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CURRENT AND FUTURE TRENDS IN NUTRIENT MONITORING

by OTT HydroMet water quality experts

Gathering Insights from Nitrate and Phosphorus Monitoring Data

Nutrients in freshwater

As fundamental components of living organisms, nitrogen and phosphorus are the nutrients of primary concern. Phosphates and nitrates occur naturally in the environment and are essential nutrients that support the growth of aquatic organisms. However, water resources are under constant pressure from both point and diffuse sources of pollution, often including excessive amounts of nutrients.

Nitrates are soluble in water and as such migrate easily. The main sources of nitrate contamination are stormwater run-off and leaching from manure or artificial fertilizers. As such, urbanization and the intensification of farming in many countries has resulted in increases in pollution potential from these sources. However, other anthropogenic sources include waste materials such as overflow from wastewater treatment plants, leakage from waste storage, soakaways and septic tanks. Phosphate contamination is derived from the same sources but can exist in elevated levels where wastewater is derived from phosphate rich cleaning products.

Elevated Nutrients

Under certain conditions, such as warm, sunny weather and slow-moving water, elevated nutrient concentrations can promote the growth of nuisance phytoplankton causing algal blooms (eutrophication). These blooms can dramatically affect aquatic ecology in several ways. High densities of algal biomass within the water column, or, in extreme cases, blankets of algae on the water surface, prevent light from reaching submerged plants, which prevents them from photosynthesizing and ultimately kills them. Also, some algae, and the bacteria that feed on decaying algae, produce toxins. In combination, these two effects can lower dissolved oxygen levels, killing fish and other organisms. Harmful algal blooms (HABs) therefore represent a major threat to water resources.

WHAT IS AN ALGAL BLOOM?

An algal bloom can be defined as a rapid increase in the population of algae in an aquatic system – marine or freshwater. Typically, one phytoplankton species dominates the bloom and whilst there is no universally recognized concentration of algal cells in a bloom, most instances of significant algal proliferation cause discoloration of the water. This may be green, yellow, brown or red, and bright green blooms may be caused by blue-green algae which are actually cyanobacteria - a phylum of (cyan colored) bacteria that obtain their energy through photosynthesis. Algal blooms have been known to trigger jellyfish blooms in ocean water, with serious negative impacts on beaches and fish farms.

When aquatic ecology is damaged by HABs, the water becomes unsuitable for recreational activities such as swimming, sailing and fishing, and more expensive to treat for drinking purposes. In some cases, it may be possible for water managers to source water from other locations, or to blend with cleaner supplies. However, where this is not possible, it becomes necessary to treat source water that is intended for drinking. This can be achieved by separating nitrates from the water, or by degrading nitrate into nitrogen gas.

Global freshwater nutrient levels

The EU Water Framework Directive (WFD) requires member states to achieve 'good status' of all water bodies (including rivers, streams, lakes, estuaries, coastal waters and groundwater) by 2015. However, according to the European Environment Agency, only 40% achieved 'good' or 'high' ecological status during the 2010-2015 monitoring period.

The EU Nitrates Directive (1991) aims to protect water quality by preventing nitrates from agricultural sources polluting ground and surface waters and by promoting the use of good farming practices. As part of the WFD, it seeks to identify and protect surface freshwaters, in particular those for the abstraction of drinking water, containing more than 50 mg/l of nitrates. River nitrate concentrations have declined steadily in Europe over recent decades.

Average concentrations of orthophosphate in European rivers have also lowered significantly in recent decades. This is due to the measures introduced by national and European legislation, in particular the Urban Waste Water Treatment Directive and the switch to phosphate-free detergents. Nevertheless, relatively high concentrations (greater than 0.1 mg P/l) are found in several regions with high population densities and intensive agriculture. Given that phosphorus concentrations greater than 0.1-0.2 mg P/l are generally perceived to be sufficiently high to result in freshwater eutrophication, the observed high values in some regions of Europe are of particular concern.

In the United States the Environmental Protection Agency (EPA) published a memorandum in 2011 confirming its ***commitment to partnering with states and collaborating with stakeholders to make greater progress in accelerating the reduction of nitrogen and phosphorus loadings to our nation's waters…Over the last 50 years, the amount of nitrogen and phosphorus pollution entering our waters has escalated dramatically… with U.S. population growth; nitrogen and phosphorus pollution from urban storm water runoff, municipal wastewater discharges, air deposition, agricultural livestock activities and row crop runoff is expected to grow. Nitrogen and phosphorus pollution has the potential to become one of the costliest and the most challenging environmental problems we face.***

WHY NITRATE IS HARMFUL?

The toxicity of nitrate to humans is mainly attributable to its reduction to nitrite. Elevated levels of nitrate in drinking water are to be avoided because, when ingested, nitrites may compete with oxygen for binding with hemoglobin in the blood, effectively starving the body's cells of oxygen. The elderly, infants and pregnant mothers are particularly sensitive to this condition, which is known as methemoglobinemia; a condition sometimes known as blue baby syndrome. Methemoglobinemia causes cyanosis and, at higher concentrations, asphyxia. The World Health Organization has a guideline value for nitrate in water of 50 mg/l. However, in 2005 the US EPA reported nitrate to be the contaminant that most frequently exceeded a federal drinking water standard, and as a result, nitrate is a regulated contaminant under the Safe Drinking Water Act with a maximum concentration of 10 mg/l. Nitrate does occur naturally in groundwater and other water resources, however, human activity can result in significantly higher levels, and this is a particular concern with private self-supplied drinking water systems, which primarily draw from groundwater.

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The EPA has since published a nutrient specific website **www.epa.gov/nutrientpollution** which provides background information as well as detailing the progress of each State toward the development of 'Numeric Nutrient Criteria,' which are specific total nitrogen (TN) and total phosphorus (TP) EPA-approved criteria for different water types.

Numeric nutrient criteria are a critical tool for protecting and restoring a waterbody's designated uses with regard to nitrogen and phosphorus pollution. These criteria enable:

- **Effective monitoring of a waterbody for attaining its designated uses**
- **Formulation of NPDES (National Pollutant Discharge Elimination System) discharge permits**
- **Development of total maximum daily loads for restoring impaired waters**

The development of water quality standards for Phosphate is complicated because it is generally necessary to set concentration levels that take into account background levels from natural sources. Not least because phosphates exist in three forms: orthophosphate, metaphosphate (or polyphosphate) and organically bound phosphate. Consequently, this may take into account the elevation of a river and other chemical factors. From a monitoring perspective, orthophosphate is measured as soluble reactive phosphorus (SRP) and is of most interest because of its availability for aquatic organism growth. Nevertheless, the other forms may play a significant role – in the slow release of P from sediments for example.

Highlighting the need for better understanding of the relationships between nutrients and ecological status, Dr. Mike Bowes from the UK's Centre for Ecology & Hydrology has published research, with others, in which the effects of varying SRP concentrations on periphyton growth rate (mixture of algae and microbes that typically cover submerged surfaces) were determined in 9 different UK rivers. In all trials, significantly increasing SRP concentrations in the river water for sustained periods (usually c. 9 days) did not increase periphyton growth rate or biomass. This indicates that in most UK rivers, phosphorus concentrations are in excess, and therefore the process of eutrophication (typified by excessive algal blooms and loss of macrophytes – aquatic plants) is not necessarily caused by intermittent increases in SRP.

Clearly, more research is necessary to more fully understand the effects of nutrient enrichment, and the causes of algal proliferation.

IMPROVING WATER QUALITY

To improve water quality and reduce nitrate and phosphorus levels storm drains are retrofitted with traps to collect debris, and retention ponds are increasingly incorporated into new development designs to help slow the flow and deposit suspended loads. Grass lined ditches provide biological filtration, and chemical treatment or filtration systems may also be employed. All of these facilities require regular maintenance.

How does nutrient monitoring data help?

As demonstrated by global initiatives to establish water quality standards for nutrients, it would be impossible to manage nutrients effectively without knowing background levels, trends, nutrient sources and loads, seasonal variation, hydrology, ecology and the effects of climate change.

Water treatment and pollution reduction infrastructure to reduce nutrient levels is costly, so it is sensible to find ways to prevent contamination in the first place. Regulatory tools such as wastewater discharge limits and limitations on fertilizer application can help in this regard, and these need to be supported by sound science, i.e. accurate monitoring data.

Since agriculture is the major source of nutrient pollution, it is important to engage with farmers to identify sustainable agricultural practices that would limit or reduce detrimental effects on groundwater and river water quality while maintaining food production and the profitability of farm businesses. Again, monitoring performs a key role; helping farmers to see the connection between fertilizer spreading and river nutrient levels. Researchers have also used monitoring to identify the benefits of other management practices – such as keeping livestock away from river banks.

By using monitoring to help identify successful management practices, regulators are able to define, implement and enforce new measures to lower nutrient pollution. For example, in April 2018, the UK government published ‘Rules for farmers and land managers to prevent water pollution’ which provides guidance and establishes a mechanism for enforcement where necessary.

The cost of developing and implementing nutrient reduction plans to restore or maintain water quality can be very high, so it is essential that such plans are based on sound science and that monitoring is available to track progress and enable refinements. The advantages of freshwater monitoring also apply to inshore marine environments which can be harmfully impacted by river nutrient loads. For example, the cost of implementing the best management practices developed by states in the Chesapeake Bay (3rd largest estuary in the world) watershed has been estimated at around US$ 900 million per year for full implementation (Kaufman et al., 2014).

Nutrient monitoring

Traditional nutrient monitoring in freshwaters has relied on discrete samples being taken at intervals for laboratory, and sometimes field, wet chemistry analysis. This low temporal frequency monitoring is often combined with modelling to inform estimates of loading, water quality standards and water quality management programs, but such models are vulnerable to uncertainties.

The collection of discrete samples is labor intensive and as a result, remote sites tend to be monitored less, which means, for example, that upland rivers and streams have been monitored less frequently. A further negative aspect of manual sampling is the delay between sampling and result – a factor which also applies to automatic samplers. Nevertheless, laboratory analysis takes place in a controlled, often accredited environment, using sophisticated analytical technology and employing reference methods. As long as the sampling is representative, the results can be precise, accurate and legally defensible.

Manual sampling has low capital costs (unless the cost of laboratory equipment is accounted for), and high operational costs. But perhaps the most important shortfall of manual sampling is its potential for missing episodic events such as storms and floods, which can have an enormous effect on nutrient loading.

Clearly, continuous monitoring, particularly in remote locations without power or data connectivity, would be the ideal monitoring solution, so why is continuous monitoring not the predominant method already?

Continuous monitoring generates enormous quantities of data. For example, weekly sampling for a single parameter generates 52 results per year, whereas continuous monitoring at a sampling rate of 15 minutes would generate over 35,000 measurements. It would therefore be necessary to run tools capable of integrating, managing and sharing large datasets. Communications capability would also be necessary if the advantages of real-time data are to be realized – identification of episodic events, alarm capability, better models, better understanding of sources, improved assessment of nutrient reduction practices and remedial measures, etc.

Both communications technology and the management of ‘Big Data’ have advanced considerably in recent years, with leading instrumentation providers now able to provide low cost communication technologies to suit every application. By including ‘cloud-based’ data management systems, data can be managed and displayed in a format that can be accessed by anyone with an internet enabled device. OTT Hydromet’s ‘Hydromet Cloud’ is an excellent example of this capability, providing users with real-time access to their data, at any time, from anywhere. Not only does this provide a secure means with which to store and share data; it also opens a new world of opportunity for leveraging the value of data. In the past, collected data enabled water resource managers to react to data, but this new capability provides opportunities for proactive measures.

So, it is now possible to collect and manage large datasets in real-time, but there are other limiting factors that are also being addressed. Power is a major consideration; wet chemistry methods generally require more power than electrovoltaic or optical sensors, so instrument developers are constantly seeking to lower power requirements and enable remote operation by battery, with local charging from solar panels for example.

The most significant limiting factor in the development of remote continuous monitoring nutrient analyzers is the measurement technology itself.

The ability to measure nutrient concentrations in-situ using field sensors was advanced in the 1970s with the development of non-chemical, ion-selective electrodes (ISEs) for nitrate and ammonium. Much of the focus on nutrient sensor development has been with nitrate given its importance in water quality and its amenability to in-situ measurements. ISEs for nitrate are relatively inexpensive and easy to use, but have much lower accuracy and higher drift than wet chemical or UV nitrate sensors. ISE sensor drift results in a frequent requirement for recalibration which makes them less suited to remote measurement. UV nitrate sensors therefore offer greater potential for continuous monitoring, and the latest instruments are delivering high levels of accuracy and precision, so current development work is focused on lowering the cost of this highly promising technology.

Phosphate monitoring currently requires wet chemistry, so mains powered analyzers are available for continuous monitoring. However, in the last few years, battery-powered, remote use, wet chemical orthophosphate sensors have been developed and have performed very well in a variety of applications. Internal QA/QC processing in conjunction with an on-board NIST standard protect the accuracy and reliability of data, and with replaceable reagent packs, instruments can be left in remote locations for up to 1,500 measurements.

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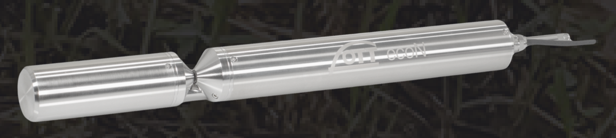
Comparison of Different Nutrient Monitoring Technologies

Sensor	Product highlights	Measurement principle	Parameters	Advantages	Disadvantages
 Ion-selective electrode (ISE)	**HYDROLAB HL7:** • Versatile and durable • Practical for simple and complex deployments • Long-term continuous and profile monitoring	Electrical potential between sensing and reference electrodes	• Nitrate • Ammonium	• Low cost • Fast response	• Low resolution, accuracy & precision • High instrument drift • Limited shelf life • Ionic interferences
 Wet chemistry	**Sea-Bird HydroCycle-PO4:** • Stablizes rapidly • Real-time QC flags and post-processing • Enables better management recommendations	Photometer/colorimetry	• Phosphate • Ammonium • Nitrate	• High resolution, accuracy & precision • In-situ calibration • Fast response • Battery power possible	• Higher capital cost • Requires reagents/site visits • Produces waste reagents
Now with SDI-12  Optical	**OTT ecoN:** • User-friendly • Low operational cost • Sensor interfaces of SDI-12, RS-485 (Modbus RTU), and Ethernet (TCP/IP) • 4 adaptable path lengths	UV absorption by photometer	• Nitrate	• High resolution, accuracy & precision • Chemical free • Fast response • Low maintenance • Spectral data	• Higher capital cost

Newly Launched: The OTT ecoN with SDI-12 Converter accessory. Learn more on otthydromet.com

Future trends

Summary

In order to reduce the impacts of nutrients in freshwater, it is important to establish measurable goals. However, before setting such goals it is important to understand the sources and how they interact with other environmental factors, as well as the cost/benefits ratio of proposed reduction measures. Research involving comprehensive monitoring programs is therefore necessary to underpin the development of water quality criteria that are founded in reliable science.

In the United States, the Association of Clean Water Administrators publishes (most recently in March 2018) a 'Nutrient Reduction Progress Tracker.' This work began in 2014 to identify a set of measures that demonstrated progress toward nutrient reduction in the nation's waters. States expressed concern that the only national metric for demonstrating progress on addressing nutrient pollution was the establishment of nitrogen and phosphorus criteria for lakes, estuaries, and flowing waters. Furthermore, States believed there was potential for more robust national metrics to demonstrate state actions taken to reduce nutrient loads in conjunction with the development of nutrient criteria. As a result, it is now possible to view the progress that States are making on the website **www.acwa-us.org**.

Nutrient reduction is heavily reliant on effective monitoring and looking back, this has been limited by a number of factors including cost, sensor technology, maintenance requirements, data management capability and telecommunications.

The future is clear

Looking forward, we are at a tipping point; many of the previous limitations no longer exist or have been minimized, so the prospects for much wider use of continuous nutrient monitoring look extremely bright. We will be able to monitor more wells, streams and rivers in even more remote locations, and with real-time data, we will be able to build fast-response, alarm-based systems that prevent ecological harm from taking place.

Improved monitoring and communication technology will increase spatial data density and thereby improve the models that underpin strategic investment. By improving our understanding of nutrient behavior, continuous monitoring will enable the effective prioritization of infrastructure investments to reduce the impacts of nutrients and the restoration of impaired waters.

The availability of data will also improve visibility and raise the profile of nutrient status among stakeholders. We can therefore look forward to a much better understanding of nutrient sources and loads, and to the creation of measurable goals… and to meeting them.

Informed decisions
are better than decisions

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