



Standard Guide for Monitoring Aqueous Nutrients in Watersheds¹

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INTRODUCTION

Various forms of nitrogen and phosphorus are plant nutrients, both naturally occurring and manmade, that can threaten water resources. Nutrients that run off or infiltrate through the soil profile can result in unfishable and unswimmable streams, lakes, and estuaries, and unsafe surface and ground water used for drinking. High concentrations of nitrate in drinking water are a threat to young infants, and surface waters can suffer from algal blooms, fish kills, and unpalatable and unsafe water for swimming and drinking. Nutrients are also added to watersheds via chemigation.

This guide recommends a process for developing and implementing monitoring projects for nutrients in a watershed. It follows Guide D 5851 with more specifics applicable to watersheds and nutrients. These guidelines are presented for use in the nationwide strategy for monitoring developed by the Intergovernmental Task Force on Monitoring (ITFM). The nationwide monitoring strategy is an effort to improve the technical aspects of water monitoring to support sound water quality decision-making. It is needed to integrate monitoring activities more effectively and economically to achieve a better return of investments in monitoring projects (1).²

Guide D 6145 is offered as a guide for monitoring actual and potential nonpoint and point source pollution within a watershed. The guide is applicable to surface water and ground water resources, recognizing the need for a comprehensive understanding of naturally occurring and manmade impacts to the entire watershed hydrologic system.

1. Scope

1.1 *Purpose*—This guide is intended to provide general guidance on a watershed monitoring program directed toward the plant nutrients nitrogen and phosphorus. The guide offers a series of general steps without setting forth a specific course of action. It gives assistance for developing a monitoring program but not a program for implementing measures to improve water quality.

1.2 This guide applies to waters found in streams and rivers; lakes, ponds, and reservoirs; estuaries; wetlands; the atmosphere; and the vadose and subsurface saturated zones (including aquifers). This guide does not apply to nutrients found in soils, plants, or animals.

1.3 Nutrients as used in this guide are intended to include nitrogen and phosphorus in dissolved, gaseous, and particulate forms. Specific species of nitrogen include: nitrate, nitrite, ammonia, organic, total Kjeldahl, and nitrous oxide. The

species of phosphorus include total, total dissolved, organic, acid-hydrolyzable, and reactive phosphorus as described in (2)

1.4 *Safety*—Health and safety practices developed for a project may need to consider the following:

1.4.1 During the construction of sampling stations:

1.4.1.1 Drilling practices during monitoring well installations,

1.4.1.2 Overhead and underground utilities during monitoring well drilling,

1.4.1.3 Traffic patterns/concerns during sampling station installation,

1.4.1.4 Traffic patterns/concerns during surveying sampling station locations and elevations,

1.4.1.5 Drilling through materials highly contaminated with fertilizers, and

1.4.1.6 Installing monitoring equipment below the soil surface.

1.4.2 During the collection of water samples:

1.4.2.1 Using acids for sample preservation,

1.4.2.2 Sampling during flooding events and ice conditions,

1.4.2.3 Traffic on bridges,

1.4.2.4 Condition of sampling stations following flood events,

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² The boldface numbers given in parentheses refer to a list of references at the end of this standard.

1.4.2.5 Sampling of water or soils, or both, highly contaminated with fertilizers,

1.4.2.6 Conditions of sampling stations resulting from vandalism,

1.4.2.7 Adverse weather conditions, and

1.4.2.8 Transporting liquid samples.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 ASTM Standards:

D 515 Test Methods for Phosphorus in Water³

D 653 Terminology Relating to Soil, Rock, and Contained Fluids⁴

D 1129 Terminology Relating to Water³

D 1357 Practice for Planning the Sampling of the Ambient Atmosphere⁵

D 1426 Test Methods for Ammonia Nitrogen in Water³

D 1739 Test Method for Collection and Analysis of Dustfall (Settleable Particulate Matter)⁵

D 3370 Practices for Sampling Water from Closed Conduits³

D 3590 Test Methods for Total Kjeldahl Nitrogen in Water³

D 3856 Guide for Good Laboratory Practices in Laboratories Engaged in Sampling and Analysis of Water³

D 3858 Test Method for Open-Channel Flow Measurement of Water by Velocity-Area Method³

D 3867 Test Methods for Nitrite-Nitrate in Water³

D 4410 Terminology for Fluvial Sediment³

D 4448 Guide for Sampling Ground Water Monitoring Wells⁶

D 4696 Guide for Pore-Liquid Sampling from the Vadose Zone⁴

D 4700 Guide for Soil Sampling from the Vadose Zone⁴

D 5092 Practice for Design and Installation of Ground Water Monitoring Wells in Aquifers⁷

D 6145 Guide for Monitoring Sediment in Watersheds³

D 5851 Guide for Planning and Implementing a Water Monitoring Program⁸

3. Terminology

3.1 Definitions:

3.1.1 For definitions of terms used in this guide, refer to Terminology D 1129 and Guide D 5851.

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *aquifer*—a geologic formation containing water, usually able to yield appreciable water.

3.2.2 *ground water*—that part of the subsurface water that is the saturated zone. **(D 653, D18)**

3.2.3 *nonpoint pollution*—a condition of water within a water body caused by the presence of undesirable materials from diffuse locations with no particular point of origin.

3.2.4 *vadose zone*—the zone of soil located between the surface and the water table that is not saturated.

3.2.5 *watershed*—all lands enclosed by a continuous hydrologic surface drainage divide and lying upslope from a specified point on a stream. **(D 4410, D19)**

4. Significance and Use

4.1 The user of this guide is not assumed to be a trained technical practitioner in the water quality field. The guide is an assembly of the components common to all aspect of watershed nutrient monitoring and fulfills a need in the development of a common framework for a better coordinated and a more unified approach to nutrient monitoring in watersheds.

4.2 *Limitations*—This guide does not establish a standard procedure to follow in all situations and it does not cover the detail necessary to meet all of the needs of a particular monitoring objective. Other standards and guides included in the references describe the detail of the procedures.

5. Monitoring Components

5.1 A watershed monitoring program of nutrients is comprised of a series of steps designed to collect nutrient data to achieve a stated objective. The purposes of monitoring may be several and include: analyzing trends, studying the fate and transport of nutrients, defining critical areas, assessing compliance, measuring the effectiveness of management practices, testing for sufficient levels, making wasteload allocations, testing models, defining a water quality problem, and conducting research **(3)**.

5.1.1 Monitoring to analyze trends is used to determine how water quality is changing over time. In some cases baseline monitoring is included as the early stage of trend monitoring.

5.1.2 Fate and transport monitoring is conducted to determine whether pollutants move and where they may go.

5.1.3 Water quality monitoring can be used to locate critical areas within watersheds exhibiting greater pollution loading than other areas.

5.1.4 Nutrient monitoring may also be used to assess compliance with water quality plans or standards.

5.1.5 Nutrient monitoring may assess the effectiveness of individual management practices in improving water quality or, in some cases, may be used to evaluate the effect of an entire nutrient management program in a watershed.

5.1.6 The testing of nutrient levels in water bodies may be used to see if sufficient amounts are present to support certain aquatic organisms.

5.1.7 Monitoring of receiving water bodies may be used to determine wasteload allocations between point and nonpoint sources. Such allocations require a thorough knowledge of the individual contributions from each source.

5.1.8 Nutrient monitoring may be used to fit, calibrate, or test a model for local conditions.

5.1.9 Nutrient monitoring may be used for research questions such as the accuracy of different types of samplers in collecting a representative sample.

³ Annual Book of ASTM Standards, Vol 11.01.

⁴ Annual Book of ASTM Standards, Vol 04.08.

⁵ Annual Book of ASTM Standards, Vol 11.03.

⁶ Annual Book of ASTM Standards, Vol 11.04.

⁷ Annual Book of ASTM Standards, Vol 04.09.

⁸ Annual Book of ASTM Standards, Vol 11.02.

5.1.10 Finally, nutrient monitoring may be used to give adequate definition to a water quality problem or determine whether a problem exists. Guide for Planning D 5851 provides overall guidance on water monitoring.

5.1.11 This guide suggests and discusses the following steps in designing a watershed monitoring program for nutrients. More detail on each step may be found in (3).

5.2 *Step 1: Water Quality Need*—The first step is to define the need for nutrient monitoring. The need statement should include several components: the potential or real water quality issue requiring attention (for example, eutrophication), the potential water resource use impairment (for example, recreation), the name of the actual water resource (for example, Long Lake), the potential threats or causes (for example, phosphorus), and the potential sources that may cause a problem (for example, agriculture) (3). Very often the need is to identify a water quality problem, but in some cases, the need may be to assess the existing water quality whether a problem exists or not. An example of a need statement might be: “The lack of recreation in Long Lake is due to excessive eutrophication caused by excessive phosphorus loading possibly from agricultural sources.”

5.3 *Step 2: Objectives*—The second step in developing a nutrient monitoring program is to define the monitoring objectives. The objectives of the monitoring study should address the water quality need or problem. An objective statement should include an infinitive verb, an object word or phrase, and some limits on the objective such as the surface or ground water resource or watershed boundaries and variables to monitor. An example of a monitoring objective might be: “To determine the effect of implementing agricultural management practices on phosphorus concentrations in Long Lake.” When several objectives are used, a hierarchical approach may be used to determine higher priority objectives. An objective tree can be used to distinguish among several objectives. To determine how several objectives can be linked, the following question can be asked: “Does the achievement of objective A contribute directly to the achievement of objective B?” If it does then objective A feeds into objective B and a diagram can be built showing all possible objectives and their linkages.

5.3.1 To assess whether objectives are being achieved, objective attributes could be determined. Attributes define the level of achievement for each objective. They answer the question of how close are we to achieving our goals? For example, are we 50 % of the way to achievement? These attributes for nutrient monitoring objectives are often binary; that is, either the objective is accomplished or not.

5.4 *Step 3: Statistical Design*—A statistical experimental design should be stated that is consistent with the objectives of the monitoring program. Appropriate experimental designs could include: reconnaissance, plot, single watershed, above-and-below, two watersheds, paired watershed, multiple watersheds, and trend stations (3). The design selected will dictate most other aspects of the monitoring project including the study scale, the number of sampling locations, the sampling frequency, and the station type.

5.4.1 Reconnaissance or synoptic designs may be used as a preliminary survey where no data exist or to assess the

magnitude and extent of a problem. This type of sampling could be used to identify critical areas as well. A critical area is one that is contributing a significant amount of nutrients to the water body of interest. Randomization in sampling locations may be important for reconnaissance monitoring. Reconnaissance monitoring could be used in a “whole aquifer” study with well placement located randomly or on a grid basis.

5.4.2 Plot designs have been commonly used in agricultural experiments for 100 years (4). Plots are generally small areas that can be replicated on the land or waterscape. Plots allow replication and control of certain variables, such as soil type. Plot designs are analyzed using Analysis of Variance (3).

5.4.3 The single watershed before-and-after approach has been sometimes used to compare water quality conditions before a watershed treatment to after. Generally, this technique is not recommended, since the results are confounded with time and climate variables, and should be avoided. For example, the water quality differences from year-to-year may be caused by climate differences not the watershed activity.

5.4.4 The above-and-below design is used after a watershed practice is in place. Sampling is conducted both upstream and downstream, or in the case of ground water monitoring, up-gradient and down-gradient from the activity of interest. Although this design is not as susceptible to the effect of climate as the single watershed design, the differences in water quality between the two stations may be partly due to inherent watershed differences such as soils or geology. If monitoring is conducted before and after the practice is installed, the design would follow the paired watershed approach described below.

5.4.5 Ground water monitoring using this approach is referred to as up-gradient versus down-gradient monitoring. This is probably the most commonly used strategy in ground water studies and is appropriate for most designs. Placement of the wells is important because ground water sites are three dimensional. Gradients may occur in both vertical as well as horizontal directions. Also due to heterogeneity at some sites, gradient directions may change over time.

5.4.6 The paired watershed approach uses a minimum of two watersheds - control and treatment - and two periods of study - calibration and treatment (5). The control watershed serves as a check for year-to-year climate variations and receives no changes in land uses or activities during the monitoring study. During calibration, the two watersheds are treated identically and paired water quality data are collected. During the treatment period, one watershed is treated with a practice while management in the control watershed remains unchanged.

5.4.7 For ground water monitoring, an above-and-below approach to the paired watershed design is recommended. During the calibration period, monitoring would take place up-gradient and down-gradient for both the control and treatment portions of the ground water formation being studied. During the treatment period, one of the areas bounded by wells would receive a practice while the other control area would remain as before.

5.4.8 The multiple watershed approach involves more than two watersheds. Watersheds with treatments already in place are selected from across the region of interest. Sampling from

these watersheds is conducted over a period of time. Groups of similar watersheds are tested against each other to determine water quality differences (3).

5.4.9 Trend stations are single watersheds monitored over time. A trend is a persistent change in the water quality variables of interest over time. It is important while using most forms of trend analysis that there not be gaps in the data set, that water quality analysis methods not change, that the hydrological control is stable, and a casual link can be made between the water quality and watershed activities. A control trend station is highly recommended where no changes in watershed activities occur during the trend investigation (3).

5.5 *Step 4: Scale of Study*—The size or scale of the monitoring program should be determined. Appropriate scales include: point, plot, field, and watershed. Points are the smallest scale considered for water quality monitoring and are characterized by obtaining single observations at a location. A rain gage represents a point sample. Plots are mesocosm (medium scale) sampling units which are appropriate if the objective is to replicate several treatments or activities. The number of plots needed for a study is a function of the number of treatments applied (3). Monitoring on a field scale implies a larger area than an individual plot. The area of a field is difficult to state because it varies greatly in different parts of the United States; however, a field is usually homogeneous in land use and general topography. Watershed scale monitoring is used for most water quality monitoring purposes. One of the most difficult decisions is the watershed size. Generally, watershed size is influenced by stream order, climate, number of land-owners, extent of a problem area, homogeneity in land use and physical attributes, aquifer boundaries, and geology (3). For lakes a plot might be a column of water confined with plastic (limnocorral). Fields in lakes are represented by bays.

5.6 *Step 5: Variable Selection*—A list of the nutrients to measure should be indicated. The specific species to monitor and whether they should be in dissolved, gaseous, or particulate forms should be described. Nutrient monitoring often requires that additional supporting parameters be monitored such as velocity, discharge, pH, and dissolved oxygen. Also, several biological characteristics of the water may need to be measured since they are involved in nutrient cycling in the watershed. Often, water quality indices or environmental indicators may be used along with nutrient monitoring in watersheds.

5.6.1 Water quality variable selection depends on the monitoring objectives, water body type, the use of the water, the land activity being investigated, the cost or difficulty in analysis, and any known or suspected nutrient issue associated with the water body. To assist in the selection of water quality variables, activity matrices have been developed (3). Other techniques for selection include ranking the variables of interest, developing correlations between variables, and determining the probability of exceeding a water quality standard (3).

5.7 *Step 6: Sample Type*—Nutrients in watersheds may be collected as grab, composite, integrated, or continuous samples. The type of sample collected is a function of the purpose in monitoring, the variables to sample, and whether

concentration or mass is the desired outcome. A grab sample is a discrete sample that is taken at a specific point and time. A series of grab samples, usually collected at different times and combined together in one sample, are considered composite samples. Composite samples may be either time-weighted or flow-weighted. A specific type of a surface water grab sample is a depth-integrated sample. Such samples account for velocity or stratification induced differences in water quality. Continuous sampling is rare because the technology is limited, but usually involves water quality variables measured using electro-metric methods, such as specific ion electrodes for ammonia and nitrate nitrogen.

5.8 *Step 7: Sampling Location*—The location of sampling should be determined at two levels: where within the watershed and where at a given station location. The monitoring program objectives, study design, and type of water body will dictate general sampling locations. To characterize a watershed outlet only requires one station. Ground water or lake characterization would require many more locations. The actual number of ground water locations can be determined based on the variability in the data as described in (3).

5.8.1 For ground water sampling, the placement of wells and the number of wells will also be influenced by the heterogeneity of the system that can be caused by mineralogical differences, geologic structure, multiple water-bearing zones, confining layers, and recharge/discharge areas. Because these differences may not be known at the time of monitoring program design, an initial geologic assessment may be needed to make final determinations of well locations. Geostatistical approaches will assist in locating wells.

5.8.2 Once the overall location has been determined, a more specific location is needed to collect a representative sample. Nutrients are known to stratify in lakes, estuaries, and in ground water systems. Therefore, sampling at different depths will yield different results. Gradients across streams may also exist due to water velocity gradients. If the velocity varies at different locations then nutrients associated with velocity will also vary, such as phosphorus bound to sediments carried by the water. Width gradients may be especially evident below the confluence of two streams. Algae also may stratify in water bodies. Sampling within stratified systems is often done to take subsamples in the different strata and then bulk the entire sample.

5.9 *Step 8: Sampling Frequency and Duration*—The sampling frequency should be based on the objectives of the study, the type of water resource being monitored, and the variability in the data being collected that may be due to storm events or seasonal changes. Nutrient data are highly variable in most surface water systems due to the influence of precipitation as well as biological activity. The temporal variability in ground water systems is typically less than for surface waters. To determine the sampling frequency a sample size calculation should be made based on the estimate of the standard deviation, the allowable difference from the mean, and Student's *t* (3). Such calculations are found in most standard statistical books. Calculations can also be made for detecting linear or step trends (6). The duration of the study will also be influenced by the study objectives. Longer durations are

needed for phosphorus monitoring than for nitrogen monitoring since phosphorus is highly absorbed and changes slowly within systems as compared to nitrogen.

5.10 *Step 9: Station Type*—Watershed monitoring of nutrients may require the design and construction of monitoring stations for stream discharge, precipitation collection, soil water and ground water sampling, biota, and sediment sampling. The monitoring program should specify what types of monitoring stations will be used. Generally, several optional methods for conducting the monitoring are available for each type of monitoring station needed. Agricultural Handbook No. 224 (7) is an important reference for designing monitoring stations. The US Geological Survey has published a series of Techniques of Water Resources Investigations (TWRI) reports that address many of the issues related to designing monitoring stations. A listing of the TWRI's is given in Appendix X1. Other guidelines may be found in (3).

5.11 *Step 10: Sample Collection and Analysis*—The monitoring study should address appropriate techniques for collecting and analyzing samples. The sample collection procedures for nutrient analysis will depend on the type of sample and the type of water resource being sampled. Grab samples are often collected in bottles that have been rinsed with collection water. Sampling from pipes may require running the water long enough to remove stagnant water. Sample collection from wells also requires purging to ensure that the water in the well represents water from the formation (See Practice D 5092, and Guide D 4448). Appropriate containers should be used and the sample should be preserved as recommended (8). Nitrogen and phosphorus samples are typically collected in plastic or glass containers. Nutrients are preserved by keeping cool (4°C) and acidifying to a pH < 2. For some species of phosphorus, filtration is also used. Transportation and storage before analysis should follow standard methods (2). Most samples are transported in the dark and in coolers. The methods of laboratory analysis should be specified. Two important analysis methods references are Standard Methods for the Examination of Water and Wastewater (2) and Methods for Chemical Analysis of Water and Wastes (8).

5.11.1 The analysis methods should include a quality assurance/quality control program. Quality assurance is the total integrated program for assuring the reliability of monitoring and measurement data. Quality assurance is composed of quality control and quality assessment. Quality control refers to activities conducted to provide high quality data. Quality assessment refers to techniques used to evaluate the effectiveness of the program. A good quality control program should include good laboratory practices including record keeping, standard operating procedures, education and train-

ing, and supervision. Quality assessment allows feedback on how well the quality control program is operating. Indicators of data quality include precision, accuracy, representativeness, comparability, and completeness. Usually such assessment involves the use of duplicate samples, spikes, internal and external audits, tests of reason, and exchange samples (3).

5.12 *Step 11: Land Use and Management Monitoring*—Since nitrogen and phosphorus can come from many sources, it is critical to monitor the sources of these nutrients to explain any water quality changes that may occur. Such sources may include precipitation, land applications, irrigation, wastewaters, and long-term stored nutrients. The proximity of these sources to the water body may also be important. The land use monitoring plan should match the water quality monitoring objectives and be consistent with the watershed boundaries being monitored. The basic approaches for monitoring land use information are personal observations, field logs, personal interviews, and remote sensing. As the size of the study area increases, the difficulty and importance of adequate land use monitoring increases.

5.12.1 A method for managing land use data should be specified and could include photos, ad hoc files, spreadsheets or data bases, or a geographic information system (GIS).

5.13 *Step 12: Data Management*—The final step in developing a monitoring program for nutrients in watersheds involves specifying the methods for the acquisition, storage, validation, retrieval, and manipulation of nutrient data. Acquisition includes the collection and entry into the data management system. Computerized data loggers have eased the complexity of this step. The storage of data should be viewed as a multilevel effort using both manual and computerized technologies. Original paper copies of collected data should be maintained. All data should be validated with a 100 % error check. Tests of reason can be used by computers or manually to see if recorded values are technically/physically possible. Data generally require some form of manipulation before being reported. Manipulation may be statistical, graphical or may include censoring values below detection limits.

5.14 *Monitoring Purposes*—Discussion of the purposes in monitoring nutrients is provided in Guide D 5851, in (3) and the ITFM reports (1).

6. Keywords

6.1 atmospheric; environmental indicators; estuary; ground water; monitoring; nitrogen; nonpoint source pollution; nutrient; phosphorus; point source pollution; soil pore water; surface water; water monitoring; water quality; watershed monitoring; vadose zone

APPENDIX
(Nonmandatory Information)
X1. OTHER PUBLICATIONS ON TECHNIQUES OF WATER RESOURCES INVESTIGATIONS

- Barnett, P. R., et al., *Determination of Minor Elements in Water By Emission Spectroscopy*, U. S. Geological Survey, TWI 5-A2, 1971.
- Benson, M. A., et al., *General Field and Office Procedures For Indirect Discharge Measurements*, U. S. Geological Survey, TWI 3-A1, 1967.
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- Kennedy, E. J., *Levels at Streamflow Gaging Stations*, U. S. Geological Survey, TWI 3-A19, 1990.
- Keys, W. S., et al, *Application of Borehole Geophysics to Water-Resources Investigations*, U. S. Geological Survey, TWI 2-E1, 1971.
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