

PRIORITY PARAMETERS FOR MONITORING OF FRESHWATER AND MARINE SYSTEMS, AND THEIR MEASUREMENT

L. J. Twomey, M. F. Piehler and H. W. Paerl

Institute of Marine Sciences, University of North Carolina at Chapel Hill, USA.

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Summary

This paper describes the priority parameters for water quality monitoring currently used by a wide range of government, educational and private agencies in a variety of aquatic systems. Water quality monitoring has become a global priority to ensure that the economic, ecological and recreational value of natural and man-made waterways are sustained. Priority parameters will differ depending on the complexity and ecosystem function of the system. However, there is similarity and considerable overlap in the commonly monitored parameters in freshwater and marine environments.

Physical parameters such as salinity, light, dissolved oxygen concentration, temperature and pH play an important role in the biogeochemistry of water bodies. Subtle changes in physical conditions can have profound effects on the water quality of the study system, which may in turn affect the spatial and temporal distribution of nutrients and/or biological communities. Additionally changes in physical processes of oceans can affect weather patterns and climatic variability. Nutrient concentration data are intrinsically linked to primary productivity and determine the spatial and temporal distribution of biological communities, particularly phytoplankton. Biological monitoring is essential to describe the community constituents and assess variability in seasonal patterns, trophic relationships and potential environmental stressors. Phytoplankton are useful biological indicators, which are commonly used in water quality monitoring. Variability

in phytoplankton community composition, biomass and physiology can reflect environmental changes related to seasonality, acute perturbations or long term environmental change. Zooplankton abundance and grazing is monitored to evaluate trophic transfer of nutrients to higher levels. Fish and large aquatic organisms are monitored because of their importance as tertiary consumers and their value as commodities. Aquatic pathogens are a public health concern for municipal water suppliers and wastewater managers. They are most often monitored indirectly by measurement of fecal coliform bacteria.

1. Introduction

As awareness of the value of aquatic systems has increased, the protection, maintenance and rehabilitation of these important resources has become a priority. Aquatic systems are important economic, ecological and recreational resources. They provide drinking water, support industrial and agricultural water usage, and sustain commercial and recreational fisheries, including rapidly expanding aquaculture ventures. Monitoring water quality provides the basic information needed to address issues pertaining to characterization of water quality trends, specific problems of water quality, development of aquatic ecosystem remediation programs, and assessment of ecosystem management activities.

Increasingly, natural aquatic ecosystems are affected by human activities, which have caused both intentional and unintentional hydrologic alterations, sedimentation, toxic contamination and nutrient enrichment. As a consequence, the deterioration of water quality has become a serious public health and environmental problem. Safety of drinking water is of global concern in the face of population increases and degradation of natural waterways. Lakes and reservoirs are predisposed to poor water quality because unlike rivers, streams and estuaries they are not regularly flushed. As a result, nutrients or pollution entering the system will typically remain there for a prolonged period. Monitoring of drinking water resources is a priority to reduce the risk of adverse human health affects from water contaminated by heavy metals, chemicals and pathogenic microbes. The alteration of ecosystem structure and function as a consequence of excessive nutrient loading has been widely reported in freshwater, estuarine and coastal systems. Decreasing species diversity and the advent of nuisance algal blooms are signs of ecosystem degradation.

Here, we describe important water quality parameters that are routinely monitored by groups worldwide including government, educational and private agencies. The applicability of these parameters to specific systems discussed herein will vary substantially depending on environmental complexity, trophic composition and ecosystem function. Undoubtedly, the selection of water quality priority parameters will differ depending on the interest and area of expertise of the reader. However, we have endeavored to provide an overview of the water quality parameters that are widely used in current freshwater and marine monitoring programs.

2. Salinity and Conductivity

Salinity is a measurement of the ionic composition of water. Saline water usually consists of four major cations, Ca^{+2} , Mg^{+2} , Na^+ , K^+ , and four major anions, HCO_3^- , CO_3^-

$^{2-}$, SO_4^{2-} and Cl^- , with other minor elements also present. Salinity of inland waters is extremely variable, dictated by the flux of ions within the water body. Ions are largely contributed to inland waters from terrestrial and atmospheric sources. Salinity of estuarine and coastal water varies depending on mixing of the relatively fresher inland waters with saltier marine waters. Oceanic salinities are largely dependent on the balance between evaporation and precipitation.

Salinity is a fundamental water quality parameter monitored by freshwater and marine ecologists because of its influence on the biota. Most aquatic organisms are adapted to only a narrow range of salinity, beyond which they cannot maintain their osmotic and ionic balance. Some species tolerate only intermediate levels of salinity while broadly adapted species can acclimate to variable salinity ranging from fresh water to seawater. In freshwater systems, problems associated with rising salinity have become a major environmental concern, with drinking and agricultural water supplies in some regions being rendered unusable without costly desalinization. Additionally, losses of habitat and other adverse effects on biota have become prominent ecological and economic issues as a result of increased salinization. Oceanographers monitor salinity to provide information on the horizontal and vertical circulation patterns of the oceans, and give insight into global hydrology and atmosphere climate variability.

The salinity of a water sample is calculated using the internationally standardized conductivity ratio defined below;

$$\text{Salinity} = \frac{\text{conductivity of seawater sample}}{\text{conductivity of standard KCl solution}}$$

where the concentration of the standard KCl solution is 32.4356 g L^{-1} , measured at 15°C and 1 atmosphere pressure. Salinity is therefore a pure ratio, the values having no dimensions or units. By decision of the Joint Panel of Oceanographic Tables and Standards, salinity should be reported as a number with no symbol. However, many scientific texts report salinity as practical salinity units (PSU), parts per thousand (ppt), or grams per kilogram (g kg^{-1}).

The average salinity of freshwater throughout the world is less than 0.2. Brackish water salinity is less than 25, whereas the surface waters of the open ocean ranges from 33 to 37, and hypersaline water is greater than approximately 40. Estuaries display a wide spatial and temporal salinity range (0 to 30).

The refractive index of water is closely related to salinity and temperature, thus interference refractometers can measure the salinity of a water sample to a precision of ca. ± 0.02 at 20°C . At other temperatures, a correction must be applied to account for changes in the refractive index associated with temperature. Modern salinity measurements are largely based on the specific conductance of the water sample, in which the resistance of the sample to the flow of an electrical current is quantified. Conductivity is the inverse of resistance, and is quantified as the electrical conductance over distance. Units are expressed as $\Phi\text{mhos cm}^{-1}$ or microsiemens (ΦS). Conductivity of electricity in water increases with increasing temperature, thus simultaneous

measurements of temperature and conductivity are necessary to enable correction. Modern conductivity sensors are coupled with temperature and depth sensors (CTD probes) to enable their rapid measurement *in situ*. Current CTD technology enables the measurement of salinity precise to $\pm 0.5\%$ of the reading.

3. Light

Light is essential for life in terrestrial and aquatic ecosystems. Solar radiation that penetrates the water column is absorbed by plants during photosynthesis, where light energy is used to convert inorganic nutrients into organic compounds. However, only a small fraction of the total solar radiation incident on the water surface is able to penetrate to depth. More than 50% of total solar energy is absorbed, scattered and reflected in the atmosphere or reflected at the water surface. Of the light that penetrates the surface, infrared radiation (>780 nm) and ultraviolet radiation (<380 nm) are rapidly scattered or absorbed and converted to heat at the near surface. Only light from the range of the visible spectrum (ca. 400-700 nm) can penetrate deeper into the water column. These wavelengths are referred to as photosynthetically available radiation (PAR) because they provide the utilizable energy for supporting plant photosynthesis. The surface illuminated area of the water column where there is sufficient irradiance to support net photosynthesis is called the photic zone. At depths below the photic zone photosynthesis is limited by the amount of PAR and respiration occurs at a greater rate than photosynthesis. This region is termed the aphotic zone. Some limnologists and oceanographers define the aphotic zone as the region where light is absent. Others suggest that the aphotic zone is the region where light falls below 1% of the surface irradiance. The exponential loss of radiant energy with increasing depth is called light attenuation. Light is attenuated through two main processes: absorption and scattering. Absorption involves the conversion of light energy to heat or chemical energy by algae, inorganic or organic particles, dissolved organic compounds or by the water itself. Scattering changes the direction of the light by reflecting it off suspended particulate material.

Total underwater irradiance is a particularly useful measure in natural aquatic systems because it represents the total amount of light available to photosynthetic organisms whether from direct or scattered sources. Commercially available irradiance sensors measure the ambient PAR as directional light from downwelling or upwelling, or as diffuse light from all directions. The light attenuation coefficient (K) can be calculated by measuring the vertical profile of light attenuation through the water column with an irradiance sensor and then determining the slope of the log transformed data. In doing so, the photic depth of the water column can be calculated to determine the depth at which photosynthesis ceases to be greater than respiration.

Prior to the development of modern day sensors, water clarity was measured using a Secchi disk. This method was first used nearly a century and half ago by Italian physicist Angelo Secchi and is still widely used by many modern day limnologists and oceanographers. The Secchi disk is a weighted flat plate, 20 to 30 cm in diameter and painted either plain white or with black and white quadrants. The disk is lowered through the water column so that its surface is visible to the operator above the water. Secchi depth is determined as the distance below the surface at which the disk is no

longer visible. When modern light sensors are unavailable, this measure is useful for visually inspecting the spatial and temporal variability of suspended particulate matter in the water column including; phytoplankton, organic material, silts and sediments. Secchi depth may be employed to make estimates of the photic depth. However, to calculate the optical property K , supplementary experiments are required using a narrow band-width underwater light detector.

Scattering and absorption of light by suspended particulate matter in the water column is known as turbidity. The concentration and size of suspended materials such as clay, silt, metabolic waste, decaying matter, plankton and other organisms reduce the amount of light transmitted in a straight line through the water. As such, turbidity is simply a measure of water clarity. Turbidity meters are widely used by limnologists and oceanographers to directly measure light scattering *in situ*. The basic turbidity meter uses a single light source located perpendicularly to a photodetector, which detects the light scattered from the source by suspended particles. More complex turbidity meters with greater accuracy incorporate additional light sources and photodetectors, or split light sources to compensate for light decay or the presence of color.

4. Dissolved Oxygen

Dissolved oxygen (DO) concentration is a fundamentally important parameter in aquatic systems. Oxygen is required by virtually all aquatic organisms for metabolism. Because it is required for the function of the biology of aquatic systems, DO concentration measurements are critical in efforts to monitor aquatic systems. DO conditions are closely related to the activity and distribution of aquatic organisms, including reproduction and feeding. DO requirements increase with ascending trophic state, for instance, organisms such as fish have maximum requirements, whereas some microorganisms, such as bacteria, can thrive in oxygen-free environments. Additionally, DO concentrations affect availability of major sources of limiting nutrients by influencing the solubility of many inorganic nutrients and metals.

DO is supplied to aquatic systems through atmospheric and photosynthetic sources and is distributed in the water column by a variety of physical processes. Consumptive processes such as aerobic metabolism and decomposition balance DO levels in aquatic systems. Measurements of DO in water bodies provide an estimate of the balance of supply and demand for DO. Non-biological factors that may affect DO concentration in aquatic systems include temperature (determines the solubility of the gas in water), light (affects the level of photosynthesis and the types of phytoplankton present), turbulence (affects the mixing of oxygen from the atmosphere), color and turbidity (affects light penetration and thus photosynthesis) and salinity (higher salinity means water has less capacity to hold DO). The biology of a system modifies the DO budget through three major processes, photosynthesis, respiration and decomposition. Photosynthesis generates oxygen as a bi-product of primary productivity and respiration and decomposition use up DO. When supplies from photosynthesis and atmospheric sources cannot keep up with demand for DO, oxygen deficits can occur and may have deleterious effects on the organisms in the system. Anoxic waters are defined as those with 0 mg L^{-1} DO and hypoxic waters are defined as those with less than 2 mg L^{-1} DO (4 mg L^{-1} DO is regarded by some as the threshold of hypoxia).

When monitoring DO in aquatic systems, the primary concern is that the instrument used is precise and accurate enough to make measurements of the gas in water at the mg L^{-1} level. Because DO measurements in aquatic systems are often made in the field, instruments used to make the measurements must also be substantial enough to function in adverse conditions. The majority of field measurements of DO are made with polarographic oxygen sensors. These sensors have platinum anodes and gold-plated cathodes that are mounted in electrolyte filled chambers covered with gas permeable membranes. DO diffuses across the membrane, into the electrolyte solution and to the electrodes. The electrical current resulting from the reduction of DO is proportional to the DO concentration in water. These instruments are fast and portable, however, they do have some limitations. They require flow of water across the membrane, therefore stirrers are often fitted to DO sensors. The sensors are also considered to be less reliable at very low concentrations of DO ($0\text{-}1 \text{ mg L}^{-1}$). Finally, polarographic sensors are not suitable for use in measurements near surfaces having steep DO gradients. Oxygen microelectrodes are very effective in these areas of steep gradients in DO and are accurate at low DO levels ($\pm 0.05 \text{ mg L}^{-1}$). However, microelectrodes are also difficult to construct, relatively expensive to purchase and quite fragile. Despite these limitations, microelectrodes fill an important analytical gap in field oxygen measurements. Recent advancements have led to more accurate and portable field DO measurements. There is still need for development of improved oxygen sensors to approach the accuracy and sensitivity of chemical approaches such as the Winkler method (iodometric method). The Winkler method relies on the oxidation of DO with a strong alkaline manganese solution, and subsequent reaction with added iodine. Iodine is liberated from solution at a concentration equivalent to DO, which may be determined by titration with thiosulfate or measurement with absorption spectrophotometry. The Winkler method can be precise to $\pm 5 \mu\text{g L}^{-1}$.

5. Temperature

Temperature is an extremely important physical property that exerts a strong influence on the biogeochemistry of the freshwater and marine environment. The rate of chemical reactions and both catalyzed and uncatalyzed cellular processes are closely controlled by temperature. Absorption and its dissipation of heat affect water density and thus stratification and vertical circulation patterns. A thermocline develops when cool high-density water becomes physically separated from warmer low-density water. Thermoclines are commonly observed features of natural aquatic systems such as the deep permanent thermocline of the oceans or seasonal thermoclines in shallow water bodies such as lakes and estuaries. Thermoclines can separate physical, chemical and biological processes and thereby alter the structure and function of the ecosystem. Additionally, water temperature affects the solubility of biologically important gasses such as oxygen and carbon dioxide. Variability in temperature largely controls seasonal community composition and global distribution of species. Heat and water are exchanged from the ocean surface to the atmosphere through conduction, convection, evaporation and precipitation. Through these mechanisms, the oceans of the world act as heat buffers for the earth's surface. The daily and seasonal variations in sea surface temperature profoundly affect global temperature and climate.

Mercury thermometers have been used by generations to measure water temperature by direct immersion. However, their accurate application is limited to surface samples. Maximum/minimum thermometers are a more precise method for determination of subsurface temperature, however these require careful calibration. Reversing thermometers are highly precise instruments typically used by oceanographers for measuring subsurface temperature. The reversing thermometer is lowered to the required depth, where a messenger is then sent down the line, which causes the thermometer to pivot and constrict the flow of mercury through the stem. When the assembly is brought to the surface the temperature can be read accurate to 0.02 °C. Most current day measurements of temperature are conducted with thermistors, which measure changes in electrical resistance with changing temperature. Thermistors provide a quick (within seconds) and reliable measure with good accuracy (± 0.15 °C) within the range of temperatures encountered in aquatic environments (-5 to +45 °C). Thermistors are required in modern CTD probes to make temperature corrected salinity measurements.

6. pH

pH is the intensity or power of acidity. Often used synonymously with alkalinity, pH quantifies the measurement of H⁺ ions (protons). pH is expressed as the negative logarithm of H⁺ ions in a water sample. The calculation of the pH of a pure water sample is shown here;

$$\text{pH} = -\log(\text{H}^+) = -\log 10^{-7} = 7$$

Pure water has 10^{-7} mol L⁻¹ of H⁺ at 25 °C, thereby giving a pH of 7, which is defined as neutral. Values below a pH of 7 are acidic, whereas values above 7 are alkaline. The pH scale runs from 0 to 14.

pH is a fundamentally important parameter for many chemical and biological processes in aquatic systems. The bacteria responsible for biogeochemical transformations in natural systems have a relatively narrow range of pH tolerance. Similarly, aquatic plants and animals have difficulties tolerating pH levels below 5.0 and above 9.0. The solubility of metals such as iron, mercury and copper can be affected by changes in pH. For instance, some Canadian lakes whose pH have been lowered by acid rain have high levels of sediment dissociated mercury, which has been transferred through trophic interactions to higher order organisms such as predatory fish (see *Acidification and Salination of Water Bodies*). Water supply and treatment facilities regularly monitor pH to ensure that pH-dependent processes such as water softening, acid neutralization and disinfection occur at optimal rates. Highly alkaline waters can contain large concentrations of dissolved solids (e.g CaCO₃), which can be detrimental to water supply facilities and residential appliances such as water heaters.

The measurement of pH is often conducted using the electrometric method, which involves the comparison of a solution with unknown pH to a standard reference solution. A glass electrode is inserted into the standard solution and the electromotive force (emf), which varies proportionally with pH, is measured. By measuring the emf in different buffers, a linear relationship can be determined and the pH of a natural water

sample can be determined by extrapolation precise to ± 0.01 . pH electrodes are affected by temperature, but the response is linear so calibration is relatively simple. Some pH meters have built in thermistors that automatically correct the pH based on the temperature of the solution. Rapid assessment of pH can also be conducted with simple colorimetric tests using litmus indicator paper of an appropriate narrow-range, which can be precise to ± 0.1 .

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Biographical Sketches

Luke Twomey is a post-doctoral research biologist at the University of Western Australia.

Higher Education

- 1995. B. Sci, (1ST class honors) Biology, Curtin University of Technology, Western Australia.
- 2000. Ph.D., Aquatic Ecology, Curtin University of Technology, Western Australia.
- 2000. Post-Doc., University of North Carolina-CH, Institute of Marine Sciences, NC.

Employment

- Part-time tutor and laboratory advisor, Curtin University of Technology, School of Environmental Biology, Western Australia
- 1996-00. Coastal Ecology Consultant, CSIRO Marine Research, Marmion, Western Australia.
- 2000. Part-time Research Associate, Planktonic particle dynamics, University of Western Australia, Center for Water Research, Western Australia.
- 2000-2002. Post-Doc., University of North Carolina-CH, Institute of Marine Sciences, NC.
- 2003-present. Lecturer, Murdoch University, School of Biological Science and Biotechnology, Western Australia.
- 2003-present. Post-Doc., University of Western Australia, Centre for Water Research, Western Australia.

He has made about 20 international conference presentations.

Michael F. Piehler gained his B.S. in Biology in 1990 from The University of North Carolina at Chapel Hill, North Carolina, and a M.S.P.H. in Environmental Sciences and Engineering in 1994. He was awarded a Ph.D. in 1997 in Environmental Sciences and Engineering, from The University of North Carolina, Aquatic and Atmospheric Sciences Section.

Appointments

- 2004-present: Program Head, Estuarine Ecology and Human Health, UNC Coastal Studies Institute, Manteo, North Carolina.
- 2003-present: Graduate Faculty Appointment, UNC Chapel Hill.
- 1998-present: Research Assistant Professor, UNC Institute of Marine Sciences.
- 1997-1998: Post-doctoral Researcher, UNC Institute of Marine Sciences.
- 1992-1997: Research Assistant, UNC Institute of Marine Sciences.
- 1990- 1991: Environmental Scientist, AScI Corporation, McLean, Virginia.

Synergistic Activities

- SERDP Ecosystem Management Project: New River-Onslow Region, Atlantic Beach, NC 2/04

- NSF Collaborative Large-scale Environmental Analysis Network for Environmental Research (CLEANER) Workshop #4, Duke Univ. 11/03.
- Selection committee for Gov. and Mrs. Dan K. Moore Graduate Fellowship, 3/02.
- Steering committee for Sustainable Shoreline Protection and Development Project, Carteret Community College, Morehead City, NC, 1/02.
- Southeastern Estuarine Rivers and Sounds Restoration Conference, Beaufort, NC 3/99.
- Participant: Estuarine restoration panel discussion. Israel-North Carolina Biotechnology Workshop, NC Biotechnology Center 8/95.

Hans W. Paerl is Kenan Professor of Marine and Environmental Sciences, at the UNC-Chapel Hill Institute of Marine Sciences, Morehead City. His research includes: microbial ecology, nutrient cycling and primary production dynamics of aquatic ecosystems, environmental controls of algal blooms, and assessing the causes and consequences of man-made and climatic (storms, floods) nutrient enrichment and hydrologic alterations of inland, estuarine and coastal waters. His recent studies have identified the importance and ecological impacts of atmospheric nitrogen deposition in estuarine and coastal environments. He was recently (Feb. 2003) awarded the G. Evelyn Hutchinson Award by the American Society of Limnology and Oceanography for his work in these fields and their application to interdisciplinary research, teaching and management of aquatic ecosystems.

Professional Preparation

- College of San Mateo, California, Biology-Biochemistry, A.A. 1967.
- University of California, Davis, California Biological Sciences, B.Sci. 1969.
- University of California, Davis, California Ecology-Limnology Ph.D. 1973.

Appointments

- Kenan Professor, Marine and Environmental Sciences, Institute of Marine Sciences, University of North Carolina at Chapel Hill, 1979.
- Visiting Scientist, Canada Centre for Inland Waters, Environment Canada, 1978.
- Research Scientist (Limnologist-Microbiologist), Dept. of Scientific and Industrial Research, Taupo, New Zealand, 1975-77.
- Postdoctoral Research Limnologist, Division of Environmental Studies, Univ. California, Davis, 1973-75.
- Research Associate, Division of Environmental Studies and Tahoe Research Group, 1971-73.
- Teaching Assistant in Limnology & Oceanography, Zoology Dept. & Institute of Ecology, Univ. California, Davis, 1967-70.

Synergistic Activities

- Co-Chair, US-European Conference on Comparative Shallow Water Coastal Ecosystems, Rostock, Germany 1996.
- Keynote Speaker. "Algal bloom dynamics in aquatic ecosystems: Synergistic physical-chemical controls" Am. Chem. Soc. meeting, San Francisco, Apr. 1997.
- Chair, 4th Int. Conference on Toxic Cyanobacteria, Beaufort, NC. Sept. 1998.
- Keynote Lecture, 8th Internat. Symp. on Aquatic Microbial Ecology, Taormina, Italy. Oct., 2002.