

Monitoring nitrate in groundwater

Nitrate nitrogen is a stable form of nitrogen found in freshwater ecosystems; it is highly soluble and can be readily used by aquatic plants and algae for growth. Nitrate occurs naturally in New Zealand groundwaters but generally at very low concentrations. However, nitrate can leach through the soil and enter groundwater systems in high concentrations in areas of intensive agriculture and horticulture.

Elevated nitrate concentrations in groundwater are a health risk to people if the groundwater is used for drinking water. It is also an issue where groundwater feeds into rivers and lakes. High nitrate in surface waters can result in eutrophication (excessive nutrients),

which can lead to extensive growth of aquatic plants and algae. In turn, this can degrade the aesthetic, recreational and ecological values of a water body. At high concentrations, nitrate can be toxic to aquatic life.

How do we monitor nitrate in groundwater?

To date, most nitrate monitoring in groundwater in New Zealand has involved taking water samples that are sent for testing in a laboratory. For information on how to collect, store and transport groundwater samples for nitrate analysis in a laboratory, see the relevant National Environmental Monitoring Standard¹.

In New Zealand, laboratory results and guidelines relative to nitrate are generally expressed as nitrate nitrogen ($\text{NO}_3\text{-N}$) concentrations².

Because 'discrete' nitrate sampling doesn't tell us what is happening between sampling events, high-frequency

nitrate monitoring using sensors in monitoring wells is currently being trialled by several regional councils. High-frequency monitoring can give us additional insights into peak concentrations and hydrological processes such as vadose zone storage and release to the water table. Monitoring at a high frequency can also increase the statistical power for change detection. We discuss the pros and cons of discrete and high-frequency sampling more below.

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 water.

¹ 'National Environmental Monitoring Standard - Water Quality, Part 1 of 4: Sampling, Measuring, Processing and Archiving of Discrete Groundwater Quality Data. Available at <https://nems.org.nz/documents/>

² Nitrate nitrogen' ($\text{NO}_3\text{-N}$) 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.

An ISE nitrate sensor operates on the principle that nitrate variation in the water will affect the electric potential of a solution in the probe³. 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.

The pros and cons of high-frequency nitrate monitoring

Because high-frequency monitoring generates significantly more nitrate data points than discrete sampling, the probability of detecting statistically significant changes within a given period is higher. This may mean that the effectiveness of nitrate loss management actions can be determined more quickly and/or with more certainty. The magnitude of this potential time saving/certainty improvement can be constrained by serial correlation and the periodicity of background variability (aka “noise”) at the monitoring site, however. The *Water quality monitoring for management of diffuse nitrate pollution*⁴ provides more information on these limitations.

High-frequency data can also yield new insights into nitrate leaching processes and the local hydrological system. For example, a sensor installed by Environment Canterbury in north Canterbury showed large spikes in nitrate concentrations following rainfall, which provided important insights into lag times, the effect of land use intensification and concentration variance.

Nitrate sensors require routine maintenance and validation sampling. The frequency of these depends on whether the sensor is fitted with an auto-cleaner to remove biofilm and/or sediment accumulation, the biochemistry of the well and the type of sensor. Quarterly site visits are generally recommended as a minimum, with more frequent visits likely to be required for sensors without auto-cleaners.

Sampling from a well. Photo supplied by Environment Canterbury.



³ <https://niwa.co.nz/publications/isu/instrument-systems-update-22-june-2018/time-for-a-closer-look-at-nitrates>

⁴ Etheridge, Z., Dumont M., and Charlesworth E. (2023). *Water quality monitoring for management of diffuse nitrate pollution. Report prepared by Kōmanawa Solutions Ltd. Our Land and Water National Science Challenge: Monitoring Freshwater Improvements, Report Z22014_01.*

Some dataloggers provide quality assurance (QA) indicators based on readings from additional sensors (e.g. turbidity). Although these QA readings are generally used to identify unreliable data within the record, the readings could be used to signal when a maintenance visit.

The recommended site visit allowance for budgeting purposes is:

- Monthly or two-monthly for sensors without auto-cleaners
- Quarterly for self-cleaning sensors

How much will it cost?

The cost of carrying out a groundwater nitrate 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. Using these estimates, monthly monitoring of nitrate in one well will cost about \$2,700 per year. Travel time can be a significant proportion of the cost and hence localised monitoring (e.g. by a catchment group) may be less expensive.

	Cost per sampling occasion
Laboratory testing for nitrate nitrogen	\$12
Staff time, vehicle expenses, field equipment	\$212
Total per sampling occasion	\$224

The visit frequency should be optimised based on:

- Validation sampling results. These should include down-hole sensor readings before and after cleaning of sensor without auto-cleaners plus an out-of-hole sensor reading in the water sample to be sent for laboratory testing⁵. If sensor and laboratory samples are sufficiently similar over a 12- to 18-month period, visit frequency could be reduced to quarterly. Conversely, divergence between laboratory and sensor results could signal the need for more frequent site visits.
- QA readings for loggers with telemetry and a QA data feed.

The cost of operating a high-frequency nitrate monitoring site will depend on several factors, such as:

- The type of sensor chosen
- The location and accessibility of the monitoring well and frequency of maintenance visits
- Whether the data are electronically transmitted (telemetered) or manually downloaded.

The purchase cost of a mid-range nitrate sensor is in the range \$15–20,000. Installation costs are likely to be relatively low for groundwater sites, in the order of \$500, assuming telemetry is not included.

Ongoing costs are in the order of \$1,600 for the first year, assuming two-monthly maintenance and validation sampling visits and allowing for some additional data processing and QA time. This could potentially be reduced to \$1,000 per year if the first year of data show that maintenance and validation sampling visits can be decreased to quarterly without compromising the integrity of the data.

⁵ This is important because the sampling process can draw groundwater from a different part of the aquifer and therefore result in a different nitrate concentration relative to the natural well throughflow under static conditions.