sites. Measurements at other depths may be required if density stratification is present or *in situ* depth profiles are being recorded (Section 7.4).

#### 4.8 Vertical Density Stratification

Density stratification is a critical feature of the aquatic environment and it affects a wide range of water quality characteristics. In most natural lakes (and many UMRS backwaters), density stratification is a seasonal or transient phenomenon that is produced most often by surface heating of the water. However, other processes can produce this phenomenon. For example, tributary inflows or groundwater may differ substantially from the main body of the river (or backwater) in temperature or in the amount of suspended or dissolved materials they carry. As a result, the density of the inflow will not match that of the main body, and density layering (stratification) will result. Because water density can be altered by dissolved or suspended material, stratification may exist even when the temperature is nearly uniform from top to bottom in the water column, and temperature inversions are indeed possible. This is sometimes accompanied by unusual subsurface currents

(e.g., flowing in a different direction or different velocity from the surface current). Unusual vertical profiles of temperature, dissolved oxygen, and conductivity may also be observed in the vicinity of groundwater inflows. Velocity measurements at depth can sometimes be useful in diagnosing such situations in the field. Whenever unexpected (e.g., inverted) profiles are observed, they should be noted in the site comments.

Water quality monitoring in the LTRMP records the presence of density stratification because of its ecological significance and because procedures must be adjusted to obtain suitable representative samples when the water column is stratified.

##### 4.8.1 Definition

Vertical density stratification is defined by the vertical rate of change in density in the water column. The density gradient can be estimated from vertical profiles of water temperature, but large vertical changes in dissolved or suspended material can interfere with this estimate.

##### 4.8.2 Method

Vertical density stratification is evaluated during routine monitoring by examining the vertical profile of temperature, dissolved oxygen, and conductivity. Requirements for sampling in vertically stratified conditions are presented in Section 7.4.

## 5. Concentration of Chemical Constituents

The concentrations of chemical constituents in the water are important in determining its suitability for aquatic organisms and human use. The chemical composition of river water reflects inputs from upstream, the biotic and chemical activity within the water column, and interactions among the water column, underlying substrate, and the atmosphere. This section details LTRMP methods for collecting and processing samples for chemical analysis. Except for dissolved oxygen, measured *in situ*, chemical analyses

are performed in the LTRMP laboratory using samples shipped from the field. Laboratory procedures used for the analyses are documented elsewhere.

Chemical constituents monitored routinely by the LTRMP have included dissolved oxygen, plant nutrients (phosphorus, nitrogen, and silica), chloride, sulfate, and selected cations (calcium, iron, magnesium, manganese, potassium, and sodium). Iron and manganese measurements were discontinued in February 1993 (Appendix A, Table A-2). Alkalinity has been recommended for inclusion in the LTRMP parameter list since 1991 as an important, fundamental water quality measure, but addition of this measurement has been deemed impractical and resources have never been allocated for implementation.

The constituents measured and the frequency of measurement in the LTRMP have varied over time (Appendix A). Additional characteristics (e.g., temperature, pH, conductivity, and turbidity) are described in Section 4. Individual chemical constituents are arranged alphabetically in the sections that follow.

### 5.1 Chloride

Chloride is one of the major anions in freshwater and because dissolved chloride is nonreactive (conservative), it can be used as a tracer of water masses and as a check in mass-balance or flux calculations. Chloride measurements (in combination with alkalinity and sulfate) are also important for determining an ion balance for laboratory QA/QC purposes. Increases in chloride can sometimes be associated with snow and ice removal operations on highways within the watershed, or with the proximity of wastewater outfalls. Concentrations of chloride usually found in the UMRS will not directly affect aquatic biota, but increasing levels may indicate a change in this situation.

#### 5.1.1 Definition

Beginning in January 1994, dissolved chloride in LTRMP was measured on a filtered sample

according to *Standard Methods* (APHA 1992) using ion chromatography. It is reported in units of mg/L as elemental chlorine.

#### 5.1.2 Sample Collection and Preservation

An appropriate depth-discrete water sample (Sections 7.3 and 7.4) is collected. The sample is filtered (0.45- $\mu$ m membrane; Section 7.8.1) in the field (same sample is used for soluble reactive phosphorus) and held on ice (approximately 4°C), until frozen within 24 hours of collection for shipment to the laboratory for analysis.

#### 5.2 Metal Cations (Calcium, Iron, Magnesium, Manganese, Potassium, and Sodium)

The dissolved metal cations analyzed by LTRMP are important in several ways. Calcium is the major cation in the UMRS followed by sodium; calcium's concentration is related to the buffering capacity of the water and can provide an indication of water source. Iron and manganese, although not measured by LTRMP at present, are important indicators of anoxia and can complex with phosphorus. Potassium is a significant minor plant nutrient and can influence the distribution of molluscs (Imlay 1973). Further discussion of these elements is provided in Cole (1979), Wetzel (2001), and *Standard Methods* (APHA 1992). Significant quantities of these constituents may be associated with particles, but the LTRMP only measures the dissolved phase (operationally defined by filtration and may include colloidal material) as encountered at the time of sample collection. Cation samples are not digested in the LTRMP, and this precludes the determination of total suspended cations.

#### 5.2.1 Definition

Metal cations are determined on filtered (0.45- $\mu$ m membrane) samples that have been preserved with nitric acid. Atomic absorption spectrometry and ion chromatography are used for analysis (APHA 1992). Analytical results for metals are reported as elemental concentrations in mg/L.

## 5.2.2 Sample Collection and Preservation

An appropriate depth-discrete water sample is collected (Section 7.3). The sample is filtered (0.45- $\mu\text{m}$  membrane) in the field, preserved with reagent grade nitric acid (Section 7.81), and is held in the dark on ice (approximately 4°C), until shipped to the laboratory for analysis.

### 5.3 Nitrogen—Ammonia plus Ammonium

Ammonia in water is a form of nitrogen readily usable by plants that can promote the growth of algae and aquatic macrophytes. This constituent is present in dissociated and undissociated forms in water. As pH increases, the equilibrium between these two forms shifts to the undissociated form and at elevated pH (i.e., above about 8), ammonia is present primarily in the  $\text{NH}_4\text{OH}$  form (nonionized, undissociated), which is highly toxic to aquatic biota (Wetzel 2001).

Accurate measurement of ammonia at low concentrations in ambient water samples is difficult. Ammonia is highly soluble in water and a filtered sample is used for the determination. However, ammonia is strongly sorbed to particles, and the filtration process may remove a significant fraction of the total in turbid waters. The partitioning between nonionized or undissociated and ionized forms of ammonia is dependent upon pH and temperature, but in the analytical procedure, both ionized and undissociated ammonia in the original sample are combined and detected colorimetrically. Because ammonia gas ( $\text{NH}_3$ ) can form and escape from the sample at higher pH, the sample is acidified immediately after collection to prevent loss to the gas phase before analysis. This preservation step also halts nitrification (biological oxidation of ammonia to nitrate), but unfortunately it also encourages ammonia gas from the atmosphere to accumulate in the preserved sample. The relative portions of dissociated and undissociated ammonia in the original sample can be calculated from the total ammonia determined in the analysis if the ambient pH and temperature of the water at the time of collection are known.

## 5.3.1 Definition

Ammonia nitrogen is defined as the total amount of ammonia (expressed as milligrams of elemental nitrogen per liter) that is detected in an acid preserved, filtered (0.45- $\mu\text{m}$  membrane) sample using an automated phenate method (APHA 1992).

## 5.3.2 Sample Collection and Preservation

An appropriate depth-discrete water sample is collected (Sections 7.3 and 7.4). The sample is filtered (0.45- $\mu\text{m}$  membrane) in the field immediately after collection and preserved with sulfuric acid (pH approximately 2.5; Section 7.8.1) and is held in the dark on ice (approximately 4°C), until shipped to the laboratory for analysis.

### 5.4 Nitrogen—Nitrate Plus Nitrite

Nitrate ( $\text{NO}_3$ ) and nitrite ( $\text{NO}_2$ ) are highly soluble forms of nitrogen in water and a filtered sample is used for the determination. In the analytical procedure, nitrate is reduced to nitrite, which can be detected colorimetrically. Any nitrite present in the original sample is also detected, so that the result ( $\text{NO}_x$ ) is the sum of both  $\text{NO}_3$  and  $\text{NO}_2$  in the sample. If desired, a separate determination on an unreduced sample can be used to determine  $\text{NO}_2$ , and  $\text{NO}_3$  can then be calculated by the difference between  $\text{NO}_x$  and  $\text{NO}_2$ .

## 5.4.1 Definition

The  $\text{NO}_x$  is defined as the total amount of nitrite (expressed as milligrams of elemental nitrogen per liter) that is detected after a filtered (0.45- $\mu\text{m}$  membrane) sample is reduced using a cadmium catalyst (APHA 1992). Thus, it includes both nitrate and nitrite present in the original sample. In the 1990s, LTRMP used differing laboratories and analytical methods for this determination (Appendix A). Ion chromatography of oxidized samples was the primary technique used for  $\text{NO}_x$  determination

in the LTRMP from June 1994 through April 1997 (Appendix A). Ion chromatography is still used on selected samples to cross-check the NO<sub>x</sub> results from the cadmium reduction method.

#### **5.4.2 Sample Collection and Preservation**

An appropriate depth-discrete water sample (Section 7.3) is collected. The sample is filtered (0.45- $\mu$ m membrane), preserved with sulfuric acid (pH approximately 2.5; Section 7.8.1), and is held in the dark on ice (approximately 4°C), until shipped to the laboratory for analysis.

#### *5.5 Nitrogen—Total*

Nitrogen is a critical plant nutrient and component of aquatic organisms that occurs in various physical and chemical forms in the water column. The operationally defined total concentration of nitrogen includes all common chemical forms of this element, both particulate and dissolved. Because nitrogen occurs in both reduced and oxidized states, independent analytical pathways have been used traditionally to measure reduced and oxidized nitrogen compounds. With this approach, total concentration is calculated as the sum of the two separate analyses. In recent years, digestion procedures have been published (APHA 1998) that use persulfate to oxidize all common forms of reduced and oxidized nitrogen to nitrate, requiring only a single analysis. This single digestion procedure has gained wide acceptance and is used by LTRMP for the determination of total nitrogen.

##### **5.5.1 Definition**

Total nitrogen concentration is determined using an automated cadmium reduction method on a whole water sample following persulfate digestion (APHA 1992).

##### **5.5.2 Sample Collection and Preservation**

An appropriate depth-discrete, whole water sample (Section 7.3) is collected. The sample is

preserved with sulfuric acid (pH approximately 2.5; Section 7.8.1) and is held in the dark on ice (approximately 4°C), until shipped to the laboratory for analysis.

#### *5.6 Oxygen—Dissolved*

Dissolved oxygen is a major determinant of habitat suitability for many aquatic species. The concentration of dissolved oxygen is dependent upon exchange with the atmosphere, photosynthesis, respiration, and various chemical reactions.

The solubility of oxygen in water (saturation concentration) is strongly dependent upon temperature, pressure (atmospheric and water), and dissolved ions. Of these three factors, water temperature has the greatest influence. As temperature rises from 0 to 30°C, the solubility of oxygen decreases by almost half (14.6-7.6 mg/L). Atmospheric pressure has far less effect; over the normal range that might be encountered (720–780 mm/Hg), solubility is increased by only 10%. The effects of dissolved material on oxygen solubility in the UMRS are generally negligible.

The dissolved oxygen concentration can be a critical habitat feature in shallow areas where high water temperatures, ice cover, or rapid respiration can result in dissolved oxygen levels below 5.0 mg/L (a commonly accepted minimum requirement for healthy aquatic biota). Inflows from groundwater and tributaries can also produce low oxygen levels. Large diurnal (24-hour) fluctuations of dissolved oxygen are common in highly productive areas (e.g., macrophyte beds and algal blooms).

An assortment of methods are available for measuring dissolved oxygen. An electrometric (amperometric) membrane method (temperature compensated) is used in the LTRMP. A number of methods are also available for calibrating dissolved oxygen sensors (e.g., U.S. Geological Survey 1999), and calibration methods for dissolved oxygen measurements in the LTRMP have evolved over time. An iodometric method (azide modification to the Winkler Method) used widely for cross-check and calibration of the electrometric technique was used by LTRMP

before July 1997, but this involves the use of hazardous materials (sodium azide, concentrated sulfuric acid, and concentrated sodium hydroxide) and was discontinued (Appendix F). Complete discussions of the electrometric and iodometric approaches to oxygen measurement are available (Wetzel and Likens 1991; APHA 1992, U.S. Geological Survey 1999).

### 5.6.1 Definition

The dissolved oxygen concentration (mg/L) in the LTRMP is determined by an electrometric (amperometric) membrane method adjusted for temperature and ambient atmospheric pressure. The measuring instrument is calibrated in an air-saturated water bath (at stable pressure and temperature), or more commonly in a water-saturated air chamber. Before 1993, various methods were used in LTRMP water quality monitoring to indicate dissolved oxygen levels that exceeded the upper detection limit of the monitoring instrument. For example, values >20 mg/L were recorded as either 21 or -9 mg/L. This coding scheme is unacceptable because valid oxygen concentrations >21 cannot be distinguished from over-range values. As of August 27, 1993, over-range values are reported as the maximum limit of the device and the over-range condition is indicated by a QF code of "2" (reading off-scale, high; Section 8.4).

### 5.6.2 Method

In the LTRMP, dissolved oxygen and water temperature are measured simultaneously in the field at the sampling depth. The instrument used for dissolved oxygen determination must meet or exceed the following requirements:

- a. Suitable precision (i.e., standard deviation of five repeated measures on a homogenous water sample must be <0.1 mg/L) and accuracy ( $\pm 0.2$  mg/L).
- b. Response time and sensitivity specified by the manufacturer.
- c. The measurements must be appropriately compensated for temperature effects on the sensor. Temperature measurements provided by the compensating thermistor

are verified quarterly against an NIST traceable thermometer (Section 4.6).

Performance in each of the above criteria is checked at least quarterly. An equipment maintenance log verifying the performance is maintained for each instrument. Maintenance is performed as recommended by the manufacturer. This maintenance is documented in the instrument maintenance sheet (Appendix J).

The dissolved oxygen is measured *in situ*. The manufacturer's recommendations regarding daily calibration and use of the equipment (including stirrer requirements) are observed as described in general guidelines that follow (also see Appendix D). A mechanical stirrer is generally required for polarographic type probes (e.g., Hydrolab [with standard membrane] and Yellow Springs Instruments) because this method of detection consumes oxygen and vigorous water movement over the membrane is needed to balance this consumption and obtain a precise and accurate measurement.

### 5.6.3 General Guidelines

All dissolved oxygen meters and sensors should be protected from physical shock and extreme heat or cold. Extra care is needed when taking dissolved oxygen measurements in the winter. The instrument probe(s) should be kept in a heated container to prevent freezing (Appendix G).

If the membrane is changed, it should not be used for at least 8 hours and preferably allowed to equilibrate overnight. If used before that time, frequent (i.e., hourly) calibration is needed to check for instrument drift.

The requirements for mechanical stirring across the face of the membrane must be closely observed. In turbulent water, additional stirring may not be necessary, but this must be verified (i.e., by observing no change in dissolved oxygen during additional stirring or agitation of the probe). Mechanical stirring is almost always required to obtain an accurate reading in quiescent waters. If mechanical stirring is not provided with the instrument, then the effect of this on dissolved oxygen measurements must be verified by comparison to a sensor equipped with

a stirrer. The data from this comparison must be properly recorded and made available to the water quality coordinator before such equipment is used for LTRMP monitoring.

Some polarographic probes (e.g., Hydrolab Datasonde3<sup>®</sup>) can be continuously powered (polarized) to allow rapid equilibration and measurement when the full unit is powered up. Polarizing batteries are not used routinely in LTRMP water quality monitoring, but if these batteries are installed, the membrane should be removed, the cell drained of electrolyte, and a fresh membrane placed over the empty cell whenever the unit will not be used for 10 days or more. This is necessary to prolong electrode life. Before the unit is returned to service, the electrolyte and membrane are replaced and the new membrane is allowed to “relax” by soaking in tap water for at least 8 hours (preferably overnight) before use.

### 5.7 Phosphorus—Soluble Reactive

The soluble reactive fraction of phosphorus includes all chemical forms of the material that pass through a 0.45- $\mu\text{m}$  membrane filter and, without prior chemical digestion, react with the reagents in the detection procedure. The SRP (also called dissolved reactive phosphorus) was once reported as orthophosphate, but it has been recognized that numerous reactive chemical forms of phosphorus (in addition to orthophosphate) can be hydrolyzed during the analysis and will behave as orthophosphate. A large majority (if not all) of the phosphorus detected as SRP is suitable for immediate uptake by bacteria, algae, and aquatic macrophytes. Before 1994, true SRP was not measured by LTRMP because filtered samples were preserved with dilute sulfuric acid, which hydrolyzes some portion of the otherwise nonreactive phosphorus species. Although preliminary tests have shown that the error introduced by this procedure is not great (<10%), data obtained from acid preserved samples are designated in the LTRMP database as soluble reactive phosphorus after hydrolysis (SRPH) by acid preservative.

### 5.7.1 Definition

The SRP is defined as the total amount of reactive phosphorus (expressed as milligrams of elemental phosphorus per liter) that is detected when a filtered (0.45- $\mu\text{m}$  membrane), nonacidified sample is analyzed with the ascorbic acid method (APHA 1992). Selected SRP samples are cross-checked in the analytical laboratory by running a parallel determination of orthophosphate on the ion chromatograph. This check is only approximate as SRP is not identical to orthophosphate.

### 5.7.2 Sample Collection and Preservation

An appropriate depth-discrete sample (Section 7.3) is immediately filtered through a 0.45- $\mu\text{m}$  membrane (glass-fiber prefilter allowed; Section 7.8.1). It is recommended that SRP samples not be preserved (APHA 1992). But if analysis must be delayed, *Standard Methods* (APHA 1992) recommends that SRP samples be frozen after the addition of mercuric chloride ( $\text{HgCl}_2$ ). In the LTRMP before January 1, 1994, SRP samples were preserved with sulfuric acid (pH <3) and held in the dark at approximately 4°C until shipped for analysis. Results obtained with this technique are recorded as SRPH (see above). After December 1993, LTRMP has held samples for SRP analysis by freezing at -10°C or colder and without the addition of  $\text{HgCl}_2$ .

Filtration membranes and glass-fiber filters can contribute significant amounts of SRP, and *Standard Methods* (APHA 1992) recommends that the filtration media be presoaked in laboratory grade water before use. Presoaking is not practical with LTRMP equipment and to avoid this interference, the first 1–10 mL of sample passed through the membrane or glass-fiber filter are discarded. In addition, the analytical laboratory conducts periodic (biannual) tests to evaluate the contribution of filter media to the analytical blank.

## 5.8 Phosphorus—Total

Phosphorus is a critical plant nutrient that occurs in various physical and chemical forms in the water column. The operationally defined total concentration of phosphorus includes all common chemical forms of the material, both particulate and dissolved. A single chemical digestion can dissolve and hydrolyze all common forms of phosphorus in an unfiltered sample to produce orthophosphate, which can then be measured precisely in a single chemical analysis.

### 5.8.1 Definition

Total phosphorus is defined as the total amount of reactive phosphorus (expressed as milligrams of elemental phosphorus per liter) that is detected using the ascorbic acid method after an unfiltered sample is digested with persulfate under acid conditions (APHA 1992).

### 5.8.2 Sample Collection and Preservation

An appropriate depth-discrete water sample (Sections 7.3 and 7.4) is collected. The sample is preserved with sulfuric acid (pH approximately 2.5; Section 7.8.1) and is held in the dark on ice (approximately 4°C), until shipped to the laboratory for analysis.

## 5.9 Silica—Dissolved

Silicon ranks second to oxygen in abundance in the Earth's crust. It appears as the oxide (silica) in quartz and sand and is combined with metals as complex silicate minerals. Degradation of silicate rocks results in silica in natural waters as suspended particles, colloidal or polymeric silica, and as silicic acids or silicate ions. For industrial uses, silica in the water is undesirable, but it is an essential nutrient required by diatoms, microscopic algae which frequently dominate the algal flora of flowing waters. Lack of silica can limit the growth of these algae, and strong correlations have been

demonstrated between silica concentration and diatom abundance (Wetzel 2001).

### 5.9.1 Definition

Dissolved silica is defined as the total amount of silicate (expressed as milligrams of elemental silicon per liter) in a filtered, unpreserved sample that reacts using the molybdate method (APHA 1992).

### 5.9.2 Sample Collection and Preservation

An appropriate depth-discrete water sample (Sections 7.3 and 7.4) is collected. The sample is filtered immediately in the field (0.45- $\mu$ m membrane), but not preserved (Section 7.8.1). Silica samples are held in a plastic container to prevent contamination by glass (a silica compound). Because silicates will precipitate under acidic conditions, acid preservatives cannot be used. The filtered sample is held in the dark on ice (approximately 4°C), until frozen for shipment to the laboratory for analysis. Silica analyses are normally performed on the same sample collected for SRP and chloride analyses.

## 5.10 Sulfate—Dissolved

Sulfate is an abundant anion in waters of the Upper Mississippi River Basin. Its concentration, in combination with other cations and anions, can be used to identify water masses. In anaerobic conditions, sulfate can replace oxygen as an electron acceptor in bacterial metabolism and is reduced to sulfide (a toxic substance). Because this is a major dissolved constituent, the concentration of sulfate is important for determining ion balance, an aspect of laboratory QA/QC.

### 5.10.1 Definition

Beginning in January 1994, dissolved sulfate in LTRMP was measured on a filtered sample according to *Standard Methods* (APHA 1992)

using ion chromatography. It is reported in units of mg/L as sulfate (SO<sub>4</sub>).

### 5.10.2 Sample Collection and Preservation

An appropriate depth-discrete water sample (Sections 7.3 and 7.4) is collected. The sample is filtered (0.45-µm membrane, Section 7.8.1) in the field (same sample is used for chloride and soluble reactive phosphorus) and held on ice (approximately 4°C), until frozen for shipment to the laboratory for analysis.

## 6. Biological Measurements

The abundance and composition of aquatic communities in the UMRS is of central concern to the LTRMP. The limnological characteristics (water quality) of the system can help to explain and predict the condition of the aquatic biota, and conversely, the condition of the aquatic biota can help to explain or interpret the results of other limnological measurements. In the LTRMP, detailed examination of biological communities in the system is largely the responsibility of other Program components (fish, vegetation, and invertebrates). However, water quality monitoring includes selected biological characteristics related to the plankton.

### 6.1 *Phytopigments (Chlorophyll-a and Phaeophytin)*

Phytoplankton (suspended algae) are a major food source for filter-feeding organisms (i.e., mussels, various macro- and microinvertebrates, and some fish) in the river. These microscopic organisms process nutrients and other materials suspended or dissolved in the water, generate oxygen during daylight, and can form nuisance concentrations (blooms) that can negatively affect river biota and interfere with multiple uses of the resource (e.g., water supply and recreation). The biomass of suspended algae is indicated by the concentration of photosynthetic pigments (e.g., chlorophyll-*a*) in the water. The most common degradation product of chlorophyll-*a* is phaeophytin, and although this decay product can

interfere with the chlorophyll-*a* determination, simple steps can be taken to circumvent this interference. Phaeophytin has been suggested as a measure (negative) of algal “health,” but may only indicate the amount of detrital material suspended in the water. Techniques more advanced than those used in the LTRMP are now available to quantify the broad range of phytopigments (and taxonomic composition of the suspended algae) in a sample (e.g., high performance liquid chromatography [HPLC]), but simple spectrophotometric or fluorometric measurement of chlorophyll-*a* is rapid, inexpensive, and widely used as an indicator of phytoplankton biomass.

Because the mass of suspended algae in the main stem and tributaries of the UMR is of fundamental importance to the ecology and management of this highly enriched system, fluorometric chlorophyll-*a* measurements are made at all sampling locations in FSS and SRS.

### 6.1.1 Definition

Two types of chlorophyll-*a* determination are used in the LTRMP and the results of these two determinations are reported as separate parameters. The spectrophotometric method for chlorophyll-*a* uses extraction of a filtered sample with 90% buffered acetone and is a well-established standard (APHA 1992) in wide use for more than 50 years. The chlorophyll-*a* obtained with this technique is termed CHLS in the LTRMP. The CHLS method is labor intensive and has a high detection limit when used in turbid waters (because of practical limits on filtration volumes), so the LTRMP also uses a fluorometric determination of chlorophyll-*a* conducted on a filtered sample extracted with a 50:50 mixture of dimethyl sulfoxide (DMSO) and acetone. The result of this method is termed CHLF. The CHLF is rapid and easily completed with a minimum of sample handling. It has been used at all FSS sites since September 16, 1998, and at all SRS sites since 1993. Samples are still collected for CHLS at a minimum of 10% of all sites (all QA/QC sites plus additional sites during SRS) to use for later calibration of the CHLF values.

## 6.1.2 Sample Collection and Preservation

An appropriate depth-discrete water sample (Sections 7.3 and 7.4) is collected in an opaque container (an amber plastic bottle with 2-L capacity is recommended for CHLS). The sample is not preserved (Section 7.8.1), but is held in the dark on ice (approximately 4°C), until filtered onto a glass-fiber filter. Filtration may be completed in the field under shade immediately after collection, or in the laboratory under subdued lighting within 24 hours. Following filtration, the filters are kept frozen in the dark until shipment to the UMESC laboratory for analysis.

### 6.1.2.1 Method—Spectrophotometric Chlorophyll Filtration

The filtration procedures for chlorophyll determinations are similar to those previously described for suspended solids analysis (Section 4.5.2), except that strict adherence to vacuum levels must be followed (suction not to exceed 0.3 atmospheres, 225–250 mm of Hg, or 5 psi), and filtration must be completed in subdued light. Even brief exposure to light can alter chlorophyll values. The limitation on filtration pressure serves two purposes. First and foremost, the goal is to avoid the rupture of phytoplankton cells (with subsequent loss of material to the filtrate). The second purpose is to avoid collapse of the filtration apparatus itself (i.e., filters, flasks, tubing, etc.). For CHLS, a 47-mm diameter filter (type A/E) is used and the maximum practical volume is filtered (20–1,000 mL commonly).

The filtration apparatus is assembled with the 47-mm glass fiber filter (type A/E) positioned with wrinkled side up. Suction is started and the filter is wetted with a small volume of reagent-grade water to seat it. In preparation for filtering, the sample is agitated in its container vigorously to resuspend any material that may have settled. The graduated cylinder used to measure the sample volume is rinsed first with a small volume of sample water before the measurement. After rinsing the cylinder, the capped water sample is agitated vigorously once more and a suitable volume (20–1,000 mL commonly) of sample is

immediately poured into the graduated cylinder (type TD). See below for guidelines on highly concentrated samples. The measured volume is then poured from the graduated cylinder onto the seated filter and suction is continued for at least 30 sec after liquid has passed through the filter to ensure that the filter is damp dry. The funnel walls are then rinsed with three successive small volumes of reagent-grade water to move any particles clinging to the walls. The filtered sample volume (excluding the reagent water used for rinsing) is recorded. The damp filter is carefully removed from the apparatus, folded in half with the filtered material inside, and transferred to a labeled and bar coded storage planchet. The planchet and filter are wrapped in aluminum foil and stored frozen in darkness until ready for shipment to the LTRMP laboratory

Several trade-offs must be made in this procedure. To maximize analytical accuracy, it is important to filter the maximum practicable volume. Once the filter has become clogged with material, the filtration rate drops abruptly and the time required to complete the filtration becomes impractical. When dealing with small filtration volumes (i.e., 50–100 mL) having high concentrations of suspended solids, a precision ( $\pm 1\%$ ) pipette (i.e., 25–50 mL) should be used to measure out the sample volume instead of a graduated cylinder. Care must be taken to ensure the sample is vigorously agitated immediately before drawing off the sample and that the sample is taken from middepth in the container. Adding repeated small volumes of sample (i.e., 20-mL increments) to the filter is generally unacceptable because measurement errors accumulate with each increment added (this is particularly true with graduated cylinders) and settling of material in the sample is increasingly likely. When repeated volumes must be used, precise and accurate ( $\pm 1\%$ ) measuring equipment is essential and the number of incremental additions should be kept to four or less. Further, the sample container **MUST** be agitated vigorously before each subsample is withdrawn. If a graduated cylinder is used to deliver a single increment of sample and filtration time is prolonged (several minutes), then special care

must be taken to ensure that all material is kept in suspension.

Large particles (>2 mm) are not included in chlorophyll measurements made by the LTRMP water quality teams. This practice may exclude some large algal colonies, but these large colonial aggregates are not uniformly distributed in the water column at the scale of LTRMP measurements, they do not arrive at the laboratory intact (easily damaged by shipping and handling), and they create aberrant, nonreproducible results. The LTRMP near-surface samples (0.2 m) are specifically intended to exclude material floating on the water surface and field teams can avoid many of these large particulates (e.g., duckweed and vegetation fragments) by proper sampling. Several methods can also be used to remove large pieces of vegetation and other debris from the whole water sample before measurement and filtration for CHLS. Passing the water through a #10 sieve (2 mm, 0.0787 inch, USA standard testing sieve) or equivalent is appropriate. Large pieces of vegetation and other debris can also be individually plucked from the sample container using clean forceps or other suitable and clean device, but in most instances another sample should be collected. The surface of the filter media should be visually examined when filtration is complete. If large particulate is present, the filter must be discarded. It is not acceptable to manually remove particulate from the filter surface or from the filtration volume after it has been measured. If not enough sample volume remains to repeat the filtration and a replacement sample cannot be obtained (i.e., filtration is conducted in the laboratory), then the sample is lost and should be appropriately flagged (QF code of “5”).

#### *6.1.2.2 Method—Fluorometric Chlorophyll-*a* Filtration*

For CHLF, a volume of 5.00 mL is filtered through a 25-mm diameter filter (type A/E). A fixed-volume precision pipet is used for sample withdrawal and delivery. The same procedures described for CHLS (Section 6.1.2.1) are used

for sample agitation and vacuum levels, as are the following additional instructions:

- a. The 25-mm glass fiber filters used for fluorometric chlorophyll-*a* are not prerinsed, but a few drops of DI water may be used to help seat the filter.
- b. You must filter exactly 5.00 mL of sample for fluorometric chlorophyll-*a*. In instances where large particles may be present, a widemouth pipette tip may be appropriate. Do not include any macroscopic vegetation or other large particulate (i.e., >2 mm) in the chlorophyll-*a* determination. Be sure to follow the exact procedures provided by the pipette manufacturer. For most models, the plunger is depressed to the first position while the pipette tip is in the air (not submerged in the sample). The plunger is released slowly and steadily after the tip is submerged in the sample. The 5.00 mL is delivered by depressing the plunger to the second position (some models require a blow out or wick step to eject the last portion of sample). Read the instructions carefully! Pipette tips are rinsed between samples. The pipette unit (not the individual tips) must be calibrated at the LTRMP laboratory or other analytical facility to ensure accuracy and precision of delivery.
- c. After the 5 mL has passed through the filter, the filter and funnel are rinsed with three successive portions of DI water (5–10 mL) to ensure that all of the sample has been flushed onto the glass-fiber filter and to ensure that any dissolved fluorescent material is rinsed away. The damp filter is then carefully removed with forceps, folded sample-side in, and inserted into a culture tube.
- d. Culture tubes are not capped for storage or shipment. Once the filter is inserted deep into the tube and the bar code label is applied, tubes can be carefully and securely wrapped in at least two layers of aluminum foil (in groups of 5 to 10) to exclude all light. The tubes are then ready

to ship to the LTRMP analytical laboratory (keep frozen in darkness until shipment).

## 6.2 Phytoplankton

Phytoplankton (drifting algae) are microscopic and near-microscopic plants that are the major source of primary production in lentic systems and are significant contributors to the food chain in large river systems, such as the Upper Mississippi River. The plankton of rivers are sometimes called potamoplankton. In ecological studies, phytoplankton have been collected with plankton nets in a manner similar to that still used for zooplankton. However, it has been found that a large portion of the active phytoplankton assemblage could pass through even the finest mesh nets. Phytoplankton samples are easy to collect and preserve, but processing of these samples is extremely time-consuming. The LTRMP approach is to collect and preserve whole-water phytoplankton samples routinely, but with the intention of processing only those samples that are later shown to be significant (as determined by other analyses or notable events). As of September 2003, none of the preserved phytoplankton samples in the LTRMP have been subjected to microscopic analyses.

### 6.2.1 Definition

The LTRMP considers all microscopic and near-microscopic algae and cyanobacteria suspended in the water column to be phytoplankton.

### 6.2.2 Sample Collection and Preservation

A suitable depth-discrete (Sections 7.3 and 7.4) sample is collected. A whole (unfiltered) sample is preserved with Lugol's iodine (Section 7.8.1). Enough preservative is added to give the sample a weak brown color (i.e., 0.2 mL per 60-mL sample)

## 6.3 Zooplankton

Zooplankton (drifting animals) are microscopic and near-microscopic animals that can be a major source of nutrition for many young and larval fish, as well as filter-feeding fish and invertebrates. This group of organisms can exert major grazing pressure on phytoplankton and can also provide nutritional links among microorganisms, organic detritus, primary producers, and higher consumers. Zooplankton sampling is not difficult, but processing of zooplankton samples can be extremely time-consuming and expensive. Consequently, the LTRMP has not routinely sampled zooplankton except in Lake Pepin, where separate funding has been provided to the Minnesota Department of Natural Resources to collect these samples.

### 6.3.1 Definition

In the LTRMP, all drifting copepods, cladocerans, and rotifers suspended in the water column and trapped by an 80-micron mesh plankton net are considered to be zooplankton. This operational definition allows some organisms (i.e., rotifers smaller than 80 microns) to escape detection.

### 6.3.2 Sample Collection and Preservation

The LTRMP zooplankton samples are collected by semiquantitative vertical tows using an 80-micron mesh plankton net. Before April 1996, samples were preserved with buffered sugar-formalin and subsequently have been preserved with 80% ethanol that is diluted by the sample volume to a final concentration of 40-50%.

## 7. Field Sampling of Physical and Chemical Water Characteristics

This section describes the general procedures used to collect water samples and make *in situ*

measurements of selected physical and chemical properties of water. For details on the overall sampling design and the scheduling of field sampling, see Section 1. Important amplifying information required for the measurement or handling of specific chemical or biological constituents is provided in Sections 5 and 6. Details on the recording of field data are presented in Section 8.

In general, water samples collected for chemical analyses receive only that level of field manipulation needed to successfully transfer them back to the field station for further processing or shipment to the analytical laboratory. *In situ* measurements of chemical and physical properties are taken in a manner that ensures that these measurements accurately represent ambient conditions in the water column at the location (horizontal and vertical) and time of sampling.

Measurements of *in situ* chemical and physical properties and the collection of samples for analysis are done near the water surface (0.2 m) at all sampling locations. Other depths are sampled as required (see Sections 7.3 and 7.4). For *in situ* measurements, care is taken to ensure that the sensors themselves are located at the assigned sampling depth. Grab samples taken for analysis are collected so that the vertical midpoint of the collected water is at the assigned depth.

### 7.1 Sampling Site Inaccessible or Unusable

River conditions, weather, and equipment failures occasionally make it impossible or unsafe to collect samples or measurements at a designated sampling location. Sections 1.6 and 1.8 describe the use of alternate sampling locations in SRS, but in FSS there are no alternate sampling locations. To document conditions that cause a sampling site to be missed during a scheduled FSS sampling week or SRS sampling episode, a data sheet (Section 8.3) that includes the date, crew leader code, recorder code, and site comment is completed for the missed location. The site comment briefly explains the situation that caused sampling to be incomplete. The number of sample rows

(NROWS; Section 8.3) on the data sheet is set to zero and no data or QF codes are entered in the depth rows. The time of sampling need not be recorded for a site that cannot be accessed. However, if a sampling time is recorded in this situation, it should be the time of arrival in the vicinity of the site. Note: Sampling times from data sheets with no detail rows completed (NROWS=0; Section 8.3) are excluded from computation of mean daily sampling times and other performance measures.

### 7.2 Shallow Water Sampling

Sampling in shallow water (<0.5 m) presents special problems because of equipment size limitations and the possibility of sample contamination with bottom material. Generally, LTRMP routine monitoring does not attempt to collect grab samples in water <0.2 m deep. The only exception is in hard-bottom, flowing-water situations (e.g., concrete weir, gravel bed, or other hard surface in a flowing tributary) where a sample can be readily obtained without contamination with bottom material. Sampling in shallow water requires special attention to the actual vertical position of the *in situ* sensors. The difference between the bottom of the sensor guard and the probes is a significant fraction of the total sampling depth in this situation. If, for example, the sensor guard is in contact with the bottom, then the instrument may not be vertical and the *in situ* probes may be displaced from their expected depth in the water column.

When approaching a shallow water site, special care must be taken to avoid disturbing the substrate. Whether using an air boat or conventional propulsion, the motor should be shut off or disengaged several meters from the sampling location and the boat allowed to drift into sampling position. Anchoring is required to obtain velocity measurements, but extreme care must be taken to avoid disturbance of the bottom. One approach to shallow-water sampling is to collect the water sample immediately after the boat drifts into position and before setting the anchor. This is, however, a compromise because it is desirable to take *in situ* readings (e.g., temperature, DO, etc.) at nearly the same

time as the water is collected. Any material that is resuspended or disturbed during approach to the site should be allowed to settle or drift clear before sampling commences.

### 7.3 Discrete-Depth Sampling

In water deeper than 0.5 m, when only a surface (0.2-m) grab sample is needed, a plastic sampling bucket or a 2-L amber bottle may be used to obtain the sample. However, for discrete-depth sampling, a horizontal Van Dorn sampler (Wetzel and Likens 1991; Lind 1979) is recommended for collecting grab samples in moving or shallow (<0.5 m) water. This device is well suited for this application because of the narrow layer of water that it samples. However, the horizontal Van Dorn sampler is not recommended for discrete-depth sampling of subsurface water in deep (>1.9 m), stratified, calm water. This is because the horizontal Van Dorn sampler fills with surface sample when it first enters the water and, unlike a vertical Van Dorn sampler, this surface water tends to be carried along in the sampler as it is lowered. In flowing water, the surface sample dragged along with the device is flushed out by horizontal water movement and the problem is eliminated. However, in calm water, the operator must move the device horizontally after it has arrived at the desired sampling depth to replace water from upper layers with water from the depth of interest. This horizontal motion may not be fully effective because (1) it can mix the layer of interest and produce a mixed-depth (rather than depth-discrete) sample and (2) the water entrapped in the device during lowering may not be fully purged. Consequently, a conventional (vertical) Van Dorn sampler or similar device is recommended for depth-discrete sampling in deep, calm water.

### 7.4 Subsurface Sampling Requirements

Water quality monitoring in the LTRMP is designed to detect patterns and changes in those limnological features that are most likely to influence river biota. Thus, the vertical

distribution of limnological characteristics in the water column is monitored within the LTRMP, but only where the vertical dimension is clearly important and monitoring can be conducted with safety and efficiency. It is well known that steep gradients in suspended sediment (and associated constituents) are common immediately above the bed of the main channel(s) in the UMRS, but the biotic significance of these gradients has not been established and vertical sampling in the main channel requires special equipment, is extremely time-consuming, and can be life-threatening. Limnological characteristics known to have major biotic significance (e.g., oxygen, water temperature, pH, dissolved constituents) generally do not exhibit pronounced vertical stratification in the main channel(s) of the UMRS except during low discharge. The LTRMP data demonstrate that surface sampling provides a good indicator of these limnological characteristics when flow velocities exceed about 0.1 m/sec. Thus, routine subsurface sampling of water quality in swiftly moving ( $\geq 0.1$  m/sec) water is not performed in the LTRMP.

Appendix H summarizes the following information and provides a useful key for assessing the need for subsurface sampling under LTRMP guidelines.

Surface measurements (0.2 m below the surface) are collected at all water quality sites. In areas where current velocity is <0.1 m/sec (which may at times include the main channel) and available water depth (AWD) is at least 0.60 m, bottom measurements of temperature, dissolved oxygen, pH, and conductivity are required to be recorded. If stratification is documented (see below and Appendix H for details), then bottom-grab samples for additional constituents may be required at fixed sites only. Measurement and recording of *in situ* parameters at additional depths (i.e., profiling) is optional; however, chemical analyses of profile samples are not routinely performed.

In FSS only, subsurface water samples are collected in low-velocity areas for chemical analysis (e.g., turbidity, suspended solids, plant nutrients) when water depth exceeds 1.9 m, and differences between surface and bottom of the water column meet any of the following criteria:

1. Temperature difference  $>1.9^{\circ}\text{C}$
2. Oxygen difference  $>3.9\text{ mg/L}$
3. Specific conductance differs from surface reading by more than 50%.

Historically, bottom-grab samples were required during SRS; however, those requirements were dropped in 1998 because stratification was infrequent and the cost of extra field and analytical effort required was large for the additional information gained.

## 7.5 Sampling During Ice Cover

### 7.5.1 Suitability for SRS Sampling

The field team leader must always judge whether the sampling point is suitable for measurement. This decision is not based on the “representative” character of the site relative to its designated stratum, but only on the ability to obtain a valid sample of the location. When ice is not present, sites  $<0.2\text{ m}$  deep are recorded, but are generally not sampled. Likewise, when ice is present, a site that would have  $<0.2\text{ m}$  of water if it were ice free is not sampled, but general site (header) information is recorded. If a representative site would have  $>0.2\text{ m}$  of water when ice free, but is frozen to the substrate (Section 7.5.3) then no additional or alternate site is used because to do so would bias the sampling (sites frozen to the substrate would tend to be overrepresented).

### 7.5.2 Sampling Requirements with Ice Cover

When a hole is cut through the ice for sampling, the water that enters the sampling hole from below the ice should be relatively clear with no indication of disturbed substrate. Care must be exercised when there is little clearance between the ice and substrate to ensure that the bottom is not disturbed while boring the access hole. In shallow water areas (e.g.,  $<1\text{ m}$ ), it is highly recommended to stop the ice auger before it completely penetrates the ice and chisel the remaining few centimeters with an ice spud. The plunge and rotation of the auger blades upon penetration through the ice may

cause undesirable sediment and water column disturbance. If this cannot be accomplished, then see guidance in Section 7.5.3. Depth definitions are complex when ice is present, and a diagram of sampling depths and definitions used in this situation may be helpful (Section 3.1, Figure 2). When sampling through the ice, the reported sampling depth ( $Z$ ) for the near-surface sample is the vertical distance between the bottom of the ice and the point of sampling (recorded to the nearest  $0.01\text{ m}$ ). Thus, in all instances, the actual depth of a near-surface sample below the level of the free-water surface is the recorded depth ( $Z$ ) plus the vertical extent of submerged ice ( $Z_{\text{ice}}$ ). Samples and measurements are normally collected  $0.2\text{ m}$  below the bottom of the ice (if possible) and the depth of the sample ( $Z$ ) is reported as  $0.2\text{ m}$ . However, if water depth and ice thickness are such that measurements and samples can only be collected between zero and  $0.2\text{ m}$  below the ice, then water samples for chemical analysis are not required and should never be taken if any possibility of substrate disturbance exists. However, *in situ* measurements are required, and the appropriate value for  $Z$  (sample depth beneath the ice to the nearest  $0.01\text{ m}$ ) is recorded. If measurements or samples cannot be collected beneath the ice, then  $Z$  is reported as zero. In some instances (e.g., shallow, flowing water), it may be possible to obtain *in situ* readings in the hole;  $Z$  is reported as zero, but water samples are not required. Near-bottom measurements are not required unless there is at least  $0.6\text{ m}$  between the bottom of the ice and the substrate (Section 7.4).

The sampling and reporting of nonsurface sampling depths when ice is present is unchanged from ice-free procedures (Section 7.4) and is referenced to the free-water surface, not the bottom of the ice. For example, if the substrate is  $70\text{ cm}$  below the bottom of the ice and  $Z_{\text{ice}}$  is  $25\text{ cm}$ , then the substrate is  $95\text{ cm}$  below the free-water surface. A surface sample is collected at  $0.2\text{ m}$  below the bottom of the ice ( $Z = 0.20$ ) and bottom measurements and samples (as appropriate) are taken  $0.2\text{ m}$  above the substrate ( $Z = 0.95 - 0.20 = 0.75$ ). All measurements except the near-surface are referenced to the free-water surface. Additional information on depth

definitions and snow and ice cover is found in Sections 3.2 and 3.8.

### 7.5.3 Ice Extends to Substrate

When ice extends into the substrate, or the bottom of the ice is in such close proximity to the substrate that a sediment and water mixture (slurry) is forced into the access hole when the ice is penetrated, then the site is considered frozen to the bottom. In this instance, the guidance in Section 7.5.1 applies to SRS sampling and an appropriate comment is recorded on the data sheet. Further,  $Z_{\max}$  at the site is reported as zero so that AWD can be correctly calculated as zero in the database. Note that submerged ice thickness ( $Z_{\text{sub}}$ ) is also reported as zero under these conditions and that  $Z_{\max}$  and  $Z_{\text{sub}}$  both receive QF codes of 5 (sample unusable or unobtainable). This approach ensures that the condition of the site is properly documented.

### 7.5.4 Unconsolidated Ice

If ice is present but does not form a continuous cover over the water surface at the sampling location, then sampling depths are the same as in open water. However, if open water sampling depths are used, then recorded ice information must indicate ice depths ( $Z_{\text{ice}}$ ) and ( $Z_{\text{sub}}$ ) of zero. This is necessary to properly interpret the recorded sampling depth ( $Z$ ).

### 7.5.5 Ice Surface Submerged

The surface of the ice is sometimes below the surface of the water because of rain, snow melt, or subsidence under the weight of the sampling team and equipment. Several alternatives are available for sampling in this situation: (1) move as much equipment and personnel as possible away from the sampling site, (2) construct a low dike of snow or ice around the sampling site to prevent over-ice water from entering the sampling hole, and (3) look for a slightly elevated spot on the ice within the sampling radius. If none of these options are suitable, then

the effect of the overlying water can be gaged by comparing the conductivity in the sampling hole to both the overlying water and to water directly beneath the ice. Carefully examining the water in the sampling hole for signs of gravity flow or convective movements can also be helpful. If the conductivity in the sampling hole is not within 5% of the underlying water or other indications of contamination by over-ice water are present, then the site is considered inaccessible and an appropriate comment entered on the data sheet. However, if some data are desired from this situation, then all the measurements should be flagged as nonrepresentative (QF code of "6") and an appropriate comment entered on the data sheet.

### *7.6 Chemical Sampling when Dissolved Oxygen is Less Than 1 mg/L*

Oxygen concentrations <1.0 mg/L are not frequently encountered in routine LTRMP sampling. However, these conditions do occur in the UMRS, particularly under ice cover in the northern reaches, in the vicinity of groundwater inflow, in dense beds of submerged aquatic vegetation, and in deep, stagnant, areas with high sediment oxygen demand. Chemical sampling from water that has a low-oxygen concentration requires special considerations because the chemical form and solubility of many constituents in low-oxygen water (particularly iron and manganese) are altered dramatically when exposed to air. For example, field teams have seen clear samples become cloudy with precipitate after being filtered or transferred to the sample bottle. As a result of this precipitation, the concentration of dissolved iron and manganese and co-precipitated materials (e.g., phosphorus) in the sample returned to the laboratory do not represent conditions in the river. The LTRMP has not targeted low-oxygen waters for specific study, and so the extra measures needed to accurately sample a wide range of chemical constituents under such conditions have not been included in routine monitoring. It is important, however, that these conditions be appropriately documented so that

the laboratory is prepared for the condition of the samples and to ensure that the resulting analytical results can be interpreted correctly. This is accomplished by recording appropriate site and sample comments on the data sheet (Section 8.3). The lab software (ScanLog32) alerts lab personnel when individual sample comments are recorded.

### *7.7 Selecting Sites for Chlorophyll-a Calibration and QA/QC*

To calibrate CHLF, samples are collected for CHLS at approximately 10% of the CHLF sampling sites. Phytoplankton samples are also collected at these locations. The selection of calibration sites is randomized to avoid bias and because more CHLS sites than QA/QC sites are required (10% vs. 5%), a subset of the CHLS sites should be used for QA/QC. In SRS, the number of CHLS sites in each sampling stratum is proportional (10%, rounded up to the nearest whole number) to the total number of sites sampled in the stratum.

#### **7.7.1 Method**

First, the required CHLS sites for each stratum are picked randomly from the list of full chemistry sites. For example in Pool 4, the 10% requirement specifies the following allocation: main channel = 3, side channel = 3, Lake Pepin = 3, and backwater = 5 (see Table 3). Randomization can be done by assigning a random number to each full chemical site in the sampling episode and then sorting the list of sites in descending order by stratum and random number. After sorting, the top sites from the list within each stratum are picked until the required number for each stratum is obtained. A simple SAS program can perform these operations (Appendix I). All the sites selected in this step are used as CHLS sites. Of these sites, one per day per work block is also used as a QA/QC site. If none of the selected sites occur in the daily work block, then an additional site for that block is picked randomly. If multiple CHLS sites are located in the daily work block, then the site with

the highest randomly assigned number is used for the QA/QC site.

The number of QA/QC sites required during the episode will generally equal the number of team days required to complete the episode. For example, seven QA/QC sites are required for a 7-day, 140-site SRS episode with one team in the field on each day. However, if sampling is completed in 4 days with two teams in the field each day, then eight QA/QC sites will be required. If an additional QA/QC site is needed beyond those originally scheduled, then the highest random number in the CHLS site list within the daily work block is used for the additional QA/QC site.

Blocks of sites are picked that can be sampled in 1 day by a single team. The 6 to 10 daily blocks are then randomly assigned to teams and to workdays. If a large area (e.g., Lake Pepin) is to be sampled on two consecutive days, then one of the blocks in the sequence is selected randomly and randomly assigned to a workday (Friday would be excluded from the random choice of days). The second block in the sequence is then sampled on the following day.

### *7.8 Sample Preparation For Shipment and Analysis*

Some processing of samples is normally conducted after samples are returned to the field station and only three containers need be collected in the field at each sampling site and depth. Two of these (60–125 mL) will contain water that is filtered and acid-preserved on-site (Section 7.8.1), the third (2 L) is unfiltered and unpreserved and may be processed in the field or returned to the field station laboratory for additional processing. The 2-L sample must be held on ice and in the dark until processing is completed (within 24 hours of collection). The unfiltered sample can be used for determination of specific conductance, turbidity, suspended solids, chlorophyll-*a*, phytoplankton, total nitrogen, and total phosphorus.

It is recommended that all the smaller (i.e., 60-mL) sample containers from a single location and depth be placed into a single zipper-lock bag or other suitable container to keep them

organized. An additional label written in pencil or waterproof ink should be placed inside the bag to identify the sampling location and depth.

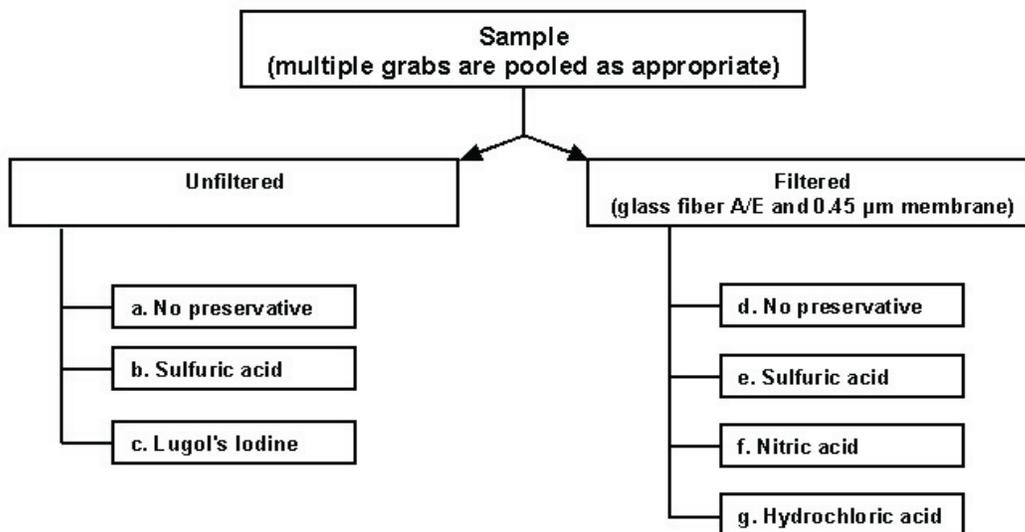
### 7.8.1 Sample Treatments

Before water samples are brought back from the field or shipped to the analytical laboratory, they receive one of the treatments listed (Figure 3) to prepare them for shipment or analysis. Note: hydrochloric acid preservation is not used presently in LTRMP but is listed for reference. All the constituents associated with a treatment are not necessarily analyzed in the LTRMP:

- a. *Unfiltered, No Preservative Added.* Suitable for turbidity measurement in the laboratory or subsequent processing for total suspended solids, volatile suspended solids, and chlorophyll-*a* measurement (Sections 4.5 and 6.1).
- b. *Unfiltered, Preserved with Sulfuric Acid (pH 2.5–3.0).* Suitable for total nitrogen, total Kjeldahl nitrogen, total phosphorus, total iron and manganese, and total organic

carbon. Although this sample is unfiltered, care must be taken to ensure that large (>2-mm) particulates (e.g., leaves or other pieces of vegetation, insects, larval fish) are excluded. This is necessary because the analytical laboratory cannot prepare a homogeneous sample for multiple determinations if large particulate material is included.

- c. *Unfiltered, Preserved with Lugol's Iodine.* Used for phytoplankton samples, Lugol's iodine is added in sufficient quantity to impart a tealike color to the sample.
- d. *Filtered, Nonpreserved.* Suitable for color, SRP, alkalinity, chloride, sulfate, and silica determinations.
- e. *Filtered, Preserved with Sulfuric Acid (pH 2.5–3.0).* Suitable for nitrate plus nitrite nitrogen, ammonia nitrogen, total dissolved phosphorus, acidified soluble reactive phosphorus (SRPH), total dissolved Kjeldahl nitrogen, and total dissolved organic carbon.
- f. *Filtered, Preserved with Nitric Acid (pH 2.5–3.0).* Suitable for dissolved metal cations.



**Figure 3.** Treatments used to prepare samples for shipment to the Long Term Resource Monitoring Program analytical laboratory.

- g. *Filtered, Preserved with Hydrochloric Acid (pH 2.5–3.0)*. Not used in the LTRMP, but suitable for some dissolved metals cations (Ca, Mg, Na, K) and dissolved organic carbon.

In addition to water samples, filtered residue is shipped to the analytical laboratory for further chlorophyll-*a* and suspended solids processing (Sections 4.5 and 6.1).

### 7.8.2 Filtration of Inorganic Chemical Samples

Two-stage filtration is used routinely in the LTRMP to prepare chemical samples for shipment and analysis of inorganic dissolved species (i.e., metals, nitrate, nitrite, ammonia, chloride, silica, SRP). Filtration for these constituents is normally completed on-site within 20 min of sample collection, or appropriate comments and QF codes are entered on the data sheet (Sections 8.3 and 8.4). To avoid cross-contamination, new filtration media are used for each sample. The first-stage filtration uses a glass-fiber (type A/E) filter, followed by a second (final) filtration through a 0.45- $\mu\text{m}$ , surfactant-free, cellulose acetate membrane filter (Nalgene® 191-2045). These steps are usually performed in a combined two-stage filter, but where necessary, the filtrate from suspended solids or chlorophyll-*a* filtration can be used as the first stage, followed by processing through a 0.45- $\mu\text{m}$  membrane. It is essential that the filtration apparatus and filtrate container be rinsed at least twice with a small volume (5–20 mL) of sample filtrate before water is kept for analysis. The initial flush of sample (5–20 mL) through the filter apparatus serves to remove carryover on the apparatus walls from the previous sample and removes most contamination that may be leached from the filter itself during subsequent filtration. If constituents from the sample adsorb to the filter media, this initial flush is intended to saturate or equilibrate the adsorption process. The flush water is discarded. The syringe filters in use by the LTRMP (Nalgene® 25-mm Syringe Filters Cat. 191-2045) have a maximum operating pressure of 75 psig/5.1 bar, which can be exceeded with the use of mechanical pressure. Extreme care must be taken to ensure that the

maximum operating pressure is not exceeded. Filtration equipment must be checked with an in-line pressure gage periodically and before initial use to ensure that maximum pressures are not exceeded.

Although two or more differing containers of filtered water (acidified, not acidified, QA/QC split, and QA/QC split plus spike) may be sent to the laboratory for each sample, the filtered water used to fill all these containers must come from a single common “pool” of filtrate. Therefore, enough water must be filtered into a common container to supply all the acidified and unacidified sample bottles for the original sample and the QA/QC (as appropriate). The common filtered sample may be held in any sample container with adequate capacity that also meets the requirements of cleanliness and material composition for the analytes being sampled.

For samples and analyses in which the phytoplankton cell contents are of little or no quantitative consequence (i.e., total suspended solids with high inorganic content), vacuums, or pressures are limited only by the limitations of the filters and filtering apparatus.

### 7.8.3 Acid Preservation of Samples

*Standard Methods* (APHA 1992) for the acid preservation of samples calls generally for pH levels <2.0, but extremely low pH has been found to interfere with automated sample analysis (i.e., because of altered reaction rates and color development) at the LTRMP analytical laboratory. Therefore, for acid preservation of samples in LTRMP water quality monitoring, a pH level between 2.5 and 3.0 is specified. Field teams verify that this level is attained by use of pH test strips in the field. Preservation is performed with reagent grade acid that is certified to contain no LTRMP analytes at concentrations >1 ppb. Care must be taken to ensure that the acid and acid-dispensing equipment does not become contaminated. The dispensing container must remain sealed and kept inside a protective outer container (e.g., plastic bag) when not in use. Immediately before acid is added to the first sample at a new location (or more than 30 min have elapsed since acid

was dispensed), a few drops of acid should be dispensed into a proper waste container to clear any contaminant from the dispenser. The dispensing device must be handled in such a way that contaminated or used acid is not drawn back into the dispenser. Disposable, powderless gloves are worn when handling acid.

Acid preservation should be performed only in the field after sample water has been placed in the sample container (add acid to water, not water to acid). Sample containers should not be “preacidified” with concentrated acid before proceeding into the field. Although this practice is attractive because it allows all acid handling to be conducted in controlled conditions and removes the need to transport significant volumes of dangerous chemicals into the field, it creates problems. Specifically, holding concentrated nitric and sulfuric acid in plastic sample containers degrades the plastic, creating a range of breakdown products, and can make the container brittle. It can also impregnate the walls of the sample container with analytes (nitrate, sulfate, etc.) that are not removed by normal washing, but leach slowly into samples during storage.

Acid preservation of filtered samples is performed as follows:

- a. *Partly Fill the Sample Bottle to be Acidified.* The sample to be acidified is processed before the nonacidified sample so that if something goes wrong (i.e., excess acid is added), the acidified sample can be discarded and additional water can be filtered into the common, unpreserved, filtrate pool (Section 7.8.2) for a second try. If the nonacidified sample were processed first and then a mistake was later made in processing the acidified sample, then the entire volume of both the nonacidified and acidified sample would have to be discarded because (1) any additional filtrate required to prepare the acidified sample would not come from the common filtrate pool used to fill the nonacidified sample container and (2) water cannot be transferred back into the common filtrate pool from

the unacidified container because of contamination risk.

- b. *Adjust the pH.* The goal is to add the minimum amount of acid required to get the sample into the proper pH range (2.5–3.0). Keep in mind that one drop (0.03 mL) of concentrated acid in 60 mL of distilled water will produce a pH of about 1.7. Therefore, depending on the buffering capacity of the sample, one drop of acid may be enough. Also, keep in mind that below pH 4.5 the buffering capacity of most water drops off dramatically (because bicarbonate has all been converted to carbon dioxide). Test the pH with a fresh test strip as needed. Beware of the contamination potential. Test strips are not inserted into sample containers, but a few drops of preserved sample are dropped onto the test strip to determine pH.

Experience over the years has shown the approximate additions of acid (Table 10) that create the proper pH in 60-mL samples from the

**Table 10.** Acid additions required to reach the desired pH for preservation of 60-mL Long Term Resource Monitoring Program water quality samples.

Acid preservative	Sample type	Volume added
Concentrated sulfuric acid	Dissolved inorganic nitrogen	1–2 drops (30–60 µL)
Concentrated nitric acid	Dissolved metals	5–6 drops (150–180 µL)
Concentrated sulfuric acid	Total nitrogen and total phosphorus	1–3 drops (30–90 µL)

Upper Mississippi and Illinois Rivers.

- c. *Add the Remaining Filtered Volume and Seal the Container.* After the acid has been added, the remaining volume of filtered water can be added to the sample bottle. With 125-mL bottles, this sequence is not critical, but because 60-mL bottles are used by the LTRMP, it will be necessary to leave enough headspace so that acid can be added without splashing any acid or sample from the container. In QA/QC

procedures, the sample bottle (volumetric flask) is filled to the volume mark with additional sample after the acid is added. This final topping off of the sample will raise the pH slightly (typically <0.1 pH unit).

Acid preservation of unfiltered samples is performed as with filtered samples except that the order of sample processing is not critical because a single pool of filtered water is not used. Unfiltered water may have slightly greater buffering capacity than filtered water because of suspended carbonates and other buffering materials and may therefore require slightly greater acid addition to reach the desired pH.

#### **7.8.4 Filling of Sample Bottles: Rinsing and Agitation**

Sample containers should be rinsed with sample twice before keeping the final sample. Adequate headspace must be left in the subsample container for preservatives and freezing. Containers should be filled to the rounded shoulder of the bottle (about 10 mL of empty space in a 60-mL bottle). Suspended particulate material in river water can settle rapidly; therefore, it is critical that whole-water samples be vigorously agitated before and during transfer to subcontainers (including transfer to filtering apparatus). In LTRMP water quality monitoring, pumps may be used for delivery of sample water to the filtration apparatus, but not for the transfer of whole water samples into subcontainers (Section 7.8.5).

Care must also be taken to ensure that contaminants (including dust, rain, and snow) do not enter the whole water or subsample container during the transfer process.

#### **7.8.5 Filtration Using a Peristaltic Pump**

Instead of using a syringe to pressure-filter a sample, a peristaltic pump may be used to transfer the water sample into the filtration apparatus under suitable low pressure. This is only applicable when the filtrate is to be analyzed; it is not appropriate when the

particulate phase of the sample is to be retained (i.e., suspended solids or chlorophyll-*a* analysis). The preferred method for obtaining filtrate by pump-driven filtration is to place a subsample (split) from the collected ambient water sample into a separate container for filtering (e.g., plastic cylinder) that serves as the source water for the pump. The main sample must be appropriately agitated immediately before the subsample is transferred into its separate container where further mixing is performed. In some situations (e.g., ice forming in the sample and on the apparatus), it may not be feasible to transfer a subsample to a separate container for filtration. In this instance, the primary sample may be used as the source water for pump filtration (and used as a whole-water sample) if precautions are taken to ensure that the filtering procedure does not alter the composition of the primary sample by selectively withdrawing particles or supernatant: (1) any whole-water subsamples should be withdrawn before filtration commences; (2) the primary whole-water sample should be agitated during filtration at least once every 60 sec or whenever the filter media is changed, whichever comes first; and (3) the primary sample is fully remixed whenever sediment is observed on the container bottom or a gradient in particulate concentration is observed in the sample container.

The following additional guidelines must be followed when filtering samples: (1) because the filters have pressure limits specified by the manufacturer and mechanical pumps can easily exceed those limits, it is imperative that pressures be checked periodically by a suitable means (e.g., in-line gage). Filter membrane rupture can occur without any visible signs of defect. (2) Mechanical devices intended to increase hand pressure by way of leverage (e.g., “can-crushers”) can produce pressures much greater than filter limits and are not easily controlled. Their use is therefore strongly discouraged. (3) Past experience has demonstrated quality control problems with some filter manufacturers; therefore, the only final-stage filter approved for LTRMP use is the Nalgene® 25-mm syringe filter (Cat. 191-2045).

### 7.8.6 Freezing of Samples for Preservation

Chlorophyll-*a*, suspended solids, soluble reactive phosphorus, silica, and chloride samples may all be preserved by freezing at temperatures at or below -10°C. Chlorophyll-*a* samples must be kept in total darkness while frozen and any exposure to acid fumes during storage must be rigorously avoided. Do not store acid in the refrigerator used to hold samples and keep the freezer or refrigerator in an area that is isolated from any acid washing or other acid use.

#### 7.9 Holding Times For Storage and Shipment of Chemical Samples

Analysis of water samples for chemical constituents should be performed as soon as practicable to avoid changes in the sample during storage. Sample holding times and conditions are published in *Standard Methods* (APHA 1992, 1998) and are observed by the LTRMP, with some exceptions (cf. Table 11). **Note that total**

**holding times are from sampling to analysis, not just the time held at the field station before shipment to the laboratory.** Keep in mind that samples may be held 1 to 3 weeks in the laboratory before analysis.

#### 7.10 Sample Containers: Size, Composition, and Integrity

All samples that are shipped to the laboratory for analysis must be placed in the appropriate size and type container (Table 11) and must be properly tagged to ensure correct storage and handling. All containers must be leak-free (with a tight seal) so that the sample does not leak out and contaminants are unable to enter. Leaking containers are sometimes difficult to detect when sample bottles are kept in an ice-water mixture, and this practice should be avoided. If a leak is detected in a sample bottle AFTER it has been immersed (i.e., in a cooler of ice-water), the sample must be discarded as contaminated—it cannot be transferred to another container.

**Table 11.** Preservatives, containers, and holding times used for water quality monitoring samples in the Long Term Resource Monitoring Program.

Constituent	Preservative	Container type and size	Holding time
Chlorophyll- <i>a</i>	Total darkness, freezing	Planchet, glass fiber 47 mm; culture tube, glass fiber 25 mm	30 days dark, frozen
Dissolved metals	HNO <sub>3</sub> , pH 2.5-3.0	Plastic (60 mL)	60 days
Dissolved Si, chloride, soluble reactive phosphorus, sulfate	Freezing	Plastic (60 mL)	For SRP, 48 hours unfrozen, 28 days frozen. For silica, 28 days (silica must be at pH >6)
Nitrate, nitrite, ammonium	H <sub>2</sub> SO <sub>4</sub> , pH 2.5-3.0	Plastic (60 mL); glass container also acceptable)	28 days
Phytoplankton	Lugol's iodine	Amber	Indefinite after preservation
Suspended solids <sup>a</sup>	Freezing	Planchet, glass fiber 47 mm	28 days after filtration, kept frozen
Total nitrogen and phosphorus	H <sub>2</sub> SO <sub>4</sub> , pH 2.5-3.0	Plastic (60 mL)	28 days
Zooplankton	Ethanol, 80%	Not specified	Indefinite after preservation

<sup>a</sup>Holding time in *Standard Methods* (APHA 1992) is 7 to 14 days.

Plastic containers can become brittle with age and after exposure to acid. This is often accompanied by discoloration of the plastic. Any containers that become discolored or inflexible should be discarded.

Before shipment to the laboratory for analysis, field samples must be processed as described previously in this section and (if necessary) transferred to appropriate containers. The LTRMP follows the specifications of *Standard Methods* (APHA 1992) regarding the composition of containers used for holding samples for analyses (Table 11).

### 7.11 Quality of Water for Cleaning and Sample Preparation

One of the most important aspects of chemical analysis is the preparation of reagent water used for dilution, washing, and preparation of blanks. Water used for cleaning of sample containers and sampling equipment or used in analysis and sample (blank) preparation in LTRMP is called deionized (DI) water and must meet published standards of purity (APHA 1998). This is gaged by the conductivity of water. Commercially available distilled water cannot be assumed to meet these standards without verification. If possible, reagent-grade water should be obtained from the LTRMP analytical laboratory or other quality controlled source. Water is prepared by the LTRMP laboratory using ion exchange and micro-filtration (0.45  $\mu\text{m}$ ) and typically has a resistivity of 17–18.2 megohm-cm at 25°C when fresh. Water used for blank preparation in the field should have a resistivity of >1-megohm-cm (<1  $\mu\text{S}$  conductivity) at 25°C. Low-quality water (APHA 1998) suitable for field washing of equipment should have a resistivity of >0.1-megohm-cm (<10  $\mu\text{S}$  conductivity) at 25°C.

### 7.12 Cleaning of Sample Containers

All containers used for sample collection, storage, or shipment must be appropriately cleaned. For the inorganic constituents analyzed in LTRMP, cleanliness can be verified by testing the conductivity of rinse water from cleaned

containers. To conduct this test, a cleaned container is rinsed with a volume of reagent-grade water (specific conductance <0.5  $\mu\text{S}$  or resistivity of >2-megohm-cm) not exceeding 40% of the total container volume (i.e., <25 mL of rinse for a 60-mL container). The resultant rinse water should have a specific conductance  $\leq 1 \mu\text{S}$  (or resistivity of  $\geq 1$ -megohm-cm at 25°C). Statistical-based quality control in which at least 10% of all bottles washed are subjected to testing provides acceptable verification of cleanliness. In July 2001, the LTRMP implemented a central facility for machine washing of all sample containers used for chemical analysis. This facility exceeds the 1- $\mu\text{S}$  standard for rinse water on clean bottles, and greater than 10% of all bottles washed are subjected to quality control tests. All batches of clean bottles are tested for compliance with the above cleanliness standards before release to the field teams.

Manual washing of sample bottles used for shipment of inorganic chemical samples to the laboratory is no longer routine in the LTRMP, and the following guidance is provided for historical reference and for use in exceptional or emergency circumstances when laboratory-washed bottles cannot be obtained. Inorganic chemical samples shipped to the laboratory in hand-washed bottles after July 2001 should be marked with appropriate QF codes and data sheet comments. Except as noted below for chlorophyll-*a* and phytoplankton, all hand-washed containers used for the analysis of chemical constituents are cleaned using (1) a soap-and-water wash with phosphate-free detergent, (2) tap water rinse, (3) acid soak, and (4) a final distilled water rinse as follows:

- a. Add a few milliliters of Liquinox® detergent (phosphorus-free; Alconox, NY) to a clean washtub or sink and fill with hot tap water. Thoroughly scrub the inside of exposed areas and the outside of glass and plasticware.
- b. Rinse off all traces of soap with hot tap water, then thoroughly rinse twice or until the glassware is free of all traces of soap. This is an important step.
- c. Using powder-free gloves, fully submerge the item in the acid bath (10% HCl) and

- soak for at least 30 min but no longer than 2 hours.
- d. Remove item and rinse immediately with reagent-grade water at least three times; do not set glass or plasticware on counter during this process.
  - e. Set cleaned item on precleaned drying area with sample surfaces facing down to prevent dust contamination. Place small items (e.g., caps, glass stoppers, forceps) and fully exposed items in a tent of foil so dust will not contaminate surfaces and to allow to dry to completion (2–3 days).

The following containers are subjected to cleaning processes that differ from those described above:

- a. *Chlorophyll-a*. Fluorimetric cuvettes are not cleaned before use. However, cuvettes with obvious soiling, chips, or scratches are discarded. It is essential that no containers used in any step of chlorophyll-*a* analysis (including sample collection) come in contact with acid or acid fumes. Note that hydrochloric, nitric, and acetic acids are volatile, and the fumes can permeate an entire room. Sulfuric acid is nonvolatile, but any trace of sulfuric acid solution left on a surface or in a container will concentrate as the water evaporates.
- b. *Phytoplankton*. Hot water (>40°C) followed by a single distilled water rinse is adequate for phytoplankton containers.
- c. *Two-liter Container for Raw Water*. Hot water (>40°C) rinse with vigorous agitation. Pressure spray or brush is used as needed to remove any adhering material. No acid or detergent can be used for these containers. Following hot water rinse, the containers receive two rinses with reagent grade water.

### 7.13 Cleaning of Sampling Devices and Tubing

Because LTRMP water quality monitoring does not include trace substances (<1 µg/L) or organic contaminants, sampling equipment and tubing need not be subjected to cleaning by caustics, solvents, or detergents between sample sites. Repeated rinsing with ambient

sample water before sample collection is usually sufficient. Tubing used for sample collection by pump is cleaned by allowing at least 5-tube volumes of sample water to pass through the tubing before sample collection. Care is taken to ensure that no particulate material has settled in the tubing. Grab-sampling devices, such as Van Dorn samplers, are cleaned by submergence at the sampling location. At the end of a sampling day, tubing should be cleaned with a rinse of 10% HCL, followed by a thorough rinse (at least 10-tube volumes) with reagent grade water.

Warning! Sampling devices (including tubing) can harbor invasive species (some microscopic) during transport among sites. Proper care must be taken to ensure that sampling equipment does not transport exotic species (e.g., zebra mussels) into pest-free areas. Flushing equipment with household bleach should suffice usually, but field teams should consult with local resource managers to ensure that specific threats are being properly addressed with this approach. Field crews must also take care that sanitation measures do not damage or contaminate their sampling equipment and should consult with the component coordinator in the development of specific sanitation procedures.

### 7.14 Bar Code Labeling of Samples and Data Sheets

A total revision of the LTRMP water quality data sheet was implemented in spring 1993. The new data sheet (Section 8, Figure 4; Appendix J) includes the use of bar codes for automated tracking of samples and data. Bar codes serve three major purposes in LTRMP water quality monitoring operations:

- a. *Streamlined Error Tracking and Correcting*. Every item of data in the database is permanently linked to the bar code on its original data sheet so that every item (or error) in the LTRMP database has a simple, unambiguous identity and can be tracked quickly and easily to its ultimate source.
- b. *Streamlined Laboratory Handling and Tracking*. The sample bar code is used to track samples through the analytical

laboratory. The analytical results from the laboratory are linked back to the data sheets by these bar codes. This allows the laboratory to easily and efficiently track samples and analytical results. It also provides a method for conducting laboratory QA/QC blind testing.

- c. *Data and Sample Accounting and Accountability.* The bar codes provide an automated method for tracking data and samples through the entire processing system. Data or samples that are lost, duplicated, overdue, or otherwise mishandled will be readily detected and appropriate corrective action can be taken.

The use of bar code labels in the LTRMP water quality monitoring has undergone revisions since 1993, but in general, the bar code labels are used as follows:

- a. Bar code labels are not taken into the field; they are attached to sheets and sample containers at the field station. A temporary labeling system is used in the field (color-coded tags are provided for this purpose).
- b. Each data sheet receives a unique data sheet bar code label; this bar code is printed (or adhesive label attached) at the top of the data sheet in the space provided.
- c. Each sample collected also has an associated bar code. One copy of the sample bar code is attached (or printed) on the data sheet in the space provided and one is attached to each bottle, planchet, etc., associated with a sample. Bar code labels are attached to sample containers in such a manner that the entire bar code (1) is visible to the scanner (i.e., not wrapped around corners); (2) appears in a single plane (flat); and (3) does not interfere with analytical instruments (e.g., fluorometer cuvettes must be labeled outside the optical section of the cuvette). For samples with color-coded tags, the bar code is attached to the tag. Although the sample bar code is the only identifying information that the analytical laboratory records or uses for individual sample identification, samples that require supplemental information for processing

(e.g., tare weight or filter volume) must be properly labeled with this additional information. Filter volumes are included in the electronic data sheet transmitted to the laboratory over the Internet. Future enhancements are planned for tare weights to be tracked by the laboratory with a separate bar code label. Additional details are provided in Section 8.6.

### *7.15 Sample Submission Procedures*

All samples for laboratory analyses are sent to the LTRMP laboratory at La Crosse, Wisconsin, by overnight courier and are preceded by electronic sample records transmitted to the laboratory over the Internet using file transfer protocol (FTP). A different transfer protocol (e.g., Virtual Private Network) will probably be implemented in 2004 to overcome the security issues associated with FTP. These records describe the number and type of samples included in the shipment, their identifying bar code numbers, and all other information recorded on the field data sheet. The electronic records (log files) are created by a field team member using computer software specifically developed at UMESC for this purpose (ScanLog32). An earlier version of this software (1994 to 2000) produced electronic files that were transmitted by field teams to the laboratory by electronic mail (e-mail). The version of the software now in use generates and transmits records directly to UMESC using the Internet and FTP. Additional details are provided in Section 8.6.

#### **7.15.1 Scanning Samples for Custody Tracking and Shipment**

Field teams use the ScanLog32 software to scan and check the bar code on each sample as it is placed in the shipment container; this is to produce a verified custody record of all samples that were placed in the shipment container and sent to the laboratory. After this final scan is complete, the shipment container should be sealed and shipped. The ScanLog32 software will notify the user when all samples have been

accounted for, and it will then print paper copies of the data sheet for local archiving and also transmit the data sheet records to the LTRMP laboratory.

### **7.15.2 Packaging Samples for Shipment**

The ScanLog32 software is tightly coupled to the concept of a sample batch (Section 8.1) and requires that samples and data be grouped in batches and that each batch be processed and sent to the laboratory as a single entity. This concept, however, does not preclude the field team from sending multiple batches to the laboratory in a single shipping container. This is an acceptable practice when multiple types of sampling (SRS, FSS, or special projects) have been conducted during the same interval (e.g., same week) and it is efficient to combine samples from multiple batches in a single shipping container (cooler). When samples are shipped this way, the batches must be kept separate and identifiable (i.e., in separate, labeled, zipper-lock bags) within the shipping container.

Successful shipment to the laboratory requires that all samples remain cold during shipment and that frozen samples not thaw before arrival at the laboratory. It is also necessary to pack the shipment so that glass containers (e.g., fluorometric chlorophyll-*a* tubes) do not break, and plachets and chlorophyll-*a* tubes are not exposed to moisture that results from sample leakage or condensation. The external surface of sample containers should be dry before shipment to make leakage obvious and to minimize damage to bar code labels and other materials in the shipment. To further protect bar code labels on frozen samples, a paper towel or other suitable moisture-absorbing material should be placed inside sealed bags of sample bottles to trap condensation and any melt water derived from frost.

To prevent thawing of frozen samples during shipment, the frozen samples should be packed toward the center of the cooler. Plastic containers of frozen coolant (commercially available or prepared using 2:1 ethylene glycol:water solution in clean plastic beverage containers with 10% headspace) should be packed around

(and among) frozen samples. Plachets and chlorophyll-*a* tubes are placed in sealed bags above midheight in the cooler (to avoid immersion if leakage occurs). Some teams have used “bubble wrap” to encase the chlorophyll-*a* tubes, but generally this is not required. The cooler should be filled with samples, coolant, and auxiliary packaging material as needed to prevent any significant free movement of the samples within the cooler during shipment.

In completing the shipping label, be careful that all necessary fields, particularly the destination address, are complete and legible. Obtain and hold the documentation provided by the carrier until the shipment arrives at the LTRMP laboratory. The outside of all shipping containers should have the name, address, and phone number of the field station permanently marked and clearly visible on multiple surfaces. This may allow the shipment to be recovered if the shipping label is defaced or removed in transit. Standard overnight delivery is used routinely. Do not ship on Friday or immediately before a federal holiday as the LTRMP laboratory will not be able to receive the samples on the following day.

## **8. Field Data Recording and Reporting**

Water quality data sheets provide the basic information collected by LTRMP water quality monitoring. The data sheet is used to record conditions and samples collected (custody) at each monitoring site and to document sites that are inaccessible or not sampled for a variety of reasons. Because the water quality data sheet, in either paper (Appendix J) or electronic form (Figure 4), is the primary source of water quality information for the LTRMP, the importance of accuracy, legibility (paper version), and completeness cannot be overemphasized. Errors on the data sheet are difficult, and sometimes impossible, to detect and correct. If illegible or incorrect data are recorded, the time spent in the field may be totally wasted. Likewise, the laboratory resources spent analyzing any samples associated with incorrect field data are lost. Program resources, better used elsewhere, are also required to track down and correct

**LTRMP Water Quality Data Sheet (Unmodified)**  
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(if possible) data sheet errors. Errors that go undetected will eventually undermine the accuracy and credibility of the LTRMP.

In 2001, the LTRMP deployed electronic data sheet software that intercepts the errors most commonly associated with field data recording and eliminates legibility issues, but the ultimate responsibility for obtaining and recording accurate monitoring data in the LTRMP still remains with the individual field team member. All field teams are to carefully examine data records before they are transmitted to the laboratory and database.

### *8.1 Sample Batches*

In LTRMP water quality monitoring, the term “sample batch” is used to describe samples and associated data that are collected within a short interval (e.g., a day or week) for a single sampling project and with a single sampling design (FSS, SRS, or special project). The temporal span of a batch is flexible; for example, an entire SRS episode, or a single day of sampling (SRS or FSS) could be processed as a single batch. However, a batch should never extend beyond a full SRS episode or an FSS period (e.g., a week), because this requires extended storage of samples before analysis. The ScanLog32 software does not impose any limit on the time span of a batch, but it will not allow samples from differing projects or sampling designs (SRS vs. FSS) to be combined into a single batch.

### *8.2 Crew Leader and Recorder Codes*

Because the individual field team leader or member has ultimate control over the quality of data obtained in the LTRMP, the individuals who lead the field team and record the data are assigned a unique code. This code is recorded on each data sheet for which the individual is responsible (either as a team leader or a data recorder). The code is assigned by the LTRMP database administrator and is permanently associated with an individual. It is not transferred

to another employee or reused after an employee leaves the Program.

### *8.3 Data Sheet Description*

The water quality data sheet (Appendix J) was substantially revised in June 1993, additional minor changes were made in July 1999, and conversion to an electronic version was completed in July 2001 (Appendix J). The 1993 revision included several major changes: (1) use of bar code labeling (see above), (2) Quality Factor (QF) codes for each data item, (3) use of wave height codes, (4) recording of substrate information, (5) recording of vegetation information, (6) optional recording of geographic position, (7) recording of samples submitted for analysis, (8) allowance for up to six sample depths (or sample types) per site, and (9) allowance for QA/QC tests to be assigned. The previously recorded depth code was eliminated from the data sheet as this classification can be readily derived from sample and water depth as needed. The next revision (1999) included an additional sample row (for a total of seven), updated the quality factor information, added a provision for recording the monitoring instrument serial number, added a capability for using an additional bar code to link the data sheet to other projects or LTRMP components, and corrected a few minor errors.

This section provides description and instructions on the use of the data sheet (Figure 4 and Table 12). Detailed descriptions of parameters and methods are provided in other sections.

### *8.4 Use of Quality Factor Codes*

Most fields on the water quality data sheet have associated QF codes that can be assigned to indicate problems or other special considerations. The electronic data sheet provides valid choices for the QF codes as pop-up or drop-down menu items. This section (Table 13) gives additional descriptions and guidance for the use of QF codes on the LTRMP water quality data sheet.

**Table 12.** Description of the Long Term Resource Monitoring Program (LTRMP) electronic water quality data sheet fields with instructions for use and reference to procedures that relate to the specific data sheet entry. Figure number references individual fields in Figure 4

Figure number	Field label	Description and coding instructions	Related section(s)
1	Field station	Numeric designator of field station 1 = Lake City, Minnesota 2 = Onalaska, Wisconsin 3 = Bellevue, Iowa 4 = Pool 26, Illinois 5 = Open River, Missouri 6 = Havana, Illinois 7 = Upper Iowa University 0 = UMESC, any location, special projects only	1.1
2	Location code	ScanLog32 provides a drop-down menu of valid choices. See appropriate sections on fixed-site sampling (FSS) and stratified random sampling (SRS) site identifiers for the syntax of the location code. In SRS, the location code may have an optional "A" suffix appended if it is an alternate site. A permanent location code dictionary is maintained in ScanLog32 for FSS (Appendix B). The SRS location code dictionaries (with associated coordinates and strata designations) are supplied quarterly by UMESC. See further instructions on the site comment field for documenting the use of alternate sites.	1.5, 1.6, Appendix B
3	MM DD YYYY	Date of site visit. Format is MM/DD/YYYY.	None
4	HH MM	Time of site visit as central standard, 24-hour clock. At the user's option, the electronic data sheet will fill this field automatically during data acquisition. Clicking on the small clock icon adjacent to these fields will update this field to the present clock time.	1.3
5	# Rows	Number of samples (depths) collected at this location. Number must match the number of sample or depth rows filled out (maximum number of records is seven). This is filled automatically by the electronic data sheet and is not accessible to the user.	3.11
6	Project code	Routine LTRMP sampling has an M project code; other codes used for special projects are obtained from the component coordinator as needed. This field is filled automatically by the electronic data sheet.	None
7	Sheet bar code	On the paper version of the data sheet, a unique data sheet bar code is attached at this location. The electronic data sheet provides this label automatically or the user can manually enter a value. Note that the serial number used for the data sheet may also be used as a sample bar code. The sheet and sample serial numbers are independent series, but typically their use is closely coordinated so that the sheet bar code and the first sample bar code on the sheet are the same.	7.14
8	Z <sub>max</sub>	Z <sub>max</sub> is always measured as the vertical distance from the free (unconfined) surface of the water to the substrate. It is reported to the nearest 0.01 m, but in water >1 m deep the value can be rounded to the nearest 0.1 m.	3.1, Figure 2
9	Secchi	Secchi disk transparency is measured to the nearest centimeter. It cannot exceed the value for Z <sub>max</sub> (e.g., if Z <sub>max</sub> = 1.10 m, then Secchi disk transparency cannot exceed 110 cm).	4.4, 4.7
10	Wave code	Numeric code based on Beaufort Scale is entered here. Valid choices appear at the bottom of the paper data sheet and as a pop-up menu on the electronic data sheet.	3.4, Table 5

Table 12. Continued.

Figure number	Field label	Description and coding instructions	Related section(s)
11	Zice cm	Ice depth—measured to the nearest centimeter.	3.2, Figure 2
12	Zsice cm	The submerged thickness of the $Z_{sice}$ measured from the bottom of the ice to the water surface, rounded to the nearest centimeter.	3.2, Figure 2
13	% Ice	Percent ice cover, rounded to the nearest 10%. If any ice less than 10% is present, a 1 is reported.	3.8.1
14	Zsnow	Snow depth ( $Z_{snow}$ ), measured to the nearest centimeter.	3.8.4
15	% Snow	Percent snow cover, measured to the nearest 10%. If any snow less than 10% is present, a 1 is entered.	3.8.5
16	Site type	Indicates the type of sampling location (this field is filled in automatically by ScanLog 32): 0 = SRS primary site 1 = SRS alternate site 2 = FSS site 3 = Other type of sampling site	1.5, 1.6, 1.7, 1.8
17	Summary code	Specifies a condition that is applicable to all measurements taken at the site. This field was not used as of date of publication. Valid choices appear as a pop-up menu on the electronic data sheet and include: Blank = Site is OK, same as code "5" 0 = Reserved for future use 1 = Obsolete (one or more of the data values for this site are suspected or known to be in error) 2 = Obsolete (possible equipment malfunction) replaced by individual quality factor (QF) codes 3 = Obsolete (site probably nonrepresentative because of local, short-term conditions) 4 = Obsolete (data analysis suggests the observation is atypical, but no reporting or transcription errors have been identified) 5 = Same as blank entry 6 = Site frozen to bottom, or close enough to prevent sample collection 7 = Site too shallow to sample 8 = Site dry (dewatered), 7 is implied 9 = Site inaccessible (and not 7 or 8)	7.1, 7.5
18	Substrate	Measured at least once per quarter at all sites in shallow, low-velocity areas (i.e., contiguous backwaters). Optionally measured at other locations. Grabs or other suitable surficial samples are used to make the determination.  This measurement is required in backwaters only, but at the discretion of the field team these measurements can also be made in channels. In FSS (other than channel sites), measurements are made at least once per quarter. They are required in backwaters during all SRS episodes.	3.9
19	Veg cover	A one-digit approximation of aquatic vegetation coverage within the sampling radius of the sampling location. Valid entries are listed on the data sheet or as pop-up menu items on the electronic data sheet. A value is recorded at every site visit. 0 = 0% 1 = 1–19% 2 = 20–49% 3 = >50%	3.10.1

Table 12. Continued.

Figure number	Field label	Description and coding instructions	Related section(s)
20	Veg density	A one-digit semiquantitative assessment of stem concentration within the sampling radius of the sampling location. Valid entries are listed on the data sheet and as pop-up menu items on the electronic data sheet. Recorded at every site visit, but left blank if no vegetation is present. Note the difference between veg cover and veg density. An area can be completely covered with a sparse stand of vegetation (e.g., <i>Nelumbo</i> ). 1 = Sparse 2 = Dense	3.10.2
21	Veg type	The type(s) of vegetation present in the immediate sample area. Valid entries are listed on the data sheet and as pop-up menu items on the electronic data sheet. Left blank if no vegetation is present. S = Submergent E = Emergent F = Floating B = Two or more of the above categories C = Combination of S, E, or F	3.10.3
22	Cross-link bar code	Optional field provided to link the data sheet to other projects or data. This identifier should also appear on the data sheet(s) from the other project(s) to which it is linked.	None
23	Method	Indicates the method used to locate sampling sites. This field is used only for special projects where sampling locations are determined in the field rather than from predefined sampling locations. This is frequently used in the LTRMP fish component, but not water quality. As of September 28, 2000, a 1 is the default provided by ScanLog32 and is the only valid entry.	1.4
24	Zone	Universal Transverse Mercator (UTM) grid zone used to determine easting and northing coordinates (see next two fields)	1.4
25	Coordinates (East/West)	UTM coordinate east of the reference meridian. Not used in routine monitoring, but available for special projects to record field-obtained site coordinates.	1.4, 1.6
26	Coordinates (North)	UTM coordinate north of the reference parallel. Not used in routine monitoring, but available for special projects to record field-obtained site coordinates.	1.4, 1.6
27	Accuracy	This field was intended originally to record the accuracy of global positioning system or other positioning system coordinates. It is not used for routine monitoring, but is available for use in special projects.	None
28	Field derived stratum	Describes the stratum in which an SRS site is actually found if it differs from the original designation. Valid choices appear on the paper data sheet and as a pop-up menu on the electronic data sheet. This designation is recorded in the LTRMP database as "field derived stratum." It is used in data interpretation, but it is not used for updating the base map or modifying the stratum code assigned to the geographic coordinates of this location.	1.6

**Table 12.** Continued.

<b>Figure number</b>	<b>Field label</b>	<b>Description and coding instructions</b>	<b>Related section(s)</b>
29	Sample type	Indicates whether routine or Quality Assurance and Quality Control (QA/QC) sampling is reported on this data sheet. Blank field or zero indicates routine sampling, <i>I</i> indicates QA/QC sampling, and that the QA/QC categories are applicable to the reported sample rows.	2.1.1, Table 4
30	Instrument code	The serial number (or other unique identifier) of the multiparameter instrument used to obtain readings in the sample rows. The electronic data sheet automatically carries this identifier forward to new sheets.	2.2 Appendix D
31	Recorder code	Three character identifier (normally numeric) for the individual who records the field data. Each field team member obtains this unique identifier from the LTRMP database administrator. It is not shared or reused.	8.2
32	Crew leader code	Three-character identifier for the individual leading the field team. Each individual field team member obtains this unique identifier from the component coordinator.	8.2
33	Site comments	Also called station comments—contains up to 80 characters of general site observations. No punctuation (commas, ampersands, or quotes) may be used in this field. An entry is required in this field if no depth rows are filled (# rows = 0), if a turbidity sample was diluted for analysis (ScanLog32 inserts comment automatically), or an alternate SRS site is being sampled. If an alternate site, then comments should indicate the original site that is being replaced. A comment should also be recorded on the sheet associated with the inaccessible or unsuitable primary SRS site.	
34	Z	Sample depth in meters, recorded to the nearest 0.01 m when <1 m; and to the nearest 0.1 m when ≥ 1 m.	3.1
35	Temp	Water temperature to the nearest 0.1 °C. Note that small negative values (-0.1 to -0.2) are possible.	4.6
36	DO	Dissolved oxygen concentration to the nearest 0.1 mg/L. Values above instrument limits (e.g., 25 mg/L) must be accompanied by a QF code of 2 (off-scale high).	5.6
37	pH	pH to the nearest 0.1 pH unit.	4.2
38	Cond	Conductivity (also called specific conductance) to the nearest whole $\mu$ S/cm.	4.1
39	Turb	Nephelometric turbidity unit (NTU; to the nearest whole NTU). This value is derived from raw instrument NTU (next field) and is the same as the raw reading if that is less than 100 NTU. Raw samples that exceed 100 NTU are diluted with deionized water to read within the 30 to 50 NTU range. The dilution factor is then applied to estimate the original NTU. Record a QF code of 8 (sample diluted) for this field when dilution is required.	4.4, 4.5, 4.7 Appendixes D and J
40	Raw NTU	Nephelometric turbidity (to the nearest whole NTU) as read from the field turbidimeter. A QF code of 8 (sample diluted) is only applied to this value if the raw value is >1,000 NTU and could not be read without dilution.	4.7 Appendixes D and J

**Table 12.** Continued.

<b>Figure number</b>	<b>Field label</b>	<b>Description and coding instructions</b>	<b>Related section(s)</b>
41	Vel	Horizontal speed of water current (m/sec) to the nearest 0.01 m/sec. If QF code of C (category measure) is used, this is a flow category measurement (numeric code from 0 to 6).	3.5, 3.6, 7.4 Appendix D
42	Dir	The magnetic compass direction from which water is flowing past the sampling point, rounded to the nearest 10°. If velocity is ≤0.02 m/sec, this reading is optional and may be left blank with a QF code of X (parameter optional) or 3 (reading off-scale, low).	3.7
43	Sample Bar code	A sample bar code is placed here if any laboratory samples are submitted for this row. This block is left blank if no samples are submitted. For the first sample row on a data sheet, the sample bar code is usually the same as the data sheet bar code. Sample bar codes are not typically assigned during data acquisition in the field, but rather when samples are being processed for shipment to the LTRMP laboratory. The electronic data sheet will assign the sample bar code automatically if the user requests it.	7.15
44	Filtered and Unfilt. (chemical sample codes)	QF code is entered to indicate type and condition of samples collected for submission to the laboratory. Blank indicates sample not submitted (QF code of 5 indicates that a normally submitted sample was unobtainable or lost before submission).	2.3,8.4, Table 13
45	QA/QC sample types	This column provides guidance as to what type of QA/QC sample is reported on each row when the sample type = 1 (QA/QC). On the electronic data sheet, these labels are enabled only when sample type = 1 (QA/QC).	2.1.1
46	Tare/Serial	Electronic data sheet or electronic custody sheet only. This is the tare weight (five digits without the leading decimal) or five-character serial number from the planchet label or laboratory bar code. This value is usually entered when samples are being prepared for shipment, rather than during field data acquisition.	4.5, 7.8.5, 7.14
47	Vol (mL)	Volume (mL) filtered for suspended solids or spectrophotometric chlorophyll- <i>a</i> (CHLS). Entered on the electronic data sheet or electronic custody sheet only. Volumes are usually entered when samples are being prepared for shipment, rather than during field data acquisition.	4.5, 6.1, 7.8.5, 7.14
48	QF	Most fields on the data sheet have an associated QF code. Valid choices are listed at the bottom of the paper sheet and appear as pop-up menu items on the electronic data sheet. Unless a problem or special condition exists, the QF code is left blank.	2.3, 4.4, 4.7, 5.6, 8.4, Table 13
49	Sample comment	Electronic data sheet only. This provides the option of adding a sample-specific comment to the data sheet. This comment is not restricted in length (several hundred characters can be easily handled) nor in punctuation. Currently, these comments are stored in the laboratory database only, not the central LTRMP database.	8.6

**Table 13.** Description of water quality data sheet quality factor codes used in the Long Term Resource Monitoring Program.

Quality factor code	Description	Cross reference
Blank	No problems and no exceptional circumstances. When used as a sample submission code, this indicates no sample submitted.	Appendix C
0	Equipment inoperative. Equipment will not function or function is so intermittent or erratic as to render data unusable. Conditions that prohibit operation are covered under quality factor (QF) code of 5.	Appendix C
1	Equipment questionable. Measurement is reasonable and probably correct, but intermittent, erratic, or erroneous instrument behavior was noted immediately before or after the measurement.	Appendix C
2	Reading off-scale (too high). Actual value was too high for the instrument to measure (not an instrument error). The instrument's maximum value is recorded. A negative sign is not used, but a QF code of 2 must be recorded.	
3	Reading off-scale (too low). Actual value was too low for the instrument to measure (below detection or negative; instrument function is normal). The lower limit of the instrument is recorded. A negative sign is not used on the data sheet. A QF code of 3 must be recorded.	
4	Sample returned to laboratory for processing. This indicates that because of instrument or field conditions, an <i>in situ</i> measurement was not taken, but the sample was returned to laboratory for measurement or processing. This QF code applies only to samples that are normally processed or measured in the field. For turbidity readings, this code is not appropriate if the determination is made within 24 hours of sample collection.	Section 7.8.2
5	Sample unusable or unobtainable. This code provides explanation for missing data at a site. Additional site comments are required. If a sampling site is inaccessible so that no data can be obtained, this is indicated by absence of data rows (data sheet NROWS field is 0) and an appropriate site comment.	Sections 1, 7.5
6	Sample not representative of ambient conditions. The best sample that could be obtained may not reflect general conditions at the site. The quality of the sample is questionable, but is probably OK. Use QF code of 7 if the problem is contamination. If the sample is obviously unsuitable, then another sample should be taken or QF code of 5 should be used if a sample cannot be obtained. If this condition applies to the site in general, an appropriate site summary code should also be recorded (Table 12).	Section 2.3, Table 12
7	Sample possibly contaminated. It is likely, but not certain, that foreign material has entered the sample bottle. Additional explanation in the site comment is recommended. This QF code is generally used only for samples that are returned to the laboratory for analysis.	Section 2.3, Table 12
8	Sample diluted for analysis (i.e., for turbidity measurement). This QF code is used exclusively for turbidity measurements. The dilution volumes and resulting factors are recorded in the sample comments. This QF code usually applies only to the calculated turbidity value that results from dilution; it is not used to flag the original raw nephelometric turbidity unit (raw NTU) instrument reading from which the diluted reading was derived, unless readings are above 1,000 NTU, and dilution is required to obtain a reading.	Section 2.3, Table 12
9	Not used.	None

**Table 13.** Continued.

Quality factor code	Description	Cross reference
A	Nonstandard (alternative) method used for collection or processing of sample or measurement. Some innovative technique was needed to obtain a suitable sample or measurement. Additional explanation in site comment is required.	Sections 3.5, 3.6, 4.5, 4.7, 5.6
C	Category measurement is being used (i.e., for current velocity measurement).	Section 3.6
D	Instrument calibration is out of limits.	Appendix C
F	Operator error resulted in missed or unusable value.	
H	Sample holding time exceeded.	
X	Optional measurement not performed, or measurement is not applicable.	

### *8.5 Data Sheet Submission*

As of July 2001, LTRMP water quality data sheets are submitted electronically from the field station over the Internet directly to the LTRMP analytical laboratory with software (ScanLog32) developed by D. M. Soballe of the Upper Midwest Environmental Sciences Center (UMESC). Following laboratory processing, data sheet information is transmitted from the laboratory to the main LTRMP database. Before July 2001 and during a transition period extending from July 2001 to December 30, 2001, paper data sheets were submitted by the field station teams to a data entry contractor following instructions provided by the LTRMP database administrator.

The ScanLog32 software includes sample custody information automatically in its electronic transmission from the field station, but from October 1995 to July 2001, electronic custody records (DOS, ASCII text files with an extension of .lb2) were sent by e-mail manually to the LTRMP laboratory. Field stations maintain archive copies (both paper and electronic) of all data sheets submitted.

### *8.6 Electronic Data Acquisition*

Water quality monitoring in the LTRMP produces a large volume of field data (6,000 data sheets) and samples (20,000 containers) each year. To process this material efficiently, the

LTRMP staff uses an automated system of data and sample management that includes (1) field computers and customized software to acquire data from manual entries and instrument outputs and (2) a customized laboratory information management system (LIMS) that relies heavily on bar codes to track samples and analytical results through the system.

As of July 2001, field data in LTRMP water quality monitoring are subjected to extensive real-time syntax and contextual checking as they are acquired in an electronic data sheet. This is accomplished using a software package (ScanLog32) that water quality teams run on a notebook computer while (1) in the field at the sampling location and (2) at the field station when processing samples for shipment to the laboratory. The software produces data and custody records that are sent electronically to the LTRMP analytical laboratory LIMS and are printed at the field station for archival purposes. The LIMS uses the electronic records (and bar code labels) to identify samples, track custody, and to guide and monitor analytical processing. After laboratory processing, the software forwards the electronic data sheets from the LIMS to the central LTRMP database.

The electronic version of the data sheet maintains the familiar “look and feel” of the paper version (Figure 4). This avoids much of the disruption related to retraining and relearning and also eliminates the need for radical changes in the established data management process. It

also allows archives based on paper records to be continued without significant change.

Error trapping was the primary goal in implementing an electronic data sheet for LTRMP water quality monitoring; rugged computers and customized software provide the field teams with real-time detection and correction of errors as data are acquired.

Although error rates were low before the use of the electronic data sheet (on the order of 1–2 per 1,000 keystrokes), data volume is large (greater than 500,000 keystrokes per year) and after-the-fact detection and correction are extremely costly (0.25 to 1.5 hours per error).

The ScanLog32 software uses two levels of real-time error checking to produce extremely low error rates (less than 1 per 10,000 keystrokes) in data that enter the data management process: (1) syntax checks are performed as data are entered into each field of the data sheet to ensure that the entry is properly formatted (valid numeric value with correct precision, etc.) and that the properly formatted value is in the range allowable for the geographic area and month of the year, and (2) more sophisticated context checks are performed when each data sheet is completed to ensure that all the required fields are filled and that all entries are consistent with each other and with the procedures established in this manual (e.g., Secchi disk transparency or sampling depth cannot exceed maximum depth of the water column; nontributary sites with current velocity  $<0.1$  m/s and available water depth  $>0.6$  m require near-bottom readings of temperature, pH, dissolved oxygen, and conductivity; snow cover cannot be present in the absence of ice cover; vegetation type cannot be specified when vegetation cover is zero). Several hundred checks of this type are performed on each data sheet in a fraction of a second as the field team member completes the entries on the form. These checks were developed in close collaboration with field team members and they incorporate much of the error detection experience and expertise accumulated by the field team members over the years.

When the software encounters an invalid or missing entry, it gives the operator an immediate indication and diagnosis of the problem. The

application's help utility, of particular value to less-experienced field technicians, provides direct access to the relevant sections of this manual.

ScanLog32 provides several documentation capabilities that are not available on the paper version of the data sheet. With ScanLog32, the user can attach an extended textual comment to any individual sample. This comment is not restricted in length (several hundred characters can be easily handled) nor in punctuation. These individual sample comments are stored in the laboratory database only, not the central LTRMP database. A parallel capability allows the laboratory staff to attach another sample comment upon receipt of the sample at the laboratory. ScanLog32 provides an electronic notepad (field log) that can be used by the field teams for recording information that is not forwarded to the laboratory. The field teams may also set (or clear) reminders that appear automatically whenever the user reopens a sample batch for processing with ScanLog32.

Detailed descriptions of the ScanLog32 software and its use in LTRMP water quality operations are provided in separate software documentation.

### *8.7 Archival Storage of Data and Associated Records*

The long-term value of the LTRMP depends on the data acquired by this program being available to users in future decades or beyond. It is essential that at least one method, not heavily reliant on advanced technology, exists to check and reconstruct the database maintained at UMESC. The LTRMP uses archived paper copies of the data sheets held at the separate field stations and at UMESC for this purpose. Copies in multiple locations ensure that LTRMP archives are never completely lost because of a localized event (fire, flood, other) or data system failure. After December 2001, the archival process was streamlined, with an original certified paper copy of each data sheet maintained only at the originating field station, and electronic copies on multiple media (compact disk, magnetic disk) as ASCII text files held at the UMESC laboratory and by the UMESC database administrator. The

content of these ASCII files is also printed out in a condensed format for archival storage by UMESC.

Additional records associated with water quality monitoring in the LTRMP (e.g., equipment maintenance logs, field notebooks) are held in safe locations at each of the field stations.

## 9. Acknowledgment

The authors of this manual have compiled and edited information provided by numerous water quality professionals associated with the Long Term Resource Monitoring Program from 1988 to 2003. These individuals provided technical information, as well as review comments and suggestions on a series of drafts that have led to this version of the manual. Without the contributions from the following individuals, several of whom have now moved to new positions, this manual could not have been completed: Robert Burdis, Minnesota Department of Natural Resources, Lake City, Minnesota; Kraig Hoff, Kevin Mauel, Troy Clemment, and Lisa Hodge-Richardson, Wisconsin Department of Natural Resources, Onalaska, Wisconsin; Lesly Conaway, Jennifer Frazier, David Herzog, and David Ostendorf, Missouri Department of Conservation, Jackson, Missouri; David Gould and Michael Steuck, Iowa Department of Natural Resources, Bellevue, Iowa; Eric Ratcliff, Brian Macias, and Mack Sitzes, Illinois Natural History Survey, Brighton, Illinois; and Jeff Arnold, Doug Blodgett, Steven Stenzel, and Rick Wright, Illinois Natural History Survey, Havana, Illinois. Our sincere thanks, and those of our Program partners and collaborators, are extended for their dedication and all-important contributions to the Long Term Resource Monitoring Program on the Upper Mississippi River System and to this manual.

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## 11. Glossary

AWD	Available water depth
BT	Sample depth code for bottom sample
BOD	Biochemical oxygen demand
Ca	Calcium
CHLF	Chlorophyll- <i>a</i> determined fluorometrically (F)
CHLS	Chlorophyll- <i>a</i> determined spectrophotometrically (S)
Cl	Chloride
DI	Deionized water
DIN	Dissolved inorganic nitrogen
DKN	Total dissolved Kjeldahl nitrogen
DMSO	Dimethyl sulfoxide
DO	Dissolved oxygen
Fe	Iron
FSS	Fixed-site sampling
FTP	File transfer protocol
GIS	Geographic information system
GPS	Geographic positioning system
H <sub>2</sub> SO <sub>4</sub>	Sulfuric acid
HNO <sub>3</sub>	Nitric acid
HCl	Hydrochloric acid
HgCl <sub>2</sub>	Mercuric chloride
JTU	Jackson turbidity units
K	Potassium
KCl	Potassium chloride
LIMS	Laboratory information management system
LTRMP	Long Term Resource Monitoring Program
MD	Sample depth code for mid-depth sample

MET	Dissolved metals sample used for cation determinations		as determined on an acid-preserved sample
Mg	Magnesium	SRS	Stratified random sampling
Mn	Manganese	SO <sub>3</sub>	Sulfite
N	Nitrogen	SO <sub>4</sub>	Sulfate
Na	Sodium	TDP	Total dissolved phosphorus
NH <sub>x</sub>	Ammonia plus ammonium	TKN	Total Kjeldahl nitrogen
NIST	National Institute of Standards	TNP	Total nitrogen and phosphorus sample container
NO <sub>x</sub>	Nitrate plus nitrite	TSS	Total suspended solids
NROWS	Number of detail rows (depths) completed on the data sheet	UMESC	Upper Midwest Environmental Sciences Center
NTU	Nephelometric turbidity units	UMRS	Upper Mississippi River System
NVSS	Nonvolatile suspended solids	UTM	Universal Transverse Mercator
OT	Sample depth code for samples from other than surface, mid-depth, or bottom	VSS	Volatile suspended solids
QA/QC	Quality assurance and quality control	WDP	Water depth, vertical thickness of the liquid layer of water between the substrate and the bottom of any overlying ice cover (obsolete)
QF	Quality factor		Water depth, vertical distance between the substrate and the free surface of the water
P	Phosphorus	Z <sub>max</sub>	Water surface
PAR	Photosynthetically active radiation	Z <sub>0</sub>	Total vertical extent of ice, total ice thickness above and below water surface
PVC	Polyvinyl chloride	Z <sub>ice</sub>	Vertical extent of ice below the water surface, submerged ice thickness
RM	River mile, measured upstream from the river mouth	Z <sub>sice</sub>	Vertical extent of snow cover
SF	Sample depth code for surface samples	Z <sub>snow</sub>	
Si	Silicate		
SRP	Soluble reactive phosphorus, dissolved reactive phosphorus, also the SRP-chloride sample bottle		
SRPH	Soluble reactive phosphorus (hydrolyzed by acid preservation)		

## Appendix A. Sampled Parameters and Sampling Frequencies

This appendix provides a tabular listing of the parameters measured and the frequency of sampling in water quality monitoring of the Long Term Resource Monitoring Program (LTRMP).

### A.1 Sample Parameters

#### A.1.1 Measurements Made *In Situ* or at Field Station

This section summarizes the period of record for measurements made at the sampling site or on samples returned to the field station (Table A-1). Samples shipped to the analytical laboratory are described in Section A.1.2.

#### A.1.2 Samples Submitted to the Analytical Laboratory

This section summarizes the period of record (Table A-2) and parameters measured (Table A-3) for samples shipped from the field to the analytical laboratory. Before 1994, chemical samples returned to the laboratory were analyzed at one of three sites: the U.S. Army Corps of Engineers Waterways Experiment

Station facilities in Spring Valley, Wisconsin (Eau Galle Reservoir); the U.S. Army Corps of Engineers Waterways Experiment Station Facility in Vicksburg, Mississippi; or the Long Term Resource Monitoring Program (LTRMP) laboratory at the Upper Midwest Environmental Sciences Center in Onalaska, Wisconsin. All analyses were transferred to the LTRMP laboratory in 1994.

### A.2 Sample Numbers and Frequency

The number of samples collected for analysis and the frequency of water quality sampling in the Long Term Resource Monitoring Program has changed substantially over time in response to availability of funds and refinements in the Program objectives. These changes must be considered in the interpretation of long-term patterns or trends in the resulting data.

#### A.2.1 April 1991 Through April 1993

Approximately 80–100 samples for chemical laboratory analyses were collected in fixed-site sampling (FSS) during each sampling

**Table A-1.** Period of record for *in situ* measurements obtained by Long Term Resource Monitoring Program water quality monitoring teams.

Parameter	1988	1989	1990	1991	1992	1993–Present
Conductivity	■	■	■	■	■	■
Current speed	■	■	■	■	■	■
Current direction	■	■	■	■	■	■
Dissolved oxygen	■	■	■	■	■	■
Ice and snow	■	■	■	■	■	■
pH				Jun ■	■	■
Secchi disk transparency	■	■	■	■	■	■
Turbidity	■	■	■	■	■	■
Water depth	■	■	■	■	■	■
Water temperature	■	■	■	■	■	■
Wave height	■	■	■	■	■	■

**Table A-2.** Period of record for measurements from routine water quality monitoring submitted by Long Term Resource Monitoring Program field stations to the analytical laboratory.

Parameter	1988	1989	1990	1991	1992	1993–Present
Total suspended solids				■	■	■
Volatile suspended solids				■	■	■
Chlorophyll- <i>a</i>				June ■	■	■
Total phosphorus				June ■	■	■
Soluble reactive phosphorus				June ■	■	■
Total soluble phosphorus				June ■	■	■ Apr 1993
Total nitrogen				June ■	■	■
Total soluble nitrogen				June ■	■	■ Apr 1993
NO <sub>x</sub> (nitrate plus nitrite)				June ■	■	■
NH <sub>x</sub> (ammonia or ammonium)				June ■	■	■
Si (silicate)				June ■	■	■
Cl (chloride)				June ■	■	■
Ca (calcium)				June ■	■	■
Mg (magnesium)				June ■	■	■
Na (sodium)				June ■	■	■
K (potassium)				June ■	■	■
Fe (iron)				June ■	■	■ Feb 1993
Mn (manganese)				June ■	■	■ Feb 1993

week. Stratified random sampling (SRS) was not yet implemented. Chemical samples were collected biweekly from April through October (15–16 sampling dates) and every 4 weeks from November through March (5–6 sampling dates), for a total of 20–21 sampling dates per year. This produced approximately 1,800 total samples and 29,000 total analyses per year.

### A.2.2 June 1993 Through December 1999

The list of FSS locations in each study reach was modified and the number of chemical parameters analyzed was reduced. In this revised design, the number of fixed sites was set at approximately 15 sites per field station, with biweekly collection of chemical samples. However, analysis of total soluble nitrogen, total

soluble phosphorus, dissolved calcium, dissolved iron, and dissolved manganese were suspended in FSS pending the switch of analytical responsibilities to the LTRMP laboratory.

The SRS was implemented in July 1993, with a full set of chemical parameters measured at only 50% of these quarterly SRS sites (120–150 per study reach). The SRS excluded total soluble phosphorus, total soluble nitrogen, dissolved calcium, dissolved iron, dissolved manganese, dissolved potassium, dissolved silica, and dissolved chloride. This eliminated two sample preparations (metals and total soluble nitrogen and phosphorus) during SRS. The reduced parameter list included all the usual *in situ* parameters (Table A-1) plus fluorometric chlorophyll-*a* and suspended solids.

**Table A-3.** Measurements performed on Long Term Resource Monitoring Program samples by participating laboratories. Each laboratory techniques are described in the procedures manuals for the Waterways Experiment Station (WES) Environmental Laboratory, and by the American Public Health Association et al. (1992). Values in parentheses represent the method detection limit.

Parameter and method	Laboratory		
	WES <sup>a</sup> -Vicksburg	WES-EauGalle	UMESC <sup>b</sup>
<b>Total suspended solids:</b> Gravimetric/105 °C	–	June 1991–June 1993 (1 µg/L)	June 1993–Present (1 µg/L)
<b>Volatile suspended solids:</b> Gravimetric/500 °C	–	June 1991–June 1993 (1 µg/L)	June 1993–Present (1 µg/L)
<b>Chlorophyll-a:</b> Fluorometric- DMSO-acetone extraction	–	–	June 1993–Present (1 µg/L)
<b>Chlorophyll-a:</b> Spectrophotometric 90% acetone extraction	–	June 1991–June 1993 (1 µg/L)	June 1993–Present (1 µg/L)
<b>Total phosphorus:</b> Automated/ persulfate/ascorbic acid	–	June 1991– Jan. 1994 (1 µg/L)	Jan. 1994–Present (1 µg/L)
<b>Soluble reactive phosphorus (acidified, SRPH):</b> Automated/ H <sub>2</sub> SO <sub>4</sub> preservation, ascorbic acid	June 1991–Dec 1993 (1 µg/L)	–	–
<b>Soluble reactive phosphorus:</b> Automated /frozen/ascorbic acid	Jan. 1994–Feb. 1994 (1 µg/L)	–	Feb. 1994–Present (1 µg/L)
<b>Total soluble phosphorus:</b> Automated/persulfate/ascorbic acid	–	June 1991–Apr. 1993 (1 µg/L)	–
<b>Total nitrogen:</b> Automated/ Devarda’s alloy	–	June 1991–Jan. 1994 (0.01 mg/L)	Jan. 1994–July 1997 (0.01 mg/L)
<b>Total nitrogen:</b> Persulfate digestion, automated cadmium reduction	–	–	March 1997–Present (0.01 mg/L)
<b>Total soluble nitrogen:</b> Automated/Devarda’s alloy	–	June 1991–April 1993 (0.01 mg/L)	–
<b>Nitrate and nitrite nitrogen:</b> Automated Cd reduction	June 1991–April 1994 (0.01 mg/L)	–	April–June 1994 April 1997–Present (0.01 mg/L)
<b>Nitrate and nitrite nitrogen:</b> Ion chromatography	–	–	June 1994–Present (0.01 mg/L)
<b>Ammonia and ammonium:</b> Automated salicylate	June 1991–Feb. 1994 (1 µg/L)	–	Feb. 1994–Present (1 µg/L)
<b>Dissolved silicate silica:</b> Automated/molybdate	June 1991–Feb. 1994 (0.01 mg/L)	–	Mar. 1994–Present (0.01 mg/L)
<b>Sulfate:</b> Ion chromatography	–	–	Jan. 1994–Present (0.1 mg/L)
<b>Dissolved chloride:</b> Automated ferro-cyanide, ion chromatography	June 1991–June 1994 Automated FeCN (0.1 mg/L)	–	June 1994–Present (0.1 mg/L)

**Table A-3.** Continued

Parameter and method	Laboratory		
	ES <sup>a</sup> -Vicksburg	WES-EauGalle	UMESC <sup>b</sup>
<b>Dissolved calcium:</b> Ion chromatography	–	–	Jan. 1994–Present (0.1 mg/L)
<b>Dissolved calcium:</b> Atomic absorption	June 1991–Oct. 1993 (0.1 mg/L)	–	Oct. 1993–Jan. 1994 (0.1 mg/L)
<b>Dissolved magnesium:</b> Ion chromatography			Jan. 1994 –Present (0.1 mg/L)
<b>Dissolved sodium:</b> Ion chromatography			Jan. 1994–Present (0.1 mg/L)
<b>Dissolved potassium:</b> Atomic absorption	June 1991–Oct. 1993 (0.1 mg/L)	–	Oct. 1993–Present (0.1 mg/L)
<b>Dissolved iron:</b> Atomic absorption	June 1991–Apr. 1993 (0.01 mg/L)	–	–
<b>Dissolved manganese:</b> Atomic absorption	June 1991–Apr. 1993 (0.01 mg/L)	–	–

<sup>a</sup>WES=Waterways Experiment Station

### **A.2.3 January 1, 2000 Through September 2002**

Because of budget constraints, the design was modified to reduce overall sampling effort by 25–35%. Frequency of sampling in FSS was reduced from biweekly to once every 4 weeks, except for a few selected sites of special concern. The number of sites visited during SRS episodes was not changed, but the number of full-chemical sites was reduced from 50% to 33% of the total sites visited.

### **A.2.4 After September 2002**

The LTRMP water quality sampling was halted on September 30, 2002, in response to budget limitations. Reduced parameter sampling at a selected subset of fixed sites resumed in late April 2003. A return to the 2002 sampling level is proposed for January 2004.

## Appendix B. Fixed-site Sampling Locations

**Table B-1.** Descriptions of fixed-site water quality sampling locations monitored by LTRMP staff from 1988 through September 2002. Period of record is included for reference, as not all sites were monitored as of the p

Field station	State	River name	River mile	Location code <sup>a</sup>	UTM zone	Northing	Easting	Habitat class <sup>b</sup>	Additional comments	First sampled	Last sampled
1	WI	Chippewa	0.1	CH00.1M	15	4917624	572933	TRIB	mid-stream	01/29/1990	09/19/2002 <sup>c,d</sup>
1	MN	Cannon	0.1	CN00.1M	15	4938767	532272	TRIB	mid-stream	01/24/1990	09/18/2002 <sup>c,d</sup>
1	MN-WI	Mississippi	738.2	M738.2F	15	4890151	595044	MC	tailwater west side	05/13/1993	09/16/2002 <sup>c,d</sup>
1	MN-WI	Mississippi	738.2	M738.2M	15	4890323	595248	MC	tailwater mid-stream	01/14/2000	09/16/2002 <sup>c,d</sup>
1	MN-WI	Mississippi	738.2	M738.2T	15	4890529	595380	MC	tailwater east side	01/14/2000	09/16/2002 <sup>c,d</sup>
1	MN-WI	Mississippi	742.6	M742.6B	15	4894604	589536	SC	Weaver Bottoms outlet	04/30/1993	12/30/1999
1	MN-WI	Mississippi	742.8	M742.8D	15	4894957	589565	SC	Weaver Bottoms outlet	04/30/1993	10/28/1997
1	MN-WI	Mississippi	743	M743.0E	15	4895083	589464	BWC	Weaver Bottoms outlet	12/02/1997	09/16/2002 <sup>c,d</sup>
1	MN-WI	Mississippi	745.2	M745.2L	15	4898404	589565	SC	Weaver Bottoms inlet	04/30/1993	12/30/1999
1	MN-WI	Mississippi	746.9	M746.9Y	15	4901280	589372	SC	Weaver Bottoms inlet	04/30/1993	12/30/1999
1	MN-WI	Mississippi	747.3	M747.3R	15	4901328	587763	SC	Murphy's Cut	04/30/1993	09/16/2002 <sup>c,d</sup>
1	MN-WI	Mississippi	752.8	M752.8M	15	4908232	585992	MC	LD 4 tailwater mid-stream	01/14/2000	09/16/2002 <sup>c,d</sup>
1	MN-WI	Mississippi	752.8	M752.8Y	15	4908119	585823	MC	LD 4 tailwater west side	04/30/1993	09/16/2002 <sup>c,d</sup>
1	MN-WI	Mississippi	752.8	M752.8Z	15	4908276	586174	MC	LD 4 tailwater east side	04/30/1993	09/16/2002 <sup>c,d</sup>
1	MN-WI	Mississippi	753.1	M753.1X	15	4908533	585096	BWC	Peterson Lake mouth	04/29/1993	09/19/2002 <sup>c</sup>
1	MN-WI	Mississippi	753.2	M753.2S	15	4908555	583985	IMP	Peterson Lake	01/30/1990	04/16/1993
1	MN-WI	Mississippi	753.2	M753.2V	15	4908931	584545	IMP	Peterson Lake	01/30/1990	04/16/1993
1	MN-WI	Mississippi	757.2	M757.2Z	15	4914360	582462	BWC	Big Lake mouth	04/29/1993	09/19/2002 <sup>c</sup>
1	MN-WI	Mississippi	757.4	M757.4O	15	4912312	580808	BWC	Robinson Lake	04/03/1991	04/16/1993
1	MN-WI	Mississippi	757.5	M757.5O	15	4912238	580650	BWC	Robinson Lake	04/03/1991	04/16/1993
1	MN-WI	Mississippi	758.6	M758.6X	15	4915943	581454	BWC	Big Lake	02/07/1990	04/16/1993
1	MN-WI	Mississippi	758.6	M758.6Y	15	4915699	581212	BWC	Big Lake	02/07/1990	04/16/1993
1	MN-WI	Mississippi	760.7	M760.7O	15	4915321	576401	MC	west side of channel wing dam	01/29/1990	04/16/1993
1	MN-WI	Mississippi	761.5	M761.5E	15	4916388	575460	MC	west side of channel	01/29/1990	04/16/1993
1	MN-WI	Mississippi	764.3	M764.3A	15	4917826	571635	MC	mid-stream	04/29/1993	09/19/2002 <sup>c,d</sup>

Table B-1. Continued.

Field station	State	River name	River mile	Location code <sup>a</sup>	UTM zone	Northing	Easting	Habitat class <sup>b</sup>	Additional comments	First sampled	Last sampled
1	MN-WI	Mississippi	764.8	M764.8G	15	4918870	570994	BWI	Isolated backwater	02/27/1990	04/23/1992
1	MN-WI	Mississippi	766	M766.0B	15	4917935	568732	IMP-L	Lake Pepin east side	01/26/1990	04/13/1993
1	MN-WI	Mississippi	766	M766.0I	15	4919038	568951	IMP-L	Lake Pepin mid-stream	01/26/1990	09/19/2002 <sup>c,d</sup>
1	MN-WI	Mississippi	766	M766.0O	15	4920225	569220	IMP-L	Lake Pepin west side	01/26/1990	04/13/1993
1	MN-WI	Mississippi	771.2	M771.2P	15	4921651	561539	IMP-L	Lake Pepin mid-stream	04/29/1993	09/19/2002 <sup>c,d</sup>
1	MN-WI	Mississippi	775.6	M775.6L	15	4924953	555572	IMP-L	Lake Pepin west side	01/25/1990	04/13/1993
1	MN-WI	Mississippi	775.6	M775.6Q	15	4925675	556373	IMP-L	Lake Pepin mid-stream	01/25/1990	09/18/2002 <sup>c,d</sup>
1	MN-WI	Mississippi	775.6	M775.6Y	15	4926279	557162	IMP-L	Lake Pepin east side	01/25/1990	04/13/1993
1	MN-WI	Mississippi	781.2	M781.2E	15	4932250	551514	IMP-L	Lake Pepin west side	01/26/1990	04/13/1993
1	MN-WI	Mississippi	781.2	M781.2O	15	4933885	551416	IMP-L	Lake Pepin mid-stream	01/26/1990	09/18/2002 <sup>c,d</sup>
1	MN-WI	Mississippi	781.2	M781.2X	15	4935516	551310	IMP-L	Lake Pepin east side	01/25/1990	04/13/1993
1	MN-WI	Mississippi	786.1	M786.1S	15	4935869	543794	IMP-L	Lake Pepin Bay City flats	01/25/1990	04/13/1993
1	MN-WI	Mississippi	786.2	M786.2C	15	4934266	543779	MC	mid-stream	04/28/1993	09/18/2002 <sup>c,d</sup>
1	MN-WI	Mississippi	786.5	M786.5D	15	4934745	542976	SC	Wisconsin channel mid-stream	04/28/1993	12/29/1999
1	MN-WI	Mississippi	787.9	M787.9H	15	4935522	540890	BWC	Dead Slough Lake	04/02/1991	04/12/1993
1	MN-WI	Mississippi	790.3	M790.3F	15	4935661	537282	BWC	Mud Lake	01/24/1990	04/12/1993
1	MN-WI	Mississippi	792.5	M792.5N	15	4936971	536344	SC	Wisconsin channel west side	11/05/1990	04/12/1993
1	MN-WI	Mississippi	793.9	M793.9P	15	4938355	534406	MC	west side of channel	01/24/1990	04/12/1993
1	MN-WI	Mississippi	795.8	M795.8L	15	4938922	532288	BWI	Isolated backwater	02/06/1990	04/06/1992
1	MN-WI	Mississippi	796.7	M796.7M	15	4939642	531626	MC	west side of channel wing dam	01/24/1990	04/12/1993
1	MN-WI	Mississippi	796.9	M796.9M	15	4939664	531047	MC	tailwater west side	04/28/1993	09/18/2002 <sup>c,d</sup>
1	MN-WI	Mississippi	796.9	M796.9N	15	4939807	531001	MC	tailwater east side	11/05/1990	09/18/2002 <sup>c,d</sup>
1	MN	Vermillion	0.1	VM00.1M	15	4938817	532303	TRIB	mid-stream	01/24/1990	09/18/2002 <sup>c,d</sup>
1	MN	Wells Creek	0.8	WC00.8M	15	4928802	553735	TRIB	mid-stream CO 2 bridge	01/13/1999	09/18/2002 <sup>c,d</sup>
1	MN	Whitewater	1.3	WW01.3M	15	4895406	586129	TRIB	mid-stream HWY 61 bridge	04/30/1993	09/16/2002 <sup>c,d</sup>
1	MN	Zumbro	0.1	ZM00.1M	15	4904640	585582	TRIB	mid-stream	04/30/1993	09/16/2002 <sup>c,d</sup>
2	WI	Black	1	B001.0N	15	4855524	640507	TRIB	Under Clinton St. Bridge	06/11/1991	06/21/1993

B-2

**Table B-1.** Continued.

Field station	State	River name	River mile	Location code <sup>a</sup>	UTM zone	Northing	Easting	Habitat class <sup>b</sup>	Additional comments	First sampled	Last sampled
2	WI	Black	1	BK01.0M	15	4855524	640611	TRIB	Fishing pier 12 m off-shore Copeland Park	06/28/1993	09/16/2002 <sup>c,d</sup>
2	WI	Black	14.2	BK14.2M	15	4868518	633202	TRIB	Mainstem Black at bike bridge Lytles landing enters Pool 7 near RM 708	05/06/1993	09/16/2002 <sup>c,d</sup>
2	WI	Bad Axe	0.4	BX00.4M	15	4820006	644226	TRIB	mid-stream HWY 35 bridge enters pool 9 near RM 675.3	06/26/1995	09/16/2002 <sup>c,d</sup>
2	WI	Coon Creek	0.6	CC00.6M	15	4834061	643626	TRIB	mid-stream HWY 35 bridge enters Pool 8 near RM 684.5	05/06/1993	09/16/2002 <sup>c,d</sup>
2	WI	Coon Creek	4.6	CC04.6M	15	4834750	647900	TRIB	mid-stream temporary exploratory site enters Pool 8 near RM 684.5	03/21/1996	05/14/1996
2	WI	La Crosse	0.1	LX00.1M	15	4853086	640435	TRIB	bike bridge north side of side Park enters Pool 8 RM 698.1	06/11/1991	09/16/2002 <sup>c,d</sup>
2	MN-WI	Mississippi	679.5	M679.5V	15	4825913	642609	IMP	west side of channel	07/22/1988	09/05/2002 <sup>c,d</sup>
2	MN-WI	Mississippi	679.5	M679.5W	15	4825899	642742	MC	high flow transect site	05/03/2002	05/03/2002 <sup>c</sup>
2	MN-WI	Mississippi	679.5	M679.5X	15	4825899	642816	MC	transect site-mid channel	01/12/2000	08/19/2002 <sup>c,d</sup>
2	MN-WI	Mississippi	679.5	M679.5Y	15	4825899	642890	MC	high flow transect site	05/03/2002	05/03/2002 <sup>c</sup>
2	MN-WI	Mississippi	679.5	M679.5Z	15	4825899	642964	MC	transect site-east side	01/12/2000	08/19/2002 <sup>c,d</sup>
2	MN-WI	Mississippi	680.8	M680.8M	15	4828251	641268	IMP	West side lower Pool 8	07/22/1988	10/09/1991
2	MN-WI	Mississippi	680.8	M680.8U	15	4828329	642397	IMP	lower Pool 8	07/22/1988	03/11/1993
2	MN-WI	Mississippi	681.3	M681.3B	15	4828911	639935	IMP	Reno Spillway	05/17/1993	09/16/2002 <sup>c</sup>
2	MN-WI	Mississippi	684.8	M684.8W	15	4834212	643275	BWI	Isolated backwater S of Stoddard	08/05/1988	05/06/1993
2	MN-WI	Mississippi	684.8	M684.8Y	15	4836629	724102	BWI	Isolated backwater S of Stoddard	08/05/1988	08/05/1988
2	MN-WI	Mississippi	685	M685.0D	15	4833329	639806	BWC	Raft Channel S of Brownsville	07/22/1988	04/06/1993
2	MN-WI	Mississippi	685	M685.0E	15	4833364	639859	BWC	Raft Channel S of Brownsville	07/22/1988	07/02/1993
2	MN-WI	Mississippi	685.9	M685.9L	15	4835599	641380	MC	Coon Slough	07/26/1988	08/04/1988
2	MN-WI	Mississippi	685.9	M685.9M	15	4835529	641422	MC	Coon Slough	07/26/1988	08/04/1988
2	MN-WI	Mississippi	686.1	M686.1V	15	4836515	642600	BWC	West side of Stoddard Bay	07/25/1988	04/06/1993
2	MN-WI	Mississippi	686.4	M686.4K	15	4844362	641015	BWC	Grassy Island	10/13/1988	07/08/1993
2	MN-WI	Mississippi	686.6	M686.6J	15	4836021	640620	MC	Turtle Island	07/22/1988	03/30/1993
2	MN-WI	Mississippi	687.6	M687.6F	15	4836807	639637	BWC	Inside Horseshoe HREP	07/22/1988	05/17/1989

**Table B-1.** Continued.

Field station	State	River name	River mile	Location code <sup>a</sup>	UTM zone	Northing	Easting	Habitat class <sup>b</sup>	Additional comments	First sampled	Last sampled
2	MN-WI	Mississippi	687.6	M687.6G	15	4836889	639753	BWC	Inside Horseshoe HREP	05/17/1989	07/02/1993
2	MN-WI	Mississippi	687.8	M687.8X	15	4837376	642793	BWC	Crosby Slough NW side of Stoddard Islands	10/06/1988	04/06/1993
2	MN-WI	Mississippi	689.2	M689.2A	15	4839410	639381	MC	Main Ch border	11/14/1991	04/06/1993
2	MN-WI	Mississippi	689.2	M689.2B	15	4839595	639543	MC	MC border	07/25/1988	10/31/1991
2	MN-WI	Mississippi	690.2	M690.2A	15	4841764	639243	BWC	Lawrence Lake Marina	08/07/1991	09/23/1991
2	MN-WI	Mississippi	690.4	M690.4A	15	4841500	639254	BWC	Lawrence lake Marina	07/01/1993	07/08/1993
2	MN-WI	Mississippi	690.8	M690.8B	15	4842150	639331	BWC	Lawrence Lake mouth (channel to upper lake)	01/12/2000	09/05/2002 <sup>c</sup>
2	MN-WI	Mississippi	691.3	M691.3B	15	4843204	639442	BWC	Lawrence Lake	08/09/1988	09/05/2002 <sup>c</sup>
2	MN-WI	Mississippi	691.6	M691.6E	15	4843992	640839	MC	CBW East Of Lawrence Lake	06/27/1991	10/09/1991
2	MN-WI	Mississippi	691.7	M691.7S	15	4843457	643127	BWI	Goose Island near culverts under entrance road	08/05/1988	03/26/1993
2	MN-WI	Mississippi	691.7	M691.7T	15	4843442	643215	BWI	Goose Island near culverts under entrance road	08/05/1988	03/26/1993
2	MN-WI	Mississippi	691.9	M691.9B	15	4843912	639676	BWC	Mid-Lawrence Lake	07/01/1993	07/01/1993
2	MN-WI	Mississippi	692.5	M692.5C	15	4845860	639855	BWC	upper-Lawrence Lake	07/01/1993	07/08/1993
2	MN-WI	Mississippi	692.7	M692.7R	15	4844961	642904	BWC	North Goose Island landing	06/24/1991	09/23/1991
2	MN-WI	Mississippi	692.8	M692.8P	15	4844944	641981	BWC	Goose Island near culverts under road	07/21/1988	07/07/1993
2	MN-WI	Mississippi	692.8	M692.8Q	15	4844887	642052	BWC	Goose Island	07/21/1988	07/07/1993
2	MN-WI	Mississippi	694	M694.0N	15	4847065	642510	SC	Goose Island	08/09/1988	07/07/1993
2	MN-WI	Mississippi	694.7	M694.7L	15	4848046	641197	MC	Coney Island	07/25/1988	07/07/1993
2	MN-WI	Mississippi	694.7	M694.7M	15	4848012	641222	MC	Coney Island	08/03/1988	06/24/1992
2	MN-WI	Mississippi	696.5	M696.5D	15	4850291	638947	BWC	Target Lake	08/17/1988	09/25/2002 <sup>c</sup>
2	MN-WI	Mississippi	696.5	M696.5F	15	4850396	639088	BWC	Target lake	07/21/1988	08/09/1988
2	MN-WI	Mississippi	696.8	M696.8I	15	4850832	639499	MC	Municipal wing dam	07/16/1991	10/22/1991
2	MN-WI	Mississippi	698.1	M698.1G	15	4852776	637410	BWI	Blue Lake	05/07/1993	05/07/1993
2	MN-WI	Mississippi	698.3	M698.3D	15	4853101	637038	BWI	Blue Lake	05/07/1993	05/07/1993
2	MN-WI	Mississippi	698.5	M698.5B	15	4853457	636664	BWI	Blue Lake	05/07/1993	05/07/1993
2	MN-WI	Mississippi	700.2	M700.2F	15	4855029	638502	SC	East Channel	07/23/1991	10/22/1991

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**Table B-1.** Continued.

B-5

Field station	State	River name	River mile	Location code <sup>a</sup>	UTM zone	Northing	Easting	Habitat class <sup>b</sup>	Additional comments	First sampled	Last sampled
2	MN-WI	Mississippi	701	M701.0B	15	4856320	637025	MC	Main Channel	07/16/1991	07/16/1991
2	MN-WI	Mississippi	701.1	M701.1B	15	4856266	637184	MC	east side of main channel transect	06/11/1991	09/25/2002 <sup>c,d</sup>
2	MN-WI	Mississippi	701.1	M701.1C	15	4856345	637101	MC	high flow only transect site	05/03/2002	05/03/2002 <sup>c</sup>
2	MN-WI	Mississippi	701.1	M701.1D	15	4856345	637028	MC	transect site-mid channel	01/12/2000	09/25/2002 <sup>c,d</sup>
2	MN-WI	Mississippi	701.1	M701.1E	15	4856345	636956	MC	high flow only transect site	05/03/2002	05/03/2002 <sup>c</sup>
2	MN-WI	Mississippi	701.1	M701.1F	15	4856345	636883	MC	transect site-west side	01/12/2000	09/25/2002 <sup>c,d</sup>
2	MN-WI	Mississippi	701.4	M701.4I	15	4856771	639027	BWC	French Lake	11/13/1991	07/07/1993
2	MN-WI	Mississippi	701.7	M701.7I	15	4856771	639027	BWC	French Lake	06/11/1991	10/15/1991
2	MN-WI	Mississippi	701.8	M701.8C	15	4857532	639936	BWC	East Channel	07/16/1991	10/22/1991
2	MN-WI	Mississippi	701.8	M701.8H	15	4857032	638944	BWC	fisheries site	10/22/1991	10/22/1991
2	MN-WI	Mississippi	702.3	M702.3A	15	4857754	635988	MC	MN side upstream of landing	07/23/1991	10/22/1991
2	MN-WI	Mississippi	702.7	M702.7T	15	4858536	637731	IMP	French Island Spillway	05/06/1993	09/16/2002 <sup>c</sup>
2	MN	Root	0.1	R000.1M	15	4846727	640647	TRIB	mid-stream enters pool 8 RM 693.6	08/17/1988	09/09/2002 <sup>c,d</sup>
2	IA	Upper Iowa	2.9	UI02.9M	15	4814694	637926	TRIB	mid-stream HWY 26 bridge enters pool 9 near RM 671	06/26/1995	09/16/2002 <sup>c,d</sup>
3	IL	Apple	2.3	AL02.3M	15	4674120	728180	TRIB	mid-stream Army Depot Rd west of HWY 84	05/03/1993	09/18/2002 <sup>c,d</sup>
3	IA	CatFish Creek	0.3	CF00.3M	15	4704017	693417	TRIB	mid-stream in Mines of Spain state park	03/25/1998	09/17/2002 <sup>c</sup>
3	IA	Elk	2.4	ER02.4M	15	4652639	732645	TRIB	mid-stream HWY 67 bridge	09/29/1997	09/18/2002 <sup>c,d</sup>
3	IL	Galena	3.6	GA03.6M	15	4698150	711420	TRIB	mid-stream off RR bridge S edge of town	12/17/1997	09/17/2002 <sup>c</sup>
3	IA-IL	Mississippi	497.2	M497.2B	15	4608462	721528	MC	LeClaire	05/19/1993	09/19/2002 <sup>c</sup>
3	IA-IL	Mississippi	508.1	M508.1F	15	4626096	723487	BWC	Shricker's Slough	05/05/1993	09/19/2002 <sup>c,d</sup>
3	IA-IL	Mississippi	511.4	M511.4B	15	4628610	728030	MC	Camanche	05/05/1993	09/19/2002 <sup>c</sup>
3	IA-IL	Mississippi	520.6	M520.6B	15	4639310	734615	MC	Clinton	07/12/1999	09/18/2002 <sup>c</sup>
3	IA-IL	Mississippi	524.2	M524.2X	15	4644447	738835	BWC	boat ramp at Mickelson's Landing	07/02/1998	09/18/2002 <sup>c</sup>
3	IA-IL	Mississippi	525.3	M525.3I	15	4646547	735895	IMP	lower Pool 13	09/11/1990	09/26/1990
3	IA-IL	Mississippi	525.5	M525.5C	15	4645596	733769	IMP	transect site west side	07/11/1990	10/05/1992
3	IA-IL	Mississippi	525.5	M525.5F	15	4645539	734965	IMP	transect site west side	08/09/1988	10/05/1992

**Table B-1.** Continued.

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Field station	State	River name	River mile	Location code <sup>a</sup>	UTM zone	Northing	Easting	Habitat class <sup>b</sup>	Additional comments	First sampled	Last sampled
3	IA-IL	Mississippi	525.5	M525.5J	15	4647031	735977	IMP	transect site mid-channel	09/11/1990	09/11/1990
3	IA-IL	Mississippi	525.5	M525.5K	15	4646192	736250	IMP	transect site mid-channel	09/11/1990	09/11/1990
3	IA-IL	Mississippi	525.5	M525.5L	15	4646920	735830	IMP	Impounded area east of main channel - fixed site	08/09/1988	09/16/2002 <sup>c</sup>
3	IA-IL	Mississippi	525.5	M525.5N	15	4647293	736505	IMP	transect site east side	09/09/1988	04/26/1993
3	IA-IL	Mississippi	525.8	M525.8H	15	4647203	735591	IMP	lower Pool 13	09/19/1990	09/19/1990
3	IA-IL	Mississippi	526	M526.0G	15	4647326	735800	IMP	lower Pool 13	09/11/1990	09/26/1990
3	IA-IL	Mississippi	529.7	M529.7L	15	4652726	736832	MC	near Smith Bay light and daymark	08/27/1991	10/21/1992
3	IA-IL	Mississippi	529.7	M529.7M	15	4652779	737208	MC	near Smith Bay light and daymark east channel border	08/04/1988	04/26/1993
3	IA-IL	Mississippi	530.2	M530.2K	15	4653724	736618	MC	east channel border below wing dam	08/05/1988	06/29/1992
3	IA-IL	Mississippi	530.3	M530.3K	15	4653780	736622	MC	east channel border on wing dam	08/05/1988	04/26/1993
3	IA-IL	Mississippi	530.9	M530.9G	15	4654588	735786	BWC	in Elk Wildlife Refuge	05/30/1990	09/19/1990
3	IA-IL	Mississippi	532.2	M532.2T	15	4656988	737891	BWC	Spring Lake	05/15/2001	05/15/2001
3	IA-IL	Mississippi	532.3	M532.3T	15	4656988	737891	BWC	Spring Lake Fixed Site	05/07/1991	09/16/2002 <sup>c</sup>
3	IA-IL	Mississippi	534.8	M534.8L	15	4660508	734751	BWC	lower end of Edick Lake	05/14/1992	11/06/1992
3	IA-IL	Mississippi	535.9	M535.9J	15	4662145	733189	BWC	lower end of Town Lake	08/04/1988	04/27/1993
3	IA-IL	Mississippi	535.9	M535.9K	15	4662054	733511	SC	lower end of Running Slough	08/04/1988	04/27/1993
3	IA-IL	Mississippi	536.2	M536.2P	15	4663472	734166	SC	Eldridge Slough	07/09/1991	11/06/1992
3	IA-IL	Mississippi	536.4	M536.4B	15	4662625	732416	BWC	Barge Lake	08/10/1988	04/07/1993
3	IA-IL	Mississippi	536.8	M536.8L	15	4663476	733596	BWC	upper end of Eldridge Slough	07/17/1990	10/01/1992
3	IA-IL	Mississippi	536.9	M536.9M	15	4663573	733888	BWC	upper end of Eldridge Slough	07/17/1990	10/01/1992
3	IA-IL	Mississippi	540.2	M540.2T	15	4668352	733781	BWC	Savanna Bay fixed site	05/07/1991	09/16/2002 <sup>c</sup>
3	IA-IL	Mississippi	541.7	M541.7L	15	4668876	731882	BWC	upper end of Savanna Bay	06/19/1995	10/09/1995
3	IA-IL	Mississippi	542.5	M542.5E	15	4669388	729999	BWC	Lower end of Pinoak Lake	08/09/1988	04/27/1993
3	IA-IL	Mississippi	542.7	M542.7C	15	4669270	729830	MC	Lower end of Pinoak Lake	12/30/1988	04/06/1993
3	IA-IL	Mississippi	543.2	M543.2L	15	4670688	730102	MC	channel border near Big Soupbone Island	09/12/1990	09/17/1990
3	IA-IL	Mississippi	543.2	M543.2M	15	4670786	730189	MC	channel border near Big Soupbone Island	09/06/1990	09/17/1990
3	IA-IL	Mississippi	543.6	M543.6G	15	4670128	728972	BWC	Upper end of Pinoak Lake	05/31/1990	10/09/1995

**Table B-1.** Continued.

Field station	State	River name	River mile	Location code <sup>a</sup>	UTM zone	Northing	Easting	Habitat class <sup>b</sup>	Additional comments	First sampled	Last sampled
3	IA-IL	Mississippi	544.1	M544.1D	15	4669899	728204	BWC	upper end of Lainsville Slough	01/13/1989	03/20/1991
3	IA-IL	Mississippi	544.2	M544.2C	15	4669840	728063	BWC	dredge cut near entrance to Lower Brown's Lake	08/05/1988	01/11/2001
3	IA-IL	Mississippi	544.2	M544.2D	15	4669884	728068	BWC	edge of dredge cut near entrance to Lower Brown's Lake	08/05/1988	04/27/1993
3	IA-IL	Mississippi	544.5	M544.5F	15	4670287	727615	BWC	deep dredge hole in Lower Brown's Lake dredge cut	09/14/1989	03/20/1991
3	IA-IL	Mississippi	544.6	M544.6E	15	4670292	727301	BWC	Lower Brown's Lake dredge cut	06/19/1995	10/09/1995
3	IA-IL	Mississippi	544.6	M544.6F	15	4670419	727542	BWC	Lower Brown's Lake dredge cut	01/13/1989	01/11/2001
3	IA-IL	Mississippi	544.7	M544.7F	15	4670569	727508	BWC	edge of Lower Brown's Lake dredge cut	01/13/1989	03/20/1991
3	IA-IL	Mississippi	545.1	M545.1H	15	4670776	726951	BWC	Dredge hole in Scarborough portion of Brown's Lake complex	05/31/1990	01/17/2002
3	IA-IL	Mississippi	545.5	M545.5B	15	4670292	726317	BWC	Upper Brown's Lake dredge cut fixed site	09/14/1989	09/16/2002 <sup>c</sup>
3	IA-IL	Mississippi	545.5	M545.5C	15	4670307	726350	BWC	Upper Brown's Lake dredge cut	01/13/1989	10/06/1992
3	IA-IL	Mississippi	545.8	M545.8F	15	4670793	726102	MC	cut from Brown's Lake inlet structure into Upper Brown's Lake	01/13/1989	10/06/1992
3	IA-IL	Mississippi	546.5	M546.5L	15	4672479	725249	MC	channel border near Maquoketa Levee Light and Daymark	09/23/1988	10/01/1991
3	IA-IL	Mississippi	546.7	M546.7P	15	4673328	725255	BWC	N of Maquoketa Levee Light and Daymark	05/29/1990	09/24/1990
3	IA-IL	Mississippi	550.4	M550.4L	15	4675310	719859	MC	west side of channel below wing dam	08/02/1988	07/01/1992
3	IA-IL	Mississippi	550.5	M550.5L	15	4675321	719815	MC	west side of channel on wing dam	08/02/1988	04/28/1993
3	IA-IL	Mississippi	551.3	M551.3M	15	4676806	719234	BWC	lower end of Crooked Slough	08/02/1988	04/28/1993
3	IA-IL	Mississippi	551.3	M551.3N	15	4676895	719457	BWC	lower end of Crooked Slough	08/02/1988	10/21/1996
3	IA-IL	Mississippi	551.6	M551.6N	15	4677202	718446	BWC	lower end of Crooked Slough	07/25/1990	10/19/1992
3	IA-IL	Mississippi	552.3	M552.3L	15	4676383	717210	MC	main channel north of Island 254 Light & Daymark	10/24/1990	10/31/1990
3	IA-IL	Mississippi	554	M554.0G	15	4678142	715730	SC	side channel downstream of Bellevue Lower Light & Daymark	07/12/1991	10/19/1992

Table B-1. Continued.

Field station	State	River name	River mile	Location code <sup>a</sup>	UTM zone	Northing	Easting	Habitat class <sup>b</sup>	Additional comments	First sampled	Last sampled
3	IA-IL	Mississippi	554.2	M554.2C	15	4678085	714831	MC	lower end of Harrington Slough	09/19/1990	09/24/1990
3	IA-IL	Mississippi	554.3	M554.3C	15	4678229	714718	MC	lower end of Harrington Slough	09/19/1990	09/19/1990
3	IA-IL	Mississippi	554.3	M554.3D	15	4678161	714925	MC	lower end of Harrington Slough	09/19/1990	09/19/1990
3	IA-IL	Mississippi	554.8	M554.8E	15	4678589	714227	MC	channel site just west of Bellevue Lower Light and Daymark	07/19/1991	10/19/1992
3	IA-IL	Mississippi	554.8	M554.8F	15	4679382	714669	MC	At Bellevue Lower Light & Daymark channel border	08/02/1988	11/17/1994
3	IA-IL	Mississippi	556	M556.0E	15	4680920	713388	MC	mid-stream near mouth of Mill Cr.	10/24/1990	10/31/1990
3	IA-IL	Mississippi	556.4	M556.4A	15	4681070	712780	MC	L and D 12 tailwater	10/15/1990	09/16/2002 <sup>c,d</sup>
3	IA-IL	Mississippi	556.4	M556.4C	15	4681712	712828	MC	tailwater west side	07/19/1991	09/08/1992
3	IA-IL	Mississippi	556.6	M556.6E	15	4681712	712960	MC	tailwater mid-stream	10/25/1990	10/19/1992
3	IA-IL	Mississippi	563.9	M563.9T	15	4692590	711305	BWC	Sunfish Lake	05/06/1993	09/16/2002 <sup>c,d</sup>
3	IA-IL	Mississippi	564.5	M564.5T	15	4693461	710457	BWC	upper end of Sunfish Lake	01/13/1994	01/25/1996
3	IA-IL	Mississippi	566.2	M566.2R	15	4695192	708476	BWC	just west of Harris Slough	01/13/1994	02/20/1995
3	IA-IL	Mississippi	574.2	M574.2D	15	4701302	698355	SC	side channel behind Nine Mile Island	05/06/1993	11/28/1995
3	IA-WI	Mississippi	582.5	M582.5B	15	4711424	693500	MC	L and D 11 tailwater	05/06/1993	09/17/2002 <sup>c</sup>
3	IA-WI	Mississippi	615.2	M615.2B	15	4738150	655880	MC	L and D 10 tailwater Guttenberg	06/22/1998	09/17/2002 <sup>c</sup>
3	IA	Mill Creek	1	MC01.0M	15	4680820	711480	TRIB	West side of Bellevue	03/26/1998	09/17/2002 <sup>c</sup>
3	IA	Maquoketa	0.1	MQ00.1M	15	4673779	722089	TRIB	at confluence with Mississippi R	09/23/1988	10/01/1991
3	IA	Maquoketa	2.1	MQ02.1M	15	4671190	720130	TRIB	mid-stream HWY 52 bridge	05/05/1993	09/18/2002 <sup>c,d</sup>
3	IL	Plum	3.2	PR03.2M	15	4662123	737762	TRIB	mid-stream HWY 84 bridge	05/03/1993	09/18/2002 <sup>c,d</sup>
3	IL	Rush Creek	1.7	RC01.7M	15	4671160	732650	TRIB	mid-stream HWY 84 bridge	05/03/1993	09/18/2002 <sup>c</sup>
3	IA	Rock Creek	0.1	RK00.1M	15	4628602	725088	TRIB	mid-stream HWY 67 bridge	06/11/1996	09/19/2002 <sup>c,d</sup>
3	IA	Rock Creek	3.7	RK03.7M	15	4630693	723012	TRIB	mid-stream	06/11/1996	09/19/2002 <sup>c,d</sup>
3	IA	Turkey	4.8	TK04.8M	15	4729939	657604	TRIB	mid-stream HWY 52 bridge	06/22/1998	09/17/2002 <sup>c</sup>
3	IA	Tete de Mortes Creek	4.1	TM04.1M	15	4692280	703053	TRIB	mid-stream HWY 52 bridge	06/24/1997	09/17/2002 <sup>c</sup>
3	IA	Wapsipinicon	2.6	WP02.6M	15	4622695	719618	TRIB	mid-stream HWY 67 bridge	05/05/1993	09/19/2002 <sup>c,d</sup>
4	MO	Bob's Creek	4.6	BC04.6M	15	4315141	695569	TRIB	mid-stream	05/03/1993	04/11/1994

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Table B-1. Continued.

Field station	State	River name	River mile	Location code <sup>a</sup>	UTM zone	Northing	Easting	Habitat class <sup>b</sup>	Additional comments	First sampled	Last sampled
4	IL	Cahokia Creek	0.4	CA00.4M	15	4298975	751328	TRIB	below spillway on S side of creek	05/05/1993	09/16/2002 <sup>c,d</sup>
4	MO	Cuivre	11.6	CU11.6M	15	4310565	695163	TRIB	mid-stream HWY 79 bridge	05/03/1993	09/18/2002 <sup>c,d</sup>
4	MO	Dardenne	1	DC01.0M	15	4303092	712694	TRIB	mid-stream HWY B bridge	05/03/1993	09/18/2002 <sup>c,d</sup>
4	IL	Creek Illinois	0	I000.0V	15	4316002	719584	MC	confluence mix	10/12/1990	12/04/1990
4	IL	Illinois	2	I002.0Y	15	4316012	719428	MC	confluence Illinois	10/12/1990	12/10/1990
4	IL	Illinois	5.7	I005.7M	15	4313347	714703	BWC	lower Swan Lake near mouth	08/04/1988	09/20/2002 <sup>c,d</sup>
4	IL	Illinois	5.8	I005.8K	15	4313556	714649	BWC	lower Swan Lake	08/04/1988	04/28/1993
4	IL	Illinois	7	I007.0W	15	4315756	712523	MC	Pere Marquette State Park	08/05/1988	09/20/2002 <sup>c,d</sup>
4	MO-IL	Mississippi	193.2	M193.2F	15	4297372	748748	MC	transect- MO side	05/05/1993	06/29/1999
4	MO-IL	Mississippi	193.2	M193.2H	15	4297202	748922	MC	transect - mid-stream	08/12/1997	06/29/1999
4	MO-IL	Mississippi	193.2	M193.2J	15	4296989	749100	MC	transect - IL side	08/12/1997	06/29/1999
4	MO-IL	Mississippi	196.9	M196.9Q	15	4302053	750631	MC	across from Shell Plant	05/05/1993	09/16/2002 <sup>c,d</sup>
4	MO-IL	Mississippi	201.7	M201.7Q	15	4305854	744970	IMP-L	Ellis Bay open water	06/03/1993	09/17/2002 <sup>c</sup>
4	MO-IL	Mississippi	202.2	M202.2N	15	4306157	743830	IMP-L	Ellis Bay shore	02/14/1990	09/17/2002 <sup>c</sup>
4	MO-IL	Mississippi	202.2	M202.2R	15	4306204	744769	IMP-L	Alton Slough	02/14/1990	04/27/1993
4	MO-IL	Mississippi	202.2	M202.2V	15	4306563	744990	IMP	channel border	07/19/1988	04/27/1993
4	MO-IL	Mississippi	202.6	M202.6T	15	4307283	744053	MC	transect site	05/30/1995	09/17/2002 <sup>c,d</sup>
4	MO-IL	Mississippi	202.6	M202.6V	15	4307404	744476	MC	transect site	07/12/1999	09/17/2002 <sup>c,d</sup>
4	MO-IL	Mississippi	202.6	M202.6X	15	4307404	744838	MC	transect site	07/12/1999	09/17/2002 <sup>c,d</sup>
4	MO-IL	Mississippi	202.9	M202.9N	15	4306696	743418	BWI	Ellis Lake	09/12/1991	04/05/1993
4	MO-IL	Mississippi	202.9	M202.9Q	15	4306774	743661	BWI	Ellis Lake	09/12/1991	04/05/1993
4	MO-IL	Mississippi	203.5	M203.5Q	15	4307244	742887	IMP	West Alton Bay	07/28/1988	04/27/1993
4	MO-IL	Mississippi	203.5	M203.5R	15	4307339	742896	IMP	West Alton Bay	07/19/1988	09/17/2002 <sup>c</sup>
4	MO-IL	Mississippi	205.8	M205.8K	15	4308992	739745	BWI	Spatardock Lake	07/27/1988	04/05/1993
4	MO-IL	Mississippi	206	M206.0S	15	4309158	739884	BWC	Brickhouse Slough	07/19/1988	09/16/2002 <sup>c</sup>
4	MO-IL	Mississippi	206.1	M206.1T	15	4309408	739967	BWI	Dresser Island	08/04/1988	09/18/2002 <sup>c</sup>
4	MO-IL	Mississippi	207.9	M207.9Q	15	4309780	737332	MC	Brickhouse Slough (levee on site now)	06/21/1990	09/27/1990
4	MO-IL	Mississippi	211.2	M211.2P	15	4311972	731978	MC	Portage	07/19/1988	04/27/1993

Table B-1. Continued.

Field station	State	River name	River mile	Location code <sup>c</sup>	UTM zone	Northing	Easting	Habitat class <sup>b</sup>	Additional comments	First sampled	Last sampled
4	MO-IL	Mississippi	212.3	M212.3X	15	4313163	731133	MC	Portage wing dam	08/09/1988	10/06/1992
4	MO-IL	Mississippi	212.4	M212.4X	15	4313146	731177	MC	Portage wing dam	08/03/1988	04/27/1993
4	MO-IL	Mississippi	219.4	M219.4U	15	4315208	720533	MC	Mason Island wing dam	10/18/1990	04/28/1993
4	MO-IL	Mississippi	219.5	M219.5U	15	4315191	720522	MC	Mason Island wing dam eddy	10/18/1990	12/10/1990
4	MO-IL	Mississippi	220.2	M220.2T	15	4315993	719428	SC	confluence Mississippi	10/12/1990	12/10/1990
4	MO-IL	Mississippi	224.2	M224.2S	15	4308859	716523	SC	Bolter Island	07/29/1988	04/28/1993
4	MO-IL	Mississippi	235.3	M235.3D	15	4309963	702654	BWI	Bernard Lake	08/07/1990	10/31/1990
4	MO-IL	Mississippi	235.5	M235.5D	15	4310285	702472	BWI	Bernard Lake	03/22/1990	09/20/2002 <sup>c</sup>
4	MO-IL	Mississippi	235.6	M235.6J	15	4310861	702973	MC	Hat Island	07/29/1988	04/28/1993
4	MO-IL	Mississippi	237.2	M237.2G	15	4312554	701683	BWC	Turkey Island Slough	07/29/1988	09/20/2002 <sup>c</sup>
4	MO-IL	Mississippi	237.3	M237.3T	15	4313769	701581	MC	Turkey Island wing dam	08/17/1988	10/13/1992
4	MO-IL	Mississippi	237.4	M237.4T	15	4313786	701569	MC	Turkey Island wing dam	07/29/1988	04/28/1993
4	MO-IL	Mississippi	240.9	M240.9M	15	4319612	700657	MC	Lock and Dam 25 Tailwater	10/10/1990	12/11/1990
4	MO-IL	Mississippi	241.3	M241.3K	15	4319635	700638	MC	Lock and Dam 25 Tailwater	10/05/1990	12/11/1990
4	MO-IL	Mississippi	241.4	M241.4K	15	4319647	700637	MC	Lock and Dam 25 Tailwater wing dam	10/05/1990	09/20/2002 <sup>c,d</sup>
4	MO	Missouri	2	MO02.0X	15	4301655	748277	TRIB	Missouri	05/05/1993	09/16/2002 <sup>c,d</sup>
4	MO	Peruque Creek	1.8	PE01.8M	15	4306271	703159	TRIB	mid-stream	05/06/1993	09/18/2002 <sup>c,d</sup>
4	IL	Piasa Creek	0.2	PI00.2M	15	4313310	735030	TRIB	mid-stream	05/04/1993	09/20/2002 <sup>c,d</sup>
4	IL	Wood	0.2	WD00.2M	15	4305319	749105	TRIB	between Rte. 143 bridge and spillway	05/05/1993	09/16/2002
5	IL	Big Muddy	0.7	BM00.7S	15	4164557	808267	TRIB	South bank	06/11/1991	09/24/2002 <sup>c</sup>
5	IL	Cache	1.1	CR01.1M	15	4112433	832994	TRIB	Mid channel	06/28/1994	05/04/1995
5	MO	Headwaters Diversion	0.5	HD00.5M	16	4125220	276500	TRIB	formerly Little R.	05/21/1991	02/26/1992
5	MO	Headwaters Diversion	0.9	HD00.9M	15	4127458	808024	TRIB	formerly Little R.	06/27/1991	09/23/2002 <sup>c</sup>

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**Table B-1.** Continued.

Field station	State	River name	River mile	Location code <sup>a</sup>	UTM zone	Northing	Easting	Habitat class <sup>b</sup>	Additional comments	First sampled	Last sampled
5	MO-IL	Mississippi	9.7	M009.7M	15	4106471	834768	MC	Natural bank	06/29/1994	05/04/1995
5	MO-IL	Mississippi	28.8	M028.8K	15	4104444	823740	MC	Bumgard side channel	05/08/1991	02/25/1992
5	MO-IL	Mississippi	30.5	M030.5J	15	4106136	822390	SC	Bumgard side channel	03/18/1991	04/01/1993
5	MO-IL	Mississippi	30.9	M030.9M	15	4107252	821148	MC	MO bank	03/19/1991	02/25/1992
5	MO-IL	Mississippi	32.2	M032.2M	15	4108748	821631	MC	MO bank	03/18/1991	02/25/1992
5	MO-IL	Mississippi	33.7	M033.7M	15	4110878	821525	MC	MO bank	06/10/1991	02/25/1992
5	MO-IL	Mississippi	34.2	M034.2M	15	4111566	821114	BWC	Santa Fe Side channel on MO bank	03/19/1991	02/25/1992
5	MO-IL	Mississippi	35.7	M035.7O	15	4114510	820513	SC	Santa Fe side channel	03/18/1991	04/01/1993
5	MO-IL	Mississippi	38	M038.0N	15	4118249	817577	BWC	Santa Fe side channel	03/19/1991	02/25/1992
5	MO-IL	Mississippi	38.1	M038.1J	15	4116525	817510	MC	revetted channel border above wing dam	03/03/1992	04/01/1993
5	MO-IL	Mississippi	38.5	M038.5J	15	4116894	817366	MC	revetted channel border above wing dam	03/19/1991	02/25/1992
5	MO-IL	Mississippi	38.5	M038.5N	15	4117455	818189	SC	Santa Fe Side channel	03/03/1992	04/01/1993
5	MO-IL	Mississippi	39.2	M039.2N	15	4118384	817415	BWC	revetted channel border	06/10/1991	02/25/1992
5	MO-IL	Mississippi	41.1	M041.1L	15	4120242	815692	MC	Unstructured natural bank	03/19/1991	02/25/1992
5	MO-IL	Mississippi	48	M048.0O	15	4128917	810930	SC	Marquette side channel lower	03/28/1991	04/01/1993
5	MO-IL	Mississippi	48.4	M048.4M	15	4128447	810505	MC	Lower Inside bend of Marquette island	03/28/1991	04/01/1993
5	MO-IL	Mississippi	48.5	M048.5M	15	4129592	810192	BWC	Cape Bend	03/28/1991	02/18/1992
5	MO-IL	Mississippi	48.9	M048.9G	15	4128578	809146	MC	Cape bend	05/26/1994	06/09/1995
5	MO-IL	Mississippi	50.7	M050.7I	15	4131395	809127	SC	Upper Marquette side channel	03/08/1992	04/01/1993
5	MO-IL	Mississippi	50.8	M050.8I	15	4131500	809039	BWC	Upper Marquette side channel	06/17/1991	03/03/1992
5	MO-IL	Mississippi	53.8	M053.8B	15	4136480	811240	MC	Main channel border revetted bank	06/17/1991	03/31/1993
5	MO-IL	Mississippi	54.2	M054.2B	15	4136988	811140	MC	Mid channel below Picayune outlet	06/17/1991	02/19/1992
5	MO-IL	Mississippi	55.9	M055.9D	15	4137754	813107	MC	channel border below wing dike	06/12/1991	02/19/1992
5	MO-IL	Mississippi	56	M056.0I	15	4136456	813140	SC	Lower Picayune side channel	03/25/1991	09/23/2002 <sup>c</sup>
5	MO-IL	Mississippi	57.9	M057.9L	15	4138345	816587	SC	Picayune side channel near hard-point	03/25/1991	03/31/1993
5	MO-IL	Mississippi	59.2	M059.2D	15	4141154	815774	BWC	Picayune side channel	06/12/1991	09/17/1991

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Table B-1. Continued.

Field station	State	River name	River mile	Location code <sup>a</sup>	UTM zone	Northing	Easting	Habitat class <sup>b</sup>	Additional comments	First sampled	Last sampled
5	MO-IL	Mississippi	59.5	M059.5I	15	4140542	817387	SC	Upper Picayune side channel	03/25/1991	09/23/2002 <sup>c</sup>
5	MO-IL	Mississippi	60.3	M060.3D	15	4142292	815843	SC	Schinemann chute 200m above closing structure	03/26/1991	03/31/1993
5	MO-IL	Mississippi	61.2	M061.2C	15	4143708	816659	MC	Main channel border	06/12/1991	03/31/1993
5	MO-IL	Mississippi	62	M062.0B	15	4144942	816178	SC	top of Schinemann chute	03/26/1991	03/31/1993
5	MO-IL	Mississippi	66.3	M066.3A	15	4150536	813525	MC	Main channel border at Trail of Tears transect site	01/14/2000	09/24/2002 <sup>c</sup>
5	MO-IL	Mississippi	66.3	M066.3B	15	4151068	813325	MC	Mid channel at Trail of Tears transect site	08/10/1995	09/24/2002 <sup>c</sup>
5	MO-IL	Mississippi	66.4	M066.4C	15	4151106	813883	MC	Main channel border at Trail of Tears transect site	03/20/1991	09/24/2002 <sup>c</sup>
5	MO-IL	Mississippi	69.4	M069.4C	15	4154920	810662	MC	channel border above wing dam	03/08/1992	03/31/1993
5	MO-IL	Mississippi	70.1	M070.1C	15	4155779	810256	MC	Main channel border at Neely's landing	06/11/1991	03/08/1992
5	MO-IL	Mississippi	70.2	M070.2A	15	4155709	809550	MC	Main channel border at Neely's landing	03/25/1991	09/24/2002 <sup>c</sup>
5	MO-IL	Mississippi	70.4	M070.4C	15	4156188	810125	MC	Main channel border at Neely's landing	07/15/1992	07/15/1992
5	MO-IL	Mississippi	75.1	M075.1C	15	4163004	807489	MC	channel border below wing dam	03/16/1992	03/31/1993
5	MO-IL	Mississippi	76.2	M076.2C	15	4164635	807529	MC	channel border above wing dam	06/11/1991	03/31/1993
5	MO-IL	Mississippi	77.9	M077.9A	15	4167389	807337	SC	Cottonwood side channel near MO bank	03/20/1991	03/31/1993
5	MO-IL	Mississippi	78	M078.0B	15	4167464	807933	MC	Outside buoy line on the inside bend of Cottonwood island	03/25/1991	09/24/2002 <sup>c</sup>
5	MO-IL	Mississippi	79.3	M079.3B	15	4168704	808215	MC	Rock piles above cottonwood island	03/20/1991	02/24/1992
6	IL	Illinois	80.2	I080.2C	15	4423724	710613	MC	LaGrange L/D near dam wall	01/20/1994	09/19/2002 <sup>c,d</sup>
6	IL	Illinois	80.2	I080.2M	15	4423711	710757	MC	LaGrange L/D mid channel	04/28/1993	09/19/2002 <sup>c,d</sup>
6	IL	Illinois	94.8	I094.8D	15	4441126	722694	SC	.	09/06/1989	04/12/1993
6	IL	Illinois	95.2	I095.2C	15	4441535	722628	MC	.	09/06/1989	04/12/1993
6	IL	Illinois	98	I098.0C	15	4444200	725466	BWC	.	09/06/1989	04/12/1993
6	IL	Illinois	99.4	I099.4C	15	4445489	727389	BWC	.	09/06/1989	04/12/1993

Table B-1. Continued.

Field station	State	River name	River mile	Location code <sup>a</sup>	UTM zone	Northing	Easting	Habitat class <sup>b</sup>	Additional comments	First sampled	Last sampled
6	IL	Illinois	99.4	I099.4D	15	445436	727389	BWC	.	09/06/1989	04/12/1993
6	IL	Illinois	106.5	I106.5X	15	4447352	739042	BWC	.	09/06/1989	04/12/1993
6	IL	Illinois	106.5	I106.5Y	15	4447313	739082	BWC	.	09/06/1989	04/12/1993
6	IL	Illinois	106.8	I106.8X	15	4447933	739451	BWC	.	10/30/1989	04/12/1993
6	IL	Illinois	107	I107.0S	15	4448554	738347	SC	.	09/06/1989	04/12/1993
6	IL	Illinois	107.2	I107.2R	15	4448885	738242	MC	.	09/06/1989	04/12/1993
6	IL	Illinois	109.5	I109.5D	15	4453509	738629	BWI	Anderson Lake 1/2 mi out ramp	09/12/1989	09/19/2002 <sup>c</sup>
6	IL	Illinois	113	I113.0T	15	4455335	743376	SC	east side of Bath Chute	09/06/1989	09/17/2002 <sup>c,d</sup>
6	IL	Illinois	121.2	I121.2W	15	4466765	749108	MC	east side near marker	09/01/1989	09/17/2002 <sup>c,d</sup>
6	IL	Illinois	121.5	I121.5X	15	4466910	749599	SC	.	09/01/1989	04/13/1993
6	IL	Illinois	122.5	I122.5X	15	4468394	750637	BWC	.	09/01/1989	04/13/1993
6	IL	Illinois	122.6	I122.6Y	15	4468389	750707	BWC	west side of Quiver Lake	09/01/1989	09/17/2002 <sup>c</sup>
6	IL	Illinois	124.8	I124.8R	15	4471935	751508	BWI	.	04/25/1990	05/25/1993
6	IL	Illinois	127.9	I127.9W	15	4473468	755714	BWI	.	04/25/1990	05/25/1993
6	IL	Illinois	128.8	I128.8F	15	4474868	755668	SC	.	08/28/1990	05/25/1993
6	IL	Illinois	128.8	I128.8T	15	4474258	756326	BWI	.	09/05/1989	05/25/1993
6	IL	Illinois	128.8	I128.8W	15	4474253	756813	BWI	.	09/05/1989	06/25/1991
6	IL	Illinois	129.8	I129.8W	15	4475007	757518	BWI	.	07/01/1991	05/25/1993
6	IL	Illinois	135.8	I135.8W	15	4483187	764092	BWI	.	10/19/1989	04/15/1993
6	IL	Illinois	135.8	I135.8X	15	4482995	764206	BWI	.	10/19/1989	04/15/1993
6	IL	Illinois	157.8	I157.8D	15	4501489	783249	MC	Peoria L/D east rock wall	04/28/1993	09/17/2002 <sup>c,d</sup>
6	IL	LaMoines	0.5	LM00.5M	15	4429191	711723	TRIB	middle near mouth	09/24/1993	09/19/2002 <sup>c,d</sup>
6	IL	LaMoines	7.2	LM07.2M	15	4428445	707351	TRIB	mid bridge on Lock and Dam Rd	01/20/1994	09/19/2002 <sup>c,d</sup>
6	IL	Mackinaw	4.4	MK04.4M	15	4491575	776765	TRIB	mid bridge 1mi off Manito Blacktop	04/26/1993	09/17/2002 <sup>c,d</sup>
6	IL	Quiver Creek	4.6	QV04.6M	15	4468071	758620	TRIB	mid bridge 1mi off Manito Blacktop	04/26/1993	09/16/2002 <sup>c,d</sup>
6	IL	Spoon	0.2	S000.2K	15	4465581	748649	TRIB	west side near mouth	12/05/1990	09/17/2002 <sup>c,d</sup>
6	IL	Sangamon	16.2	SG16.2C	15	4438599	743373	TRIB	mid bridge Hwy 78	04/10/1992	09/19/2002 <sup>c,d</sup>
7	IA-WI	Mississippi	646.9	M646.9X	15	4784632	653383	MC	Gordons Bay Landing	09/21/2001	10/16/2002 <sup>c,d</sup>

Table B-1. Continued.

Field station	State	River name	River mile	Location code <sup>a</sup>	UTM zone	Northing	Easting	Habitat class <sup>b</sup>	Additional comments	First sampled	Last sampled
7	IA-WI	Mississippi	647.9	M647.9X	15	4785905	654366	MC	LD 9 at first roller gate	06/28/1996	08/22/2001
7	IA-WI	Mississippi	663.4	M663.4E	15	4803341	645390	MC	Big Slough at Lansing bridge	04/19/1996	10/16/2002 <sup>c,d</sup>
7	IA-WI	Mississippi	666.3	M666.3N	15	4806582	644210	BWC	Big Lake at Lansing (backwater)	04/19/1996	08/07/2001
7	IA-WI	Mississippi	667.8	M667.8F	15	4808265	641825	BWC	Botsford (backwater north of Lansing)	04/19/1996	08/07/2001
7	WI	Wisconsin	5	WS05.0Y	15	4762468	659005	TRIB	Highway 18 Bridge	04/19/1996	10/16/2002 <sup>c,d</sup>
7	IA	Yellow	1.5	YL01.5Y	15	4772580	646725	TRIB	Effigy Mounds	04/19/1996	10/16/2002 <sup>c,d</sup>

<sup>a</sup>The following list is the codes for fixed-site sampling locations in the Long Term Resource Monitoring Program. The “xx.x” designation is the distance in miles (and tenths) upstream from the confluence of the tributary and the main stem of the Mississippi River (or Illinois River, where applicable). See Sections 1.5.1 and 1.5.2 for further explanation of the location codes.

APxx.xM	= Apple River, Missouri	HDxx.xM	= Headwaters Diversion, Missouri	Rxxx.xM	= Root River, Minnesota
ALxx.xM	= Apple River, Illinois		(formerly Little River)	RCxx.xM	= Rush Creek, Illinois
BCxx.xM	= Bob’s Creek, Missouri	Ixxx.xM	= Illinois River, Illinois	RKxx.xM	= Rock Creek, Iowa
BFxx.xM	= Buffalo River, Wisconsin	IWxx.xM	= Iowa River, Iowa	Sxxx.xM	= Spoon River, Illinois
BKxx.xM	= Black River, Wisconsin	KKxx.xM	= Kaskaskia River, Illinois	SGxx.xM	= Sangamon River, Illinois
BMxx.xM	= Big Muddy River, Illinois	LMxx.xM	= LaMoines River, Illinois	SKxx.xM	= Skunk River, Iowa
BXxx.xM	= Bad Axe River, Wisconsin	LRxx.xM	= Little River, Missouri (replaced by HD above)	SXxx.xM	= St. Croix River, Minnesota/Wisconsin
CAXx.xM	= Cahokia Creek, Illinois	LXxx.xM	= La Crosse River, Wisconsin	TMxx.xM	= Tete de Mortes Creek, Iowa
CFxx.xM	= CatFish Creek, Iowa	Mxxx.xM	= Mississippi River (main stem)	TKxx.xM	= Turkey River, Iowa
CNxx.xM	= Cannon River, Minnesota	MCxx.xM	= Mill Creek, Iowa	UIxx.xM	= Upper Iowa River, Iowa
CCxx.xM	= Coon Creek, Wisconsin	MKxx.xM	= Mackinaw River, Illinois	VMxx.xM	= Vermillion River, Minnesota
CHxx.xM	= Chippewa River, Wisconsin	MOxx.xM	= Missouri River, Missouri	WDxx.xM	= Wood River, Illinois
CRxx.xM	= Cache River, Illinois	MQxx.xM	= Maquoketa River, Iowa	WWxx.xM	= Whitewater River, Minnesota
CUxx.xM	= Cuivre River, Missouri	PExx.xM	= Peruque Creek, Missouri	WPxx.xM	= Wapsipinicon River, Iowa
DCxx.xM	= Dardenne Creek, Missouri	PIxx.xM	= Piasa Creek, Illinois	WSxx.xM	= Wisconsin River, Wisconsin
DMxx.xM	= Des Moines River, Iowa	PRxx.xM	= Plum River, Illinois	YLxx.xM	= Yellow River, Iowa
ERxx.xM	= Elk River, Iowa	QVxx.xM	= Quiver Creek, Illinois	ZMxx.xM	= Zumbro River, Minnesota
GAXx.xM	= Galena River, Illinois				

<sup>b</sup>BWC = backwaters, contiguous; BWI = backwaters, isolated; IMP = impounded areas; IMP-L = Pepin or Swan Lake; MC = main channel; SC = side channels; TRIB = tributary

<sup>c</sup>As of publication date, sampling was planned to resume or continue at these sites in 2004

<sup>d</sup>These sites were sampled for a reduced set of variables every 4 weeks from April to December 2003.

## Appendix C. Instrument Performance Quality Factor Codes

The performance of water quality monitoring instruments in the Long Term Resource Monitoring Program is rated on a graduated scale from fully acceptable to nonoperational. A quality factor code is assigned to each reading based on performance of the instrument in the field (if noticeably aberrant) and on calibration checks at the end of the sampling day (Table C-1).

**Table C-1.** Criteria for assigning quality factor (QF) codes to instrument readings in Long Term Resource Monitoring Program water quality monitoring based on deviations from calibration after sampling (down calibration). A blank QF indicates that readings are fully within requirements, 1 indicates acceptable, but slightly degraded performance, D indicates performance below acceptable standards, 0 indicates that readings cannot be used, but are recorded for diagnostic purposes and documentation only.

Parameter	Deviation (+/-) required for quality factor			
	Blank	"1"	"D"	"0" (zero)
Dissolved oxygen (mg/L)	< 0.24	0.25-0.50	0.51-1.0	>1.0
pH (units)	< 0.20	0.21-0.25	0.26-0.30	>0.30
Conductivity (µS)	< 14	15-20	21-27	>27
Turbidity <sup>a</sup>	≤2% of cal. standard	3-5% of cal. standard	6-10% of cal. standard	>10% of cal. standard

<sup>a</sup>Turbidity deviations of <1 nephelometric turbidity unit from calibration standard receive a blank QF code.

## Appendix D. Field Instrument Maintenance and Calibration

In general, maintenance and calibration of field instruments in the Long Term Resource Monitoring Program (LTRMP) is performed according to the manufacturer's instructions. This appendix provides more detailed and specific guidelines.

### *D.1 Acoustic Depth Finder*

Acoustic depth finders should be calibrated before first use and any time behavior seems questionable or after a major repair or alteration has been performed on the device. Some nonlinearity has been observed in these devices so that conversion to actual depth may not be precise. Water temperature can also make a small difference in calibration.

A calibration table or figure should be created for each acoustic depth finder in service. The measurements needed for this calibration should be taken in quiescent water (velocity <2 cm/sec) using a calibrated sounding line (such as used for Secchi disk transparency measurements). The sounding line with acoustic target attached is lowered over the side (or transom) and is centered as much as possible in the signal cone of the depth finder's transducer. Positioning of the crew members and cargo in the boat should be arranged to ensure the transducer is pointed vertically downward and does not change during the calibration process. A clear and distinct return signal from the target should be apparent. Using at least 5 depths, the reading of the instrument and the actual depth to the target are recorded. If possible, the maximum depth used in this exercise should encompass the maximum depth observed in the field. A linear regression of the actual depth on instrument reading can then be used to correct the acoustic sounder readings or verify its performance. Deviation of sounder readings from actual depth should be less than 10%. This check should be performed initially at high and low temperature extremes, and then at least once per year on each instrument.

### *D.2 Multiparameter Monitoring Instrument*

Since 1993, LTRMP water quality monitoring has used multiparameter monitoring instruments (Hydrolab Corporation, Loveland, CO) for *in situ* measurements of water temperature, dissolved oxygen, pH, and specific conductance. Routine maintenance of these probes is crucial to obtaining good quality data; therefore, LTRMP multiparameter instruments undergo maintenance and cleaning on a monthly basis, or as instrument performance and fouling dictate. A check list is provided for documentation of the monthly maintenance procedures (Appendix J). Specific instructions for care, maintenance, and calibration of the individual probes on these instruments are described in the instrument manuals (Hydrolab Corporation 1991*a,b*, 1997) and should be consulted for additional details. The instructions provided here augment or supplant those given in the instrument manuals.

#### **D.2.1 Dissolved Oxygen**

The LTRMP has used three calibration methods for electrometric dissolved oxygen sensors: saturated air and saturated water for daily or site-specific calibrations and the Winkler Method (azide modification) for quarterly calibrations and equipment cross-checks. The Winkler Method has great reliability and demonstrated accuracy (i.e., 0.2 mg/L). However, it is too time-consuming for frequent laboratory or field use and requires the use of toxic and hazardous materials (i.e., sodium azide). Therefore, saturation methods are used for all oxygen meter calibrations in LTRMP. The air saturation method can be done on-site relatively quickly and with acceptable accuracy and precision; it requires atmospheric air that is saturated with water vapor. The saturated water method is less vulnerable to method errors and is preferred over atmospheric air saturation.

Air or saturated water calibration is conducted before and at the end of the sampling day to keep

track of daily machine drift. Drift, determined from daily down-calibration procedures, is tracked on a control chart (Appendix J). If drift is outside of acceptable limits, then the data for the whole sampling day must be flagged with appropriate QF codes (Appendixes C and J). In addition, if a nontemperature-compensated probe is used (i.e., required for YSI model 57®, but not Hydrolab DataSonde3® or Minisonde®), then a saturated air calibration should be performed at ambient temperature before each measurement. The initials of the crew leader on the calibration sheet and crew leader code on the data sheet provide verification that the dissolved oxygen meter was calibrated according to these instructions.

Dissolved oxygen meter calibration must be checked quarterly using an air-saturated water bath. The zero point of the instrument is also checked quarterly using a sodium sulfite solution with cobalt chloride catalyst. When oxygen concentrations <1 mg/L are encountered or anticipated in the field, the zero point of the instrument must be checked on that sampling day. All the intermediate results (i.e., date, temperature, barometric pressure, calculated saturation value) are recorded on the quarterly dissolved oxygen calibration and performance sheet (Appendix J).

#### *D.2.1.1 Calibration with Saturated Air or Water*

- a. If using saturated water for calibration, aeration of low-ionic-strength (i.e., deionized) water should be started at least 1–2 hours before calibration.
- b. Follow the daily check-out and maintenance guidelines for the instrument, such as battery charge, membrane condition, and meter function, to prepare it for use.
- c. Allow the instrument to warm up as required by the manufacturer’s instructions.
- d. Place the probe in the calibration chamber. If the probe itself is immersed in the standard, use low-ionic-strength water (<500 µS) to avoid any interference because of salinity or salinity corrections. Tap water may suffice; but deionized (DI) water is often necessary.

- e. Turn the instrument on and monitor the temperature and dissolved oxygen readings in the calibration chamber or tank. If appropriate, ensure that the salinity correction is disabled. The probe, water, and air must all be in thermal equilibrium (same temperature) and the calibration media (air or water) must be at oxygen saturation.
- f. Obtain the atmospheric pressure (sea-level-corrected) by calling the nearest weather station or referring to a calibrated barometer. Local pressure changes associated with weather systems can have the same effect as moving up or down in altitude more than 1,000 ft (300 m). Use Table D-1 (assumes standard lapse rate of 1.07 inches of Hg/1,000 ft or 27.18 mm of Hg/1,000 ft) to convert the barometric pressure obtained from the weather service into absolute pressure (standard pressure at sea level is 760 mm of Hg). For example, local barometric pressure at Cape Girardeau is reported as 30.21 inches or 767 mm of Hg (to convert from inches to millimeters, multiply by 25.4). The absolute pressure needed to calculate oxygen solubility is therefore 767 – 11 = 756 mm of Hg. Using the YSI table (Yellow Springs Instrument Company, Inc., Yellow Springs, OH), this equates to a correction factor of about 0.99.

**Table D-1.** Standard barometric pressure correction for altitude.

<b>Site</b>	<b>Altitude (ft)</b>	<b>Correction (mm)</b>	<b>Standard pressure (mm)</b>
Lake City	750	-20	740
Onalaska	700	-19	741
Bellevue	650	-18	742
Great Rivers	420	-12	748
Cape Girardeau	400	-11	749
Havana	430	-12	748

- g. Obtain the temperature of the calibration media.

- h. If using a table look-up method, find the proper temperature and pressure or pressure correction factor on the chart and determine the air-saturated value for dissolved oxygen.
- i. Adjust meter to read saturated oxygen concentration. If the Winkler Method cross-check is not required, skip steps j and k below and record all intermediate results on the calibration sheet (Appendix J).
- j. Perform a triplicate determination of oxygen concentration in the saturated container using the Winkler Method (see above). All replicates should be within 0.1 mg/L of their mean value. Discard and repeat any errant determinations. Resolve any discrepancy between the triplicate Winkler Method results and the calculated saturation value (perform additional Winkler determinations if necessary). Adjust the meter to read proper concentration.
- k. Perform a zero point check using a sodium sulfite solution as described below. Record all intermediate results on the calibration sheet (Appendix J).

#### *D.2.1.2 Zero-Point Determination using Sodium Sulfite*

Sulfite ( $\text{SO}_3$ ) ions will react with dissolved oxygen in the presence of trace amounts of cobalt ion (catalyst) to form an anoxic solution. This solution can be used to check the zero oxygen setting of the dissolved oxygen meter. Because sulfite is a strong reducing agent, it can interfere with Winkler determinations by reducing iodine to iodide (result will be lower than actual value) and so should not be used to check the zero point of a Winkler determination. The zero point of most electrometric oxygen meters is quite stable and needs to be checked infrequently (monthly). However, whenever near-zero oxygen readings are anticipated in the field, the meter should be checked in this range.

The method for preparing and using a sulfite solution for zero point checking is as follows:

Use DI water. To a suitable volume (200–500 mL) of water, add a small amount (about 100 mg or one quarter teaspoon) of sodium sulfite (a few crystals may remain undissolved

at the bottom of the container). Next add two drops of cobalt catalyst (0.001 M solution of cobalt chloride). The oxygen concentration in the solution will rapidly drop toward zero. Submerge the oxygen probe in the solution (use a calibration cup if appropriate). Avoid agitation and after immersing the sensor, seal the solution and sensor off from the air if possible. Within 2 min, the oxygen meter should register 0.0 mg/L of oxygen. If the meter does not register between 0.0 and 0.2 mg/L, or if the reading is not stable, proceed with additional maintenance or repair as specified in the instrument manual. Once the check is complete, rinse the sensor thoroughly under tap water to remove any trace of the anoxic test solution. Now repeat the measurement of air saturation with DI water (bucket or exposed membrane method). The meter reading should return to the saturated value within 2 min.

#### **D.2.2 Dissolved Oxygen Electrode Cleaning**

The silver and silver chloride electrode used in the dissolved oxygen probe requires occasional cleaning. This is indicated by loss of linearity (instrument calibrated at one concentration does not read correctly at another) or readings that are consistently high- or off-scale. The procedure is as follows:

- a. Remove the dissolved oxygen membrane and discard the electrolyte.
- b. Fill a syringe with 10% ammonium hydroxide solution.
- c. Carefully fill the dissolved oxygen cell with ammonium hydroxide, using caution to keep the ammonium hydroxide solution from contacting the gold cathode.
- d. Allow the solution to remain in the sensor cell for 10–15 min.
- e. Remove the ammonium hydroxide carefully from the sensor cell; use the syringe to draw the solution back out or use a quick turning motion to eject the solution from the cell without it contacting the gold cathode.
- f. Rinse the sensor cell thoroughly with reagent grade water—repeat at least three times. After the first rinse, allow the cell

to overflow with rinse water during the rinsing process.

- g. Refill the dissolved oxygen sensor cell with reference electrolyte and replace the membrane.
- h. Allow the membrane to stabilize (relax) for at least 8 hours (preferably overnight) after replacement. Calibrate instrument before use.

### D.2.3 Temperature

Calibration of the temperature probe is checked quarterly by comparison to a traceable thermometer and to other units in use in the LTRMP. Results of this cross-check are held at each field station.

### D.2.4 pH

Several factors must be considered in calibrating and using a glass membrane pH probe:

- a. *The pH is Temperature Dependent.* The actual pH of a calibration buffer varies with temperature. This is described in a table that usually accompanies the buffer container. For example, at 5°C, a pH 10 buffer has an actual pH of 10.26. In general, calibration buffers and the pH probe should be stored at the same temperature (20–25°C). In any event, the probe and the sample (or buffer) must reach thermal equilibrium before an accurate reading can be made. There is no need to refrigerate buffer solutions; and if this is done, it complicates and degrades the calibration process. When checking for drift in the instrument's calibration (e.g., in measure mode), the actual temperature and pH of the buffer must be considered. No meter used by the LTRMP can perform this check automatically.
- b. *Under Field Conditions, Acceptable pH Precision is ±0.2.* Standard buffers have a precision of ±0.02 pH units and most field-grade probes and conditions allow a precision of about 0.10 pH units. Therefore, pH readings outside of ±0.2 are

unacceptable (±0.10 or better is desirable) for LTRMP water quality monitoring.

- c. *The Response of pH Probes is Slower at Low Temperatures.* Low temperature and the presence of interfering materials (i.e., phosphate and colloidal clays that clog the pores on the glass membrane) can greatly slow the response of the probe. Little can be done about the temperature effect except to allow longer times for equilibration, but regular cleaning in dilute hydrochloric acid and nondamaging solvents (e.g., alcohol) can help with the clogging. Samples cannot be warmed to room temperature to accelerate the pH measurements (see item a above).

#### D.2.4.1 Daily Calibration

A glass-membrane pH meter requires frequent calibration and maintenance. The glass membrane in the measurement electrode is extremely delicate and subject to chemical and biological fouling and breakage. The pH reference electrode is vulnerable to contamination and is sensitive to pressure (depth) effects.

Calibration and maintenance procedures can vary significantly among models and must be performed in strict conformance with the operator's manual for the specific model being used (Hydrolab 1991*a,b*, 1997).

Calibration of the pH sensor is performed by first setting the zero point (pH 7) and then setting the slope using a buffer with pH 4 or 10. In the LTRMP, the pH 10 buffer is more suitable for slope calibration because it represents the range more likely to be encountered in the field. A back-check to pH 7.0 after setting the slope is highly recommended. Drift, determined from daily down-calibration procedures, is tracked on a control chart (Appendix J). If drift is out of acceptable limits, then the data for the whole sampling day must be flagged with appropriate QF codes (Appendixes C and J). If the pH sensor will not calibrate or shows excessive drift outside the performance criteria for pH meters, it should be serviced or replaced in accordance

with the manufacturer's instructions (Hydrolab Corporation 1991*a,b*, 1997).

### D.2.5 Conductivity

Conductivity is calibrated each day at the start and end of sampling and as indicated by unusual instrument performance. At least two standard solutions are used and procedures follow the manufacturer's instructions (Hydrolab Corporation 1991*a,b*, 1997). Drift, determined from daily down-calibration procedures, is tracked on a control chart (Appendix J). If drift is out of acceptable limits, then the data for the whole sampling day must be flagged with appropriate QF codes (Appendixes C and J).

Instruments used for conductivity measurements in LTRMP water quality monitoring must meet or exceed the following requirements:

- a. The device must have a maximum error not more than 1% or 1  $\mu\text{S}/\text{cm}$ , whichever is greater (APHA 1992).
- b. The device meets all of the response and sensitivity criteria published by the manufacturer.
- c. Criteria 1 and 2 above are checked and met for each sampling day.
- d. The equipment automatically compensates for temperature and displays specific conductance at 25°C.

### D.3 Nephelometer

Maintenance and calibration requirements differ among types of nephelometers. However, nephelometers in general require frequent calibration and maintenance (e.g., both daily and monthly).

Nephelometer cuvettes should be rinsed with distilled water after each day's use and washed with mild soap once a week. A final rinse with distilled water is recommended to avoid water spots. For *in situ* instruments (i.e., Hydrolab DataSonde3<sup>®</sup>), the probe should be rinsed with mild soapy water at the end of each sampling day. Instruments taken into the field must be protected from excessive vibration or jarring

(keep in padded container while in transit); in cold weather, instruments must be kept above freezing. This can be accomplished by keeping the instrument in an insulated container (e.g., a cooler) or provided with a heat source (Appendix G).

### D.3.1 Daily Checklist

- a. Check battery or power supply as applicable.
- b. Perform a daily calibration—check against three Gelex standards and record in the daily calibration control chart (Appendix J).
- c. If the calibration is out of acceptable limits as indicated on the calibration control chart, then the meter must be recalibrated with formazin or Hach StablCal<sup>®</sup> standards according to procedures in the following section. If the meter is not recalibrated, then the appropriate QF codes must be assigned (Appendixes C and J).

### D.3.2 Calibration of Hach 2100P with Hach StablCal<sup>®</sup> Stabilized Formazin Standards

Instructions are provided here for calibration of the Hach 2100P meter with Hach StablCal<sup>®</sup> Stabilized Formazin Standards because they are safer and more convenient to use than manually prepared formazin. However, these procedures may optionally be used with formazin prepared according to instructions in Section F.2.3.4. If you are preparing your own standards, then once the necessary standards are ready, proceed with step "e."

- a. The StablCal<sup>®</sup> standards are good for 24 months from the date of manufacture. This ensures 12 months of use. For long-term storage (more than 1 month between use), refrigerate at 5°C. Store away from direct sunlight. Vials should be stored in their original kit with the cover on.
- b. Always allow the standards to acclimate to ambient instrument temperature before use (not to exceed 40°C).
- c. Shake the 20-, 100-, and 800-NTU StablCal<sup>®</sup> standards vigorously for 2–3 min if they have been sitting for more than 1 week. DO NOT SHAKE OR INVERT

- the <0.1-NTU standard. Let standards sit undisturbed for 5 min.
- d. Invert StablCal® standards two to three times (except <0.1 NTU) and let sit 2–3 min. Oil and wipe outside of StablCal® standards, read, and record as formazin readings (pre-cal).
  - e. Oil and wipe outside of daily Gelex® standards, read, and record as Pre-cal Gelex® standard values.
  - f. Insert a clean cell filled with reagent grade water. Press **I/O**.
  - g. Press **CAL**. The CAL and S0 indicators will display and the 0 will flash. If the blank value was set to zero at the last calibration, then the display will be blank; otherwise, the value for the previous calibration will be displayed.
  - h. Press **READ**. The meter will count from 60 to 0 and then measure the turbidity. If using formazin standards, the meter will use the blank to calculate a correction for the subsequent standards. If the DI water used is >0.5 NTU, an E1 will appear. If this happens, clean cell and use new DI water. The display will automatically move to the next standard. Remove the 0 standard.
  - i. The display will show S1 (with the 1 flashing) and either 20 NTU or the value of the previous S1 standard. If using formazin and the value is incorrect, edit by pressing **RIGHT ARROW** until the number that needs editing flashes, then use the **UP ARROW** to scroll to the correct value. For StablCal® standards, it should read 20 NTU. Insert either a well-mixed formazin 20 NTU standard or the 20-NTU StablCal® standard. Press **READ**. The meter will count from 60 to 0, measure the turbidity, and then store the value. The display will automatically move to the next standard. Remove the cuvette.
  - j. The display will show S2 (with the 2 flashing) and either 100 NTU or the value of the previous S2 standard. If using formazin and the value is incorrect, edit by pressing **RIGHT ARROW** until the number that needs editing flashes, then use the **UP ARROW** to scroll to the correct value. For StablCal® standards, it should read 100 NTU. Insert either a well-mixed formazin 100-NTU standard or the 100-NTU StablCal® standard. Press **READ**. The meter will count from 60 to 0, measure the turbidity, and then store the value. The display will automatically move to the next standard. Remove the cuvette.
  - k. The display will show S3 (with the 3 flashing) and either 800 NTU or the value of the previous S3 standard. If using formazin and the value is incorrect, edit by pressing **RIGHT ARROW** until the number that needs editing flashes, then use the **UP ARROW** to scroll to the correct value. For StablCal® standards, it should read 800 NTU. Insert either a well-mixed formazin 800-NTU standard or the 800-NTU StablCal® standard. Press **READ**. The meter will count from 60 to 0, measure the turbidity, and then store the value. Remove the cuvette and press **CAL** to accept the calibration. The instrument will return to measurement mode automatically.
  - l. Immediately after performing the formazin or StablCal® standard calibration, re-measure any Gelex® standards used with this specific meter and record the new value on the Gelex® standard. Remember Gelex® standards are associated with a specific instrument; they cannot be used on another instrument without separate calibration for that instrument.
  - m. Record the calibration on the calibration sheet and prepare a new control chart. Check the Hach 2100P manual if any error messages occur or for more complete calibration instructions.

#### *D.4 Velocity Meter (Marsh McBirney Model 201D)*

Maintenance and calibration requirements for the Marsh McBirney Model 201D include the following (see manufacturer's instructions for a complete discussion):

- a. Move the selector switch to **CAL** position.
- b. Set the time constant switch to **2**. After 10 sec, the readout should be on or between 9.8 and 10.2. If it is not, check the

battery pack connections and the batteries. If this does not resolve the problem, technical servicing may be required.

*D.5 Velocity Meter (Marsh-McBirney  
Flo-mate™ Model 2000)*

Notes:

- a. Never turn the selector switch past the CAL position when the probe is out of the water.
- b. Clean the sensor with clean water or mild dish soap and water if needed after each field day.
- c. Be extremely careful not to scratch the sensor surface in any way; treat it as if it were an optical surface.
- d. Do not store the meter for an extended time without removing the batteries.
- e. The sensor is delicate. Care should be taken when handling it, as banging or jarring of the sensor may cause serious damage.

The Marsh-McBirney Flo-mate™ Model 2000 velocity meter requires limited maintenance and calibration. Calibration checks must be made at the factory, or by comparison to a recently calibrated meter at least annually, or whenever meter performance is questionable. Documentation of these performance checks and calibrations is maintained at the field station. It is essential to keep the sensor clean of any contaminants, especially oil and grease. Instructions in the instrument manual should be followed exactly for daily cleaning of the sensor and checking the zero point (Marsh-McBirney 1994).

## Appendix E. Equipment List for Water Quality Monitoring

The equipment used in the Long Term Resource Monitoring Program (LTRMP) water quality monitoring has evolved over time (Table E-1). The items listed here are the typical configuration used by most field teams, but where other equipment has been documented to meet the necessary performance requirements it has occasionally been substituted by some participants. The following list does not constitute a commercial endorsement of the equipment or vendors by the LTRMP, the U.S. Geological Survey, or any LTRMP participants.

**Table E-1.** Major field equipment items used in the Long Term Resource Monitoring Program by water quality monitoring teams.

Manufacturer	Model	Description and use
Hydrolab Corporation, Loveland, Colorado	Minisonde4, Datasonde3 (phased out in 2002)	Temperature, dissolved oxygen, specific conductance, pH
Omnidata International, Inc., Logan, Utah	Polycorder 286LX handheld DOS computer	Data display for Datasonde3 Phased out in 2002
Hach Company, Loveland, Colorado	2100P portable turbidimeter	Nephelometer for turbidity measurements
Marsh-McBirney Inc., Frederick, Maryland	Flo-mate™ Model 2000 water flowmeter	Electromagnetic velocity meter
Marsh-McBirney Inc., Frederick, Maryland	201/201D portable water flowmeter	Electromagnetic velocity meter
Biohit, Inc.	Biohit Proline pipette fixed volume 5,000 µL	Fluorometric chlorophyll- <i>a</i> volume
Itronix®, Spokane, Washington	XC6260 Pro	Laptop PC, platform for electronic data sheet, and instrument interface
Itronix®, Spokane, Washington	GoBook MAX™	Laptop PC, platform for electronic data sheet, and instrument interface

## Appendix F. Previous Methods and Equipment

This appendix describes selected procedures and equipment no longer used in the Long Term Resource Monitoring. This information is provided to help interpret historical data obtained with these methods and equipment and to guide operation of nonstandard equipment when necessary.

### *F.1 Previous Methods*

#### **F.1.1 Winkler Method for Dissolved Oxygen (discontinued in July 1997)**

The Winkler Method generates elemental iodine in proportion to the amount of dissolved oxygen in the original sample. This iodine is extremely volatile and is generated when the sample is acidified in step f below. After acidification, iodine can escape from the sample, and the dissolved oxygen as determined by the titration of the iodine will be erroneous (low). Excess iodide in the sample helps to stabilize the solution and reduces iodine losses, but the sample must be titrated without delay. The amount of iodine generated is measured by titration with thiosulfate solution. Thiosulfate solution, even when stabilized is not truly stable and its strength must be checked weekly against a standard biiodate solution (available from Hach Chemical, Loveland, CO; method described below).

Water samples for the Winkler Method of dissolved oxygen determination are collected from a specific depth using a discrete sampler (Section 7.3) and then analyzed following *Standard Methods* (APHA 1992). The sample must not be agitated or allowed to come into contact with the air after collection. The sample is transferred from the sampling device to a biological oxygen demand (BOD) bottle (250 to 300 mL) by a tube that extends from the sampler to the bottom of the BOD bottle. The BOD bottle is allowed to overflow with the sample for approximately 10 sec while minimizing turbulence and ensuring that no bubbles are formed. The BOD bottle is tilted slightly and a

glass stopper wetted with leftover water from the sample is inserted so that no bubbles are entrained.

Chemical analysis of the bottled sample exactly follows the azide modification of the Winkler Method described in *Standard Methods* (APHA 1992) and is described below. Collected samples should be fixed immediately by addition of manganese and azide reagents (injected below the sample surface). If the samples are quickly taken past the acid addition and properly water-sealed, they can be stored in darkness and at temperatures between 20 and 30°C for up to 12 hours before the remainder of the analysis is completed.

**CAUTION: THE CHEMICALS USED FOR THE WINKLER METHOD ARE TOXIC AND CORROSIVE, SO BE SURE TO WEAR PROTECTIVE CLOTHING AND USE SAFE LABORATORY PROCEDURES.**

- a. Remove stopper and add 1 mL of the manganous sulfate first and then 1 mL of the alkaline iodide azide solution to each BOD bottle (add reagents in this order—inject reagents below the water surface in the bottle).
- b. Insert the glass stoppers in the BOD bottles and mix by inverting gently. This should be done over a sink, as some overflow will occur when the stopper is inserted. Before proceeding to the next step, wait for the precipitate to settle until the upper third of the bottle contains only clear solution.
- c. After the precipitate has settled, remove the stopper from one BOD bottle, add one 3-g powder pillow of sulfamic acid (or 1 mL of concentrated sulfuric acid), and replace stopper on bottle immediately. Repeat for each BOD bottle. Gently mix by inverting the bottles until all solids are dissolved. This should be done over a sink as some overflow

will occur. If necessary and if proper water seal is carefully maintained, the sample may now be held for up to 12 hours before proceeding with steps d–i.

- d. Fill the titration buret with standardized sodium thiosulfate solution (0.025 N).
- e. Pour the solution from the BOD bottle into a volumetric flask (203-mL polypropylene) and then into a 500-mL Erlenmeyer flask for titration. Begin to titrate IMMEDIATELY. The use of 203 mL instead of 200 mL is to compensate for the addition of fixing agents to the original sample volume. A volumetric flask is used instead of the entire BOD bottle volume because BOD bottles are not particularly precise in their dimensions.
- f. Titrate the flask solution to a pale yellow color.
- g. Add 2 drops of starch indicator to the flask solution. A blue color should appear.
- h. Titrate carefully until the solution is clear.
- i. REPEAT steps g–h for each BOD bottle.

Each milliliter of sodium thiosulfate (at 0.0250 N) used in the titration equals 1.0 mg/L of dissolved oxygen (DO). If the thiosulfate is not exactly 0.0250 N, then a correction factor must be applied (see below).

#### *F.1.1.1 Thiosulfate Standardization*

A 200-mL sample (not 203 mL as used in DO titrations) of standard biiodate solution (0.00125 N; available from Hach Chemical in 4-L bottles) is measured out with a volumetric flask and added to a 500-mL Erlenmeyer flask. A powder pillow (3 g) of sulfamic acid or 1 mL of concentrated sulfuric acid is added and the sample is swirled. The sample in the Erlenmeyer flask is now exactly equivalent to a 10-mg/L DO sample; proceed with the titration as in steps d–i above. Repeat this determination three times, recording the results. A correction factor for the actual strength of the thiosulfate solution is then calculated by dividing 10 by the average volume of titrant used in this standardization test (e.g.,  $10.0/10.40 = 0.961$ ). This correction factor is then applied to sample titrations performed with this thiosulfate solution. For example:

$$\text{DO mg/L in sample} = (\text{milliliters of titrant}) \times (\text{correction factor})$$

### **F.1.2 Nitrogen—Total Kjeldahl**

In the LTRMP, total Kjeldahl nitrogen (TKN; organic nitrogen plus ammonia nitrogen) is determined from an unfiltered sample. In the analysis, all forms of organic nitrogen are reduced (by Kjeldahl digestion) to ammonia, which is then measured quantitatively. Any ammonium or ammonia ( $\text{NH}_x$ ) present in the original sample becomes part of the TKN. A separate analysis for ammonia on an undigested portion of the sample is used to determine the concentration of  $\text{NH}_x$  before digestion, and the concentration of organic nitrogen in the sample can be calculated by the difference. The LTRMP discontinued Kjeldahl nitrogen analyses after analytical responsibilities were transferred to the LTRMP laboratory from the Waterways Experiment Station in 1993. However, TKN can be estimated from subsequent measurements by subtracting  $\text{NO}_x$  measurements from total nitrogen values.

#### *F.1.2.1 Definition*

The TKN is defined as the total amount of ammonia or ammonium nitrogen (expressed as milligrams of elemental nitrogen per liter) that is detected after an unfiltered sample is subjected to Kjeldahl digestion (APHA 1992).

### **F.1.3 Nitrogen—Dissolved Kjeldahl**

Total dissolved Kjeldahl nitrogen (DKN; organic nitrogen plus ammonium nitrogen) is determined as for TKN (Section F.1.2), but a sample is filtered in the field for the analysis. This constituent was measured in the LTRMP from June 1991 to April 1993 (Appendix A).

#### *F.1.3.1 Definition*

The DKN is defined as the total amount of ammonia or ammonium nitrogen (expressed as milligrams of elemental nitrogen per liter) that is detected after a filtered (0.45- $\mu\text{m}$  membrane)

sample is subjected to Kjeldahl digestion (APHA 1992).

*F.1.3.2 Sample Collection and Preservation*

An appropriate depth-discrete water sample (Section 7.3) is collected. The sample is filtered (0.45- $\mu$ m membrane) and preserved with sulfuric acid (pH approximately 2.5; Section 7) and is held in the dark on ice (approximately 4°C), until shipped to the laboratory for analysis.

**F.1.4 Nitrogen—Total Dissolved**

In the LTRMP, total dissolved nitrogen is not a separate analytical measurement, but is calculated by adding DKN and NO<sub>x</sub> concentrations (see appropriate sections).

**F.1.5 Phosphorus—Total Dissolved**

The “total dissolved” concentration of phosphorus includes all common chemical forms of the material, both particulate and dissolved, that pass through a 0.45- $\mu$ m membrane filter. A single chemical digestion is used to dissolve and hydrolyze all common forms of phosphorus in a filtered sample to produce orthophosphate, which can then be measured precisely in a single chemical analysis.

*F.1.5.1 Definition*

Total dissolved phosphorus (TDP) is defined as the total amount of reactive phosphorus (expressed as milligrams of elemental phosphorus per liter) that is detected with the ascorbic acid method (APHA 1992) after a filtered (0.45- $\mu$ m membrane) sample is digested with persulfate under acid conditions (APHA 1992).

*F.1.5.2 Sample Collection and Preservation*

An appropriate depth-discrete water sample (Section 7) is collected. The sample is filtered (0.45- $\mu$ m membrane), preserved with sulfuric acid (pH approximately 2.5), and is held in the

dark on ice (approximately 4°C), until shipped to the laboratory for analysis.

*F.2 Previous Equipment*

This section provides information on equipment that was used previously in the LTRMP for water quality monitoring so that the data that was collected with this equipment may be properly interpreted.

**F.2.1 Cole-Palmer Model 4070 Conductivity Meter**

This section does not describe this instrument, but rather the methods used in the LTRMP for its calibration. Because the conductivity of standard potassium chloride (KCl) solutions varies with temperature, and some early model conductivity meters were not temperature compensated, a table (Table F-1) was provided to make this correction manually if necessary. This table was also used to verify the performance of the automatic temperature compensation feature on meters with this capability.

**Table F-1.** Conductivity of a 0.005 M KCl (potassium chloride) solution at various temperatures. Conductivity at 25°C is defined as 717.5  $\mu$ S/cm.

Temperature	Conductivity
20	646
21	660
22	674
23	689
24	703
<b>25</b>	<b>717.5</b>
26	732
27	746
28	761

When calibrating the instrument, a zero or low cal check is normally done first. This is accomplished by having the sensor dry in air or in distilled water. Select **COND** for display and

press the **CAL LOW** key. The unit will display 00.0. Press the **CAL LOW** key again and the instrument will take a zero reading on each of the three ranges.

The next step in calibration is to do a span or **CAL HIGH**. We first rinse the sensor thoroughly in distilled water and dry it so as not to cross contaminate the standard solution. Place the sensor in the calibration solution and allow the sensor to equilibrate for several minutes (stir sensor periodically). Select **COND** for display and press **CAL HIGH** key. The unit will display the value of the last calibration solution. If this is different than the solution value presently being used, adjust the display for the proper value with the **UP** or **DOWN ARROW** keys.

There are several considerations when doing a span function. First, the value of the standard solution should be greater than 20% of the range selected (i.e., higher than 0.400 on the low range; higher than 4 on the midrange; between 40 and 70 on the high range). The instrument must be operating on the same range as the calibration entry value. Assuming we will be using a 1.408-mS/cm solution at 25°C, the instrument should be operating on the low (0–1.999 mS/cm) range before the **CAL HIGH** key is pressed for the first time. This must be verified because the unit will not change ranges once the calibration sequence is begun.

Once the appropriate range is established and the **CAL HIGH** key is pressed, adjust the displayed value to that of the calibration solution. Pay attention to the position of the decimal point. It must correspond to the instrument's selected operating range. When using the 1.408-mS/cm standard, the **CAL HIGH** value must be entered with three decimal places, otherwise the slope that is calculated will be in error. If the original **CAL HIGH** value is not on the appropriate range, just press the **ARROW** key that points in the correct direction of adjustment. The cal number will begin to change in that direction, slowly at first and then more rapidly. Watch the position of the decimal point. It will change as the decades change. When the decimal point is in the correct position for the desired range, release the **ARROW** key and then depress it again. This will

slow the rate of change so that the desired value is not overrun by a large amount.

It is good practice to disable the auto-shut off feature during a **CAL HIGH** procedure. This will keep the unit from turning off if the operator is diverted in the middle of the calibration. Once the calibration solution value has been inputted, press the **CAL HIGH** key again and the unit will establish a proper slope, store its new calibration data, and return to the measurement mode.

#### *F.2.1.1 Daily Calibration*

The conductivity meter is calibrated daily using a 0.01 M KCl solution. The procedure is as follows:

- a. Set the **MODE** switch to **SET K**.
- b. Adjust the display to the correct cell constant by using a small screwdriver inserted through the hole in the back of the meter.
- c. Obtain a factory premixed KCl solution (certified to National Bureau of Standards).
- d. Rinse the cell with some of the solution.
- e. Place the cell in the solution.
- f. Set the **MODE** to **mS**.
- g. Measure the resistance or conductivity of the solution by adjusting the **MODE** to progressively more sensitive ranges until the highest possible reading is obtained.

There is no need to correct the reading to 25°C as the meter does this automatically.

Maintenance of the conductivity meter involves daily cleaning of the cell in a mild dish soap.

Winter maintenance includes keeping the cell and meter in an insulated box in a warm environment (Section 4.3).

If the readings become erratic or when a sharp endpoint cannot be obtained, check the cell's platinum electrode. If the black coating is flaking or dirty, the cell needs to be replatinized or replaced until it can be replatinized (remember to **SET K** for the new cell).

#### *F.2.1.2 Replatinizing Procedure*

It is strongly recommended that this procedure not be attempted by field station personnel. The

LTRMP will maintain limited ability to perform this procedure on equipment for which it is feasible.

- a. Clean the cell in a solution of 1-g chloroplantinic acid and 12-mg lead acetate in 100-mL distilled water.
- b. Immerse the cell in the solution.
- c. Connect both probes to the negative side of a 1.5-V dry cell battery.
- d. Connect the positive side of the battery to a piece of platinum wire and dip into the solution.
- e. Continue the electrolysis until both probes are coated with platinum black.
- f. Rinse with distilled water.
- g. The cell is now ready for use.

### **F.2.2 Orion 230A pH Meter**

This pH meter recognizes standard buffers and has the temperature-pH information that appears on the buffer label already programmed into its internal memory. In autocalibrate mode, the meter will (a) recognize the type of buffer that it is in (if pH is even close), (b) determine the actual temperature of the buffer, and (c) use the corrected pH value of the buffer at that temperature to calibrate itself. For example, if you manually enter pH 10 for a standard buffer solution at 5°C (to get the meter within the appropriate range), you will see the pH jump to 10.26 when the meter completes its self-calibration. Some have incorrectly interpreted this behavior as a malfunction of the instrument. In manual mode, the pH buffer values are FORCED into the instrument by pressing the YES key after each digit is entered. For correct results, these values must accurately reflect the pH of the buffer at that temperature. The primary purpose of manual mode is to allow the use of nonstandard buffers.

Additional details are provided in the Orion instruction manual (part number 213376-001, 1991 edition; pages 13–16).

The LTRMP field stations reported frequent problems with the thermistor probe on this meter and with fouling of the pH electrode (unacceptably slow response or inability to calibrate). Frequent cleaning and checking of

the probes were required. Replacement of the original probes with more robust versions was recommended.

### **F.2.3 Hach Model 16800 Turbidimeter and Hydrolab Datasonde 3<sup>®</sup> Equipped with Turbidity Sensor**

For Hach Model 16800 turbidimeters that are taken into the field, calibration must be checked against secondary (field) standards at each site or whenever the instrument is subjected to significant vibration or bouncing (i.e., during travel between sites). Calibrations are performed according to manufacturer's instructions.

#### *F.2.3.1 Daily Checklist*

- a. Check battery or power supply as applicable. When operating in cold weather, ensure that heater batteries are fully charged.
- b. Perform a zero nephelometric turbidity unit (NTU) or stray light check as applicable.
- c. Calibrate the instrument against an appropriate set of standards that adequately cover the range likely to be encountered in the field. If both low (approximately 10 NTU) and high (100–1,000 NTU) turbidity conditions are likely to be encountered, the instrument should be checked in both ranges. With the Hach Model 16800, use the cell riser when measuring at the 100- or 1,000-NTU range and be sure that the dot on the cuvette faces forward. Note that the nominal value for secondary Gelex<sup>®</sup> standards is not precise and is instrument-dependent. The formazin equivalent for a specific combination of Gelex<sup>®</sup> standard and nephelometer must be determined at regular intervals (see below). Calibration values for Gelex<sup>®</sup> standards are marked on top of the cap.

Note: All turbidity standards have a limited shelf life; only unexpired standards can be used for calibration. If calibration requires a major adjustment of the instrument, the secondary standard is checked against another set of secondary or primary

(formazin) standards. If the instrument still does not function properly, the water quality coordinator should be notified to coordinate repair and replacement.

#### *F.2.3.2 Method (Hach Model 16800)*

Grab samples for turbidity are collected using the appropriate depth-specific sampler (Section 7.3). The LTRMP does not require that turbidity measurements be made in the field, but turbidity should be measured at the time of collection or as soon as practicable to avoid changes in the sample characteristics that might result from particle precipitation, flocculation, dissolution, growth, or decomposition. If the measurement is delayed, samples are kept from freezing, held in the dark at about 4°C, and measured within 24 hours of collection. The steps for measuring turbidity on a grab sample are as follows:

- a. A grab sample is collected (Section 7) and inspected to ensure that it has not been contaminated with bottom sediment or contains large debris or vegetation fragments. If the bottom sediment has been disturbed or the sample is otherwise contaminated, then another sample is collected, either in an undisturbed section of the site or after the water current has cleared the disturbance.
- b. The sample should be gently inverted several times immediately before measurement. This resuspends any settled particulates without introducing air bubbles into the sample.
- c. The cuvette is rinsed with sample water, and then an appropriate volume of sample is carefully poured into the clean cuvette. Avoid creating air bubbles while pouring the sample, and do not handle the cuvette in the optical area as oils from the skin will cause an erroneous reading.
- d. Carefully wipe the cuvette with a piece of cheesecloth or other soft material (laboratory wipes may scratch the glass) and place into the nephelometer. Maintain a consistent orientation of the cuvette (i.e., one surface always facing forward).
- e. Record the turbidity measurement. If the reading is unstable (i.e., fluctuates more than  $\pm 5\%$  because of settling of material or movement of large particles), refill the cuvette from the same, well-mixed, grab sample and repeat the reading. Allow the instrument to settle from the shock of cuvette movement before taking the reading (1–2 sec), but do not wait long enough for the material to settle from the sample ( $>5$  sec). Be sure that the grab sample is properly agitated before refilling the cuvette (see step b). If highly unstable readings are encountered (not because of instrument malfunction), three determinations from the same sample container are averaged. However, if one of these readings deviates substantially ( $>20\%$ ) from the other two, disregard the deviant reading and take another.
- f. When turbidity is too high to measure directly (off scale), then a sample dilution is used. Dilution is performed with volumetric pipettes (1–10 mL), a volumetric flask (100 mL), and a beaker (150–250 mL). For a 0.1X dilution, 10 mL of the sample is added to a clean (not necessarily dry) 100-mL volumetric flask. Distilled water is then added to bring the total volume up to 100 mL. The flask is swirled when about one-half the distilled water is added and then again when three-fourths of the distilled water has been added. The 100-mL mixture is poured into the beaker to ensure good mixing (do not introduce air bubbles). The diluted sample is then read in the turbidimeter as usual, with the reading divided by the dilution factor (e.g., 30 NTU/0.1 = 300 NTU in original sample).  
If turbidity is still too high to read, a greater dilution factor must be used. **DO NOT FURTHER DILUTE A SAMPLE THAT HAS ALREADY BEEN DILUTED—START FRESH.** To achieve a 0.050X dilution, pipette exactly 5.00 mL of a well-shaken sample into a clean (rinsed with distilled water) volumetric (100-mL) flask and add distilled water as above to make

100 mL of mixture. The NTU reading in this example is divided by 0.05 (or multiplied by 20).

If even greater dilution is needed (extremely unlikely), dilute 2.50 mL of original sample to 100 mL in the cleaned volumetric flask and divide the NTU reading by 0.025 (multiply by 40).

In the sample comment section of the data sheet, record the dilution volumes used (i.e., 10/100). Keep in mind that dilution with distilled water can alter the particulate materials in the sample, so dilution should be kept to a minimum.

#### *F.2.3.3 Comparison of Secondary Standards for Hach Model 16800*

The following section is applicable if secondary standards are used for field calibration. When field calibrations are required (i.e., with Hach Model 16800), each field station maintains two sets of secondary Gelex® standards. One set is normally used in the field, and the second set is kept in the laboratory. These two sets of standards are compared to each other monthly to verify their condition. Important notes: (1) turbidity standards have a limited shelf life; only unexpired standards can be used for calibration, and (2) Gelex® turbidity standards are not interchangeable among instruments (i.e., a single Gelex® standard may give slightly different turbidity readings in two properly functioning nephelometers that have just been calibrated to the same formazin standard).

- a. Calibrate the nephelometer using the unexpired set of laboratory Gelex® standards for 100 and 10 NTU, remember to use the cell riser when measuring solutions in the 100- or 1,000-NTU range and orient the dot on the cuvette so that it faces forward). The formazin equivalent values for the Gelex® standards are recorded on the cap. If the nephelometer requires major readjustment to calibrate or if the instrument cannot be adjusted to the proper reading, then the nephelometer may be malfunctioning or the standards may be inaccurate. To resolve the source of the problem, attempt to calibrate the instrument using fresh formazin

standards. If the instrument is the source of the problem, have it repaired or replaced. Replace defective laboratory standards after consultation with the water quality coordinator.

- b. Insert the field secondary standard for the high range (80–100 NTU) and take five readings. Rotate the standard about 60° between readings. Repeat for the low NTU (5–10 NTU) field secondary standard.
- c. Record the range of readings obtained with each field standard and the nominal value recorded on the cap.
- d. If the average of the five readings differs from the cap value by greater than 5% or the range of values is greater than 10%, inspect the field standard for scratches, chips, fingerprints, bubbles, etc. If the standard is scratched, apply silicone oil to the scratch; if the vial is dirty, clean with distilled water and a piece of velvet or cheesecloth; if bubbles have formed, the standard is no longer usable and should be replaced. After cleaning or applying oil, remeasure the standard. If the difference between the cap value and the reading remains greater than 5%, the standard must be rechecked against a formazin primary standard (see below). If the range of five readings after cleaning and oiling exceeds 10% of the average value, the secondary standard must be discarded. Substitute the laboratory standard for field use and order a new Gelex® standard for the laboratory.
- e. All preceding steps must be documented in the turbidity calibration and maintenance log book.

#### *F.2.3.4 Calibration with Formazin (Hach Model 16800 or Hydrolab Datasonde 3® Equipped with a Turbidity Sensor)*

**WARNING: FORMAZIN CAN BE HAZARDOUS TO YOUR HEALTH. ALWAYS HANDLE IT WITH RUBBER GLOVES**

This calibration is performed as required by the instrument being used. It is performed at least once per quarter or whenever the instrument

or secondary standard does not calibrate satisfactorily. Formazin calibration is also required whenever the systems electronics or optics are significantly altered (i.e., lens cleaning, focus adjustment, potentiometer adjustment, etc.).

A formazin calibration is performed (and recorded in the turbidity calibration and maintenance log book) only after the instrument has received its daily check and routine maintenance (e.g., is properly focused, charged, and the lens cleaned) as follows:

- a. Following the guidelines in Table F-2, prepare formazin standards using volumetric flasks (500 and 1,000 mL), prepare 80- and 8-NTU dilutions (4:200 and 2:1,000, respectively) from the concentrated formazin (4,000-NTU) standard. Use low turbidity water (i.e., filtered, deionized) and volumetric glassware (not graduated cylinders or transfer pipettes). Contrary to instructions in some instrument manuals, the LTRMP does not prepare turbidity standards by repeated dilutions. Each dilution must be prepared directly from the original (4,000-NTU) standard. The dilutions have a shelf life of only 2–3 hours, so the calibration process must be completed before that time has elapsed.

**Table F-2.** Instructions for preparation of formazin standards for specific nephelometric turbidity units (NTU).

NTU	Dilution instructions
20	Pipette 1 mL of 4,000-NTU formazin into a clean 200-mL volumetric flask. Dilute to line with deionized water, insert stopper, and mix.
100	Pipette 5 mL of 4,000-NTU formazin in 200-mL volumetric flask. Dilute to mark with deionized water and mix.
800	Pipette 20 mL of 4,000-NTU formazin in a 100-mL volumetric flask. Dilute to mark with deionized water and mix.

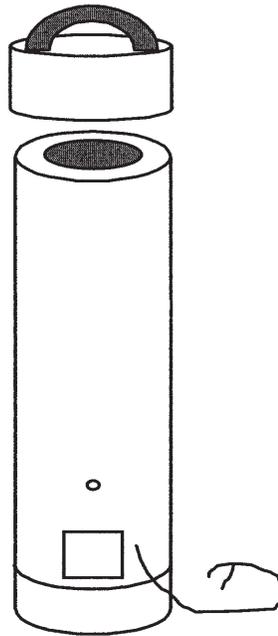
Note: Concentrated formazin standards have a guaranteed shelf life of only 1 year after receipt. They should be kept cool, held in the dark (i.e., in the refrigerator), and labeled with the date they were originally received, not the date they were opened. Be sure to use the unexpired standards for calibration. Use gloves and clothing protection when mixing formazin solutions. Wash hands immediately after any contact with formazin.

- b. Pour the entire volume of diluted standard from the volumetric flask into a clean beaker or flask that will allow the sample to be gently stirred. Swirl suspension gently to ensure uniform distribution of the formazin.
- c. Ensure that the nephelometer is properly zeroed and focused according to manufacturer's instructions (as applicable).
- d. Insert standard (or submerge probe). Adjust the nephelometer according to manufacturer's instructions.
- e. Remove the formazin standard and insert a comparable secondary standard into the nephelometer. Proceed as in steps b–d of the monthly comparison of secondary standards above.
- f. Repeat steps d and e for additional standards as appropriate.
- g. If appropriate (see manufacturer's instructions), check the range or span calibration on the instrument while the formazin primary standards are still usable.
- h. Whenever internal adjustments, lamp replacement, or lens cleaning is performed, the instrument and its secondary (Gelex®) standards must be recalibrated against a formazin primary standard.

## Appendix G. Sonde Holder for Use in Subfreezing Temperatures

When sampling is performed under subfreezing conditions, multiparameter instruments, such as the Hydrolab Datasonde, must be kept from freezing, yet still be stored in an aqueous environment to prevent drying of the probes. Several options are available to achieve this depending on ambient temperatures. If conditions are only slightly below freezing, then an insulated tube with water initially at around 20–25°C should prevent significant icing problems throughout a day of sampling. For slightly cooler conditions, a small volume of alcohol may be added to the insulated tube to lower the freezing point (note that the pH will require longer equilibration time than normal when stored in alcohol).

For extreme conditions (subzero Fahrenheit), a heated tube will prevent freezing of the sonde. The “Hot Tube” was developed specifically for use at the northern Long Term Resource Monitoring Program field stations and consists of an insulated “tube-within-a tube” design (Figure G-1). It runs off of a 12-V battery and provides a few watts of heat to prevent excessive icing in the tube. The thermostat is adjusted to keep the water in the tube at about 4°C, thereby eliminating long temperature equilibration times at each site. The Hot Tube can be constructed locally from PVC tubing, nickel-chromium wire (heating element), fiberglass insulation, an LED (to indicate “heating on”), and a simple thermostat.



**Figure G-1.** Heated tube used to hold multiparameter monitoring instrument in subfreezing temperatures.

## Appendix H. Key to Subsurface Sampling Requirements for Off-Channel Areas

This key can be used to determine if subsurface (>0.2 m) measurements or samples are required at a sampling location. The key is applicable to all areas (including MC) other than tributaries.

### Is velocity $\geq 0.1$ m/sec?

Yes. No subsurface samples are required.

No. **Is there sufficient depth for a subsurface sample at least 0.2 m deeper than the surface sample (i.e., AWD  $\geq 0.60$  m)?**

No. No further samples required.

Yes. ***In-situ* measurements required. Does the difference between surface and bottom readings (0.2 m above sediment) meet any of the following criteria:**

- (1) Temperature difference  $>1.9^{\circ}\text{C}$
- (2) Oxygen difference  $>3.9$  mg/L
- (3) Specific conductance difference  $>50\%$  of surface reading

No. Record readings, but no subsurface water sample required.

Yes. **Is maximum depth ( $Z_{\text{max}}$ )  $>1.9$  m?**

No. Record readings, but no subsurface samples required.

Yes **In fixed-site sampling only, water samples required for turbidity, suspended solids, and nutrients.**

## Appendix I. Program Code to Randomize Chlorophyll-a Sampling Sites

This code is an example of a program that can be used with the SAS® software system to generate a randomized list of sampling sites. It uses a stratified random sampling location coordinates file as input. In this example, a location file for Pool 26, 2002, spring episode, primary sites is used.

```
Data Sites;
  * define the sites file;
  infile 'c:\usr1\logfiles\SRSSites\P26w02so.dat' dsd stopover;
  * read from the input file - site is a character variable;
  input site $ stratum easting northing;
  * Assign a random number with a seed based on the clock;
  Rand1 = ranuni(-12345);
  run;

* Create a separate site order for each sampling stratum;
Proc sort data=sites; by stratum rand1;
run;

* Make a hard copy of the results;
Proc print;
title1 'Randomized Chlorophyll Calibration Sites';
id stratum;
var site easting northing;
run;
```

## Appendix J. Water Quality Forms

This appendix provides copies of the forms (Forms J-1–J-8) used by water quality monitoring in the Long Term Resource Monitoring Program (LTRMP). Some of the forms shown here are provided only for reference and are no longer used routinely. All the forms are subject to change and the LTRMP water quality coordinator at the Upper Midwest Environmental Sciences Center (UMESC) should be contacted to obtain present version(s).

From 1993 to 2003, the LTRMP database administration provided all the bar code labels used by the field stations. Every effort is made to ensure that bar code label sheets are properly printed and distributed to the field stations, but no system is completely foolproof and the accidental use of erroneous bar codes to label data or samples could have serious consequences. To provide a second level of error checking, each field station maintains a log of water quality bar code serial numbers received from the LTRMP staff at UMESC (Form J-6). As each new packet of bar code labels is received by the field station, the beginning and ending serial numbers in the packet are recorded in the field station log, and the entry is initialed by the individual making the log entry. In addition, each packet is inspected carefully to ensure that the two prefix digits in the serial number correctly indicate the component and field station. Any exceptions are brought immediately to the attention of the component coordinator who takes corrective action and issues a new packet of correct bar code labels. Erroneous bar code sheets are destroyed.

The field data acquisition software (ScanLog32) may be used by field teams to print bar codes locally, but this feature had not

been implemented as of the printing date of this manual. When implemented, it will permit local printing of bar codes, track bar code use, and guard against duplication of serial numbers (Form J-6). Field teams will still be required to exercise caution to ensure that the software is functioning correctly and that they are producing proper labels.

In addition to daily calibrations, the performance of dissolved oxygen (DO) meters is routinely checked against another standard. During the first years of the Program, this was accomplished on a monthly basis by comparing DO meter readings to Winkler titrations performed on the same water. The Winkler procedures were problematic, so a replacement for the Winkler titration procedure was proposed (Memorandum dated January 20, 1997) and later implemented (May 1997). The new procedure provided a “bench sheet” (Form J-7) with step-by-step instructions for completing a quarterly performance test of DO and temperature probe functions. The new procedure compares the “air-calibration” technique, used for daily DO calibration, to readings taken in an air-saturated water bath. Strict limits for changes in atmospheric pressure, air temperature, and water-bath temperature must be met and documented before the cross-check is completed. The revised procedure provides further DO probe performance checks by testing anoxic response in a solution of sodium-sulfite/cobalt-chloride, and subsequent return to saturated-bath conditions (i.e., hysteretic error). Thermistor response is also compared during the quarterly procedure to a National Institute of Standards certified thermometer.



Hydrolab Serial Number \_\_\_\_\_

UP Calibration:

Date: \_\_\_\_\_ Hydrolab Date \_\_\_\_\_ Reset (Y/N) \_\_\_\_\_  
Time (CST): \_\_\_\_\_ Hydrolab Time \_\_\_\_\_ Reset (Y/N) \_\_\_\_\_

DOWN Calibration:

Date: \_\_\_\_\_ Hydrolab Date \_\_\_\_\_ Reset (Y/N) \_\_\_\_\_  
Time (CST): \_\_\_\_\_ Hydrolab Time \_\_\_\_\_ Reset (Y/N) \_\_\_\_\_

Conductivity: UP DOWN Dissolved Oxygen: UP DOWN

Hydrolab Reading (uS/cm): \_\_\_\_\_ Temperature \_\_\_\_\_

High Standard (uS/cm): \_\_\_\_\_ Atmospheric Pressure (alt. corrected) \_\_\_\_\_

Hydrolab reset to: \_\_\_\_\_ Saturation Value from table (mg/L) \_\_\_\_\_

Low Std (if required) \_\_\_\_\_ Hydrolab Reading (mg/L) \_\_\_\_\_

Hydrolab Reading \_\_\_\_\_ Hydrolab Reset to (mg/L) \_\_\_\_\_

pH:

Turbidity:

Hydrolab Reading (7) \_\_\_\_\_ Hydrolab Reading (NTU) \_\_\_\_\_

pH 7 value @ temperature \_\_\_\_\_ NTU Standard (NTU) \_\_\_\_\_

Hydrolab Reset to \_\_\_\_\_  
Kaolin \_\_\_\_\_  
Formazine \_\_\_\_\_  
Other \_\_\_\_\_

Hydrolab Reading (10) \_\_\_\_\_

pH 10 value @ temperature \_\_\_\_\_ Hydrolab Reset to (NTU) \_\_\_\_\_

Hydrolab Reset to \_\_\_\_\_

UP Calibration: External Battery Voltage \_\_\_\_\_ Internal Battery Voltage \_\_\_\_\_ Stirrer OK Y/N \_\_\_\_\_

Down Calibration: External Battery Voltage \_\_\_\_\_ Internal Battery Voltage \_\_\_\_\_ Stirrer OK Y/N \_\_\_\_\_

Remarks (e.g., servicing performed/questionable performance)

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Technician Performing UP Calibration: \_\_\_\_\_

Technician Performing DOWN Calibration: \_\_\_\_\_

EMTC 06/14/94

**Form J-2.** Long Term Resource Monitoring Program hydrolab calibration sheet.





Field Station: \_\_\_\_\_  
Name of Analyst: \_\_\_\_\_  
USFWS Number: \_\_\_\_\_

Date: \_\_\_\_\_  
Serial Number: \_\_\_\_\_  
Date last Charged: \_\_\_\_\_

1. Review check list:

- \_\_\_\_\_ 80 NTU formazine standard at room temperature
- \_\_\_\_\_ 8 NTU formazine standard at room temperature
- \_\_\_\_\_ Cuvettes clean and scratch free
- \_\_\_\_\_ Meter warmed up at least 30 min
- \_\_\_\_\_ Focusing template adjusted for proper light
- \_\_\_\_\_ Zero point set and checked for all scales
- \_\_\_\_\_ Span control set to midrange (10 turns counterclockwise, 5 clockwise)

2. 0–100 NTU RANGE

- a. Insert cell riser
- b. Insert 80 NTU formazine standard and adjust circuit board potentiometer to 80 NTU reading
- c. Remove formazine, insert Gelex<sup>®</sup>, and measure its value at three different orientations. Record each reading. Replace value on cap if necessary.
- d. Prior Gelex<sup>®</sup> value: \_\_\_\_\_
- e. Current readings: a.(dot forward) \_\_\_\_\_ b. \_\_\_\_\_ c. \_\_\_\_\_

3. 0–10 NTU RANGE

- a. Remove cell riser
- b. Insert 8 NTU formazine standard and adjust circuit board potentiometer to 8 NTU reading
- c. Remove formazine, insert Gelex<sup>®</sup>, and measure its value at three different orientations. Record each reading. Replace value on cap if necessary.
- d. Prior Gelex<sup>®</sup> value: \_\_\_\_\_
- e. Current readings: a.(dot forward) \_\_\_\_\_ b. \_\_\_\_\_ c. \_\_\_\_\_

Comments:

\_\_\_\_\_

Signature

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**Long Term Resource Monitoring Program**  
**Quarterly DO Meter Calibration & Performance Check**

Model \_\_\_\_\_ Serial # \_\_\_\_\_ Date(mm/dd/yy) \_\_\_\_\_  
 Technician \_\_\_\_\_ Signature \_\_\_\_\_

**Water Bath Preparation ( $\geq 4$  liters &  $\leq 100 \mu\text{S}$ )**

Aeration Time ( $\geq 1$  hour) \_\_\_\_\_ @ rate ( $\geq 100$  ml/min) \_\_\_\_\_ ml/min Conductivity \_\_\_\_\_  $\mu\text{S}$

**Calibrate Meter (Routine Method)**

1. Calibrate Conductivity and DO with routine methods. DO calibration must be done in air or *separate* uncontrolled bucket.
2. Set meter to log readings for one hour at five minute intervals (or capture readings to file with communications software, e.g., Pibterm)

<u>Conductivity</u>		<u>Dissolved Oxygen</u>	
Cond. Standard _____ $\mu\text{S}$	Temperature _____ $^{\circ}\text{C}$	DO Meter reading _____ mg/L	
Cond. Reading _____ $\mu\text{S}$	Local Pressure _____ mm-Hg	DO reset to _____ mg/L	
Cond. Reset to _____ $\mu\text{S}$	Saturation value from table _____ mg/L		

**Verify Atmospheric and Water Bath Stability**

1. Place probes in controlled water bath prior to beginning of logging run. Record conductivity of controlled water bath (above). After logging is complete, attach hard copy output to this form.
2. Record water and air temperature during logging run with traceable thermometer at intervals indicated in table. Water temperature must be  $\pm 2^{\circ}\text{C}$  of air temperature. Record altitude-adjusted (local) pressure as indicated.

Time	Air Temperature $^{\circ}\text{C}$ ( $\pm 1^{\circ}\text{C}$ over previous 30 min.)	Water Temperature $^{\circ}\text{C}$ ( $0-25^{\circ}\text{C}$ , $\pm 0.5$ over previous 30 min.)	Local Pressure ( $< 5$ mm-Hg change over 1 h)
Start:			
30-min:			n/a
60-min:			

**Check DO Meter for Drift**

1. Use routine calibration method (air or separate, uncontrolled bucket) to check for DO probe drift.
- Temperature \_\_\_\_\_  $^{\circ}\text{C}$  Local Pressure \_\_\_\_\_ mm-Hg Saturation Value From Table \_\_\_\_\_ mg/L  
 Meter Reading \_\_\_\_\_ mg/L - Reset To \_\_\_\_\_ mg/L = Drift \_\_\_\_\_ ( $\pm 0.2$  mg/L) Pass/Fail

**Check Meter in Controlled Bath**

1. Return probe to controlled water bath. Allow to equilibrate at least five minutes, but no longer than ten minutes.
  2. Record temperature with traceable thermometer and meter. Subtract meter reading from thermometer reading.
  3. Record initial DO reading, then re-calibrate in the controlled bath and record Reset Value. Subtract the Reset Value from the initial reading.
- Bath Temp. (Thermometer) \_\_\_\_\_ - Bath Temperature (meter) \_\_\_\_\_ = \_\_\_\_\_ (Within  $\pm 0.1^{\circ}\text{C}$ ) Pass/Fail  
 Initial DO Reading (bath) \_\_\_\_\_ - DO Reset Value (bath) \_\_\_\_\_ = \_\_\_\_\_ (Within  $\pm 0.2$  mg/L) Pass/Fail

**Check Low Oxygen Response**

1. Anoxic Conditions:  
 Prepare anoxic solution (sodium sulfite w/catalyst): Fill storage cup 2/3 full with deionized water. Add about 100 mg (1/4 tsp) sodium sulfite (some crystals may not dissolve). Add two drops of catalyst (0.001M cobalt chloride). Screw storage cup on meter and begin timing. Avoid agitation after probe is sealed off from air. DO should drop to 0.0 mg/l within two minutes.  
 Meter Reading \_\_\_\_\_ mg/L ( $\leq 0.2$  mg/L) Pass/Fail  
 Response Time \_\_\_\_\_ s. ( $\leq 120$  s) Pass/Fail
2. Saturated Conditions:  
 Remove cup and immediately begin timing. Rinse probe thoroughly (tap water) to remove sulfite and catalyst solution, and return to bath.  
 Meter Reading \_\_\_\_\_ mg/L (Within  $\pm 0.2$  mg/L of saturation value) Pass/Fail  
 Response Time \_\_\_\_\_ s. ( $\leq 120$  s) Pass/Fail

Comments/Steps taken to repair defective meter \_\_\_\_\_  
 \_\_\_\_\_  
 \_\_\_\_\_  
 \_\_\_\_\_

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**MONTHLY MAINTENANCE CHECKLIST: Multiparameter Water Quality Sondes**

Year: \_\_\_\_\_

Meter SN: \_\_\_\_\_

Instructions: Routine maintenance is critical for good instrument performance, and should be conducted monthly. This form is only for documentation of maintenance--consult the User's Manual for instructions specific to your sonde type. Individual configurations may vary, therefore all procedures may not apply.

Required Monthly Maintenance*		Month											
Sensor	Maintenance Procedure	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
	Day:												
	Technician Initials:												
Turbidity <small>(not approved for routine monitoring)</small>	Guard/Retainer Cleaned												
	Lenses Cleaned (alcohol)												
Conductivity <small>(consult manual for your probe type)</small>	Electrodes Polished												
	*Cell Block Washed												
	*O-rings Checked												
	*Annular rings cleaned (detergent, alcohol)												
*pH	Glass Electrode cleaned (alcohol)												
	Reference Electrolyte Replaced												
	Porous Junction Flushed and Checked												
*D.O.	Electrolyte and Membrane Replaced												
Sonde body	Washed (soap & water)												
	Submersible Junctions Greased												
	Polarizing Batteries (IN/OUT)												

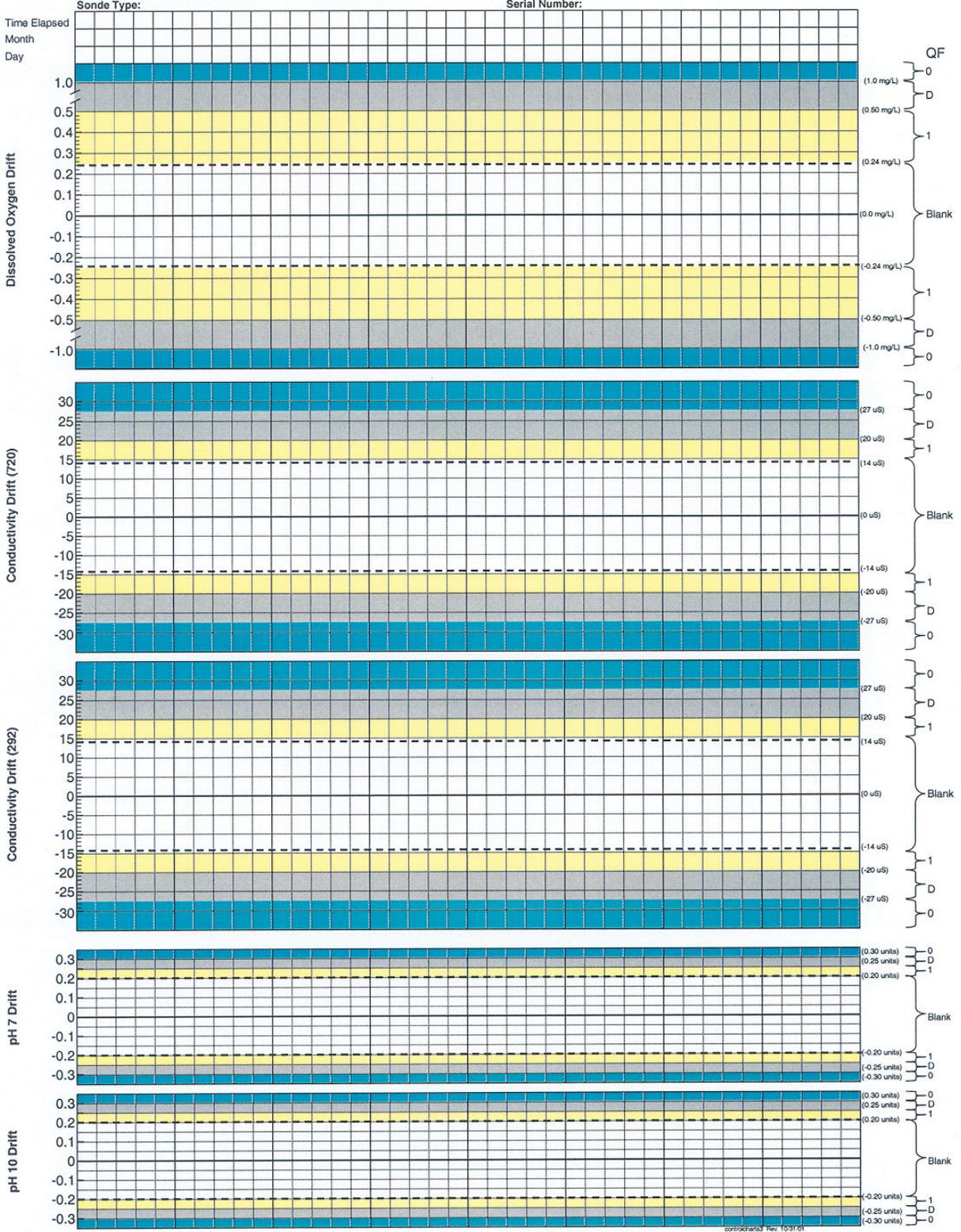
Date	Additional Maintenance and Comments (continue on reverse)

Rev. 10/2003

**Form J-8.** Monthly maintenance checklist for multiprobe instruments

LTRMP Water Quality Instrument Calibration Control Chart

Year:



Form J-9. Control charts with quality factor flags for documenting daily multiprobe calibration drift

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The Long Term Resource Monitoring Program (LTRMP) for the Upper Mississippi River System was authorized under the Water Resources Development Act of 1986 as an element of the Environmental Management Program. The mission of the LTRMP is to provide river managers with information for maintaining the Upper Mississippi River System as a sustainable large river ecosystem given its multiple-use character. The LTRMP is a cooperative effort by the U.S. Geological Survey, the U.S. Army Corps of Engineers, and the States of Illinois, Iowa, Minnesota, Missouri, and Wisconsin.

