Nutrient Requirements for the National Water Quality Monitoring Network for U.S. Coastal Waters and their Tributaries

Nutrients Workgroup

Members

Jane Caffrey, co-Chair
Center for Environmental Diagnostics and Bioremediation
University of West Florida
Pensacola, FL 32514

Tamim Younos, co-Chair
Virginia Water Resources Research Center
Virginia Tech
Blacksburg, VA 24061

Michael Connor
San Francisco Estuary Institute
Oakland, CA 94621

Gary Kohlhepp
Michigan Department of Environmental Quality
Water Bureau
Lansing, MI 48909

Dale M. Robertson
U.S. Geological Survey
Water Science Center
Middleton, WI 53562

Jonathan Sharp
College of Marine and Earth Studies
University of Delaware
Lewes, DE 19958

David Whitall
NOAA, National Centers for Coastal Ocean Science
1305 East West Hwy, SSMC 4, 9110
Silver Spring, MD 20910

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Introduction:

The National Water Quality Monitoring Council (Council) has produced a design for the National Water Quality Monitoring Network for U.S. Coastal Waters and their Tributaries (the Network) as called for in the U.S. Ocean Action Plan. The Network is a framework for linking water quality monitoring in coastal bays, estuaries and the Great Lakes with observations in upland areas and offshore waters, and includes freshwater flows and contaminant input from inland and coastal rivers, groundwater, and atmospheric deposition. Wetlands and coastal beaches are also included in the design. A description of the Network design is available at http://acwi.gov/monitoring/network/design.

Nutrients in the design document:

Issues the Network was designed to address include nutrient enrichment, oxygen depletion, and habitat degradation. Table 3-1 in the Network report indicates that the following resource components should be monitored for nutrients: estuaries, near shore coastal waters, offshore coastal waters, Great Lakes, rivers, groundwater, and atmospheric deposition.

The Interagency Working Group charged the Nutrients Workgroup with several tasks.

1. Determine the specific constituents to be monitored and the performance requirements for analytical methods. Specify details such as total or dissolved nutrients in water and whether samples of sediment are to be analyzed. The goal is to provide guidance on nutrient concentrations and loads and to establish a basis for determining trends over time.
2. The Network is intended to provide data that will be collected primarily by Federal and State agencies. Thus, the methods used should be operational rather than approaches designed for research purposes. In recent years, the parameters measured and the performance limits of agencies and academic institutions have become increasingly similar.
3. The list of constituents to be monitored should be broad enough to address major management issues at regional and national scales but should not be so extensive as to make the Network prohibitively expensive. It is expected that at the local level, the basic Network design will be augmented by additional sample collection and analyses.

It is recognized that ambient nutrient concentrations in estuaries, near shore coastal waters, offshore coastal waters, Great Lakes, and rivers are of a similar nature. Concentrations of various forms of nutrient elements in groundwater and atmospheric deposition are often considered as loading parameters for input into aquatic systems. Wetlands are important to aquatic systems as either nutrient loading sources or sinks. Although the network design for the groundwater, atmospheric deposition and wetlands components are not complete, the Nutrients Workgroup recommendations include preliminary nutrient parameter recommendations for these components. The final recommendations for these components will be decided in consultation with those working groups.

The Nutrients Workgroup's recommendations are described below.

Nutrient requirements

The Nutrients Workgroup has developed a tiered list of nutrient parameters with corresponding analyses (Table 1). Tier I parameters represent the required constituents; Tier II parameters represent the constituents that would add significant value but may not be essential to some programs. The requirements for the river, Great Lakes, estuary, nearshore coastal and offshore coastal components are the same. However, some related analyses will differ between freshwater and marine systems. For example, conductivity will be measured in freshwater systems, while salinity will be measured in marine systems.

For all of the components except for wetlands, the Nutrients Workgroup recommends water sampling only. The Nutrients Workgroup does not recommend nutrient analysis in sediments except for wetlands. Sediments are very heterogeneous for many parameters on quite small spatial scales (meter or less).

Recommendations

Dissolved inorganic nitrogen (DIN) is comprised of nitrate plus nitrite and ammonium. These forms of nitrogen are readily available to phytoplankton and often control the formation of blooms. Total dissolved nitrogen (TDN) is comprised of dissolved inorganic nitrogen (DIN) and dissolved organic nitrogen (DON). Because there is no reliable way to measure DON directly, it is usually calculated from measured TDN and DIN values (DON=TDN-DIN). There is evidence that DON, particularly urea, may be important in triggering harmful algal blooms. The Nutrients Workgroup recommends that TDN be measured. The advantage of measuring TDN is that it provides a better estimate of the nitrogen that is likely to be most available to phytoplankton. The measurement of TDN plus particulate nitrogen (PN) is usually used to calculate total nitrogen (TN=TDN+PN). Because there is a significant historic dataset of total nitrogen values for a variety of systems, the Nutrients Workgroup recommends that total nitrogen (TN) be measured. These additional analyses would provide more detailed information about the sources of nitrogen in the system.

Phosphorus is also very important as a limiting nutrient, particularly in freshwater as well as tropical and subtropical estuarine marine systems. Total phosphorus (TP) is comprised of ortho phosphate, dissolved organic phosphorus and particulate phosphate (PP). Total dissolved phosphorus (TDP) includes dissolved organic phosphorus and ortho phosphate. Ortho phosphate is the dissolved inorganic form of phosphorus. Ortho phosphate concentrations are often very low and ortho phosphate is rapidly recycled. Similarly, the Nutrients Workgroup recommends that total phosphorus (or total dissolved phosphorus and particulate phosphorus (TP = TDP + PP)) be measured. As with nitrogen, the measurement of TDP gives more detailed information about the most available pools of phosphorus.

Dissolved silica controls the growth of diatoms and changing N:Si ratios in freshwater flow have been associated with changes in estuarine and marine phytoplankton communities (an increasing ratio is generally related to fewer diatoms relative to the other taxa).

In addition, the Nutrients Workgroup recommends that specific response variables and ancillary variables should be monitored. Chlorophyll *a* and dissolved oxygen concentrations are critical response variables that need to be monitored. Salinity or conductivity, while not response variables, are critical parameters that should be monitored. The ancillary analyses that would be useful to monitor include dissolved organic carbon, dissolved inorganic carbon, pH, total suspended sediments, particulate carbon, and photosynthetically active radiation. Dissolved organic carbon is a mixture of refractory and labile compounds. It is important in controlling the availability of trace metals as well as bacterial productivity of systems. Total suspended sediments and photosynthetically active radiation provide information about the light available for phytoplankton growth. Dissolved inorganic carbon and pH have traditionally been considered more significant in freshwater than marine waters. However, with the increasing atmospheric carbon dioxide concentration, ocean acidification is an increasing concern.

Groundwater and atmospheric deposition can be important sources of nutrients for many aquatic systems. Usually nitrate plus nitrite is the dominant form of nitrogen from these sources, although ammonium can be important in some systems.

The Nutrients Workgroup has also developed performance requirements including expected ranges and detection limits for the specific analytes discussed here (Table 2). It should be recognized that nutrient concentrations in many freshwater streams and rivers far exceed the detection limits listed in Table 2. However, nutrient concentrations in many estuaries and coastal areas are near or below these limits. Laboratories performing nutrient analyses should follow the method detection limit determination outlined in 40CFR part 136 Appendix B. If 90% of the network samples analyzed by that laboratory are above the method detection limit, that method detection limit may be used rather than the detection limit in Table 2. However, if some areas within the sampling region or some times of year are consistently below the laboratory determined method detection limit, a better method with a lower detection limit needs to be used.

Table 1 - Required nutrient parameters for National Water Quality Monitoring Network

Component	Nutrient Analyses		Related analyses	
	Tier 1	Tier 2	Response Variables	Ancillary Analyses
Rivers, Great Lakes, Estuaries, Nearshore Coastal, Offshore Coastal	Total nitrogen* Dissolved ammonium Dissolved nitrate plus nitrite Total phosphorus[+] Dissolved ortho phosphate Dissolved silica	Total dissolved nitrogen Total dissolved phosphorus Particulate nitrogen Particulate phosphorus	Chlorophyll *a* Dissolved oxygen Conductivity/salinity	Dissolved organic carbon Dissolved inorganic carbon pH Total suspended sediments Photosynthetically active radiation Particulate carbon
Groundwater	Dissolved nitrate plus nitrite	Dissolved ammonium Dissolved ortho phosphate		Dissolved organic carbon
Atmospheric deposition	Dissolved nitrate plus nitrite Dissolved ammonium Dissolved ortho phosphate			Major ions pH
Wetlands (sediment only)	Particulate nitrogen Ammonium Dissolved ortho phosphate Particulate phosphorus		Chlorophyll *a*	Particulate carbon

* May be determined by analysis of total dissolved nitrogen and particulate nitrogen (TN=TDN+PN)

[+] May be determined by analysis of total dissolved phosphorus and particulate phosphorus (TP=TDP+PP)

n.b. Dissolved refers to samples that are filtered through GF/F (or equivalent) filters before analysis. Total nitrogen (or phosphorus) refers to unfitered samples. Particulate nitrogen (or phosphorus or carbon) refers to samples collected on filters which are then analyzed.

Table 2 - Performance requirements

Analyte	*Range*	*Detection limit*
Dissolved ammonium	0.007–0.50 mg N L^{-1}	0.007 mg N L^{-1}
Dissolved nitrate plus nitrite	0.007–10.0 mg N L^{-1}	0.007 mg N L^{-1}
Dissolved ortho phosphate	0.001–5.0 mg P L^{-1}	0.001 mg P L^{-1}
Dissolved silicate	0.003–4.0 mg Si L^{-1}	0.003 mg Si L^{-1}
Particulate nitrogen	0.01–100 %	0.01%
Particulate phosphorus	0.005–5.0 mg P L^{-1}	0.005 mg P L^{-1}
Total dissolved nitrogen	0.001–10.0 mg N L^{-1}	0.001 mg N L^{-1}
Total nitrogen	0.03–15.0 mg N L^{-1}	0.03 mg N L^{-1}
Total dissolved phosphorus	0.01–5.0 mg P L^{-1}	0.01 mg P L^{-1}
Total phosphorus	0.01–10.0 mg P L^{-1}	0.01 mg P L^{-1}
Chlorophyll *a*	0.01–150 µg L^{-1}	0.01 µg L^{-1}
Dissolved oxygen	0–15 mg L^{-1}	0.1 mg L^{-1}
Total suspended sediments	1–20,000 mg L^{-1}	10 mg L^{-1}
Conductivity/salinity	0–1,000 mS cm^{-1}	1 -100 µS cm^{-1}
Dissolved organic carbon	0.22–50 mg C L^{-1}	0.22 mg C L^{-1}
Dissolved inorganic carbon	3–24 mg C L^{-1}	3 mg C L^{-1}
pH	1–12 pH	0.01 pH
Particulate carbon	0.01–100 %	0.01%
Photosynthetically active radiation (400 -700 nm)	0.01–10,000 µmol m^{-2} s^{-1}	0.01 µmol m^{-2} s^{-1}

Dissolved inorganic nitrogen (DIN)
Dissolved organic nitrogen (DON)
Total nitrogen (TN)
Total dissolved nitrogen (TDN)
Particulate nitrogen (PN)
DIN = NO3NO2 + NH4
TDN = DIN + DON
TN = TDN + PN
DON = TDN - DIN

Total Phosphorus (TP)
Dissolved inorganic phosphate (DIP)
Ortho phosphate (oPO4)
Particulate phosphate (PP)
Total dissolved phosphorus (TDP)
DIP = oPO4
TP = TDP + PP
TDP = DOP + oP04
TP = oPO4 + DOP + PP