

Nitrogen in water is an essential nutrient for the growth of plants and algae. Whilst nitrogen is naturally present at low levels in rivers, excessive nitrogen can result in eutrophication of water bodies. Eutrophication (excess nutrients) can lead to extensive growth of aquatic plants and algae, which can impact the ecological health, recreational, cultural and food-gathering values of a river.

In a river, nitrogen can be present in various forms (chemical species).

Total nitrogen (TN) is the sum of all forms of nitrogen: nitrate nitrogen (NO₃–N), nitrite nitrogen (NO₂–N), ammoniacal nitrogen (NH₄–N) and organic nitrogen (nitrogen in amino acids and proteins).

Nitrate nitrogen is a stable form of nitrogen found in freshwater ecosystems; it is highly soluble and can be readily used by vascular plants and algae for growth. However, at high concentrations, nitrate can be toxic to aquatic life. The major sources of nitrate in freshwater systems include diffuse discharge from agricultural

areas and wastewater discharges (from municipal sewerage treatment plants, septic tanks and industry). Atmospheric deposition and decaying plant debris are also sources of nitrate in freshwater bodies.

Ammoniacal nitrogen is the concentration of nitrogen present as either ammonia (NH₃) or ammonium (NH₄⁺) and, at high concentrations, is toxic to aquatic life. Elevated ammoniacal nitrogen concentrations in rivers and streams are often due to point source discharges, such as raw or poorly treated sewage or dairy shed effluent. The toxicity of ammoniacal nitrogen increases as water pH and temperature increase.

How do we monitor nitrogen in waterways?

To date, most nitrogen monitoring in rivers and streams in New Zealand has involved taking water samples, usually on a monthly basis. The samples are then tested in the laboratory. In New Zealand, laboratory results and guidelines relative to nitrate are generally expressed as nitrate nitrogen concentrations.¹

For information on how to collect, store and transport river water samples for nitrogen (TN) analysis in a laboratory, see the relevant National Environmental Monitoring Standard².

However, this 'discrete' sampling doesn't tell us what is happening in between sampling occasions, and the results will depend on conditions at the time of sampling. It is possible to monitor nitrate concentrations on a high-frequency basis, by installing a sensor in the waterway. High-frequency monitoring can help

detect overall changes quicker and more robustly, and the sub-hourly data means that reliable estimates of nitrate loads can be made. However, the initial set up and ongoing maintenance costs are higher than conventional (discrete) sampling.

There is currently no reliable technology for high frequency monitoring of total nitrogen or ammoniacal nitrogen at concentrations routinely encountered in New Zealand streams and rivers. However, it may be possible to determine the ratio of nitrate to total nitrogen at a site and use this ratio to estimate total nitrogen from nitrate sensor records. A sampling programme involving analysis of both nitrate and total nitrogen in samples taken under a range of conditions (flow, season, temperature, etc.) would first be required to determine this ratio.

 $^{^{1}}$ 'Nitrate nitrogen' (NO $_{3}$ –N) refers to the nitrogen portion of the total nitrate (NO $_{3}$) in a sample. Some countries tend to express nitrate results and guidelines as total nitrate concentrations. For example, the World Health Organization's drinking water standard for nitrate concentration (50 mg/L) corresponds to 11.3 mg/L when expressed as nitrate nitrogen concentration. Thus, care should be taken when interpreting results from the laboratory and comparing them to international guidelines.

² National Environmental Monitoring Standards - Water Quality Part 2 of 4: Sampling, Measuring, Processing and Archiving of Discrete River Water Quality Data. Available from https://nems.org.nz/documents/

High-frequency nitrate monitoring: how it works

There are two types of high-frequency sensors for nitrate monitoring: ultra-violet (UV) spectral sensors and ion selective electrode (ISE) sensors.

UV spectral sensors operate on the principle that nitrate absorbs radiation in the UV region of the electromagnetic spectrum at a characteristic wavelength of about 220 nm. Pulses of UV light are transmitted through a sample path of water (typically 20 mm), received by the sensor and spectrally analysed. The amount of UV absorbed by the water in the sampling zone is proportional to the concentration of nitrate in the water³.

An ISE nitrate sensor operates on the principle that nitrate variation in the water will affect the electric potential of a solution in the probe. This change is then transmitted to the meter, which converts the electric signal to a scale that is read in millivolts.

The millivolts are then converted to nitrate concentration. The accuracy of the electrode can be affected by high concentrations of chloride or bicarbonate ions in the sample water, and fluctuating pH.

The nitrate concentration data, measured by either type of sensor, are recorded and stored in a datalogger. The datalogger may then transmit the data to a central location (such as a base station PC), or data can be manually downloaded during a site visit.



How much will it cost?

The cost of carrying out a nitrogen monitoring programme based on discrete sampling will depend on how often samples are collected, the location of the site and laboratory charges for analysing the samples. Some approximate costs for a single sampling occasion, based on average results from a survey of regional councils in 2022, are shown in the table (excluding the cost of purchasing a vehicle). Using these estimates, the operational cost for monthly monitoring of total nitrogen, nitrate and ammoniacal nitrogen will be about \$2,800 per year. In addition, some sampling equipment may need to be purchased.

	Cost per sampling occasion
Laboratory testing	\$25 for total nitrogen \$16 for ammoniacal nitrogen \$12 for nitrate-nitrogen
Staff time – sampling and subsequent data processing	\$140
Operational costs – mileage* and consumables (courier charges, ice)	\$40
Total per sampling occasion	\$235

^{*}Based on regional council estimates of average distance to a monitoring site



 $^{^3\} https://niwa.co.nz/publications/isu/instrument-systems-update-22-june-2018/time-for-a-closer-look-at-nitrates$

Running a high-frequency nitrate monitoring site will be more expensive than sampling, due to the purchase cost of the equipment and staff time for installation, maintenance and data processing. The exact cost will depend on many factors:

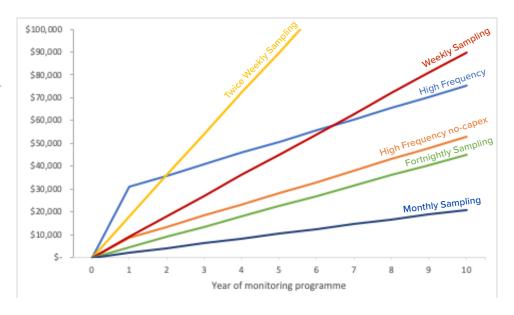
- · The type of sensor chosen
- · The remoteness of the monitoring site
- Characteristics of the monitoring site, e.g., is it prone to excessive aquatic weed growth? Is there an existing structure for mounting a nitrate sensor?
- Whether the data are electronically transmitted (telemetered) or manually downloaded.

The approximate costs associated with setting up and running a nitrate sensor in a river are shown in the table (excluding the cost of a vehicle). The cost of the sensor will depend on the type selected; the cost shown in the table is for a mid-range sensor. The costs will be highest in the first year, due to the purchase and initial installation cost. Depending on the performance of the sensor, additional calibration and validation sampling may be required.

	Year 1	Year 2+
Nitrate sensor	\$20,000	
Telemetry unit	\$1,000	
Installation cost	\$4-5000	
Ongoing maintenance (including staff time and consumables)	\$3,300	\$3,200/year
Ongoing telemetry costs	\$400	\$400/year
Calibration/validation sample laboratory costs	\$90 (six samples)	\$90/year
Staff time for data processing, QA/QC	\$2,000	\$1,200/year
Total	~\$31,000	~\$4,900/year

For more information on the cost of running a highfrequency nitrate monitoring site, or a nitrogen sampling programme, see the Monitoring Costs document on the Monitoring Freshwater Improvements website.

The graph compares the estimated cost of operating a high-frequency nitrate sensor site to the cost of a sampling programme (various sampling frequencies shown) over a 10-year period. The 'High-frequency no capex' represents a scenario where the user already has a sensor and does not need to purchase one. Although the initial cost of setting up the sensor is high, after about 6 years of monitoring the total amount spent will be about the same as if samples were collected weekly. Therefore, if the intention is to monitor more frequently than weekly it may be cheaper to install a sensor. Note, however, that a sensor may need to be replaced after 7-10 years.



Monitoring Freshwater Improvement www.monitoringfreshwater.co.nz

Research Team | Te hunga i whai wāhi mai