OPTICAL NITRATE SENSOR SELECTION

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Front cover: Field service of an optical nitrate sensor on the Mararoa River, Southland [Andrew Willsman, NIWA].

Back cover: Sunset over Barkers Creek in-stream bioreactor, South Canterbury [Phil Abraham, ESR].

CONTENTS

ABSTRACT

The growing commercial availability of optical nitrate sensors creates opportunities to measure nitrate concentrations and fluxes at frequencies and spatial scales that were not previously feasible. However, it can be challenging to select the right sensor for a particular application. Commercially available sensors use differing hardware and software designs which affect their performance and usefulness across different water types.

This chapter provides information to help people select a sensor. It describes the sensors' basic operating principles, identifies key sensor features, compares sensor hardware and software, summarises key sensor selection questions, demonstrates how pathlength selection is critical to success, and showcases the variety of deployments undertaken across Aotearoa New Zealand. Most field sites are unattended and visited on a monthly schedule, which creates extra challenges that do not occur at attended sites (such as water treatment plants). The chapter does not address field maintenance, data editing or data verification procedures in detail.

BACKGROUND

Obtaining information about water quality dynamics over short timescales (such as daily cycles, or during a storm or rain event lasting a few days) using conventional discrete samples or field measurements may be costly and logistically challenging to undertake frequently. Fortunately, high frequency water quality (HFWQ) sensors can be deployed on site to measure indicators (e.g., nitrate, dissolved oxygen) and provide detailed insights into water quality dynamics at scales of interest (minutes to hours). However, these sensors can create different technical challenges, and unattended deployments can be resource hungry. HFWQ monitoring projects are more likely to succeed if they have (1) clearly defined objectives, (2) robust data collection systems, and (3) well thought-out methods for managing raw data and converting it into knowledge for decision-making.

This chapter provides detailed guidance on optical nitrate sensor selection. It sits alongside guidance chapters on HFWQ Use Cases, Resourcing, Sensor Selection and Automated Anomaly detection as part of the *High Frequency Water Quality Monitoring Guidance* project.

PURPOSE AND SCOPE

This chapter provides information on sensor selection for measuring nitrate concentrations in-situ, at high frequency in rivers and lakes. It will help regional council staff shorten the learning curve for new users, support them to select an appropriate sensor, and enable them to accelerate the collection of high-quality nitrate concentration data using optical sensors.

RELATED RESOURCES

Useful reading that expands on the detail in this chapter can be found in the following documents:

- USGS Techniques and Methods 1-D5 (Pellerin et al. 2013) which also provides guidance on sensor selection and operations.
- NIWA Envirolink Tool report (Hudson and Baddock 2019) which provides advice on collection, management and use of optical nitrate data, focusing on TriOS sensors.
- Massey University report (Burkitt et al. 2017) on a sensor comparison (Hach Nitratax & TriOS OPUS) on the Manawatu River.
- ESR journal paper (Burbery et al. 2021) demonstrating different applications of optical nitrate sensors, including spatial surveys.

SENSOR SELECTION STEPS

Sensor selection involves a sequence of steps (Figure 1). Figure 1 also links this chapter to other guidance chapters. Many factors must be considered when selecting an optical nitrate sensor suitable to meet a user's monitoring objectives.

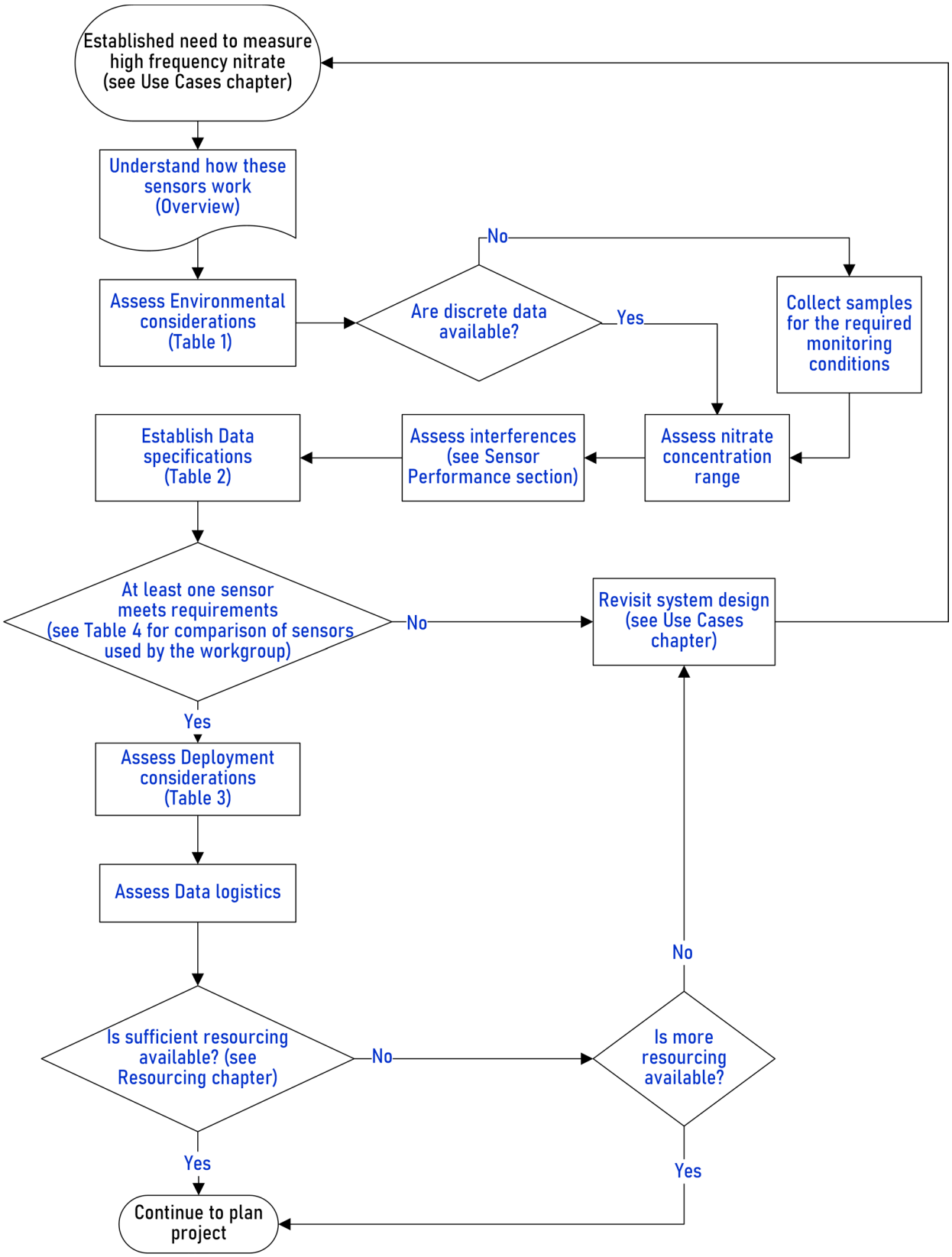


Figure 1. Suggested sequence of steps to guide optical nitrate sensor selection.

OPTICAL NITRATE SENSOR OVERVIEW

Nitrate may be measured directly by light absorbance in the ultraviolet spectral region of 200–240 nm without addition of chemical reagents. Optical nitrate sensors can measure across a wide concentration range, have rapid response times (seconds to minutes), have low power demands, and are compact, portable and robust. They measure light attenuation ('weakening') in the 200–240 nm wavelength range as it passes through the water. The higher the nitrate concentration, the more it attenuates the light beam and increases the measured absorbance.

The principle

The Beer-Lambert law (or Beer's law) is the relationship between absorbance and concentration of an absorbing substance. The general Beer-Lambert law is usually written as:

$$A = \varepsilon_\lambda \times L \times c \qquad \textbf{Equation 1}$$

where A is the measured absorbance, ε_λ is absorbance at a specific wavelength (the molar absorptivity of the absorbing substance at a specific wavelength λ), L is the pathlength and c is the analyte concentration.

Consider a solution receiving a beam of light passing through an absorbing sample of known concentration (Figure 2 A); if I_o is the light intensity emitted and the I is the intensity of light detected after passing though the pathlength, L, then the fraction of light transmitted, or the transmittance, T, is:

$$T = \frac{I}{I_o} \qquad \textbf{Equation 2}$$

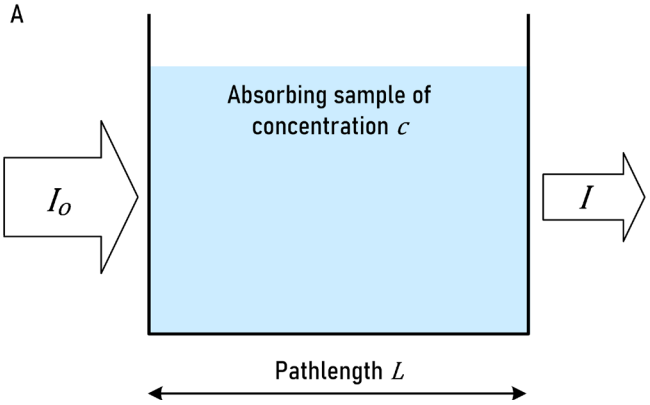
Transmittance has values between 0 and 1 but is often reported in percentage units. If no substances in the solution absorb light of the wavelength of interest, I_o and I will be equal, so transmittance will be 100%. If I is less than I_o then the substances in the sample have absorbed or scattered some light and transmittance will be less than 1.

Absorbance has a logarithmic relationship to transmittance; an absorbance of 0 corresponds to a transmittance of 100%, and an absorbance of 1 corresponds to 10% transmittance (Figure 2 B).

The transmittance is converted to absorbance, A, through the following relations:

$$A = -\log_{10} \frac{I}{I_o} = -\log_{10} T \qquad \textbf{Equation 3}$$

A



B

Transmittance	Transmittance (%)	Absorbance
1	100	0
0.1	10	1
0.01	1	2
0.001	0.1	3
0.0001	0.001	4

Figure 2. (A) Transmission of light through a sample solution. I_o is the light intensity emitted and I is the light intensity after it passes through the sample. **(B) Relationships between absorbance and transmittance.**

Absorbance is a dimensionless quantity and should be unitless. However, it is quite common to see units of AU or a.u. stated after the absorbance.

Absorbance is proportional to the pathlength (Figure 3). For a given pathlength, high concentration samples have high absorbance, whereas absorbance will be proportionately lower for a dilute sample. Absorbance will be low when the light passes through a very dilute solution along a short pathlength, say 10 mm. But passing the same light across a 50 mm pathlength of the same solution will yield a higher absorbance because the light will interact with more molecules as it passes through the solution.

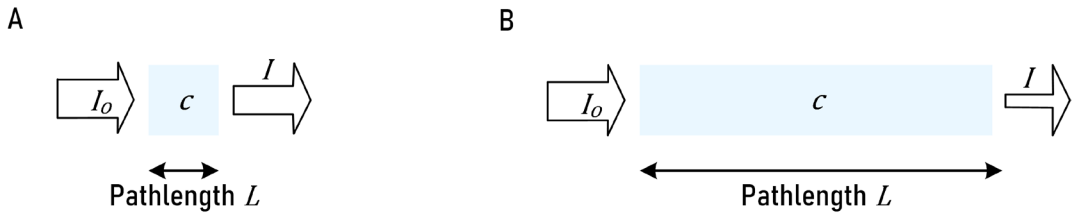


Figure 3. Transmission of light through a sample solution of known concentration for two different pathlengths. (A) Short pathlength with limited interaction with molecules yields high transmittance and low absorbance. (B) Longer pathlength with greater interaction with molecules results in lower transmittance and higher absorbance.
I_o is the light intensity emitted and I is the light intensity after it passes through the sample.

The concentration of an absorbing substance is obtained by rearranging Beer's Law (Equation 1):

$$c = \frac{A_\lambda}{\varepsilon_\lambda \times L} \qquad \textbf{Equation 4}$$

The unknown concentration of an analyte can be determined by measuring the amount of light that a sample absorbs and applying Beer's Law. If the absorptivity coefficient is not known, the unknown concentration can be determined using a calibration curve that defines the relationship between absorbance and concentration, derived from a series of standards of known concentrations.

However, there is no guarantee that the absorbance is entirely due to the material of interest, and any interferences will reduce the light intensity. These may be in dissolved or particulate form. Nitrate has a strong spectral signature up to 240 nm (Figure 5 A), but in natural waters there are other substances which also absorb light in the wavelength range of interest – mainly organics and nitrite, bromide and other ions. In addition, suspended particles scatter light, which also attenuates light intensity.

Optical nitrate sensors

An optical nitrate sensor consists of a light source which transmits light across the sample path to the detector (Figure 4). As the measuring beam passes through the sample path, the light is partially absorbed or scattered by the water. The detector picks up the remaining light and measures its intensity (I). The measured light intensity passing through the sample is compared to the intensity measured passing through ultrapure water (I_o) – almost no light will be absorbed by ultrapure water.

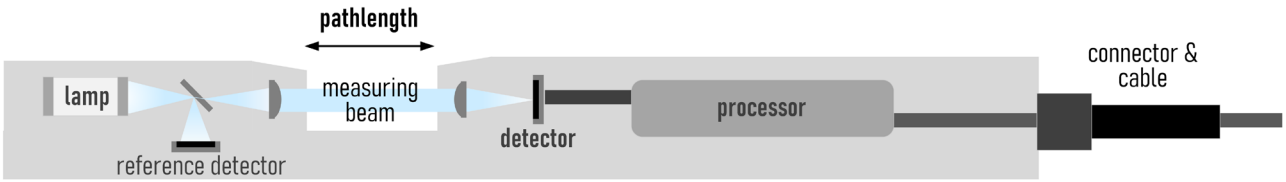


Figure 4. Generic diagram of a two-beam (split beam) UV spectrometer.

The light received by the detector is split up into wavelengths and guided to the photodiodes in the detector. Target wavelengths for optical nitrate sensors are typically in the 205–220 nm region, which is where nitrate has a long shoulder on a curve shaped like the right-hand side of a normal distribution (Figure 5 A). At higher concentrations a secondary nitrate peak at 310 nm may also be exploited. To assist with accounting for interferences, all optical nitrate sensors also measure absorbances at one or more longer wavelengths; these are typically in the ultraviolet light range (usually 254–360 nm) and sometimes into the visible light range.

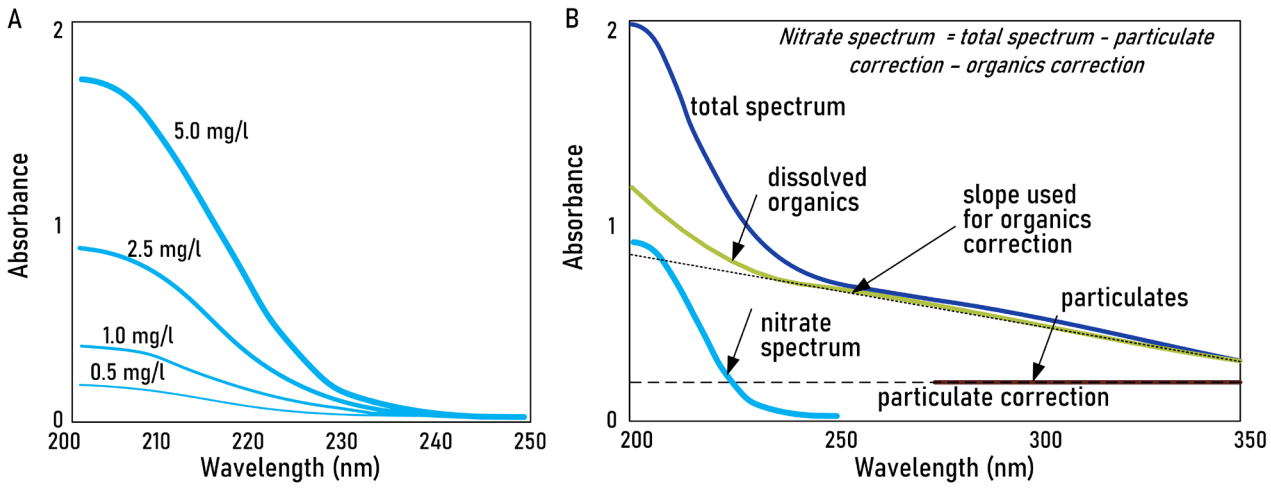


Figure 5. (A) Nitrate absorbance curve for four concentrations (after Pellerin et al., 2013). (B) Generalised total spectrum measured by a spectrophotometer, comprising particulates, dissolved organics and nitrate components. The total spectrum may be corrected for dissolved organics (green line) and particulate interferents (brown line) to provide a nitrate spectrum (blue line).

An on-board processor converts the raw signal (the total spectrum) to a calculated nitrate concentration using an algorithm that is specific to the instrument, pathlength and water matrix. In a sophisticated spectrophotometer, the algorithm 'filters' out the signals caused by other light-absorbing or scattering substances from the total spectrum to provide the nitrate spectrum (Figure 5 B), using absorbances measured at multiple wavelengths. Less sophisticated photometers use a similar method but with an algorithm that uses fewer wavelengths (typically two or three).

Most sensor models currently available have a two-beam setup that accounts for the lamp intensity loss between measurements and over time; one beam measures the sample and the other takes a reference measurement (Figure 5 A). This helps maintain sensor stability and minimises drift over time.

SENSOR PERFORMANCE

Optical nitrate sensors can measure across a wide concentration range but are less sensitive and accurate than laboratory analytical techniques. This is because laboratory samples are filtered prior to analysis to remove key interferences from the sample. Samples presented to optical nitrate sensors are not physically filtered, but instead raw sensor data are statistically 'filtered' after measurement.

Manufacturers often determine the measurement specifications for their sensor using nitrate standards in ultrapure water (resistivity 18.2 Mohm-cm), which is unlikely to reflect natural waters in the field. The precision stated by the manufacturer (i.e., the accuracy of repeated measurements) is typically calculated for samples with high nitrate concentrations and low interferences.

The field performance of an optical nitrate sensor is determined by:

- interferences, i.e., the presence of material that scatters light (suspended particles) and absorbs it (such as other ions, organics)
- pathlength
- instrument noise (electronic fluctuations in lamp, detector and circuitry)
- calculation algorithms.

Pathlength and interferences are the key criteria to consider when selecting a sensor; performance can also be improved by managing the other factors. For example, advanced users can develop custom algorithms, and with some sensors it is possible to take readings with the lamp off (known as dark counts) to reduce instrument noise (e.g., Shi et al. 2020, Nehir et al. 2021). It is also possible to use coarse screens and settling tanks to reduce interferences and improve the performance of unattended sensors (e.g., Khandelwal et al. 2020).

More on interferences

The absorbances measured in natural waters will represent multiple absorbance spectra that include nitrate, organics and particles, and these spectra will overlap (Figure 5 B). When these substances are present in amounts that excessively reduce light transmission through the water sample, nitrate calculation may be unreliable or impossible. In addition, any biological and chemical fouling of the sensor lenses will also reduce light transmission (see Fouling Management section for examples and guidance).

In freshwater, the key interferences, or matrix effects, are:

- Dissolved constituents such as nitrite, bromide and dissolved organic matter. These interferences absorb light in the same UV light range as where nitrate is absorbed. This means that for samples containing the same nitrate concentration, waters with high dissolved organic matter will have higher absorbance values than water with low organic matter. Without correction for high organics, erroneously high nitrate concentrations would be reported.
- Suspended particles scatter light and reduce the amount of light that can reach the detector. For example, when river water becomes turbid during flood events, all the light from the lamp may be scattered before it can reach the detector. Without careful correction, unrealistic 'nitrate' concentrations would be reported.

Nitrate absorbs light as it passes across the measuring window from the lamp to detector; organic matter also absorbs light, and particles scatter the light. So organic matter and particles increase the absorbance (A) (or reduce the light intensity, I, measured at the detector) and this effect is commonly called 'false nitrate'. To remove this 'false nitrate', the absorbance by organics (usually estimated ~254 nm) and scattering (estimated at >350 nm) are 'filtered' from the measured total absorbance. This 'filtering' is typically referred to as correction or compensation.

The 'filtering' is possible because scattering by particles is usually assumed to be nearly constant in the overall UV-visible spectral range, increasing the absorbances by a constant value (see Figure 5 B). Therefore, the interference can be easily corrected by subtracting the absorbance contribution of the particulates from the total absorbance values. The particulates will vary in concentration, shape, size and composition through time, so each nitrate measurement must be accompanied by at least one wavelength measurement which is used to correct for particulates. This particulate or 'turbidity' correction is measured in part of the spectrum where nitrate does not absorb and where only light-scattering particles are contributing to absorbance — typically this is at wavelengths >360 nm.

Correction for organics is more complex, largely because of the range of organic substances that may occur in natural waters and the differences in absorbance spectra of these substances. However, the combined dissolved organics matrix is generally characterised by a decreasing concave shape across a wide range of wavelengths. Optical nitrate sensors typically use the slope of the concave spectra to derive an organics correction (see Figure 5 B).

Pathlength

The range of an optical nitrate sensor is determined by the distance between the lenses, which is known as the pathlength. With a longer pathlength, say 50 mm, lower nitrate concentrations can be measured (Figure 6), but the concentration range over which measurement is possible is limited. Furthermore, longer pathlength sensors are also sensitive to interferences as there are more opportunities for absorption and scattering in the sample pathlength between the lenses. Although shorter pathlengths tend to work best for waters with higher interference concentrations, there are several trade-offs: nitrate concentrations need to be higher to be detectable, and shorter pathlength devices have a lower resolution.

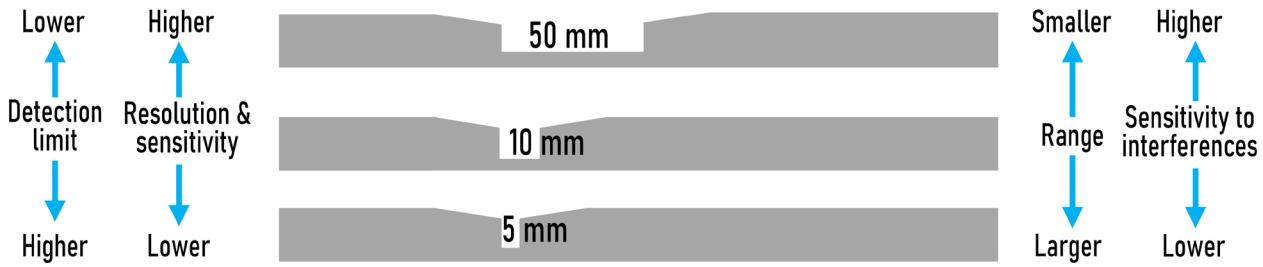


Figure 6. Relationship between sensor pathlength and detection limit, resolution, range and sensitivity to interferences.

For some applications it may be necessary to operate two sensors with different pathlengths to ensure that nitrate measurements occur successfully during changing conditions. For example, given the same model of sensor, a long pathlength sensor (with a range of say 0–2 mg/l nitrate) might operate well in a river most of the time, but during floods when suspended particles interfere with light transmission, a shorter pathlength sensor (with a range of say 0–20 mg/l nitrate) may be required. The two independent records of nitrate concentration estimates would be combined to create a record of continuous nitrate concentrations over a range from sub mg/l through to approximately 20 mg/l. Data gaps may still occur at peak flood flows due to interferences, but with a shorter pathlength, gaps should have a shorter duration (see Case study 1 – Side-by-side pathlength comparison).

Some sensor models have fixed pathlengths (see Table 4) which cannot be changed, while others have replaceable lenses and the pathlength can be changed. Changing the lens or pathlength requires a new reference measurement in ultrapure water (I_o).

Instrument design

Optical nitrate sensors all operate in the ultraviolet (UV) and visible (Vis) light ranges and can be grouped into photometers and spectrophotometers. Photometers measure the intensity of light of each wavelength individually, while spectrophotometers often include a monochromator which separates the light into many wavelengths. Optical nitrate sensors in the photometer group contain two or three photodiodes that operate at predefined wavelengths to measure light intensity. Spectrophotometers contain more advanced optics and measure the intensity of a light beam at many wavelengths (typically 256) to produce a spectrum across the UV or UV-Vis range.

Instrument noise and degradation of the light source over time is minimised by measuring absorbance at multiple wavelengths using dual light beams and more sophisticated software. Many optical nitrate sensors have dual or split light beam designs. The light beam is split by a half mirror, and one beam passes through the sample and is measured at the detector, while the other beam is measured by a reference detector. The ratio of the values from both detectors is used to compensate for any light source energy variability. Some sensors measure and store dark current (instrument noise when the light source is off) and these may be included in calculation algorithms.

Most optical nitrate sensors used in New Zealand have a xenon lamp light source. A xenon lamp contains two electrodes enclosed in a glass bulb filled with xenon gas. High voltage is applied to the electrodes, which momentarily releases sparks to create a very intense light flash lasting for a few nanoseconds. It is difficult to produce the same intensity of flash repeatedly, so most measurements are the average of a series of flashes. Xenon lamps can make around 500,000 flashes and have a full lifetime of around 2000 to 3000 hours. Other light sources used in optical nitrate sensors include LEDs and deuterium lamps. The shortest wavelength currently achievable with an LED is 235 nm, which is on the tail of the nitrate absorbance curve (see Figure 5 A). LEDs are low-cost (relative to xenon lamps), have low power consumption, and are small, robust and have a narrow output band (~ 10 nm). A deuterium lamp is used in the Sea-Bird SUNA V2 sensor, which is widely used in freshwater and marine environments in the US. Deuterium lamps are stable in the UV range, have short warmup times, and have a full lifespan of around 1000 hours (see Johnson and Coletti 2002 for more details).

Algorithms

Nitrate concentration is calculated from the absorbances using statistical techniques (on-board and/or post-processed). Each sensor model uses a unique combination of hardware and software (Figure 7). Once the raw absorbances are measured, the values are typically corrected for particulates (Step 1) then organics (Step 2) to give a corrected spectrum (see Figure 5 B). The nitrate concentration is then calculated from the corrected absorbance values. The user-ready nitrate values are then reported along with any metadata provided.

Algorithms are customised for different water matrices (e.g., groundwater, river water, wastewater, brackish and marine water) because each of these typically present different interferences. For example, algorithms intended for use in brackish and marine samples will correct the measured spectra for bromide interferences before calculating nitrate. Some sensors are supplied with variants of the algorithms for low or high organic matter content (e.g., TriOS), which the user can implement in the user interface (UI).

The proprietary algorithms which correct the spectra for interferences may use pre-selected wavelengths or wavelengths which are selected on-board for each measurement. Sensors using on-board selection may take longer to calculate nitrate values as they iterate groups or bins of wavelengths.

Most sensors report metadata on the quality of the measurements and output the raw absorbance values. This metadata can be used for real-time and delayed quality control. If absorbance limits for a sensor are specified, then real-time quality control can be implemented based on absorbance thresholds.

When the manufacturer's algorithms underperform, it may be necessary to create a site-specific algorithm. Algorithms are developed using advanced statistical techniques which relate the absorbance values or spectra to discrete lab results. Updated algorithms can also be applied retrospectively to absorbance data.

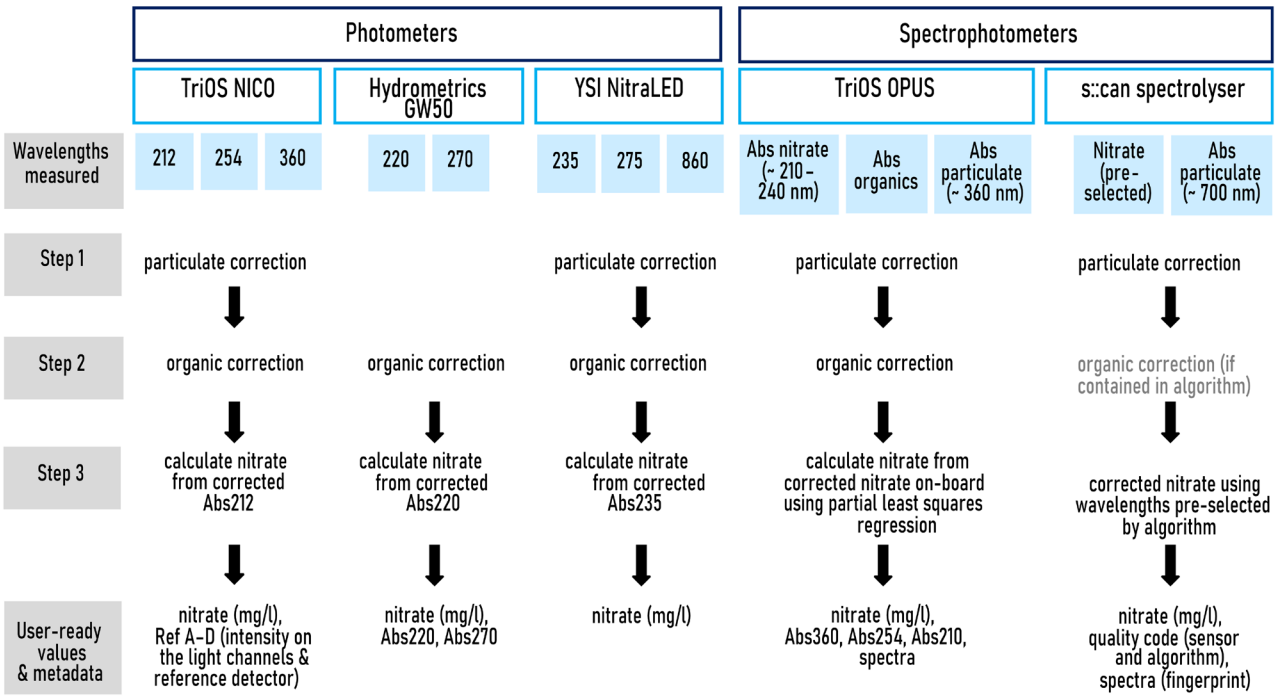


Figure 7. Overview of calculation steps for several photometers and spectrophotometers. AbsYYY is the absorbance measured at YYY wavelength. Spectrophotometers measure the full spectra and tend to use more than one wavelength in algorithms.

CASE STUDY 1 – SIDE-BY-SIDE PATHLENGTH COMPARISON

A joint NIWA and Environment Canterbury (ECan) project, funded by MPI's Sustainable Land Management and Climate Change (SLMACC) Freshwater Mitigation Fund and ECan, operated optical nitrate sensors at the Te Ahuriri constructed wetland inlet and outlet.

At the wetland outlet a 10 mm pathlength TriOS OPUS sensor was installed. It could not perform well during floods when particulate-laden water (see Figure 8 A) prevented emitted light from reaching the detector. Therefore, to assess the value of a shorter pathlength in such situations, a 5 mm pathlength sensor was deployed and run alongside the first sensor. The purpose was to assess whether it would reduce over-ranging and achieve a more continuous data record. The two TriOS OPUS sensors (10 and 5 mm pathlengths, both fitted with ZebraTech wipers) were deployed side by side in PVC housings (Figure 8 B) for 10.5 months.

A

B

Figure 8. (A) Particulate-laden water during a large flood event (27 July 2022) at the outlet of the Te Ahuriri constructed wetland [Hamish Carrad, ECan]. (B) Side-by-side TriOS Opus sensors in perforated housings (arrow) on a bracket at the wetland outlet [Patrick Butler, NIWA].

The nitrate time series was pre-processed to assign quality codes (good, fair, poor) using the absorbance criteria supplied in the TriOS OPUS manual. The following data and analysis methods were used to compare the sensors' performance:

- In addition to calculated nitrate, the OPUS outputs three absorbance values: Abs210, a key nitrate wavelength; Abs254, an organics correction wavelength; and Abs360, a particulate correction wavelength. Absorbance values at these three wavelengths provide useful metadata for each measurement.
- Absorbances limits provided by TriOS were used to assign quality codes. Poor quality data is defined as >3 at 210 nm and >0.8 at 360 nm, and fair quality data is 2.5–3 at 210 nm and 0.5–0.8 nm at 360 nm (the horizontal lines on Figure 9 A and B).
- Sensor performance was compared for periods when both sensors were operating. If either sensor was faulty, unable to return a value or out of the water (and turned off) during summer, then the concurrent value on the other sensor was also removed from the analysis. Overall, 11.7% of the data was unavailable for use in the comparison; 88.3% of the 15-min data collected were compared.
- The percentage of record coded as good, fair or poor using the absorbance limits was calculated.

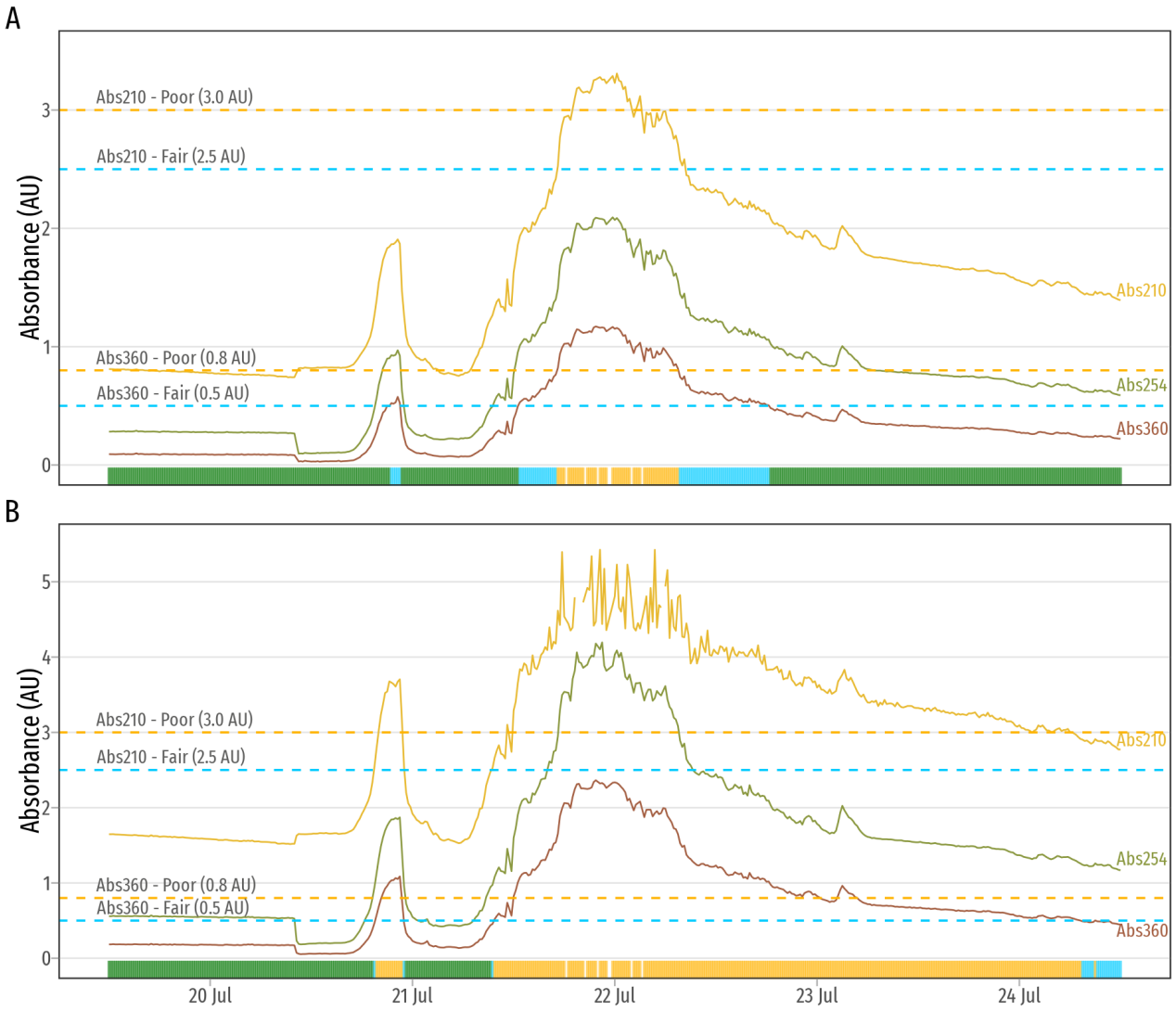


Figure 9. Sensor pathlength comparison at Te Ahuriri constructed wetland outlet for a 5-day period in July 2022. (A) Time series of TriOS OPUS 5 mm pathlength absorbances (210, 254 and 360 nm) with absorbance limits (dashed lines) and data quality summary (good, green bars, 75%; fair, blue bars, 14%; poor, orange bars, 11%). **(B) Time series of TriOS OPUS 10 mm pathlength absorbances with absorbance limits and pathlength data quality summary** (good, green bars, 35%; fair, blue bars, 4%; poor, orange bars, 60%).

Over the 10.5 month period, the side-by-side comparison of the 10 mm and 5 mm pathlength sensors found that:

- The 5 mm pathlength sensor returned 99% good data, while the 10 mm pathlength sensor returned 95% good data (2% fair, 3% poor).
- Both sensors performed well during smaller flood events, but they were unable to measure all three key absorbance wavelengths during the two largest flood events (21 and 27 Jul 2022). Two July 2022 events (one small, one large) are used to illustrate how interferences create data gaps during such events (Figure 9).
    - During the smaller flood event (20 Jul 2022; Figure 9), the 5 mm pathlength sensor took measurements throughout the event, with a short 1-hour period of fair (blue bars) data when the Abs360 (brown line) was >0.8. In contrast, the 10 mm pathlength sensor returned poor quality data for 3 hours, as indicated by orange bars in Figure 9 B, due to Abs210 and Abs360 both being over their respective absorbance limits (orange dashed horizontal lines).
    - During the larger event (21–24 Jul 2022; Figure 9), the 5 mm pathlength sensor crossed both absorbance limits (orange dashed horizontal lines in Figure 9 A) at a similar time and was unable to measure for about 12 hours (orange bars, Figure 8 A) due to interferences. The 10 mm pathlength sensor also crossed the poor absorbance limits but for a longer period (Figure 9 B; Abs210 >3.0 for 2.5 days; Abs360 >0.8 for 1.5 days; unable to measure for 2.5 days as indicated by orange bars).

At this site a 5 mm pathlength would be the best choice in order to shorten data gaps due to interferences during flood events. Some events, particularly larger ones, will still have data gaps, but with a 5 mm pathlength they will be brief.

More general recommendations include:

- Identify and field test the chosen pathlength to ensure the sensor will generally operate within specifications at critical times (e.g., flood events).
- Telemeter metadata (such as Abs210, Abs254, Abs360) so that these can be used to grade data.
- Ensure you have a robust method for filling data gaps when the sensor cannot measure due to interferences.

CASE STUDY 2 - SELECTING THE RIGHT PATHLENGTH

In 2014, Environment Southland identified a need to characterise sediment and nutrient loads to meet the requirements of tightened water quality legislation. After evaluating the available optical nitrate sensors, it selected TriOS OPUS sensors. In addition to basic sensor specifications, two other factors made the OPUS a sensible choice: (1) other absorbance parameters (such as dissolved organics) could be added with a software update, and (2) locally based technical support was available.

One of the key considerations in selecting a sensor was choosing the right pathlength. Pathlength choice needs to consider the nature of the environment to be measured, the expected nitrate range and the data requirements (e.g., baseflow or flood events). In relatively clean, unpolluted water, a longer pathlength is best so there is a greater volume of water in the measuring window. This allows a more accurate reading at lower nitrate levels. Conversely, if higher nitrate concentrations are expected, a shorter pathlength will sample a smaller volume of water and allow a more accurate reading. Because the nitrate level can vary greatly in rivers, it's usually not possible for one pathlength to cover all scenarios. Therefore, it's important to select a pathlength to match the range of nitrate that meets the data requirements.

At two sites, a 10 mm pathlength TriOS OPUS was initially installed, but in fact the shorter 5 mm pathlength was more suitable for that measuring environment. The shorter pathlength was then used, and the switch can be seen clearly in Figure 10, which shows how the correct pathlength improves data quality.

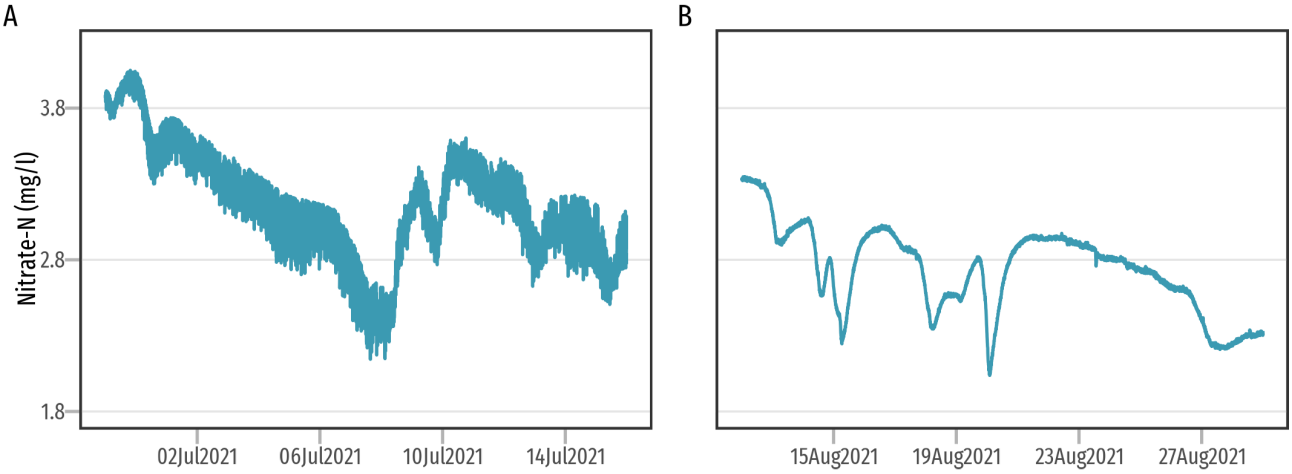


Figure 10. TriOS OPUS nitrate time series from Waituna Creek. (A) Period measured with a 10 mm pathlength sensor. (B) Period measured with a 5 mm pathlength sensor (after a lens swap and new ultrapure water value).

During a large flood event the measuring environment can change dramatically, and a 10 mm pathlength is no longer appropriate. During these times the OPUS usually returns an error reading as it cannot resolve an optical value in such extreme conditions. Ideally a second OPUS with a shorter pathlength will be available. When that isn't possible, the user must choose whether measuring extreme events or more normal flows is the highest priority.

FEATURES TO LOOK FOR

Sensor hardware and on-board software will affect the instrument's range and resolution, its metadata output and its tolerance to matrix interferences. The workgroup identified numerous optical nitrate sensor features which new users should evaluate prior to purchase (Figure 11). The key features are sensor hardware (lenses, cables, materials), software (user interfaces (UI), outputs, metadata) and user support (documentation and people). These key sensor features are the basis for the next two sections, Key questions to consider and Sensor comparison table.

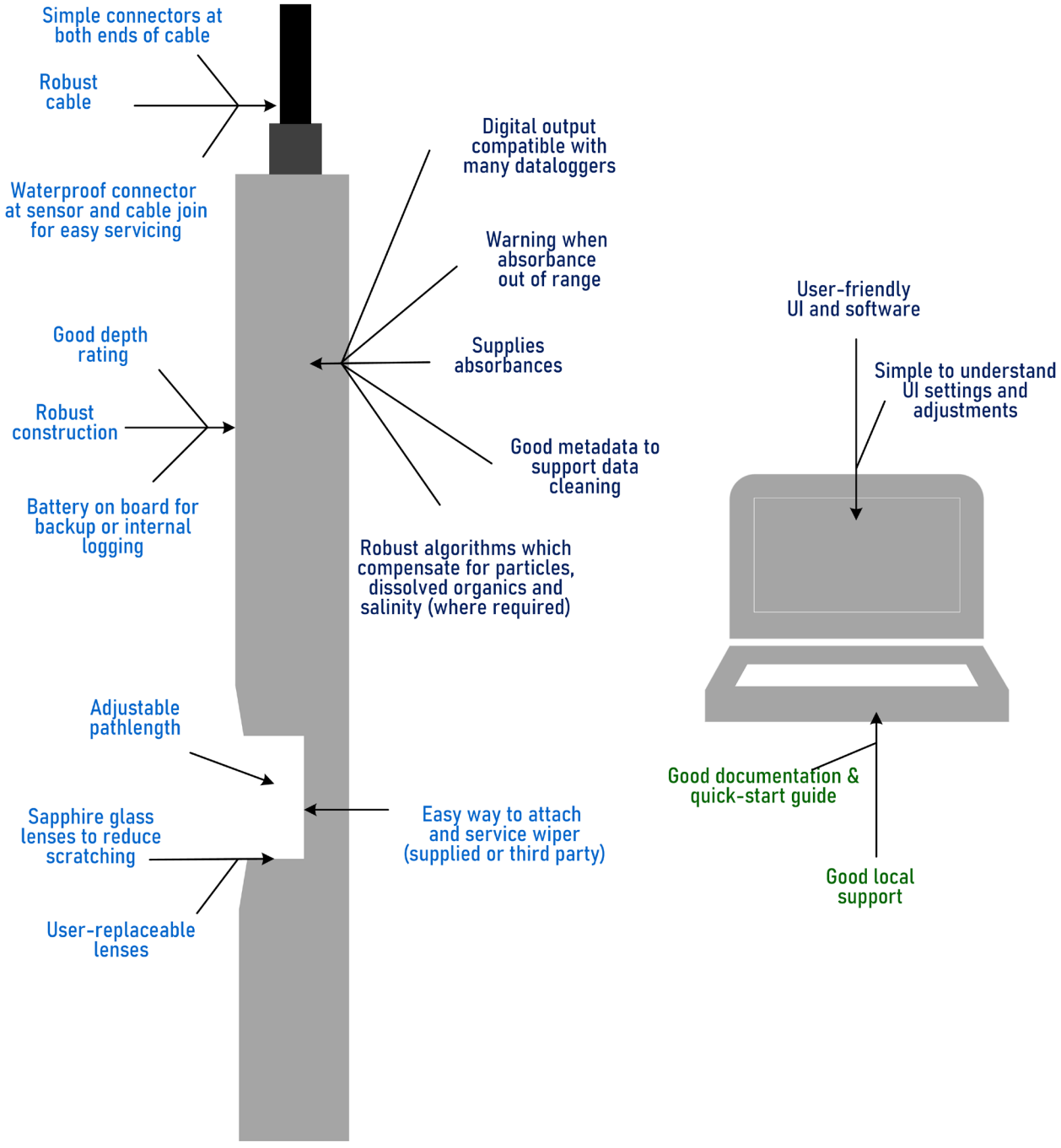


Figure 11. Key optical nitrate sensor features – hardware (blue), software (navy) and user support (green).

KEY QUESTIONS TO CONSIDER

Each candidate optical nitrate sensor should be considered against the monitoring objectives and deployment requirements. These sensors are complex and there are many factors to consider and challenges to overcome, so the key questions are grouped in three tables – Environmental conditions (Table 1), Data specifications (Table 2) and Deployment considerations (Table 3).

Environmental conditions

Table 1. Environmental conditions: Considerations and challenges to help guide sensor selection.

Key questions	Consequences	Possible solution
What is the expected nitrate range?	- Incorrect selection may result in low-resolution data.	- Nitrate-N concentration >20 mg/l: consider a shorter (<10 mm) pathlength. - Nitrate-N concentration <1 mg/l: consider a longer pathlength (say 50 mm) but also consider interferences. - Consider using more than one sensor to cover the full range of expected nitrate-N concentrations.
Are sediment concentrations high?	- Sensor lenses may be damaged. - Light may not be able to reach the detector.	- Consider using a pre-filtering system if SPM concentrations >1 g/l or pumice is present, as both can scratch lenses. - Use measured turbidity or discrete suspended sediment concentrations to estimate whether interferences will be significant during high flow events. Take care to assess the comparability of the sensor's 'particulate limits' as turbidity values are not numerically comparable (see Davies-Colley et al. 2021). You will need to work out how values from different turbidity sensors relate. For example, the EXO NitraLED 'turbidity limit' is 200 FNU (EXO sonde turbidity), which would be >350 FNU measured with a Hach TL2310 lab benchtop meter. - If particulates will be high during critical measurement periods, use <10 mm pathlength.
Does the water have a high organic concentration or colour?	- Light may not be able to reach the detector.	- For high DOC (>5–10 mg/l), use a spectrophotometer and record the full spectra so you can develop custom algorithms if required. For very high DOC (>30 mg/l) also use a shorter pathlength of <10 mm. - Use high organics algorithms if available.
Does the water contain iron, manganese, runoff from asphalt surfaces?	- The sensor and lenses may be chemically fouled.	- Plan how to identify the presence of chemical fouling on the lenses and in the data. - Plan how to remove chemical fouling. This may require advice from the manufacturer. Use an LED-lit magnifying glass to check the lenses after cleaning (to protect your eyes, ensure the sensor is not powered). - Keep the sensor body clean by wrapping in duct tape. This will reduce your cleaning effort considerably and ensure your focus is on keeping the lenses clean.
Are algorithms available for the water matrix?	- Algorithms might not calculate nitrate correctly.	- Check the types of water the sensor can operate in. Algorithms are different for fresh, brackish and marine waters. - Some manufacturers will not allow brackish/marine algorithms to be loaded onto stainless steel sensors. - Some manufacturers do not have brackish/marine algorithms.
Is the environment corrosive?	- Sensor may corrode.	- Stainless steel body material is good for freshwater applications. - For estuarine and marine sites, select a titanium sensor casing (if available). Some manufacturers will not supply brackish or marine algorithms for stainless steel sensors. - For saline waters use a spectrophotometer, record the full spectra and purchase brackish or marine algorithms. - For geothermal waters, check with the manufacturer directly.
What are the flow conditions?	- Turbulence may form bubbles, reducing data quality.	- Carefully select a site to avoid turbulence. For example select a deep, slow-moving section of a large river. - Consider operating the sensor ex-situ by pumping water to the sensor using either a flow cell or flushable water bath. Note: (1) flow cells may become clogged with sediment during flood events, (2) if a wiper is required in addition to a flow cell, consider using a custom flow cell (see Fouling Management section), and (3) high sediment concentrations may necessitate frequent pump replacement.
What is the site's temperature range and maximum depth?	- Sensor might not perform as expected.	- Check maximum sensor depths (Table 4). Check cable options too. - Most sensors have an operating range of 0–40 °C.

Data specifications

Table 2. Data specifications: Considerations and challenges to help guide sensor selection.

Key questions	Consequences	Possible solutions
What sensor performance is required for study?	- The sensor may not be able to measure nitrate.	- Low nitrate-N detection limit needed (<0.5 mg/l): use >10 mm pathlength. - High nitrate accuracy required (<±0.5 mg/l): use a longer pathlength (>10 mm) (and where possible record all absorbance values). - Check the detection limit (DL), limit of determination (LOD) and precision for each pathlength. For the TriOS OPUS there is an order of magnitude difference between the 1 mm (DL 0.3, LOD 0.5, precision 0.05) and 10 mm pathlengths (DL 0.03, LOD 0.05 and precision 0.005).
What is the required observation interval?	- Sensor may not be able to take measurements at required frequency.	- Check observation interval exceeds sensor measurement interval. For sensors with on-board statistics (e.g., TriOS sensors), the calculation time in challenging water matrices can be ~2 min.
Are real-time data required for decision-making?	- Data delivery requirement not met.	- Telemeter data AND use sensor with on-board statistical concentration calculation and matrix compensation OR develop a stable site-specific adjustment/relationship to convert raw data to nitrate. - Select a sensor which outputs raw absorbances so real-time QC is possible.
How many measurements are needed to meet study goal?	- Sensor lamp lifespan may be reduced by frequent measurements. - Infrequent measurements may result in data gaps.	- Consider sensor minimum observation period and interval. Check if the number of lamp flashes per measurement can be adjusted. - Check whether there is sufficient on-board memory space if data is not telemetered or a backup is required.
Are data gaps acceptable? What size gaps are acceptable for decision-making?	- Large gaps, or gaps at critical times, may render data less useful for decision-making.	- Consider how you will fill gaps in the record during periods when environmental conditions reduce light transmission and prevent nitrate calculation. There are numerous options: (1) multiple sensors with different pathlengths (see Case study 2), (2) operate rising stage samplers/Nalgene stormwater samplers or autosamplers and analyse samples when a sensor gap occurs, or (3) model nitrate concentrations. - Telemeter data and metadata to detect sensor failure. Consider resourcing a spare sensor to cover system technical malfunctions.
What metadata does the sensor provide to assist with data grading?	- Data values returned may be outside of sensor operational limits.	Note: Some sensors return numeric values, while others return NA or negative values when the sensor is not able to measure nitrate. - Check the sensor metadata values which accompany each value. Some sensors will only output a quality code (which will be proprietary) with each measurement. Check if the sensor outputs raw absorbances (or intensities) as these can provide a lot of information on sensor suitability and performance. - Be wary of any sensor which does not output absorbances, because this means no post-processing will be possible.
Are concentrations during river flood events required?	- Data gaps.	- Consider operating two sensors with different pathlengths to ensure nitrate measurement is possible under all conditions (note there are pathlength-range-resolution trade-offs, see Figure 6). - Use an autosampler or stage height samplers (e.g., Nalgene bottles) to collect samples during critical periods when the nitrate sensor is likely to be out of range due to interferences.
Is the spectral data required?	- Post-processing is best done with spectral data.	- Use a sensor capable of storing spectra for each measurement. - Consider if telemetry of spectra is required. Storage, telemetry and retrieval may be challenging with >260 values per sample. Check if manual download of spectra is possible (check Table 4).
Is the site a long-term operation?	- Selecting a sensor with a non-replaceable lens may be costly. - Long service times if sensor must return to manufacturer.	- Select a sensor which has user-replaceable lenses to reducing servicing costs at long-term sites where lens damage is likely. - Use a sensor that either can store spectra (if algorithms for other variables are of interest) or has additional algorithms (such as TOC/DOC). Storing spectral data will enable new algorithms to be developed and applied to historic data. - If the site is long term, consider sensor servicing timeframes. Sending a sensor to the manufacturer for repairs can take months.

Deployment considerations

Table 3. Deployment considerations: Considerations and challenges to help guide sensor selection.

Key questions	Consequences	Possible approach
How will you manage fouling?	- Data quality will be reduced.	- Consult the Fouling management section for more details. - Consider using a flow cell or flow tank if the site can be regularly serviced. Some 12 V DC pumps can last ~18 months (e.g., Abyss 12 V pump). - Consider how wiper frequency may vary seasonally.
How will you access the sensor for cleaning?	- Users will be unable to clean the sensor.	- Select sensor model/option with a SubConn® connector to disconnect the cable from the sensor. - Select a sensor with a removable mounting rod system (e.g., fibreglass rod) which makes installation in a PVC pipe simpler (compared to a clamp).
Access to instrument across the range of environmental conditions?	- Users will be unable to service or retrieve the sensor. - A sensor located near the riverbed may be damaged by during floods.	- Consider if access to sensor is required during floods. Sensors can be buried during floods in rivers with high sediment loads. - Consider the minimum water depth required for the sensor to operate. Schedule the install during summer low flows so the PVC housing can be secured adequately and set at a low level. - Consider how water level may change seasonally and how to mount the sensor to overcome changing water levels.
What are the power options?	- Data gaps due to power failure.	- If no mains power, select a sensor able to run on solar or battery power. - If using solar power, check whether the sensor operates at 12 or 24 V. - If sensor can be battery powered, check how long the batteries will last.
Does the sensor have user-replaceable lenses?	- Whole sensor replacement required if lenses cannot be replaced.	- Consider maintenance costs and time savings of user-replaceable lenses. - Sensors with replaceable lenses can be converted to a different pathlength. Check the limits of possible changes. Ensure a new ultrapure water value is recorded before using the sensor after a change. - If user-replaceable lenses are not available, take care to identify a suitable deployment location if high sediment concentrations will occur. Avoid deploying the sensor close to the riverbed or in high velocity zones which carry more sediment.
What are the data download options?	- Slow data download speeds prevent downloads or telemetering data.	- Assess whether the user can access/swap the internal SD card. - Check transfer speed of data from sensor to computer (warning: some spectral data downloads are very slow!).
Can the sensor be integrated into existing site infrastructure?	- Additional cost if additional equipment (e.g., new logger, solar systems) required.	- Use a sensor which integrates with existing data collection platforms. - If no housing/logger available, select sensor with sufficient memory. - If no mains power, select sensor able to run on battery and/or solar power.
What is your anticipated site visit schedule?	- Inadequate verification samples across the full range of conditions. - Data loss due to fouling, burial, sensor loss.	- Consider using an automatic sampler to extend verification dataset beyond baseflow conditions. Consider using a refrigerated automatic sampler at remote sites to assist with preserving samples (compared to adding ice to samplers). - Telemeter data and metadata to enable daily checking of sensor performance and issues.
Do you have the technical expertise to manage the sensor?	- Frustration, wasted time, poor data quality.	- These are complex sensors. Pre-deployment checks and deployment should be well planned. - Select a sensor with on-board statistical concentration calculation and matrix compensation.
Do you have the level of technical expertise required to create site-specific algorithms?	- Data loss as absorbances cannot be converted to good quality nitrate data.	- Check access to resources for advanced data processing of spectrophotometer data (e.g., R, Python or MatLab and a data scientist). If in-house expertise is not available, check if an external provider is available. Some manufacturers may offer support to help develop algorithms.
What is the level of technical expertise available in New Zealand?	- Time lost due to slow service from overseas.	- Consider where you can access help at short notice – you will need it! - Sign up to manufacturer's support portal to download latest versions of manual and special support documents. - Subscribe to manufacturer's newsletter to stay up to date.
How user-friendly is the software interface?	- Time wasted due to software challenges.	- Test drive the software interface. - Request training and ongoing support as part of your purchase.

SENSOR COMPARISON TABLE

Table 4. Comparison table of optical nitrate sensors used by the workgroup (in 2023). At least one sensor user contributed to each column. All costs in NZD. See notes below table for detailed additional comments on each sensor. To evaluate a different sensor, gather information from brochures, manuals, manufacturer and other users.

Sensor	s::can Spectrolyser V2 s	TriOS OPUS	TriOS NICO	YSI NitraLED	Hydrometrics GW50
Cost (sensor & cable) $: < 10K, $$: 10–20K, $$$: 20–30K	$$$ [s]	$$$	$$	$ (+ $$ [e])	$
Sensor basics					
Sensor type	UV-Vis spectro-photometer	UV spectro-photometer	photometer	photometer	photometer
Environments (Marine, Brackish, Surface water, Groundwater)	M B S G [a]	M B S G [a]	S G [a]	S	G
Pathlengths available	1,5,35	1,2,5,10 or 10,20,30,40,50	1,2,5,10 or 10,20,30,40,50	10	10
Pathlength adjustable	Yes	Yes	Yes	No	No
Range for 1 mm	0–700 [s]	0.03–100	0–60		
Range for 2 mm		0.15–50	0–30		
Range for 5 mm	0–100 [s]	0.06–20	0–12		
Range for 10 mm		0.03–10	0–6	0–10	0–50
Range for 35 mm	0–15 [s]				
Range for 50 mm		0.006–2	0–1.2		
Robustness	Yes	Yes	Yes	Yes	Yes
Light source	xenon	xenon	xenon	LED	xenon
Diameter (mm, without wiper)	44	48	48	47, 76.2	42.2
Internal power option	No	No	No	Yes	No
Depth rating (<20, <100, <250)	< 20 m	< 20, < 250 m	< 20, < 250 m	< 100, < 250 m	<20 m
Cable removable	Yes	Yes	Yes	Yes	No
In-built wiper	No	No	No	Yes	No
Lenses user replaceable	Yes –1 & 5 mm	Yes	Yes	No	No
Lifespan (15-min obs)	> 6 y	> 6 y [t]	> 6 y [t]	New product	< 4 y
User experience					
Accuracy in 'real water' lab tests [b]	Within specs with a suitable algorithm [s]	Within specs	Within specs	Within specs for high visual clarity water	Not tested
Development of custom algorithms	Before & after	Before & after	Before & after	Before	After
Measurement quality known	Yes	Yes	Yes	No	Yes
Indicators available	Many	Many	Several	Nitrate	Nitrate
Raw absorbances	Yes	Yes	Yes	No	Yes
Simple to set up	No	No	No	No	No
Metadata usefulness	Good	Good	Good	NA	Good
Communication protocols	RS-485 [s]	RS-232, Modbus RS-485, TCP/IP	RS-232, Modbus RS-485, TCP/IP	SDI-12, RS-232, Modbus RS-485 or RS-232, USB	SDI-12, RS-232, Modbus RS-485
Requires adaptor	Yes	Yes	Yes	Yes	No; adaptor for Modbus RS-485
Raw file format	Text	Text	Text	Proprietary	Text
Absorbances	Text	Text	Text [t]	–	Text
Resolution (decimal places)	3	3	3	2	3
Ability to post-process	Yes	Yes	Yes	No	Yes
User-controlled averaging	Yes	Yes	Yes	Yes	Yes
Averaging can be turned off	Yes	Yes	Yes	No	Yes
Manual(s)	Excellent	Good	Good	OK [e]	Good
Warranty (years)	1 y	1 y	1 y	2 y	1 y
NZ servicing/minor repairs	Yes	Yes	Yes	Yes	Yes
Major repairs	Austria	Germany	Germany	US	NZ

Table 4 Notes:

[a] With appropriate casing materials and algorithms.
[b] NIWA 2021 sensor tests in clear waters and with clay, silt and colour interferences.
[e] EXO Nitra-LED notes: (1) NitraLED on an EXO3 with conductivity/temperature, turbidity & wiper. (2) New guidance available 2024.
[s] Spectrolyser V2 notes: (1) Spectrolyser V3 now available. Algorithms are now purchased individually. (2) Ranges for surface water algorithms. (3) V3 has additional communication protocols – WLAN and Bluetooth.
[t] TriOS NICO and OPUS notes: (1) Integrated cable requires care. NIWA and ES have lost TriOS sensors (prior to Subconn® option) by water ingress into sensor via damaged cable. (2) Some older NICO sensors do not store Ref A–D values. (3) After many xenon lamp shots, the inside of the lenses may develop a coating that reduces the sensor's performance unless a new ultrapure water reference is used.

FOULING MANAGEMENT

Fouling must be actively managed on all optical sensors. Nitrate sensors have two lenses, and both must be cleaned to ensure light can pass across the measuring window. Even a slight buildup on either lens will degrade the sensor's ability to return nitrate values and will reduce accuracy. A light beam weakened by fouling of the lenses may not reach the detector. In freshwater environments, fouling is likely to be a combination of algae, sludge, invertebrates and, in some environments, chemical buildups (see Figure 12, Figure 16 B & E, Figure 19 F).

Figure 12. Sludge and invertebrates fouling a sensor [Andrew Willsman, NIWA].

Brush wipers

The workgroup unanimously recommended using robust brush wipers where possible. Brush wipers operate well on many unattended optical nitrate sensors across New Zealand – they are effective and the brushes are easy to replace. Other recommendations include:

- For shorter pathlength instruments (< 10 mm), a single brush wiper works well (Figure 13 A).
- For longer (> 10 mm) pathlengths, wipers are available with dual brushes (Figure 13 B).
- Brushes with bristles in twisted wire loops generally work well for river applications where flow can remove material from the brush. However, there is a risk of them catching debris that brushes across the lenses. Longer bristles overcome this risk.
- Work with a specialist wiper manufacturer to design a brush if current options are not suitable. For example, Hamish Carrad (ECan) worked with ZebraTech to develop a different style of brush for 5 mm pathlength sensors. The brush has long bristles and no fixed central wire, which ensures material does not build up in the brush and scratch the lens (see Figure 13 C).
- Brush wipers can be used inside custom flow cells (see Figure 13 D).

A

[Patrick Butler, NIWA]

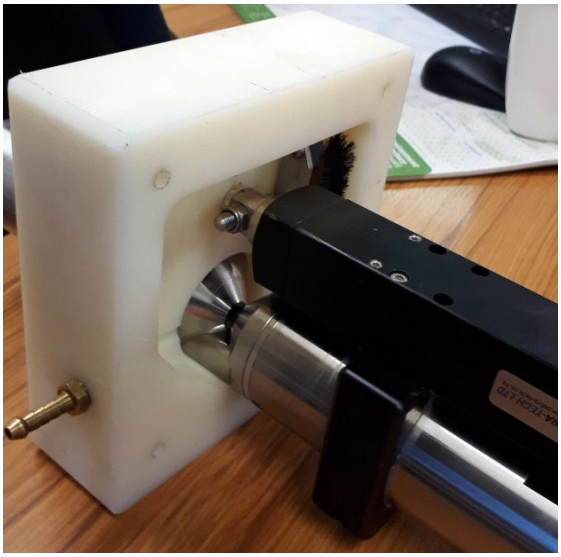
B

[Jeremy Rutherford, NIWA]

C

[Hamish Carrad, ECan]

D



[Hamish Carrad, ECan]

E

[Andrew Willsman, NIWA]

Figure 13. (A) Classic brush wiper. (B) Dual lens brush wiper on a 50 mm pathlength sensor. (C) A redesigned long-bristled ZebraTech Hydro-Wiper for 5 mm pathlength. (D) Custom flow cell with brush wiper. (E) Worn wiper brush.

Additional practical tips for managing fouling

Experienced users suggest:

- Design the deployment to minimise debris buildup on the wiper, which could then scratch the lenses.
- Orient the wiper rest position downstream so that debris does not trail in the optical window.
- Wipe as frequently as infrastructure allows, preferably before each measurement.
- Telemeter sensor metadata to monitor for fouling (such as ensuring the TriOS OPUS 360 nm absorbance is < 0.8).
- Select a wiper which can provide metadata on brush position (e.g., home position) to detect if the wiper has been stuck over the lens.
- Use acetone to remove organic residue from lenses (but check manufacturer recommendations).
- Create cleaning routines which include a check or test.
- Actively maintain the fouling system as there will be seasonal variations. For example, during summer low flows it may be challenging to maintain clean lenses.
- The shells of NZ mud snails, pumice or sediment caught in wipers can scratch the sapphire glass lenses.
- Remember, for all optical sensors, a dirty lens leads to data loss!

CASE STUDY 3 - TRIOS W55 WIPER

NIWA trialled TriOS W55 wipers on 10 mm pathlength sensors at several constructed wetland monitoring sites (see Figure 14 and Figure 15) and found them effective, but maintenance was challenging. The wiper blades need replacing frequently (TriOS recommends every 4–5 weeks) and were fiddly to fit in the field. In addition, damage to a wiper blade of this style were not easy to detect visually.

A

[Patrick Butler, NIWA]

B

[Hamish Carrad, ECan]

Figure 14. (A) & (B) A W55 wiper blade on a TriOS OPUS at Te Ahuriri constructed wetland, Canterbury.

A

[Hamish Carrad, ECan]

B

[Hamish Carrad, ECan]

Figure 15. (A) Clean TriOS OPUS lens at Te Ahuriri constructed wetland. (B) Worn wiper resulting in a dirty lens at Te Ahuriri constructed wetland.

The effect of a worn wiper blade is, however, visible in the data – Abs360 ramps up rapidly (see Figure 16) as fouling builds on the lenses. A worn blade may be able to maintain Abs360 below 0.8 for up to 7 days, so daily data checks and a rapid response are recommended to prevent poor quality data. While the W55 V2 wiper features a blockage detection and removal feature, these wiper blades are probably best suited for attended monitoring with regular blade replacement.

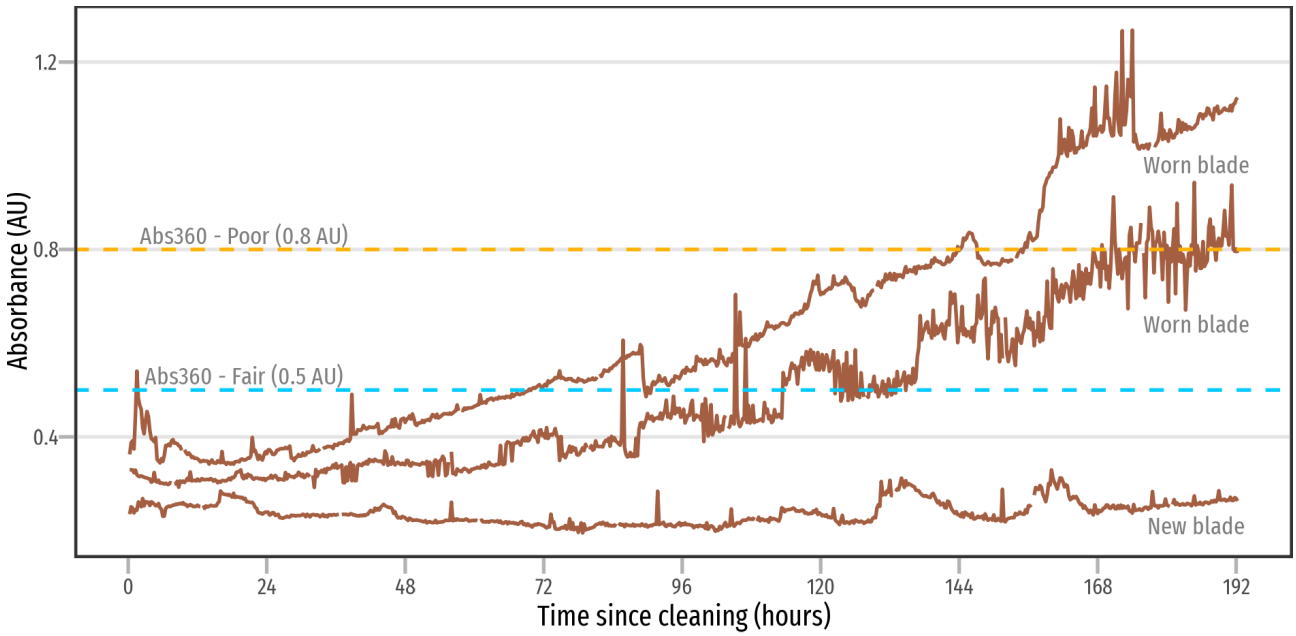


Figure 16. Absorbance at 360 nm for three 8-day baseflow periods (Oct 2022–Feb 2023) at Page wetland outlet, Tasman. The periods with worn W55 blades show rapid ramping up of Abs360, while the undamaged wiper blade cleans the lenses effectively and maintains Abs360 < 0.3.

CASE STUDY 4 – AIR CLEANING

Environment Southland (see Case study 2 for background) used compressed air cleaning to manage fouling on TriOS OPUS when it was installed in April 2015 (Figure 17 A). The release of the air blast was controlled by the TriOS TriBox3 (a controller), and the compressed air was supplied from cylinders rented from BOC Ltd (Figure 17 B). Although the compressed air line was approximately 30 m long, it provided good pressure and flow through the OPUS measuring window (Figure 18 A).

Two weeks later a coarse copper mesh guard was added to cover the optical window area (Figure 18 B) to try to discourage biofilm growth on the lenses. This mesh was then removed as its presence did not have a noticeable effect on biofilm growth. In addition, it made manual cleaning difficult, acted as a debris trap and was observed to disrupt the water flow past the measuring window.

A

B

Figure 17. (A) First installation of TriOS OPUS sensor showing air pipe (running along the white PVC and attaching to sensor with the black nozzle) for compressed air cleaning. (B) Compressed air cylinders rented from BOC Ltd for air cleaning [Environment Southland].

A

B

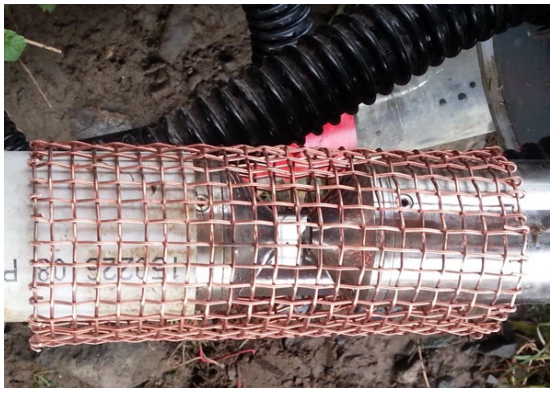


Figure 18. (A) Bubbles erupting on the surface showing a good pressure through the 30 m long air line. (B) Copper mesh placed around the optical window to (unsuccessfully) discourage periphyton growth [Environment Southland].

Renting gas cylinders was an ongoing expense and changing them every couple of weeks was resource intensive, so a 12 V compressor was designed and built (Figure 19 A). This compressor worked well for a few months but was ultimately power hungry and difficult to maintain. Additionally, the compressor sometimes ran past its cut-off pressure and drained the site batteries, plus moisture built up in the air line during colder weather.

Compressed air cleaning was abandoned after it proved to be ineffective at keeping the lenses clean during the summer months (Figure 19 B). A ZebraTech wiper unit was installed which required a re-design of the probe holder (Figure 20).

A

B

Figure 19. (A) 12 V compressor built and used to avoid ongoing cost of cylinder rental. (B) Fouling on and around the measuring window despite compressed air cleaning [Environment Southland].

Environment Southland uses wipers on all optical nitrate sensors, and they are mostly effective at keeping the lenses clean. At some sites the wiper makes a noticeable difference, and by checking Abs360 it is immediately evident when the wiper fails or is struggling to maintain clean lenses (Figure 21). Some other lessons learnt include:

- Some of the wiper units have failed, mostly due to an internal gearing issue which can be quickly repaired by ZebraTech.
- Use of SubConn® cables allows a wiper unit to be swapped out for a replacement without having to pull cables through their protective cases.
- Debris often gets stuck on the bristles, so the brush requires careful positioning. If the brush's home position is upstream of the measuring window, caught debris can obstruct the window. A solution is to ensure that the home position is downstream of the optical window, but sometimes this can be tricky to achieve.

Figure 20. Re-designed probe holder with ZebraTech Hydro-Wiper. The feet of the wiper are used to anchor the whole setup [Environment Southland].

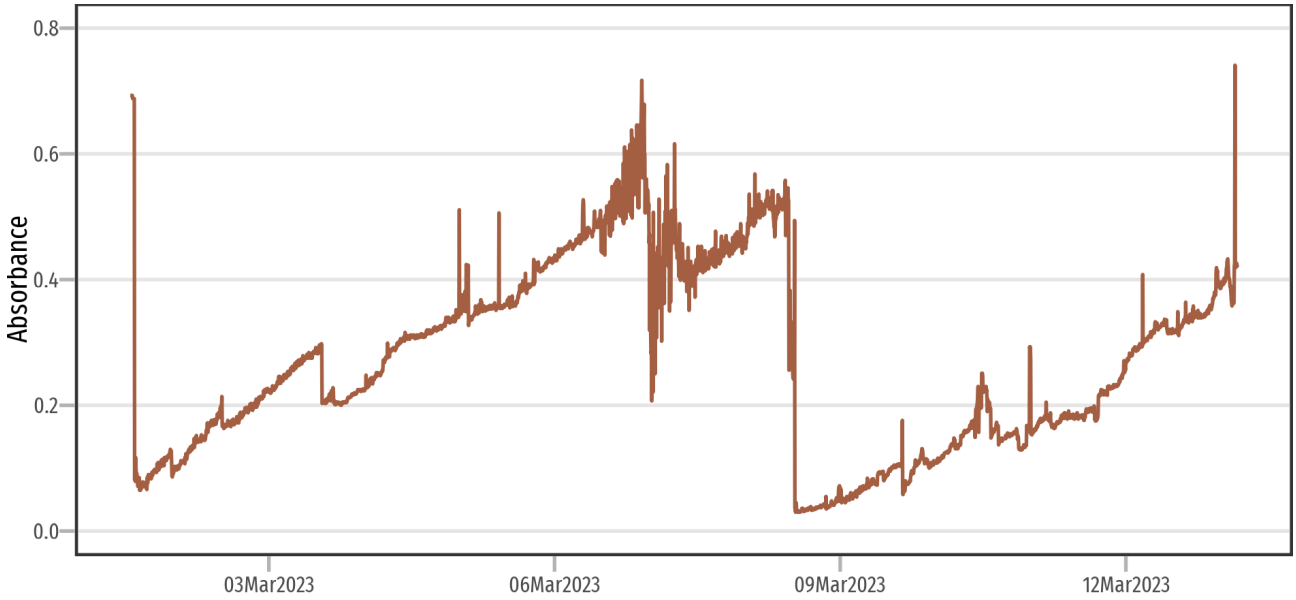


Figure 21. A wiper failure is visible in the absorbance data as fouling on the lenses causes Abs360 to ramp up to around 0.5 between weekly cleans.

DATA LOGISTICS – GETTING THE DATA

Optical nitrate sensors use a range of communication protocols, including analog (4–20 mA), SDI-12, RS-232, RS-485 (Modbus) and sometimes Ethernet (TCP/IP) or Bluetooth LE (Table 4). On-board logging, either as the primary logger or a backup for telemetry, is possible for most optical nitrate sensors. The YSI EXO NitraLED can use, but does not require, an external power source as EXO sondes can operate on battery power.

Workgroup recommendations include:

- If possible, connect using Modbus or SDI-12. Experienced users have had problems using the analog signal with TriOS sensors (see Case study 5 below).
- While it can be useful to have a proprietary controller in the lab, you can use a computer to communicate with most sensors (manufacturer's software may be required).

Useful metadata

We recommend that in addition to the nitrate value, some metadata is also telemetered and archived alongside the data. Any quality code or absorbance value can be used to monitor fouling and assist with data grading. For example, collecting Abs360 from a TriOS OPUS will indicate inadequate fouling management if the value exceeds 0.8 under normal flow conditions (not floods), while during floods a value > 0.8 will indicate high matrix interferences preventing light reaching the detector.

Spectrophotometers measure and typically also store the full spectra (UV or UV-Vis) on-board by default. Downloading this spectral data regularly provides the ability to post-process the data and create a site-specific algorithm if required. New algorithms can be developed using a partial least squares regression of discrete sample data and spectra (all wavelengths).

Downloading the spectral data from some sensors is time-consuming in the field. For example, the TriOS interface hardware and software (UI) are not designed to prioritise high transfer speeds (> 10 Mbps). While waiting until the on-board memory is full (> 2 GB) to download all the spectral data would appear efficient, the downside is that the download time will be lengthy. During the download the sensor is tasked with organising and serving hundreds of thousands of measurements as either multiple files or a single large file. This could potentially leave the user having to wait many hours for data to download, and normal sensor operation will be paused during this time. Valuable spectral data may be lost or excessive technician time may be required unless resourcing is adequate to support one of the following options: (1) downloading the spectral data using a '*little and often*' approach, (2) implementing a capable telemetry system, (3) operating multiple sensors which can be regularly swapped and downloaded in the office, or (4) operating a separate device which can be left on site to download the data (ensure the device's battery life is adequate to download all the data).

CASE STUDY 5 - ANALOG VS MODBUS

Environment Southland found that one of the initial drawbacks of opting for the TriOS equipment was that it does not support SDI-12 communication, providing a choice between only analog and Modbus. Environment Southland's loggers didn't have Modbus capability, so four TriBox3 units were also purchased and their analog channels were used to transfer data to the logger. While the analog channels were relatively simple to set up (as the TriBox3 lets you hold an output value for setup purposes), it was clear that the resolution of the data was suboptimal (Figure 22 A). To rectify this, new data loggers were purchased, allowing the digital Modbus protocol to both control the OPUS probe and receive the digital data straight from the instrument itself. This setup uses a lot less power (no TriBox3 required), and the switch from analog to digital communications clearly improved the data resolution (Figure 22 B).

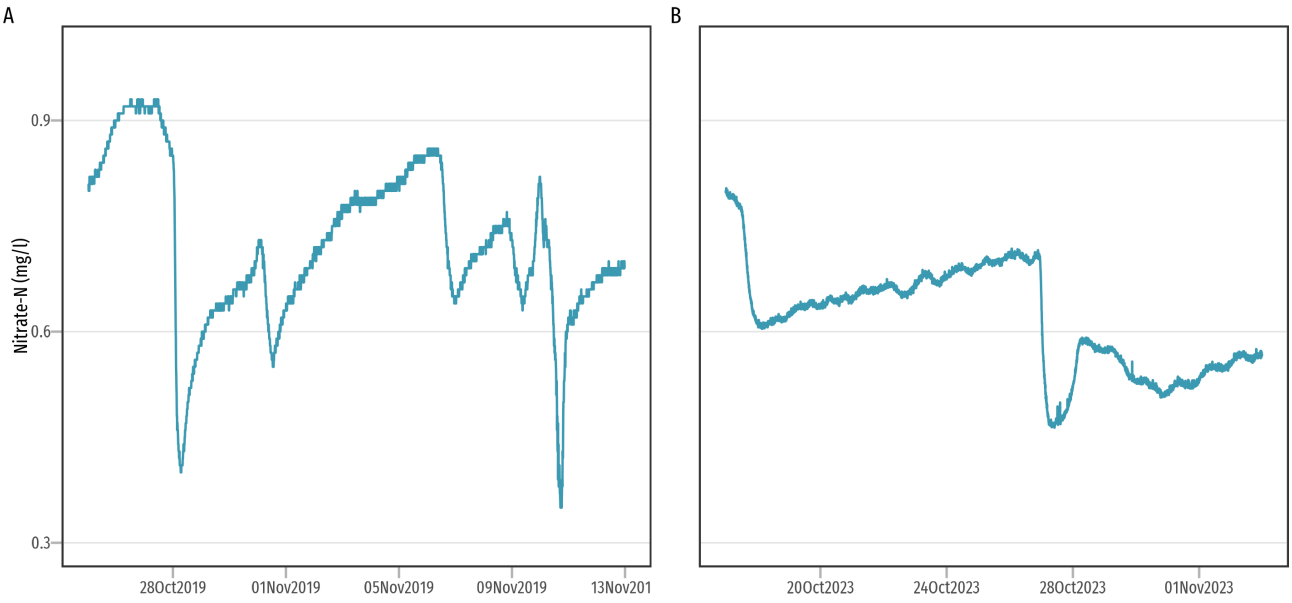


Figure 22. The effect of data communication protocol on data resolution. (A) Stepped data because of low resolution analog data logger communications. (B) Improved data resolution after switching to Modbus communication.

SENSOR VERIFICATION

It's vital to verify a sensor's nitrate values against discrete water quality samples across the full measurement range. The presence of interferences in the water and the ability of sensor algorithms to 'filter' these interferences can result in bias (a systematic shift in one direction from the true value) relative to discrete lab values. By comparing concurrent sensor and discrete values, this bias can be quantified, and if required a site-specific linear adjustment can be applied. The term 'local calibration' is sometimes used for this adjustment, but this term can mean either a linear adjustment or a new algorithm, hence the more specific term 'site-specific linear adjustment'. A site-specific linear adjustment is calculated using linear regression between the discrete values and cleaned sensor values. Pellerin et al. (2013) suggest that four criteria should be met prior to correcting any bias: (1) the error is systematic rather than random, (2) there are >20 discrete samples for comparison, (3) the relationship between the sensor and discrete values has a high r^2 value (>0.8), and (4) the slope of the regression between the discrete and lab values is close to one.

CASE STUDY 6 – SENSOR VERIFICATION

During a joint NIWA and council project (TRC, ECan, BOPRC, TDC, HBRC), funded by MPI's SLMACC Freshwater Mitigation Fund, optical nitrate sensors were operated at constructed wetlands' inlets and outlets. For this project, a sensor verification report developed in R retrieves the nitrate sensor and discrete sample data from Aquarius Time Series and prepares a series of statistics and plots (such as scatterplots, Bland-Altman and control charts) to verify the nitrate sensor data. The discrete samples were collected under both baseflow and event conditions. The verification script may need to be run more than once; the first run will identify any samples or data which need checking and helps identify appropriate editing options (see Pellerin et al. 2013), and subsequent runs check the outcomes of any corrections or edits.

The example below shows data from the Awatuna constructed wetland in Taranaki. The first verification report revealed that results from most discrete samples were plotting above the dashed 1:1 line (Figure 23 A), indicating that the nitrate sensor was reading values consistently above the lab samples. Eight values (of 56) were outside the

verification limits of 3x the manufacturer's stated accuracy (as suggested by Pellerin et al. 2013). This suggests that a correction is required.

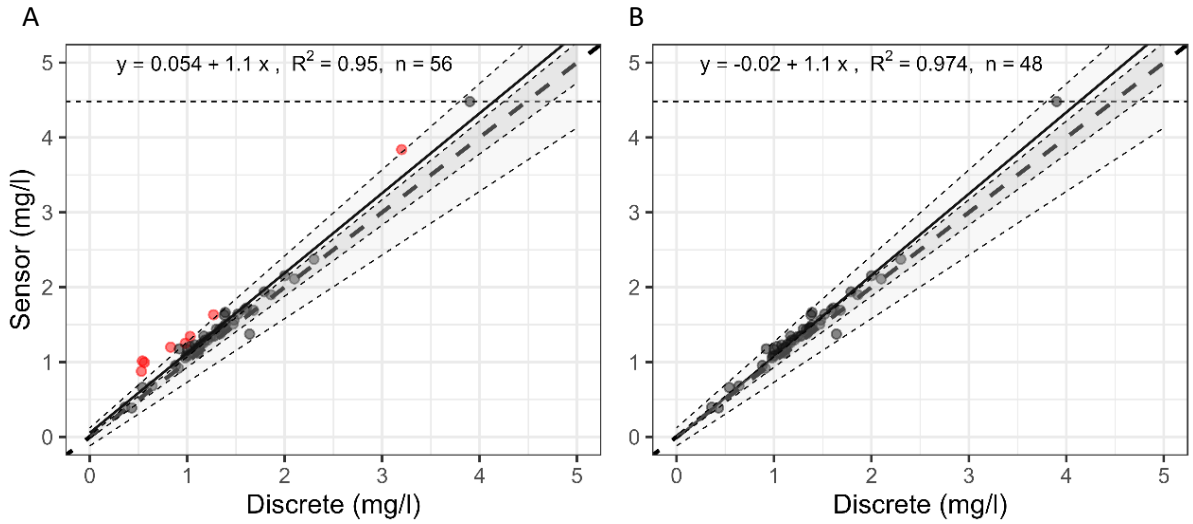


Figure 23. Plots extracted from the NIWA sensor verification report for the Awatuna constructed wetland inlet TriOS OPUS sensor (26 May 2021–16 Apr 2024). (A) Scatterplot of the verification dataset with 1:1 line (dashed), 1x accuracy limits (mid grey band), 3x accuracy limits (light grey) and samples inside (grey circles) and outside (red circles) the 3x accuracy limit**. (B) Scatter plot of verification dataset values within the 3x limit.**

A site-specific linear adjustment was made to the nitrate sensor time series to correct the overestimation. After the adjustment, only three event sample nitrate values were outside the 3x accuracy limits (red circles in Figure 24 A).

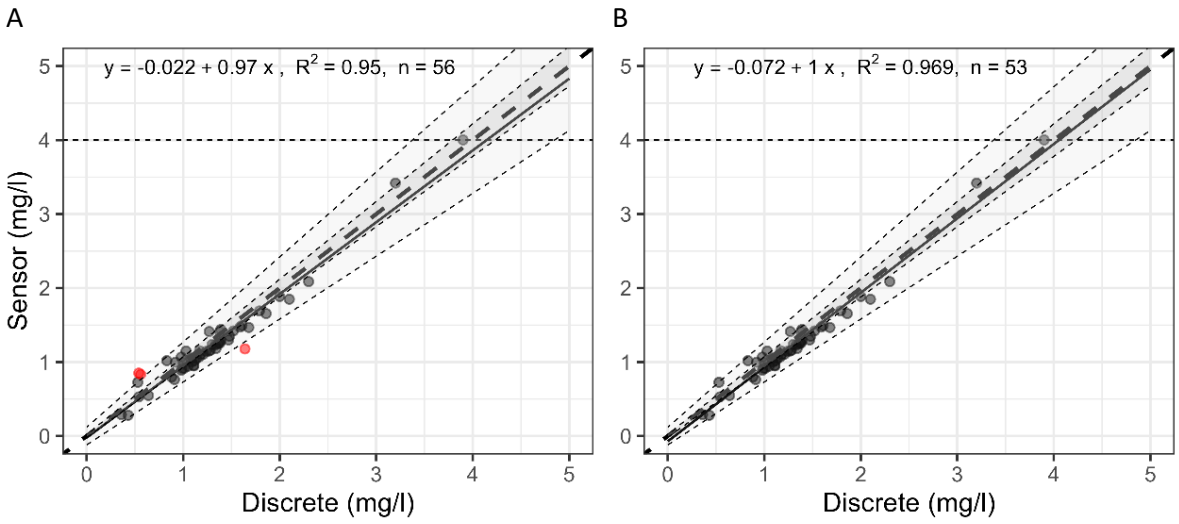
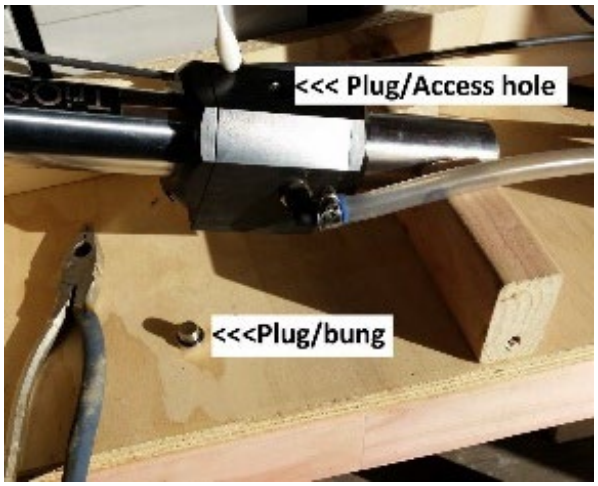


Figure 24. Plots extracted from the second NIWA sensor verification report for the Awatuna constructed wetland inlet TriOS OPUS sensor (26 May 2021–16 Apr 2024). (A) Scatterplot from the second verification report after a linear adjustment was applied. (B) Scatterplot of samples within the 3x accuracy limit.

DEPLOYMENT OVERVIEW

This project does not cover deployment in detail. However, good quality data depends on careful deployment design. The photos on this page demonstrate a range of deployments undertaken in New Zealand.

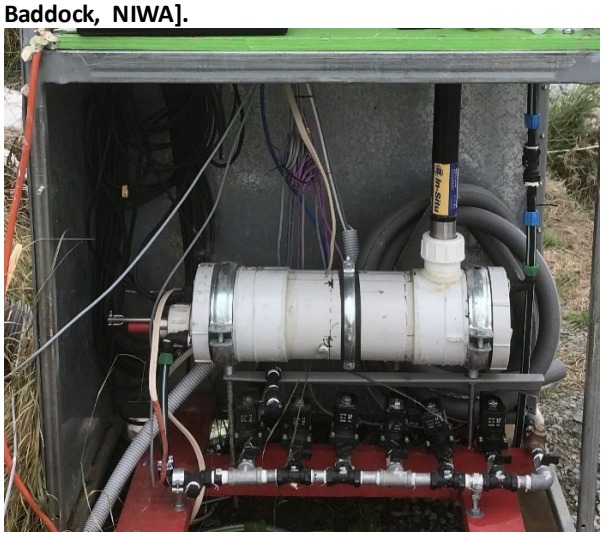
Bankside setup for one sensor on a large river [Andrew Willsman, NIWA].



Flow cell on a TriOS OPUS supplied by an Abyss 12V pump [Andrew Willsman, NIWA].

Bankside setup for multiple sensors on a large river with TriOS sensor removed for cleaning [Evan Baddock, NIWA].

Adjustable sensor depth setup in low energy environment – Te Ahuriri constructed wetland [Brent Williams, NIWA].



Manifold setup for monitoring multiple groundwater wells with a nitrate sensor in a flow cell [Phil Abraham, ESR].

Stream survey of the Silverstream water quality, Canterbury (see Burbery et al. 2021) [Kurt McBeth, ESR].

SUPPORT FOR NEW USERS

All New Zealand sensor reps are helpful and approachable; some will be able to give detailed operational guidance, while others will need to defer to colleagues. The National Nitrate Sensor User Group (hosted by NIWA) is a forum for all regional council, research organisation and university staff who wish to share their expertise and help others troubleshoot optical nitrate monitoring.

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