Review of high frequency water quality data

Advice regarding collection, management and use of nitrate-nitrogen data

Prepared for Environment Southland, Otago Regional Council and Environment Canterbury

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Prepared by:
Neale Hudson
Evan Baddock

For any information regarding this report please contact:

Neale Hudson
Environmental Chemist/Group Manager
Catchment Processes
+64-7-856 1772
neale.hudson@niwa.co.nz

National Institute of Water & Atmospheric Research Ltd
PO Box 11115
Hamilton 3251

Phone +64 7 856 7026

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Executive summary

Interest in the use of high frequency (continuous) in-situ nitrate-nitrogen (nitrate-N) sensors is starting to increase in New Zealand, with NIWA and several regional councils now managing several deployments in riverine environments. Use of in-situ sensors reflects a growing recognition that monthly spot (discrete) water quality measurements obtained from traditional State of the Environment (SoE) monitoring programmes cannot capture or characterise rapid changes in water quality that can affect human and aquatic health.

In 2017/18 NIWA, Environment Southland (ES), Otago Regional Council (ORC) and Environment Canterbury jointly scoped a project for NIWA to review the data collected from some existing in-situ nitrate-N sensor deployments. The council contribution to the project was provided through an MBIE Envirolink Large Advice Grant and required NIWA to prepare guidance and other information, including:

- An overview of the principle for measuring nitrate-N, with specific attention to the effect that factors such as optical pathlength and water matrix have on routine measurement.
- Documentation of key learnings from practical experience and the technical literature that will eventually contribute to a comprehensive guidance document or Standard Operating Procedure, likely to become one of the series of National Environmental Monitoring Standards (NEMS) documents that have been developed by multi-agency consortia.
- An overview of some existing data from Southland and Otago rivers, including the uses to which these data may be put.

A workshop was convened in the latter stages of the project to discuss the experiences of practitioners involved with sensor deployment, operation and maintenance, and to present some of the outcomes from the data analysis.

Ultra-violet (UV)-visible spectroscopy is a well-established procedure for measuring nitrate-N in water. The limitations of the procedure have also been well-documented. Coupling miniaturised spectrophotometers with data algorithms has overcome some of these challenges for specific classes of water, allowing routine unattended collection of in-situ data. Factors likely to influence performance of in-situ nitrate-N sensors include interferences (specifically dissolved organic matter and suspended sediment), the algorithms used to convert spectral data into nitrate concentration values, the trade-off between optical pathlength, sensor accuracy and detection limit, and evaluation of instrument precision and accuracy.

The basic requirements of draft procedures for instrument selection, preparation, deployment and management in the field have been identified. Several quality assurance requirements are described, including the importance of local calibration (optimising calibration to account for specific water matrix effects), use of calibration standards, and the requirement for routine sensor inspection and cleaning. Requirements for analysis of high frequency nitrate-N data are also covered, including data management, handling and graphical procedures. The large volume of data potentially derived from spectrophotometers provides several challenges that may not be encountered when dealing with hydrometric data, or with water quality data derived from discrete grab samples. The logical

next step is development of a formal procedures document, most likely in the form of a NEMS. The information in this document will assist with this.

Several case studies are presented covering the Kakanui, Aparima and Mataura rivers which describe data handling procedures in detail, and the effects of several routine operation procedures (e.g., cleaning events, location of deployment within-channel or adjacent to channel), and the effects of transient spikes. Specific uses of continuous data are presented, including:

Evaluating the relationship between discrete grab sample and continuous data

In all cases, good relationships between grab water quality samples and spectral data were achieved over a wide range of nitrate-N concentration values, and under a wide range of river discharge conditions. In several cases, a bias between grab sample estimates and in-situ sensor results was demonstrated, but the bias was consistent over the concentration range, and could be addressed simply using regression techniques to produce corrected data.

Understanding flow and concentration dynamics, and how this knowledge may be used to identify contaminant mobilisation processes within catchments

High frequency sensors provide information-rich data sets that allow discharge-concentration relationships to be determined during multiple flood events under different seasonal conditions. This information provides insights regarding contaminant mobilisation, which may be used to guide the selection and use of mitigation strategies.

Understanding short-term variability and potential drivers of this variability

High frequency data reveal diurnal trends in nitrate-N concentration similar to those previously identified for water quality variables such as dissolved oxygen and pH. Published work reveals that these data may be used to provide information regarding nutrient cycling and short-term ecological processes. Although the latter may be of limited immediate use to most councils, high frequency data are immediately useful for nitrate load or flux estimation (summarised below).

Trend assessment

Assessment of long-term trends in concentrations of key water quality variables (e.g., nitrogen and phosphorus) is an essential component of water resource management, and underpins national and regional policy and regulatory activities. Although the record of data assessed in this report was too short for estimating long-term trend, the high frequency data will ultimately be very useful when making these assessments. The case studies indicate that for a medium-sized New Zealand river (e.g., Kakanui), estimates of concentration at frequencies greater than fortnightly appear necessary to provide trend estimates over two-year periods. As a corollary, this information implies that very high frequency measurement (say sub-hourly) is not necessary for this purpose.

Nitrate-N load estimation

Well-established modelling techniques exist to estimate nutrient annual loads or flux (instantaneous loads) using grab sample concentration data and continuous river discharge data. The performance of these models is improved by collection of flow-related samples, particularly during storm events and during influential seasonal conditions. Having demonstrated robust relationships between high-frequency sensor values and grab sample concentration data, it is possible to estimate nitrate-N loads very simply as the product of estimated concentration and river flow or discharge. The case studies indicate that reasonable estimates of annual nitrate-N load may be derived from sensor data collected at daily frequency. The uncertainty in the load estimation decreases as the frequency of concentration measurement increases.

A key finding from assessing different applications of the case study data was that it is important to determine the appropriate measurement frequency. In several case study examples, subsets of data derived from five and ten- minute frequency data were generated, and these were used to repeat load estimation and trend assessments. Comparison of the results derived from these subsets help identify "suitable" measurement frequencies. It is apparent that unless very short-term information requirements exist (e.g., providing event-based load estimates), it is difficult to justify measurement in larger rivers at frequencies greater than one hour. Case study results suggest that daily measurements appear adequate for most purposes. Reducing measurement frequency provides several benefits:

i. fewer measurements will prolong the life of the lamp used as the basis of the measurement, and delay onset of drift in the lamp intensity

ii. fewer data will be generated, requiring less storage volume, and

iii. analysis will also be easier – several of the data sets used for the case studies contained in excess of 200,000 rows of data, which adversely affects computer performance when using commonly-used software such as Excel.

In several cases it was necessary to aggregate five- and ten-minute frequency data to hourly or daily average values – the results obtained using these aggregated data were practically indistinguishable to those derived from the raw data, which confirms that for many purposes, much of the high frequency data are redundant.

Development of Standard Operating Procedures (SOPs)

Review of SOPs derived specifically for nitrate sensors from other agencies, as well as those related to continuous measurement of other water quality variables in New Zealand identified key elements that were summarised as a draft or skeleton SOP. We recommend that this is further developed in consultation with regional council practitioners in the same manner that National Environmental Monitoring Standards have been developed for several continuously measured water quality variables. Key findings include:

- Instruments must be calibrated using appropriate standard solutions and zero measurement in spectrally pure water must be performed prior to deployment.
- All optical surfaces must be kept as clean as possible to avoid attenuating the light signal, which will cause drift in instrument response. Use of mechanical wipers is essential, supplemented by physical cleaning of the sensor with appropriate chemicals when necessary.
- Monthly site visits, during which instrument inspection and cleaning, collection of validation samples and where necessary, verifying instrument responses in spectrally pure water, air (i.e., without any light attenuation) and using one or more calibration samples, might be undertaken, appears adequate. Where possible, verification of instrument performance using a similar instrument would be useful.
- Full calibration of an instrument is a task better suited to a laboratory environment; provided the instrument is performing adequately, this task is probably not required more than once annually.

More work is needed to guide the effective and efficient use of in-situ continuous nitrate-N sensors and associated data processing and analysis. For example, research within NIWA is exploring the interplay between suspended sediment, dissolved organic material and accuracy of sensor measurements. This is being undertaken at both laboratory and field-scale, and the findings are likely to contribute further to the development of standard procedures that could be included in a future NEMS addressing topics such as nitrate-N sensor selection, deployment and operation, and data processing, interpretation and use.

1 Introduction

Internationally there is a trend toward use of high frequency (continuous), in-situ measurement of water properties (e.g., temperature, electrical conductivity, turbidity, dissolved oxygen). Recently, this has included measurement of contaminants such as nitrogen (N), specifically nitrate-N. New Zealand is following suit, recognising that monthly discrete (spot) water quality measurements and samples obtained from traditional State of the Environment (SoE) monitoring programmes cannot capture or characterise rapid changes in water quality that can affect human and aquatic health. For example, a significant proportion of an annual nitrate load may be transported during short-duration runoff events that occur outside of routine sampling visits. This makes it difficult to accurately estimate the true annual load of nitrate-N lost from a catchment.

While continuous monitoring of water temperature, conductivity, dissolved oxygen and turbidity are now becoming common-place in New Zealand, continuous monitoring of nitrate-N remains relatively new. High frequency nitrate-N data are increasingly important to regional councils for several reasons, including:

- improving estimates of the impacts of land use on water quality through better characterisation of temporal variation in concentrations – including identification of peak runoff concentration and potential to improve source identification
- reducing uncertainty in the examination of trends in nitrate-N concentrations
- improving the accuracy of estimated nitrate-N loads, which are key to
  - establishing water quality limits under the National Policy Statement for Freshwater Management (NPS-FM), and to
  - meeting regional and national freshwater objectives
- calibrating nitrate-N surface water and groundwater transport models
- improving ability to predict downstream water quality (e.g., river intakes used for potable and industrial supply), and
- identifying periods when nitrate-N concentrations or loads require additional management.

This report focuses on continuous nitrate-N monitoring in rivers and reviews data from some existing in-situ nitrate-N sensor deployments. Preparation of the report was jointly funded by an Envirolink Large Advice Grant (MBIE Contract No. C01X1717) lodged by Environment Southland (ES), Otago Regional Council and Environment Canterbury, and NIWA Strategic Science Investment Funding (SSIF).

1.1 Report purpose and scope

This project draws on both international literature and recent New Zealand field trials to produce preliminary guidance regarding in-situ continuous nitrate-N measurement in riverine waters, including provision of guidance on associated data processing, analysis and use. Specifically, this report provides:

1. An overview of the principles of continuous nitrate-N monitoring, including monitoring programme design, and applications/uses for fresh water management.
2. A comprehensive assessment of existing riverine monitoring applications in New Zealand (the Mataura and Aparima rivers in Southland (operated by NIWA and ES respectively), and the Kakanui River in Otago, operated by ORC).
    - 2.1 Lessons learned regarding field deployment and maintenance, including different cleaning systems – wiper versus compressed air, sensor placement, and
    - 2.2 Understanding localised temporal variations in nitrate concentration as a result of mixing and flow/current variation and biomass attenuation.
3. Identification of information that should be included in a draft procedure for sensor calibration and validation, considering data derived from wet-chemical nitrate-N analysis vs. in-situ measured data, local calibration requirements, etc.
4. Identification of information that should be included in a draft procedure for data processing and QA (e.g., adjustment of baseline drift, addressing data spikes, production of a synthetic record to fill 'gaps' etc.).
5. Data analysis and interpretation, including data visualisation methods, and interpretation of hysteresis (i.e., the relationship between variable concentrations in the rising and falling limb at multiple percentiles of discharge, which is informative regarding the mobilisation of contaminants during rainfall events), and flushing analyses.
6. Guidance on reporting and use of these data, including brief commentary on the implications for reporting continuous vs traditional grab/spot samples (e.g., nutrient load calculations, compliance monitoring), and of flow adjustment in trend analysis.
7. Guidance on identifying where and when continuous monitoring is most appropriate, and using this information to temper community expectations that this equipment should be a "routine monitoring tool" on each of "their" rivers.
8. A summary of the outcomes of a workshop involving field and science staff from NIWA, and councils who have implemented continuous water quality monitoring, or are considering doing so.

1.2 Report outline

This report is divided into eight principal sections:

Section 2 provides an overview of continuous nitrate monitoring, including various techniques available to measure nitrate-N continuously, typical performance of in-situ analysers, and situations where hyperspectral instruments have been used.

Section 3 describes hyperspectral measurement in more detail, factors that impair measurement, and typical precision and accuracy.

Section 4 discusses instrument selection, deployment, measurement and associated activities.

Section 5 introduces the case studies, data used for these studies and the techniques that were applied to these data.

Section 6 is a case study of data supplied by Otago Regional Council with special emphasis on the Kakanui River at McCones site. Flow concentration relationships, the effect of cleaning, load estimation and trend assessment are discussed.

Section 7 is the Aparima River case study (Environment Southland data). Load estimation is a key focus, as well as how these data may be used to better understand contaminant mobilisation and in-river processes.

Section 8 is a case study of data collected by NIWA for the Mataura River, Southland. Within-river and out-of-river deployment of instruments is discussed, an assessment of measurement frequency is discussed.

Section 9 discusses management of the time series data generated by two brands of instrument, and time series data management generally.

The guidance is not complete because it reflects current best available knowledge and experience, and guidance may always be improved as technologies are developed, or new techniques arise. Aspects of the guidance are expected to contribute to a potential National Environmental Monitoring Standard (NEMS) for continuous nitrate-N measurement and further continuous water quality monitoring initiatives. Materials that may contribute to development of standard procedures are include in the text, as well as in Appendix G. Appendix H through Appendix J contain figures and text provided by experienced practitioners derived from their experience with deployment and operation of this equipment. We anticipate that this information may be used immediately by anyone considering continuous nitrate-N monitoring.

2 Overview of high frequency nitrate-N monitoring

This section provides an overview of continuous nitrate monitoring, including various techniques available to measure nitrate-N continuously, typical performance of in-situ analysers, and situations where hyperspectral instruments have been used.

2.1 Recent developments in continuous monitoring

Considerable development in the technologies required for continuous monitoring has occurred over the last 15 years, and continuous monitoring of water quality is being increasingly implemented, and many of the citations in this report describe the evolution of this technique.

In contrast with traditional river water quality monitoring, which is typically based on monthly sample collection and subsequent laboratory analysis, continuous water quality monitoring generates a high frequency time series of water properties (e.g., temperature, electrical conductivity) or contaminant concentrations or loads (e.g., nitrogen, phosphorus). Typically, this might be high temporal resolution data at a fixed site, but it also includes continuous spatial monitoring or mapping of water quality variables in lakes or estuaries (e.g., by depth-profiling or using portable or movable equipment). Many water quality variables can be monitored continuously by a range of sensors, including non-spectrometric sensors (e.g., ion selective electrodes, thermistors, or combinations of sensors such as multi-water quality variable sondes), spectrometric sensors (including fluorescence, absorptiometry e.g., portable UV/Vis spectrometers, beam transmissometers) and portable wet laboratories and microbiological analysers. Several sensor types related to nitrate-N measurement are discussed briefly in Section 2.2.

High frequency monitoring has the potential to contribute significantly to national and international aquatic science. High frequency monitoring of physical water quality is reasonably mature (e.g., temperature, dissolved oxygen, pH, and turbidity (Gippel 1989; Gippel 1995; Grayson et al. 1996), whereas routine high frequency nutrient monitoring is not much more than one decade old (Jordan et al. 2005; Jordan et al. 2007), and real-time *E. coli* monitoring is arguably still emerging from the field-testing phase (Stott et al. 2016).

The National Environmental Monitoring and Reporting (NEMaR) project commissioned by the Ministry for the Environment (MfE) in 2011[1] identified national freshwater monitoring protocols for core river water quality, river bio-monitoring and lake monitoring variables. Through an expert-panel process, the project also identified a selection of key water quality variables that were recommended for national State of Environment (SoE) monitoring and reporting. Most of these variables are currently a component of regional and national river water quality monitoring. Table 2-1 lists the recommended core and supporting water quality variables, and identifies those that are currently amenable to continuous monitoring.

[1] http://www.mfe.govt.nz/publications/fresh-water-environmental-reporting/freshwater-monitoring-and-quality-assurance-report

Table 2-1: Key water quality variables, including those amenable to in-situ analysis. Green shaded cells are key variables identified in the NEMaR programme, and tan shaded cells are supporting variables identified in the NEMaR programme. Blue shading indicates those variables currently amenable to continuous monitoring. EC = electrical conductivity.

Water quality variable	Technique used for continuous measurement				Laboratory method	Notes
	Non-spectro. sensor	Fluorescence	Absorptiometry	Surrogate		
Temperature	A					[A] Thermistor
Dissolved oxygen (DO)	B					[B] Optical/ Electrochemical)
Visual clarity			C	D		[C] Beam atten. [D] Turbidity
Oxidised nitrogen (NOx)	E					[E] Ion selective electrode
Ammoniacal nitrogen						
Total nitrogen (TN)				F		[F] Turbidity
Dissolved reactive P (DRP)						
Total phosphorus (TP)				G		[G] Turbidity
E. coli bacteria		H	H	I		[H] Enzymatic procedure [I] Turbidity
Conductivity/ salinity	J					[I] EC principle; Water tracer
Turbidity					Beam atten.	
Total suspended solids				K		K Turbidity
Coloured dissolved organic matter (CDOM)		L				[L] fDOM; Water tracer
Rhodamine WT						Water tracer
Bromide	M					[M] Ion selective electrode; Water tracer
Dissolved organic carbon (DOC)						
Total organic carbon (TOC)						
Biochemical oxygen demand (BOD)						
Chlorophyll-*a*						
Blue-green pigments						

Several other variables which have a well-established role in water quality assessment are also listed. This list of variables amenable to in-situ measurement continues to grow in response to advances in measurement technology. For example, near real-time measurement of *E. coli* in freshwater has been demonstrated in New Zealand recently (e.g., Stott et al. 2016; Stott R. et al. 2017), and continuing work has more clearly identified performance criteria for this method.[2]

2.2 Developments in continuous nitrate-N monitoring

Moorcroft et al. (2001) reviewed nitrate-N measurement in a range of matrices using several broad categories of measurement principles. These included gas chromatographic, chemical, electrochemical, and spectrophotometric procedures. Some of these are not suitable for in-situ environmental monitoring; several of the more appropriate techniques are discussed briefly below.

2.2.1 Ion-Selective Electrodes

Ion-Selective Electrodes (ISE) comprise an ion-specific (i.e., nitrate anion, NO_3^-) half-cell, and a reference half-cell. The voltage difference between the two electrodes is proportional to the nitrate ion concentration. The two half-cells are integrated into one device, analogous to the well-known pH electrode.[3]

The device is relatively inexpensive, easy to use, has a wide measurement range and is insensitive to interferences from colour or particulate materials. However, this measurement approach has several limitations, including low resolution, accuracy and precision (repeatability), sensor drift (especially at low concentrations), and interference from other ionic (charged) water constituents (e.g., chloride). Continuous measurement using this technology is therefore likely to require high maintenance effort.

2.2.2 In-situ wet chemical nitrate sensors

An example of this technology is the YSI 960 Nitrate Monitor, which has been available since approximately 2005. The system is based on the principle of flow injection analysis (FIA), which is widely used for laboratory nitrate-N and nitrite-N (NNN or NO_x) measurement. A series of precise, low-volume pumps mix an aliquot of water with user-prepared reagents that undergo reaction with the nitrate ion to produce a coloured solution. The intensity of the colour is proportional to the concentration of nitrate in the sample.

The device measures NNN, i.e., cannot differentiate between forms of soluble oxidised nitrogen. The sample aspiration and colour-formation is time dependent, restricting the frequency of measurement to approximately 15 minutes. The instrument requires reagents and generates waste, which necessities periodic maintenance. The manufacturer claims that analyses will be possible for one-month at a one-hour measurement frequency. The use of blanks and standard solutions enables automatic on-site drift compensation.

[2] Dr Rebecca Stott, unpublished results from 2017/18 NIWA internal SSIF projects FWWQ1818 and FWWQ1823.

[3] http://www.google.co.nz/url?sa=t&rct=j&q=&esrc=s&frm=1&source=web&cd=1&ved=0CCoQFjAA&url=http%3A%2F%2Fwww.hach.com%2Fasset-get.download.jsa%3Fid%3D7639984588&ei=l2MsVK7ICoeAiwK4pYDwCg&usg=AFQjCNFq683z0Ibxsfraa3qYq5hxruho0Q&bvm=bv.76477589,d.cGE

The "typical" nitrate-N concentration measurement range is 0-5 mg/L, but may be extended to approximately 10 mg/L with pump and dilution modifications. The linear measurement range extends to approximately 6 mg/L, less than the measured in some eutrophic streams in New Zealand (e.g., lower Hinds River, Canterbury). Accuracy is typically ±5% (dependent on the light path in the measurement cell), ranging from 0.2 to 0.02 mg/L. An independent trial of the device in saline waters concluded "In general, however, it appears that the fundamental technology has the capability to successfully measure in situ nitrate concentrations under a variety of field conditions."[4]

Although not noted as limitations by the trial, the method does require the use of hazardous materials, and generates wastes that must be disposed of appropriately. The effects of particulate materials were not noted, because the waters tested were relatively clean.

A more recent approach to i*n-situ* measurement of nitrate-N is provided through use of microfluidics, alternatively known as "lab-on-a-chip" (Ogilvie et al. 2011; Beaton et al. 2012; Clinton-Bailey et al. 2017). The technique allows the manipulation of small volumes of fluids (tens of µL) through microchannels, typically tens to hundreds of micrometres wide. In a recent application by Beaton et al. (2017), fluid handling was performed with a custom-built device comprising a three-channel syringe pump and 14 solenoid valves attached directly to the chip, using a system controlled with a custom microcontroller-based electronics package. A conventional wet-chemical analytical process was used, based on the Griess assay. Following cadmium reduction (to convert nitrate to nitrite), diazotization with sulphanilamide and subsequent coupling with N-(1-naphthyl)-ethylenediamine dihydrochloride (NED), an intensely coloured azo dye is formed. The latter is commonly used for colorimetric nitrite analysis because it is not subject to interferences in oxygenated seawater (Beaton et al. 2012). The technique is sensitive, accurate and precise (demonstrating similar performance to laboratory scale instruments). The analytical limit of detection was estimated to be 1.6 µg/L, over a measurement range that extended to 21.7 mg/L as nitrate-N. Other attractive features of the devices are small size, low power consumption, and extended periods of unattended operation (up to 26 days demonstrated by Beaton et al. (2012), who considered that 12 weeks of operation was feasible if a conventional filter was used to reduce particulates). Measurement frequency was 300 s (five minutes) – although Ogilvie et al. (2011) demonstrated that frequencies of 24 s were possible (~140/hour). Currently these devices are research equipment, but recent developments using 3-D printing techniques and mobile phone applications create the potential for cheaper and more widespread adoption and use (e.g., Jayawardane et al. 2014; Kudr et al. 2017; Li et al. 2017; Martinez-Cisneros et al. 2018).

2.2.3 Ultraviolet (UV) spectrophotometric determination of nitrate

Analysis of nitrate-N using UV spectroscopy is discussed in greater detail in Section 3.2. In-situ analysers (discussed in the next section) rely on UV spectroscopy, and have achieved relatively widespread use because of the miniaturisation of the equipment, coupled with the development of sophisticated data mining techniques and algorithms that have allowed several of the shortcomings in the basic analytical approach to be overcome.

2.2.4 High frequency, hyperspectral instruments

Several manufacturers supply high frequency hyperspectral in-situ analysers that may be used for continuous nitrate measurement. These include:

[4] https://drum.lib.umd.edu/bitstream/handle/1903/13731/[UMCES]CBL%2008-043.pdf;jsessionid=D672FF26E615EA2212DC526B886583EE?sequence=3

- **Spectra::lyser**, manufactured by s::scan in Austria (https://www.s-can.at/), who have a range of instruments designed for stationary and field deployment. Several pathlength and wavelength ranges are provided.
- **TriOS** (http://www.TriOS.de/en/products/sensors.html) who have a range of instruments designed for stationary and field deployment. Several wavelength ranges are provided, and a larger range of pathlength options exist than for the Spectra::lyser.
  - The TriOS OPUS device measures over the wavelength range 190 – 360 nm with 0.9 nm resolution. It allows measurement of several different water quality variables.
  - The TriOS NICO is similar but is optimised for nitrate measurement with turbidity compensation.
- **Nitratax sc Nitrate Sensors** (https://www.hach.com/nitrate-sensors/nitratax-sc-nitrate-sensors/family?productCategoryId=35546907021). This equipment is designed principally for wastewater treatment plant applications, but has been successfully deployed in the field.
- **SUNA V2 UV nitrate sensor** (http://www.seabird.com/nutrient), designed for high turbidity freshwater systems, as well as marine environments, and is able to measure to depths of 500 m.
- **Digital ISE sensor for nitrate** (https://www.wtw.com/en/products/product-categories/sensor-technology/digital-iq-sensors-online/iq-ise-sensors-for-nitrate.html?mobile=1). A range of products exist, optimised for freshwater or wastewater applications. Higher resolution instruments are recommended for resolving the nitrate and nitrite peaks and for optimal accuracy.

2.3 Uses of high-frequency water quality data for water quality assessments

Advances in the capability of *in-situ* sensors allow us to monitor water quality in rivers and estuaries at time scales at which changes occur; data communications allow us to report and evaluate this information in near real-time.

High frequency data can assist in identifying water quality drivers. For example, seasonal, diel, event and within-event, finer time scale patterns may be interpreted in terms of contaminant mobilisation, delivery and availability. Use of several instruments within a catchment creates the potential to better understand within-stream nutrient processing and attenuation. It also has the potential to allow identification of “contaminant hotspots”, reaches where elevated inputs of nutrient may occur.

Collecting these data requires rethinking monitoring programme design, having regard for:

- the selection of sensors that are most fit for purpose (which sensor(s) should I use?)
- the timing of data collection, and the duration of measurement (when should data collection commence, and for how long do I need to collect data?)
- the spatial distribution and number of sensors required (where should the sensor(s) be deployed, and how many do I require?)

Although the additional data provided by continuous instruments may prove useful in itself, it is better to consider the information requirements before purchase and deployment of the instruments, to ensure that all the prerequisites for providing high quality data will be satisfied.

2.3.1 Better characterisation of catchment water quality

In many catchments in New Zealand, collection of water quality data has principally been directed by SoE monitoring, which often has a primary objective of detecting and quantifying temporal trends, typically over a five- to ten-year period. These data are generally collected through a pseudo-random monitoring programme design, having little regard for flow at the time of sampling. The timing of sample collection aims to have more or less equal time spacing between samples, rather than targeting a range of flow conditions. Data tends therefore to better represent base-flow conditions, because high-flow conditions tend to be transient, and less likely to be sampled. For many variables, however, the bulk of the load may be delivered during high flow events, following rainfall.

In other circumstances, there may be a strong seasonal component to the delivery and generation of contaminant loads. For example, seasonal rainfall causes a pulse of groundwater that increases the concentration (and load) of nitrogen to be discharged from shallow groundwater to many river systems (e.g., Figure 2-1).

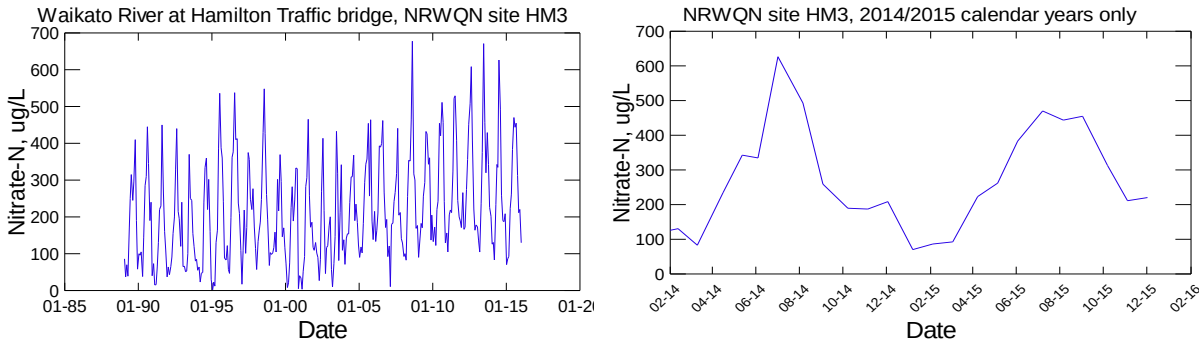


Figure 2-1: Example of seasonal variation in nitrate-N concentration, Waikato River at Hamilton. These data were derived from the National River Water Quality Network operated by NIWA.

Estimation of the "true" annual nitrate-N load delivered from the Waikato River catchment should therefore have regard for this seasonal distribution in the load. Although a pseudo-randomised monitoring programme will provide an estimate of the seasonal load, it may not be as effective as use of data that targets periods of elevated nitrate-N concentration and elevated flow as part of an annual monitoring programme. In some cases, rigid monthly sampling creates the potential to miss collecting water samples during key periods of interest, or fail to characterise the water quality dynamics of the catchment of interest (i.e., use of monthly SoE data in load calculation is best supplemented with additional event-based data). Some of the consequences of rigid monitoring programme design and operation are indicated in Figure 2-2:

- Figures A and B involve fixed time interval sampling and fixed collection times for six discrete samples – the average or median concentration of the water quality variable derived from these two data sets will be different, but only because of the timing of sample collection, and neither monitoring programme indicates that a regular concentration cycle exist.

- Figure C indicates a less rigid sample collection frequency, and collection of 1/3 more samples (8) – the increased number of samples, and variable timing better characterises the range of concentrations. The number of samples is still inadequate to demonstrate the recurring cycle, or frequency of the cycle.

- Figure D identifies and "perfectly" represents the range and duration of concentrations over the regular cycle that exists. The monitoring effort is considerable, relative to the other monitoring programme designs – 101 samples vs 6, 6 and 8 for Figures A, B and C, respectively.

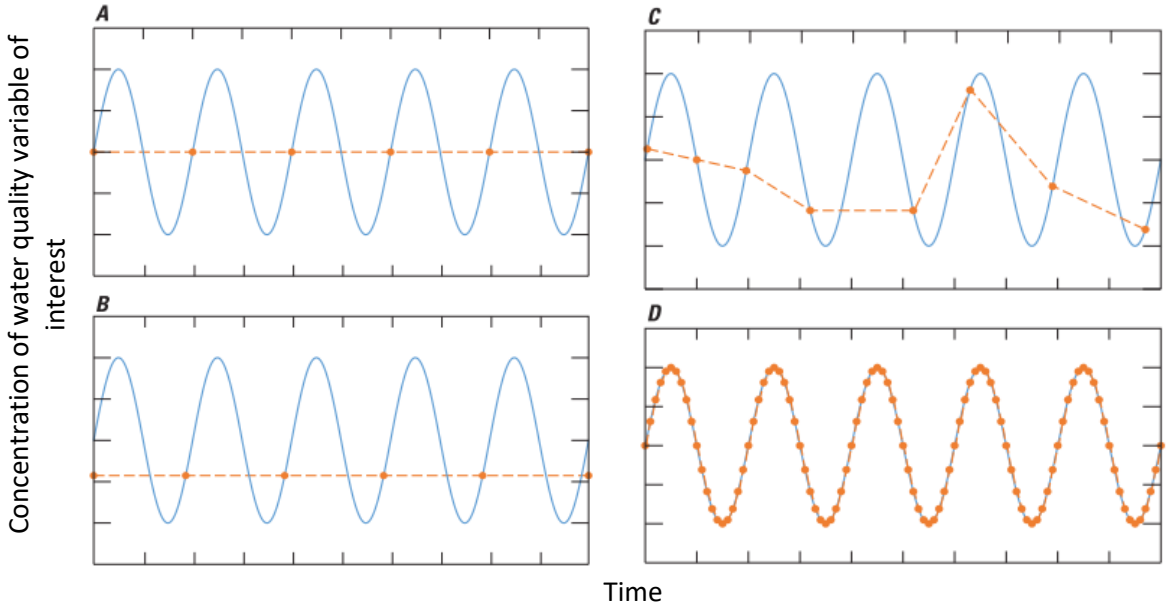


Figure 2-2: Schematic demonstrating the influence of frequency of discrete sample collection on characterisation of water quality constituent dynamics in a system. The phenomenon of "aliasing" is demonstrated by low frequency grab sampling (A–C). High frequency in-situ measurements (D) provide a more accurate depiction of the system. Based on Figure 3 of Kraus et al. (2017).

The challenge of identifying and characterising periods of poor water quality for variables subject to recurring diurnal or seasonal cycles is well-established (e.g., for dissolved oxygen concentration). This has relied on the use of bulk manual sampling or automatic samplers and – more recently – the development of accurate, high frequency measurement equipment that may be deployed and left to operate over extended time periods.

Techniques for targeting periods of high flow or periods of elevated nitrate-N concentrations exist. These include:

- More frequent manual grab sampling during the periods of interest.

- Use of automatic samplers to undertake flow-related sampling, with the sampler triggered according to stage height or discharge, or rate of change in either of these metrics.

The first of these methods is expensive, requiring more frequent site visits, and is dependent on human intervention. It may not be possible to sample the flood of interest because of health and safety concerns, or the critical sampling period may occur at night, or the person tasked with responding to the event of interest may not be available at the time required. The second option is less expensive, but will incur additional outlay and setup costs. Both approaches require analysis of additional samples in the laboratory. The use of in-situ measurement devices creates the prospect of far more frequent monitoring sampling frequency of minutes), while not necessarily requiring analysis of large numbers of additional grab samples.

2.3.2 Load estimation

Load estimation involves calculation of the instantaneous load or flux of material transported in river water. It is a fundamental metric that underpins water quality limit setting requirements in the National Objectives Framework of the National Policy Statement for Freshwater Management 2014 (New Zealand Government 2014; New Zealand Government 2015; New Zealand Government 2017). While freshwater values are related to numeric attribute concentrations values, management of land-based activities requires load calculation.

Catchment yield, or the mass of contaminant delivered from the catchment is the product of concentration and flow. The accuracy of load estimation is often limited by the quantity and representativeness of water quality data. For example, the annual load calculated from scenarios A-C in Figure 2-2 will differ from each other, and will be very different to the load calculated using the data indicated in scenario D. It may not be feasible or affordable to manually collect the number of samples indicated in scenario D, but it may be possible to use a suitable sensor to collect data over several key periods at high frequency, thereby improving the annual load estimate.

The loads estimated from regression and other statistical procedures may also be used to direct catchment modelling, by assisting with model setup and identifying the sub-catchments and land uses where implementation of various mitigation strategies is likely to be most effective.

Understanding the timing at which various proportions of the overall load are delivered to the river reach, lake or estuary of interest, is also valuable. It allows the efficacy of the mitigation strategy to be “tuned” so that the maximum water quality or ecological benefit may be achieved at lowest cost.

2.3.3 Spatial surveys

Instruments deployed from boats have been used to determine spatial trends and identify contaminant or nutrient gradients in large rivers, lakes, wetlands and estuaries. Crawford et al. (2015) revealed previously unknown variability in several factors in streams, rivers, and lakes. They also detected land-water connections in a small lake, inferred the role of main-channel vs backwater nutrient processing in a large river, and detected sharp chemical changes across aquatic ecosystem boundaries in a stream/lake complex. Fichot et al. (2011) used hyperspectral data to determine spatial patterns in dissolved organic carbon (DOC), and to determine the probable source of DOC in marine waters.

Uses of these data include identification of contaminant hotspots or sources, areas or zones where nutrients may be consumed or transformed at higher rates. Dense spatial data also allows the representativeness of fixed water quality monitoring sites to be assessed. High frequency data may reveal subtle features or characteristics in water that may not be feasible to obtain in other ways. Using other techniques, the cost of obtaining these data or information at high spatial scale may be prohibitive. For example Viswanathan et al. (2016) utilised isotopic analysis of oxygen and nitrogen

in nitrate-N and oxygen in water, coupled with collection and analysis of multiple grab water samples to provide a level of spatial information that could conceivably be obtained at much lower cost and with less effort using portable equipment. Surveys of this nature have been undertaken to identify the location of nitrate-N inputs to surface water (from points sources (tributaries, drains and tile drains), and upwelling groundwater etc.,) estimate nitrate-N removal rates along river reaches, and determine other in-stream processes (Williams 2013; Hensley et al. 2014; Aubert et al. 2016; Hensley and Cohen 2016; Rode et al. 2016; Kunz et al. 2017).

2.3.4 Other uses of high frequency data

Several other uses (some related to the points described in detail above) may also be identified for high frequency nitrate assessment, including:

- Identifying contaminant spills, and transient or irregular water quality events.
- Quantifying the water quality benefits arising from Good Management Practices (GMPs) – not just changes in median or average concentrations, but decrease in concentration or load maxima, decreased variability, and reduced frequency of poor water quality events (Viaud et al. 2004).
- Identifying the timing, magnitude and duration of nutrient transport and linking these to hydrological conditions (Bende-Michl et al. 2013; Schwientek et al. 2013), and identifying periods when better management of concentration or loads of contaminants is required (Stamm et al. 2013).
- Using hysteresis analysis to infer source-transport relationships (e.g., McKergow and Davies-Colley 2010; Hughes et al. 2012; Lloyd et al. 2013; Bieroza and Heathwaite 2015).
- Improving estimation of the impacts of land use on water quality by better identification and differentiation of point and diffuse pollution sources using high frequency coloured dissolved organic matter (CDOM) fluorescence (Old et al. 2012) or nitrate-N.
- Undertaking spatial surveys to identify source and sink areas or river plume dispersion (Hudson et al. 2009), including use of continuous sensors to trace water masses labelled with tracers in a wide range of science and applied applications (e.g., Drummond et al. 2014).
- Continuous monitoring of pathogens, e.g., using turbidity as a surrogate for *E. coli* (Davies-Colley et al. 2008; McKergow and Davies-Colley 2010) and other microbial contaminants (e.g., Stott et al. 2011; Stott et al. 2016; Stott R. et al. 2017).
- Improving understanding of hyporheic exchange of water and particles in streams and rivers, which is important to the dynamics of fine particles, nutrients and microbes (e.g., Drummond et al. 2014), and better identifying hydrological pathways (e.g., Schwab et al. 2014).
- Developing new or refined load estimation techniques (e.g., López-Kleine and Torres 2014), new surrogates and analysis algorithms (e.g., Etheridge et al. 2014b), and

general improving of data processing techniques e.g., algorithms for specific calculations.

- Providing high quality data over a range of flows (e.g., Jordan et al. 2005; Jordan et al. 2007).
- Guiding the frequency and timing of discrete sample collection – once a more representative record of water quality variable concentrations is available, these data may be subsampled to identify a sampling regime that will allow the concentration or load of the variable to be adequately characterised (Bowes et al. 2009; Cassidy and Jordan 2011; Wade et al. 2012).
- Exploring catchment scale-sample frequency relationships. On larger rivers that are less dynamic, sampling at frequencies of days to weeks may be sufficient (Burt et al. 2011), whereas it may be necessary to collect data at much higher frequency to represent smaller, more dynamic, catchments (Johnes 2007).
- Guiding sensor selection (e.g., Bende-Michl and Hairsine 2010), including use of lower cost, possibly less sophisticated or accurate sensors, for more wide scale deployment (e.g., UV nitrate sensors rather than full UV-NIR spectral sensors; passive samplers (Jordan et al. 2013) or microfluidic samplers (Cogan et al. 2013)).
- Checking, augmenting and extending routine (discrete) SoE monitoring for short or critical time periods (e.g., to check model predictions in relation to NOF guidelines (Davies-Colley et al. 2013).

In general, information derived from monitoring increases as sampling frequency increases (Halliday et al. 2015) – the challenge is to find a balance between the high (in cases, excessive) cost of high frequency monitoring and the extent of information required. This is addressed through monitoring programme design.

3 Measurement of nitrate-N using UV-visible spectroscopy

This section provides a brief overview of the principle of nitrate-N measurement and then explains measurements by UV spectroscopy. Measurement interferences, algorithms applied in different water matrices and sensor path length are all discussed, along with instrument precision and accuracy.

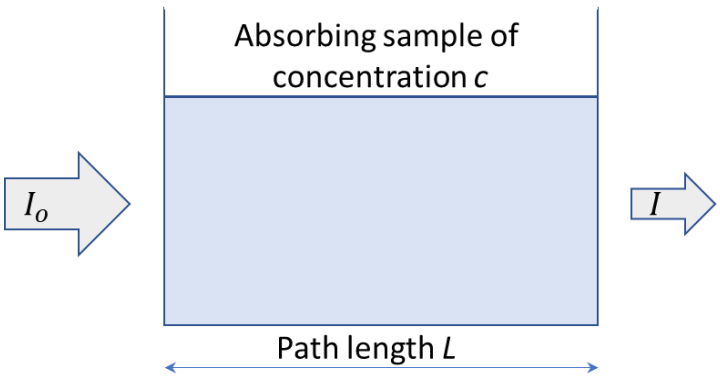
3.1 The measurement principle

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

$$\mathrm{A} = \varepsilon(\lambda) \times \mathrm{L} \times \mathrm{c}$$

where A is the measured absorbance, $\varepsilon(\lambda)$ is a wavelength-dependent absorptivity coefficient, L is the path length, and c is the analyte concentration.

Consider a solution receiving a beam of light:



Where I_o is the **initial light intensity** and I is the **light intensity** after it passes through the sample.

Measurements are usually made in terms of **transmittance** (T), which is defined as:

$$\mathrm{T} = \frac{I}{I_o}$$

The relationship between A and T is:

$$\mathrm{A} = -\log \mathrm{T} = -\log \frac{I}{I_o}$$

The concentration of an absorbing substance may be obtained by rearranging the previous equations:

$$c = \frac{A_\lambda}{\varepsilon_\lambda \times L}$$

Where c is the concentration of absorbing material, A_λ is the absorbance at a specific wavelength (λ), ε_λ is a constant (the molar absorptivity of the absorbing substance at a specific wavelength λ), and L is the path length.

Absorption instruments can usually display the data as either transmittance, %-transmittance, or absorbance. An 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 working curve that defines the relationship between absorbance and concentration, derived from a series of standards of known concentration.

- If no substances in the solution absorb light of the wavelength of interest, I_o and I will be equal, absorbance will be 0 absorbance units and transmittance will be 100%.
- If high concentrations of substances absorbing light occur in solution (interferents), absorbance will be significant, and transmittance will be less than 100%.
- If a substantial amount of particulate or suspended material is in solution, considerable light scattering and attenuation of the incident light intensity may occur. Absorbance may still be low, but transmittance may be reduced substantially.

The latter two points present challenges to the use of absorbance measurement of any material – there is no guarantee that the absorbance is entirely due to the material of interest, and any suspensoid will reduce or attenuate the light intensity. Both of these factors must be accounted for when measuring the concentration of a substance, including nitrate-N.

3.2 UV spectroscopic analysis of nitrate-N

Nitrate absorbs in the UV region of the electromagnetic spectrum, with peak absorbance at 220 nm. Nitrite-N absorbs strongly as well, but at a slightly longer wavelength. For both forms of oxidised N, the absorption is proportional to the concentration of NO_x^- ions in the water. In natural waters (and particularly in seawater), the peak absorbance occurs as a shoulder on a strong background absorbance signal. Measurement of nitrate-N using UV therefore requires discrimination of a small shoulder peak on a large background signal. There is also a temperature dependence (with absorbance increasing with temperature). As indicated in Section 3.1, interference is possible from dissolved organic materials that absorbs light at the same wavelength, and the presence of particulate materials in the sample, which will attenuate the incident light and decrease instrument sensitivity.

UV spectroscopy has been used for nitrate-N determination in water samples for considerable time (e.g., Bastian et al. 1957; Armstrong 1963), and is described in Standard Methods as "suitable for screening uncontaminated water (low in organic matter)" (e.g. method 4500-NO3-B, APHA-AWWA-WEF 2018)[5]. The occurrence of many potential interferences has promoted use of other measurement techniques, but UV spectroscopy continues to be used for laboratory assessment. Utilisation of the second derivative of the UV spectrum has proved useful (Pons et al. 2017), particularly for samples where the concentration of nitrate-N are greater than approximately 10× that of organic nitrogen (Crumpton et al. 1992).

The relationship between UV absorbance and second derivative and nitrate-N concentration is shown in Figure 3-1 and Figure 3-2 for various sample matrices.

[5] Commonly abbreviated to APHA 4500-NO3-B in New Zealand.

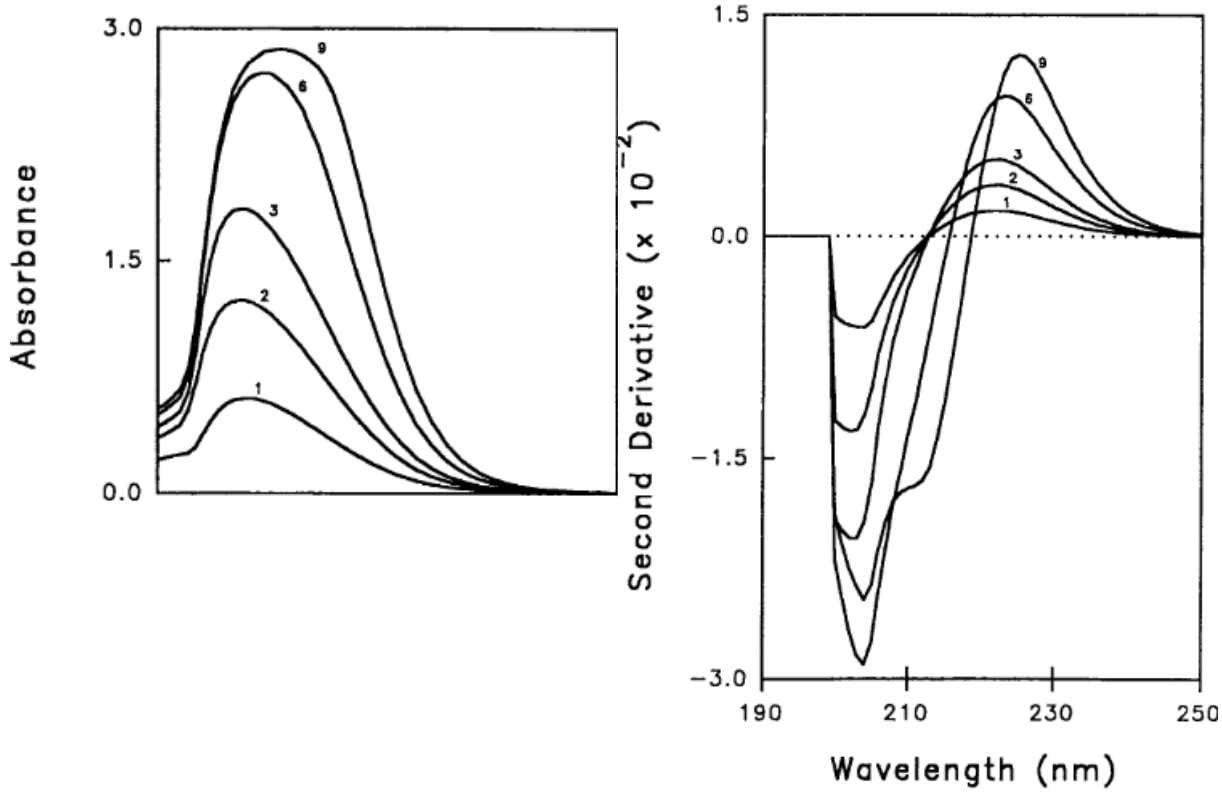


Figure 3-1: Relationship between absorbance (left) and second derivative (right) and wavelength for various nitrate-N concentration. Reproduced from Figure 1 in Crumpton et al. (1992). The curves represent standards containing 1, 2, 3, 6 and 9 mg/L as nitrate-N.

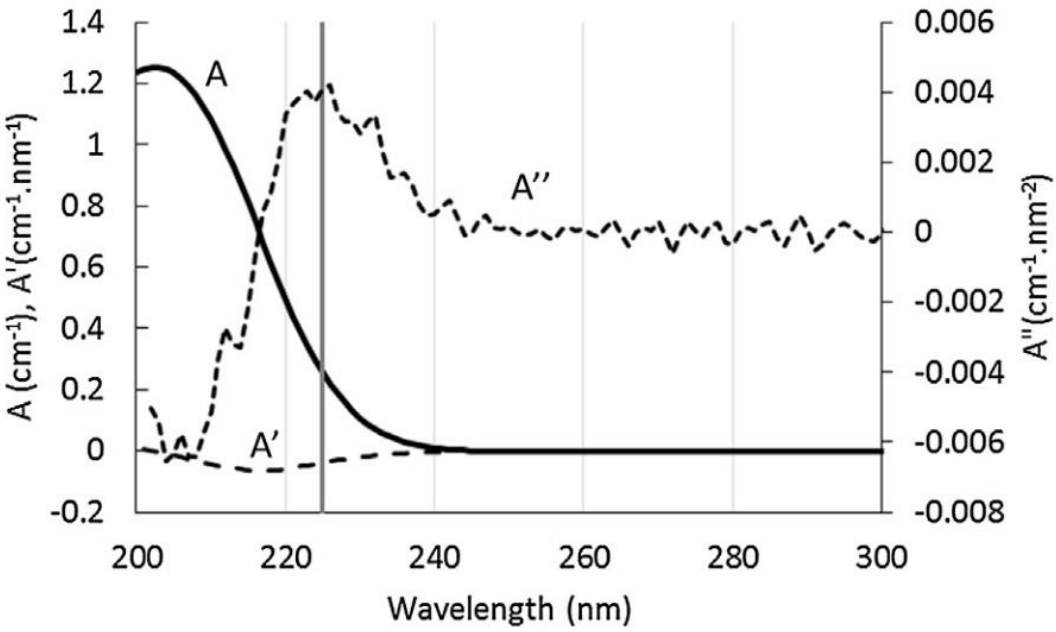


Figure 3-2: Relationship between absorbance (A), first derivative (A') and second derivative (A''), and wavelength for a 2.0 mg/L nitrate-N standard solution. Reproduced from Figure 2 in Pons et al. (2017).

Figure 3-3 shows the relationship between UV absorbance and wavelength for a series of nitrate-N standards, using method APHA 4500-B. A linear relationship is evident for absorbance at 220 nm and nitrate-N concentration (inset).

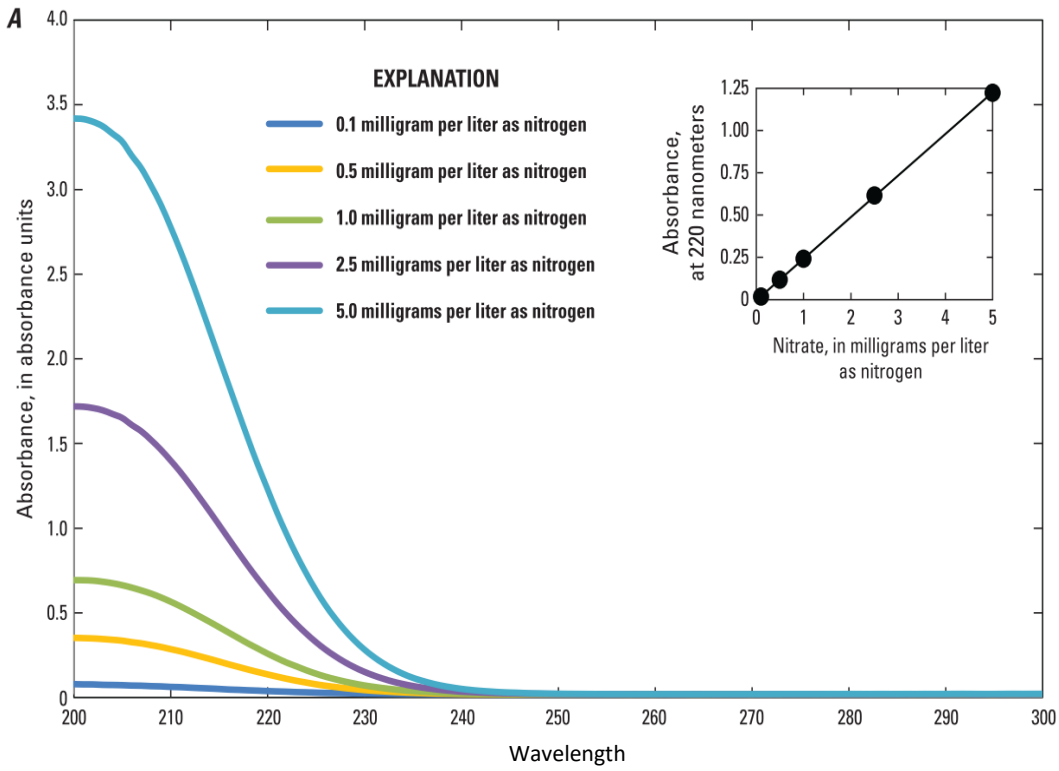


Figure 3-3: Relationship between absorbance and wavelength for a series of nitrate-N standards obtained using method 4500-B of Standard Methods (APHA-AWWA-WEF 2018). Reproduced from Figure 3A in Pellerin et al. (2013).

Figure 3-4 shows the relationship between nitrate-N concentrations reported by a commercial nitrate sensor (Hach Nitratax Plus) and values obtained from laboratory analysis of a series of nitrate-N standards. A strongly linear relationship is evident over a concentration range from 0 to 12 mg/L. The Hach instrument uses dual beam technology and a 5 mm light pathlength. The measuring range is 0.1-25 mg/L as N (the total of nitrate-N plus nitrite-N). Bennett et al. (2014) describe how these instruments are used as part of the suite of continuous water quality sensors in Kansas, USA.

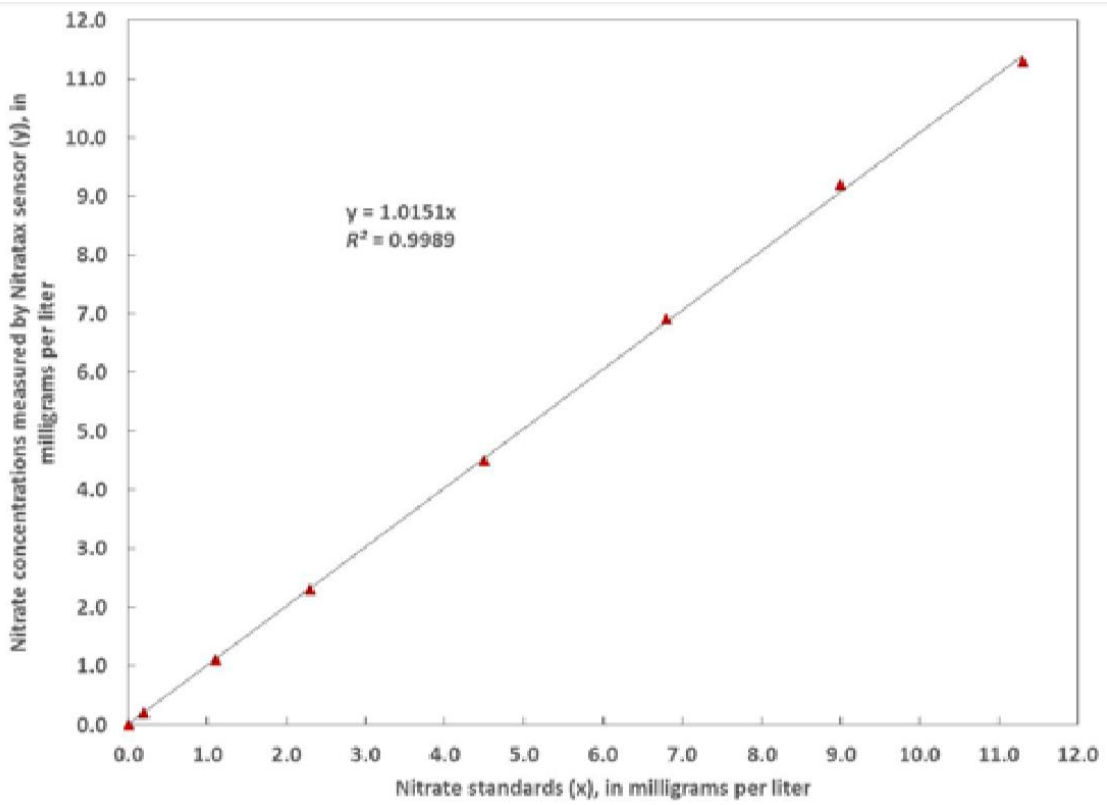


Figure 3-4: Relationship between nitrate-N concentrations measured using a Hach Nitratax Plus sensor and laboratory measured nitrate-N standards. Reproduced from Figure 16 in Bennett et al. (2014).

Proprietary algorithms supplied by instrument manufacturers are used to compensate for two principal interferences on measured nitrate-N concentrations – particulate materials (which attenuate light by absorbance and reflection), and light absorbance by other dissolved substances. These interferences are discussed next.

3.2.1 Interference by particulate materials

Figure 3-5 illustrates the effect that particulate materials (suspensoids) have on measurement performance (Pellerin et al. 2013). This figure shows results for two instruments with different pathlengths (2 mm (Hach Nitratax) and 10 mm (Satlantic SUNA), used to measure a solution containing 1.0 mg/L nitrate-N and increasing amounts of suspended silt, which increases the turbidity. The Nitratax measures two wavelengths (220 and 350 nm) and incorporates a reference beam, whereas the SUNA measures over a wavelength range from 190-370 nm, and does not have a reference beam. Both instruments incorporate an algorithm that compensates for interferences.

- Both instruments demonstrate increased reported concentration of nitrate-N as the turbidity increases.
- The dual-wavelength instrument appears less able to compensate for the increased light scattering at lower turbidity:
  - A turbidity of 100 NTU appears to have increased the reported nitrate-N concentration by 10%, rising to 20% when turbidity exceeds 300 NTU.

- Once the thresholds of approximately 100 NTU and 300 NTU are exceeded, the reported nitrate concentration appears reproducible.
- The shorter pathlength (Hach Nitratax instrument) reduces the light attenuation caused by particulates, allowing the instrument to provide estimates of nitrate-N in highly turbid water (up to 850 NTU).

- The range of measured wavelengths and the algorithm used by the SUNA instrument provided similar and reasonably accurate nitrate-N estimates over a wider turbidity range (0-2000 NTU) – i.e., is better able to compensate for light attenuation by particulate materials
  - The SUNA instrument appears to inadequately compensate for turbidity when <200 NTU.
  - The instrument is less able to compensate for increasing turbidity once a threshold of 350 NTU is exceeded – 10% increase in reported nitrate-N at 350 NTU, and approximately 12% increase at 450 NTU.
  - The longer light path allows for greater light attenuation, reducing light transmission to below the measurement threshold at approximately 500 NTU.

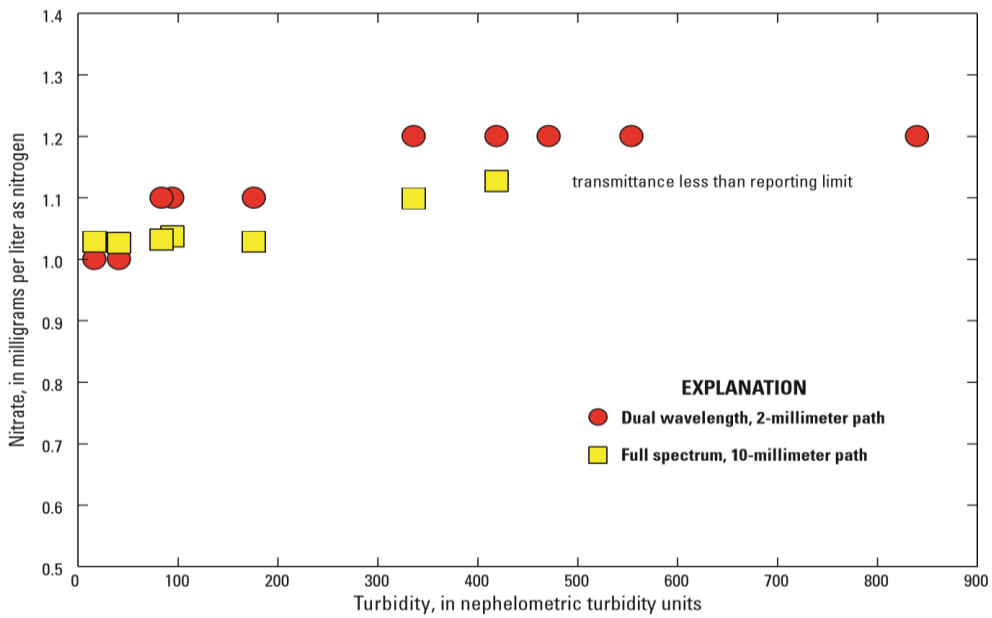


Figure 3-5: Effect of particulate material on nitrate-N concentration for 1.0 mg/L solution containing suspended silt. Reproduced from Figure 12 in Pellerin et al. (2013). Data obtained from dual wavelength Hach Nitratax, 2 mm pathlength (red dots) and full UV spectrum Satlantic SUNA 10 mm pathlength (yellow squares). Transmittance was less than reporting limit for the 10 mm pathlength instrument at approximately 450 NTU.

Similar results have been obtained in a series of laboratory trials conducted recently in the NIWA Hamilton Water Quality Laboratory.[6] These results are currently being reviewed in conjunction with the local instrument representative and will be documented in an internal NIWA report during 2019.

[6] Greg Olsen, Stephan Heubeck, James Sukias, Mike Crump and Neale Hudson. Unpublished results obtained from NIWA SSIF projects FWWQ1823 and FWWQ1909. These trials involved use of four Spectra::lyser devices, manufactured by s::scan.

3.2.2 Interference by Dissolved Organic Carbon

The same Hach and Satlantic instruments were used to assess the effect of dissolved organic carbon (DOC) on measured nitrate-N concentrations. These data are summarised in Figure 3-6:

- The full spectrum (and associated algorithm) provided by the SUNA instrument provides reasonably consistent estimates of nitrate-N over a wide DOC concentration range (increasing from 0.9 to 1.0 mg/L nitrate-N as DOC increased from 0 to 25 mg/L).
- The two wavelength Nitratax instrument failed to compensate for increasing DOC once a threshold of approximately 2.0 mg/L DOC was exceeded, showing an almost ten-fold increase in sensitivity to DOC than the SUNA instrument.
- The algorithm used by either instrument appeared to over-compensate for DOC at low nitrate-N and DOC concentrations.
- The linear relationship between measured nitrate-N and DOC by the Nitratax instrument potentially allows for post-measurement compensation, but would require water samples to be analysed for DOC.

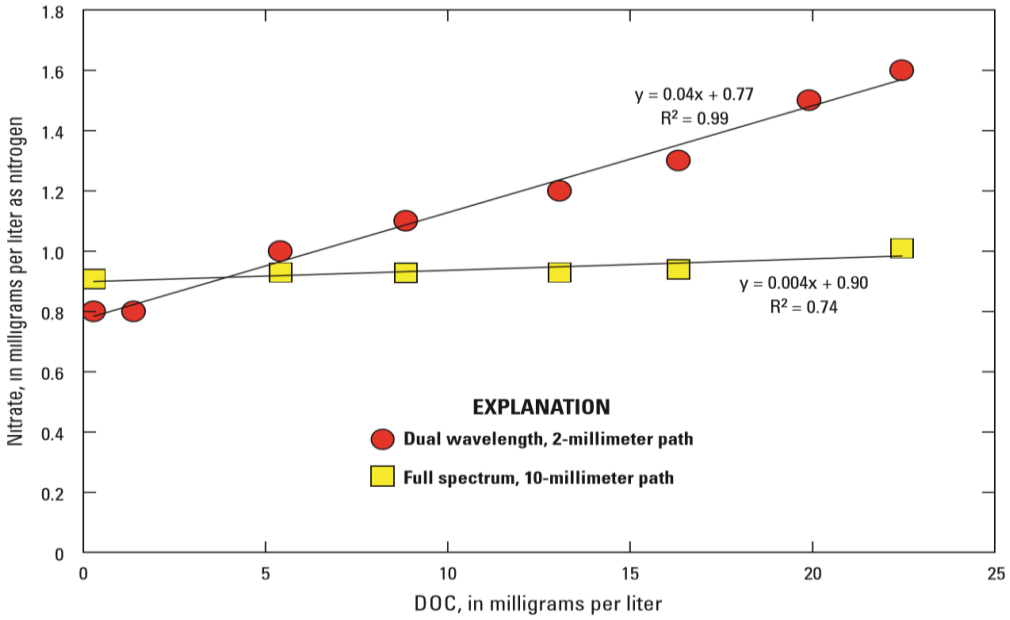


Figure 3-6: Effect of DOC on nitrate-N concentration for 1.0 mg/L solution containing increasing amount of humic substance. Reproduced from Figure 9 in Pellerin et al. (2013). Data obtained from dual wavelength Hach Nitratax, 2 mm pathlength (red dots) and full UV spectrum Satlantic SUNA 10 mm pathlength (yellow squares).

Similar results have been obtained in a series of laboratory trials conducted recently in the NIWA Hamilton Water Quality Laboratory.[7] These results are currently being reviewed in conjunction with the local instrument representative and will be documented in an internal NIWA report during 2019.

[7] Greg Olsen, Stephan Heubeck, James Sukias, Mike Crump and Neale Hudson. Unpublished results obtained from NIWA SSIF projects FWWQ1823 and FWWQ1909.

3.2.3 Selection of compensation algorithm

Some instrument manufacturers supply several user-selectable algorithms to improve calibration and quantification of nitrate-N in various sample matrices. Figure 3-7 demonstrates the effect that selection of an inappropriate algorithm may have on measurement accuracy. The algorithms represent three very different sample matrices:

- The drinking water calibration is intended for clean waters having low turbidity, and low DOC concentrations – it is not intended to compensate for significant DOC concentrations. The algorithm does not compensate for DOC, reflected as a linear increase in apparent nitrate-N concentration as the DOC concentration is increased.
- The wastewater ("influent") calibration is intended to compensate for both turbidity and elevated DOC concentrations. The algorithm over-compensates for DOC once a threshold of approximately 2.0 mg/L DOC is exceeded.
- The river water calibration is intended to compensate for turbidity and moderate DOC concentrations, which it does tolerably well (R^2 0.74).

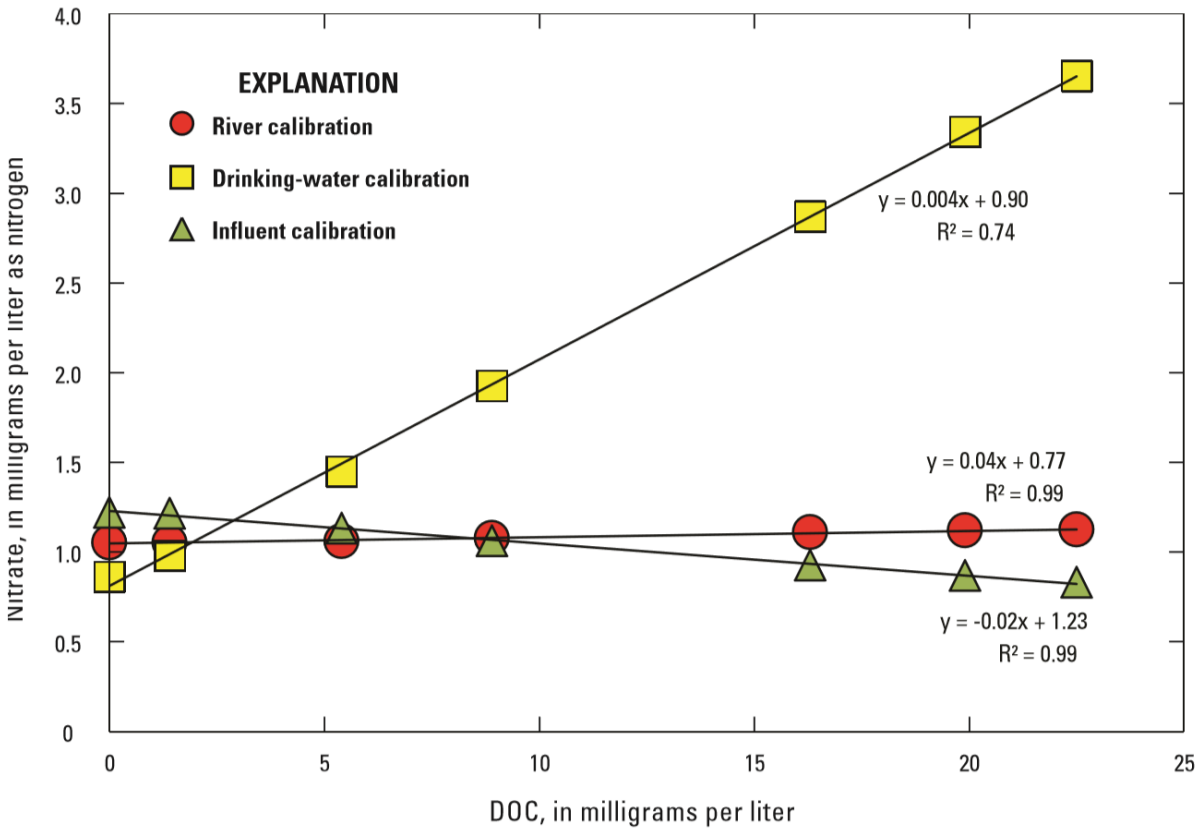


Figure 3-7: Effect of selected compensation algorithm on reported nitrate-N concentration for 1.0 mg/L solution containing increasing amount of DOC. Reproduced from Figure 10 in Pellerin et al. (2013). Data obtained from dual wavelength s::can Spectra::lyser with 5 mm pathlength after application of three calibration algorithms. Note that the equations associated with the relationships above appear to be incorrect – this is being queried with the report authors.

In recent field and laboratory trials conducted by NIWA, several difficulties were encountered with interferences such as particulates and high total nitrogen concentrations in one particular stream water (Matahuru Stream inflow to Lake Waikare, Waikato Region). Very poor correlation between s:scan Spectra::lyser estimates of nitrate-N and grab sample nitrate-N were observed. These results are currently being reviewed in conjunction with the local instrument representative. It is unclear currently what the source of the problem was, but it appears to be related to several factors, including: instrument calibration, zero adjustment, and selection of light pathlength, and dissolved and particulate interferences in a very unusual (humic-rich) sample matrix. The outcomes of this work will be documented in an internal NIWA report in 2019.

3.2.4 Sensor path length

Figure 3-5 demonstrated the effect that pathlength may have on measurement of nitrate in various natural waters. Quantification of nitrate-N requires sufficient light to be transmitted through the water sample to the sensor. Excess suspensoids reduce light transmission and can limit the measurement of nitrate-N in samples with elevated turbidity. Because nitrate itself absorbs light strongly in the UV spectrum some indication of the likely range of nitrate-N concentrations should be determined before purchasing and deploying a sensor. This would allow selection of an appropriate sensor and path length. Figure 3-8 provides a series of curves indicating the relationship between transmittance and nitrate-N concentration for five pathlengths. These values are derived from Beer's law, and should be considered indicative – they do not account for other matrix effects, such as suspensoids concentrations. The figure indicates the trade-off between detection limit and measurement range:

- If stream concentrations are low, and low nitrate-N values are to be quantified accurately, a longer path length will be required, but this will limit the measurement range – for example, a 35 mm pathlength will probably over-range at concentrations greater than 15 mg/L (this will effectively be the upper limit of quantification).
- If a wide measurement range is required, accurate quantification during periods of low concentrations will be compromised – a larger proportion of results less than the measurement threshold will be obtained.
- If measurement over a wide concentration range is required, and accuracy at low concentration is required, it may be necessary to deploy two instruments. If the concentration ranges are strongly related to season, it may be possible to match instruments to the seasonal conditions, swapping short- and long pathlength instruments at appropriate times in an annual monitoring programme.

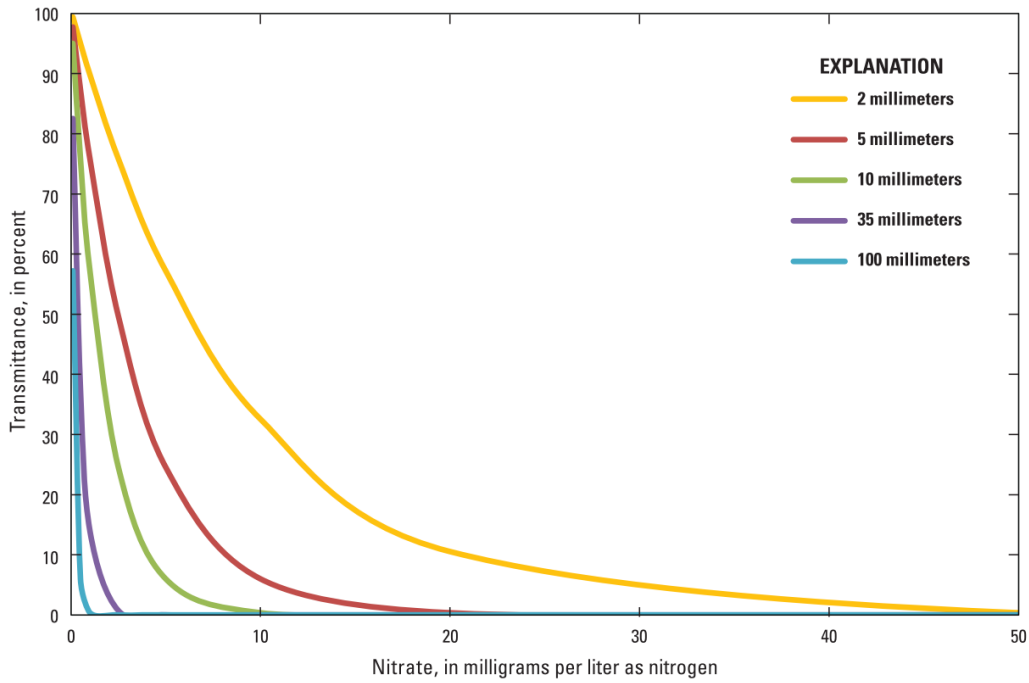


Figure 3-8: Theoretical relationship between transmittance and nitrate-N concentration according to sensor pathlength. Reproduced from Figure 7 in Pellerin et al. (2013).

Information regarding pathlength and measurement range is available from several instrument manufacturer websites. A table of values for the TriOS OPUS device is provided in Figure 3-9.

Parameter	Measurement principle	Unit	Factor	path length [mm]						
				0.3	1	2	5	10	20	50
absorbance	spectral	AU**	-	0.01...2.2	0.01...2.2	0.01...2.2	0.01...2.2	0.01...2.2	0.01...2.2	0.01...2.2
absorbance	spectral	1/m	-	50...7300	15...2200	7.5...1100	3...440	1.5...220	0.75...110	0.3...44
Nitrate N-NO3	spectral	mg/L	-	1.0...330	0.3...100	0.15...50	0.06...20	0.03...10	0.015...5	0,006...2
Nitrate NO3	spectral	mg/L	-	4.43...1460	1.33...440	0.67...220	0.27...88	0.13...44	0.067...22	0.030...9
Nitrite N-NO2	spectral	mg/L	-	1.7...500	0.5...150	0.25...75	0.1...30	0.05...15	0.025...7.5	0.01...3
Nitrite NO2	spectral	mg/L	-	5.6...1650	1.65...500	0.82...250	0.33...100	0.17...50	0.083...25	0.033...10
DOCeq	spectral	mg/L	-	17...3300	5.0...1000	2.5...500	1.0...200	0.5...100	0.25...50	0.1...20
TOCeq	spectral	mg/L	-	17...3300	5.0...1000	2.5...500	1.0...200	0.5...100	0.25...50	0.1...20
CODeq	spectral	mg/L	-	100...7300***	30...2200***	15...1100***	6.0...440***	3.0...220***	1.5...110***	0.6...44***
BODeq	spectral	mg/L	-	100...7300***	30...2200***	15...1100***	6.0...440***	3.0...220***	1.5...110***	0.6...44***
KHP	spectral	mg/L	-	17...13300	5.0...4000	2.5...2000	1.0...800	0.5...400	0.25...200	0.1...80
SAC254	Single wavelength	1/m	-	50...7300	15...2200	7.5...1100	3.0...440	1.5...220	0.75...110	0.3...44
COD-SACeq****	Single wavelength	mg/L	1.46	75...10600	22...3200	11...1600	4.4...640	2.2...320	1.1...160	0.44...64
BOD-SACeq*****	Single wavelength	mg/L	0.48	24...3500	7.2...1050	3.6...525	1.44...210	0.72...105	0.36...52.5	0.15...21
TSSeq*****	Single wavelength	mg/L	2.6	130...4300	40...1300	20...650	8.0...260	4...130	2.0...65	0.8...26

Figure 3-9: Relationship between pathlength and measurement range for several water quality variables for the TriOS OPUS instrument. Reproduced from the TriOS website https://www.trios.de/en/opus.html.

Recent laboratory trials conducted in the NIWA Hamilton Water Quality Laboratory identified that it is essential to understand the instrument response to nitrate-N over a wide concentration range – this includes the algorithm and reported concentration. For example, it was identified that a revision to the software used in the s::scan Spectra::lyser device caused the instrument to report apparent nitrate concentrations over a wide concentration range. These were observed as an "inverted U" – reported nitrate concentrations increased in response to increasing nitrate-N concentrations until the upper limit of quantification was reached, but thereafter, reported nitrate concentrations decreased in response to continuing increase in actual nitrate concentration in solution. The previous versions of the software would alert the user to this phenomenon, whereas the current version of software fails to do so, continuing to provide apparent nitrate concentrations that are incorrect. As a consequence, it is possible to obtain a reported nitrate-N concentration at two different actual nitrate-N concentrations.[8] This is not an instrument malfunction or failure – it should be regarded as a software-imposed limitation. It highlights the importance of thoroughly understanding the measurement principle, the nature of interference, and the instrument-specific algorithms that are used to compensate for interferences. Using these instruments as a "black-box" could lead to recording spurious or inaccurate data. The NIWA results are currently being reviewed in conjunction with the local instrument representative and will be documented in an internal NIWA report during 2019.

3.2.5 General comments

In-situ continuous measurement of nitrate-N has been used for considerable time (e.g., Finch et al. (1998)). The issues outlined above are to some extent overcome using several different techniques: use of several wavelength signals to compensate for interference from particulate and dissolved organic material, by temperature compensation (mainly for sea waters, owing to effect on bromide interference) (Langergraber et al. 2003; Sakamoto et al. 2009; Caradot et al. 2015; Uusheimo et al. 2017), and by development of alternate calibration algorithms (Etheridge et al. 2014a; Etheridge et al. 2014b; Lepot et al. 2016).

From the material presented above and in other technical literature, caution is required when selecting and using in-situ sensors. All waters have different spectral properties, and more or less compensation may be required. Work done at NIWA using the Spectra::lyser devices has demonstrated the need for caution when calibrating an instrument. Care is required to ensure that the blank water is of sufficient optical purity, and it is important to ensure that the calibration algorithm is appropriate. A "Global calibration" file is supplied with the instrument, in addition to the other calibration files referred to in Figure 3-7. It is unwise to assume that the "Global calibration" file is appropriate for all natural waters, or indeed for a single river or stream under all seasonal conditions, until successfully demonstrated. Techniques such as standard additions[9] allow some of these measurement issues to be resolved, but a good understanding of the strengths and weaknesses of the technique is required to ensure that one source of error is not replaced with another (Ellison and Thompson 2008).

[8] Greg Olsen, Stephan Heubeck, James Sukias, Mike Crump and Neale Hudson. Unpublished results obtained from NIWA SSIF projects FWWQ1823 and FWWQ1909.
[9] E.g., "Standard additions - Royal Society of Chemistry" www.rsc.org/images/myth-reality-technical-brief-37_tcm18-214868.pdf

3.3 Instrument precision and accuracy

Instrument precision and accuracy are subject to several factors, including electronic noise and matrix effects. Unless the instrument develops a fault, electronic noise is largely out of the control of the operator. Should a fault develop, erratic behaviour such as transient spikes, failure to record or generate a signal, or substantial drift over time may occur. These faults require expert attention from a qualified service agent or the manufacturer.

Errors associated with matrix effects may however be managed and addressed by the operator. When determining precision and accuracy, it is important to remember how these are evaluated by the manufacturer. Typically, they are determined under ideal conditions, using samples and standards created with ultra-high purity water and reagents, measured under stable, ideal conditions, and with minimal interferences from the matrix. Often precision and accuracy are estimated using nitrate-N concentrations well within the potential measurement range of the sensor. In reality, sample concentrations are measured in environmental samples where nitrate concentrations may vary widely, and where the matrix is subject to continual subtle or substantial variation over various time scales. The measurement principle makes it essential to account (as far as possible) for light absorbing and light scattering materials. These dissolved and particulate substances interfere with transmission of light from the source to detector. The instrument design, components and software used to measure nitrate-N attempts to minimise these matrix effects.

The discussion in section 3.2 (and sub-sections) identified several factors that should be considered before sensor selection and deployment, and during operation. Recognising and addressing these factors will help ensure that data of adequate accuracy and precision are collected.

4 Sensor selection, deployment and maintenance

Evaluation of the performance of specific instruments is not within the scope of this report. Considerable resources have been used by the USGS to identify factors that should be considered prior to purchasing and deploying nitrate sensors, and once data acquisition is in progress. Several publications are available that summarise the outcomes of detailed assessment of field and laboratory trials, which include comparison of the performance of several instrument types.

The USGS has invested heavily in continuous nitrate sensors, and several readily accessible texts have been have published that provide useful guidance regarding instrument selection, typical performance in laboratory and field situations, and collection and management of time-series data generally, and hyperspectral analysers specifically. Key points from several reports are listed Table 4-1, and some are discussed in detail in later sections.

Table 4-1: Useful reference and guidance materials that should be considered by anyone wishing to undertake continuous monitoring using a nitrate sensor. These reports are available on the USGS website at https://www.usgs.gov/products/publications/official-usgs-publications.

(Snazelle 2015; Snazelle 2016)	Equipment from several different manufacturers were assessed in laboratory and field situations. Non-linear response with concentration was observed, and the effects of temperature (minor), turbidity and dissolved organic matter were observed. The importance of applying data correction protocols was stressed. For all instruments tested, proprietary algorithms addressed the effects of turbidity increase on measured nitrate-N better than effects related to dissolved organic matter concentrations. Accuracy specifications were used to identify trends or drift in sensors as a response to changes in sample matrix.
(Bergamaschi et al. 2017)	Use standard operating procedures to ensure consistency of data collection, instrument operation and sample collection, handling and analysis. Use these procedures to ensure that suitably trained staff conduct field and office activities consistently over time, and across the team.
	Examine incoming data daily; establish normative ranges; determine whether data falls with defined ranges. For burst sampling, estimate the reproducibility of data within the burst (assess coefficient of variability against predetermined criteria). Compare results from nearby stations to determine whether changes or shifts in data are due to sensor drift or malfunction. Collect grab water samples on each visit to provide points against which high frequency time series data may be “anchored’. Use automatic sampler samples to validate instrument performance over hydrological events, periods of high constituent variability etc.

	Implement techniques for infilling missing data or correcting data that are obviously erroneous. This may include use of other continuously-measured water quality variables, such as electrical conductivity, water temperature and solar radiation. For this to be meaningful, it is essential that strong relationships be demonstrated between covariant water quality variables. An example of suitable techniques include those demonstrated by Smith (2018). Collect adequate metadata – this includes site information, and details regarding the equipment used for surveys or deployed at a specific location. Independent auditing of site operation and data allows systematic errors to be detected, and also provides an opportunity for review of the fitness for purpose of the programme to provide the required information.
(Wagner et al. 2006)	General principles applicable to all continuous water quality monitoring sensors, specifically site selection and sensor placement, and data review, evaluation and correction procedures.
(Pellerin et al. 2013)	Developed specific techniques for deployment, operation and data quality assurance. Identified the trade-off between sensitivity, accuracy and concentration range over which measurement is possible. Useful definitions provided: **Accuracy:** the degree of agreement between measured nitrate-N and the true value. This is pathlength, instrument noise and matrix dependent. **Precision:** the range or scatter of results provided by the instrument when making repeated measurements of the same sample under the same conditions. These measurements may occur within a short space of time, or over a period. **Measurement range:** the difference between greatest and least measurable value. No single instrument is able to measure across the 0-100 mg/L range identified by manufacturers for the continuum of pathlength setup/sample matrix. Range is principally dependent on pathlength. **Detection limit:** the lowest value measurable for a given sensor/pathlength combination at 99% confidence level. Detection limit is principally dependent on pathlength, detector sensitivity and instrument noise. True detection is determined through instrument specific calibration and repeated measurement.

	Resolution: the minimum difference between measured values reported by the instrument. **Matrix effects:** constituents in the sample that absorb or scatter light, interfering with light transmission to the detector. **Instrument performance:** the net effect of combined influences defined above; best determined through measurement of standards and spiked matrices before deployment and after servicing.
(Bennett et al. 2014)	Provides an example of a quality assurance plan developed to guide staff within a specific jurisdiction. Describes the standards, policies and procedures used for the collection, processing, storage, analysis and release of continuous water quality data. Addresses requirements such as health and safety considerations, staff training and data correction procedures. Several appendices are included that provide detailed instructions in appropriate cleaning and calibration processes. Examples of records that should be considered for collection and storage are also provided.

Chapter 5 Section D, "Water Quality" of Book 1, "Collection of Water Quality by Direct Measurement" (Pellerin et al. 2013) is a very useful guidance document. It is accessible on the USGS website[10], and all prospective and current users are directed to this document.

The National Environmental Monitoring Standards (NEMS) website[11] should also be consulted – standards have been published for continuous dissolved oxygen[12], water temperature and turbidity, and they identify and address very similar criteria to those relevant to use of nitrate sensors. The requirement for Standards for several other water quality variables suitable for continuous measurement has also been identified, and as these Standards are developed they will assist with activities such as selection, calibration and operation of nitrate sensors.

4.1 Sensor selection

The section "Sensor selection" of Pellerin et al. (2013) is informative. A series of questions are provided to guide the process – the key ones are:

1. What is the expected range of environmental conditions at the site?
2. What data specifications for nitrate-N concentration at the site exist?
3. What site requirements and logistical considerations exist?

These questions should be relatively easy to answer using currently available information, and information and statements regarding the purpose of monitoring that have been gathered. Table 3 of Pellerin et al. (2013) identifies specific water quality characteristics that should be assessed when

[10] https://pubs.er.usgs.gov/publication/tm1D5
[11] http://www.nems.org.nz/
[12] http://www.nems.org.nz/assets/Documents/NEMS-15/Dissolved-Oxygen.pdf

selecting the measurement solution – it has potential to be converted into a flow chart that could aid decision making.

Pellerin et al. (2013) reminds prospective users that unique criteria and considerations may apply at each site, and these need to be addressed in a site-specific manner. This may extend to bypassing, revising and adding to the "out of the box" tools provided with the hardware.

4.2 Instrument performance verification – pre-deployment activities

Pellerin et al. (2013) recommend that equipment performance should be verified prior to deployment. This includes visual inspection on receipt, recording serial numbers, ensuring that cables, peripherals and connectors are undamaged. The sensor windows deserve special attention, because damage to them will impair any subsequent measurement.

Operation of the equipment should be assessed in a laboratory or other controlled environment. Key steps include:

1. Measuring the "nitrate" concentration in air and in suitable quality water. High quality "spectrally pure" water is required for this purpose. If required, zero the instrument.
2. Using a range of suitable standard solutions similar to those likely to be measured in the river(s) of interest:
    i. Ensure a linear measurement performance over the range of concentrations expected on site.
    ii. Assess the accuracy of the measurement – the difference between the standard concentration and the instrument reported concentration (expressed as absolute or proportional (%) difference) – "sample accuracy".
    iii. Assess the precision of measurement from the standard deviation of the difference between known and measured concentrations of a standard solution ("analytical precision").
3. Compare the values from step 2 with those provided in the manufacturer's specifications, and remedy deviations as required.
4. Repeat steps in 2) using representative samples of water from the intended deployment site to which known amounts of nitrate-N have been added (matrix spikes).
    i. Analysis of these samples provides recovered "sample accuracy" and "sample precision".
    ii. Care should be taken to maintain particulate material in suspension, and to monitor turbidity over the duration of the measurement.
    iii. Spiked matrix samples should be discarded daily, to minimise the effects of biological activity.
5. Where elevated turbidity and/or DOM is likely, the spiked matrix samples should be further modified to represent the particulate and DOM concentrations likely at the site. Instrument performance should be verified in response to these sample matrix changes as well.

4.3 Instrument deployment

Stable sites that represent the water of interest are essential. The principles and techniques outlined by Wagner et al. (2006) regarding deployment of other continuous sensors may be transferred to nitrate sensors as well. The NEMS for Dissolved Oxygen and Turbidity measurements are other useful references.

Infrastructure requirements that should be considered for safe and reliable operation of equipment follow. Several of these are illustrated with photographs in Appendix H and Appendix I.

Suitable scaffolding, channel, and conduit for keeping the sensor and associated cables in place in a secure manner, but without altering the site characteristics or hindering measurement, and without impairing future sensor recovery, inspection or calibration. These requirements need to be assessed on a case-by-case, site-specific manner, but with regard to general in-situ water quality monitoring principles.

Pumped vs in-river deployment of sensors, and when should an out-of-channel deployment be considered?

Preventing fouling and obscuring of the sensor optical windows requires specific attention. Wiper units may be mounted on the sensors to clean windows and remove detritus. Air jets may be used to remove deposited materials as well. Mounting the sensor so that the optical windows are vertical, and underneath the sensor body will minimise deposition on the windows, or adherence of air bubbles on the windows themselves.

The choice of automatic cleaning device requires careful consideration. Should the stream or river contain significant suspended sediment load, use of compressed air for cleaning may not be appropriate. It is possible that entrainment of particulates with the compressed air could cause the optical windows to be “sand-blasted”, causing physical abrasion to the glass. This would cause serious damage to a key component of the optical measurement system, leading to drift, inaccuracy, and shortening of the instrument life. These problems are far less likely when a mechanical brush or wiper is used to remove detritus or biofilm.

Transfer of data – proprietary software and specific controllers and hardware may be required, which could potentially complicate data transfer. The distance of the sensor from the logger will under some circumstances determine cable length, type and signal type (analogue or digital).

Power requirements – some equipment was designed for process monitoring and control, and meeting power requirements in the field may prove challenging. Power requirements will be determined on a site-by-site basis, according to measurement frequency, requirement for ancillary devices and controllers (e.g., solenoid valves for cleaning, wipers, pumps to provide water to sensors located out of the river channel etc.).

Data collection frequency – nitrate sensors allow high frequency measurement, analogous to other water quality sondes. The ability to collect data at high frequency does not however necessitate high frequency data collection. Unless very short duration or transient changes in nitrate concentration need to be assessed, there is little benefit in collecting data at high frequency. This is discussed in the three case studies presented in subsequent sections. Once again, useful guidance is available from the NEMS (specifically the DO measurement document, which recommends that data are collected at 15-minute frequency), and (Pellerin et al. 2013; Chappell et al. 2017). Burns et al. (Burns et al. 2016) provide an example of uses of high-frequency data, and demonstrate how optimal

measurement frequency may be determined. Their work describes daily nutrient dynamics in detail. Generally, this level of understanding exceeds the requirements of resource managers, but if such information is required, it is probably better obtained using fixed-duration, dedicated deployment campaigns.

Pellerin et al. (2013) differentiate between sampling interval (the time between discrete measurements), and the reporting interval (the time between individual data points stored in an archive). It is recommended that data are collected in "burst mode", where several measurements are recorded at high frequency over a finite period of time, which are then averaged to provide a reported value. The discrete data recorded during the "burst" may be used to assess uncertainty of the reported value, or emerging problems arising from window fouling and lamp deterioration.

The reporting interval will be a compromise between excessively frequent measurement and loss of information. The latter should be defined in a monitoring programme design document. Excessive measurement increases power requirements, and shortens the lamp life.

4.4 Maintenance

General principles regarding maintenance of other equipment deployed in rivers should be considered. Some of the experiences of practitioners are included in Appendix H and Appendix I, which should be read in parallel.

1. **Frequent review of data** retrieved from the field is recommended. Daily inspection of nitrate-N sensor data, or automated assessment of the record to detect obvious performance issues is essential. This will assist in early identification of sensor problems, including fouling, damage or failure, as illustrated in Appendix J.

2. **Collect validation samples.** These are submitted to a laboratory for independent assessment of nitrate-N concentrations.

3. **Field maintenance of sensors** includes site and instrument inspection, cleaning (including removal of deposited minerals, if necessary). The frequency of inspection may be determined principally by budget constraints, but should also have regard for historical issues, which may indicate that more or less frequent inspection is required. The workshop discussion indicated that monthly inspection appears adequate for larger rivers, but in smaller streams with lower flows, more frequent inspection and cleaning may be required (illustrated in Appendix J). Site inspection activities should include measurement of field blanks and calibration samples, and collection of grab samples for laboratory analysis. In the case studies presented later in this document, validation samples were typically collected monthly to coincide with routine SoE discrete water sampling or site maintenance, with additional samples collected using autosamplers to target specific rainfall events. Pellerin et al. (2013) identify several steps that should be considered for inclusion with site inspection protocols (refer to Appendix H through Appendix J).

3.1 **Site inspection** – examination of the site, river channel, infrastructure, etc. Pay specific attention to changes in water level relative to instrument depth, light levels and other factors that will directly affect sensor measurements.

3.2 **Collect field readings** with another suitably calibrated instrument of the same make and model, preferably located adjacent to the installed instrument for a period of time. If this is not possible, collect a sample for laboratory measurement using similar equipment.

3.3 **Collect a field measurement with the fixed sensor** prior to cleaning and calibration. If nitrate-N concentrations are variable, collect a sample in a large container for measurement before and after cleaning.

3.4 Remove the sensor from the measurement location.

3.5 **Inspect the sensor for signs of damage**, lens scratching and fouling, etc. Take photographs as required. Specifically assess:

i. Fouling, staining and scratching of optical windows.

ii. Damage to seals around windows.

iii. Damage to the sensor housing.

iv. Damage to wipers or compressed air ports.

v. Damage to cables, compressed air lines, etc.

vi. Evaluate the efficacy of in situ cleaning (e.g., air sparging or automated wipers) and note whether chemical staining is evident or if chemical cleaning is required.

vii. In out of channel configurations, inspect the pump and associated cables and piping, as well as the flow-through chamber. In some environments, particulate clogging and abrasion of pumps and impellers may require attention.

3.6 **Clean sensors** – optical windows should only be cleaned with soft-bristle brushes or lint-free lens paper. Dilute hydrochloric acid may be used for chemical cleaning (minerals), and ethanol may be used for removal of organic contaminants. The sensor must be rinsed with water, distilled water and high purity water for subsequent checks. Wipers and ancillary devices should also be cleaned, taking care to only use cleaning agents that will not damage components.

3.7 **Perform fouling check** – measure nitrate concentrations after replacing the sensor in the river, or using a sample collected earlier (step 2.2 above). Where necessary, these measurements may be used to make adjustments for fouling (e.g., Wagner et al. (2006), or other suitable procedures).

3.8 **Perform a baseline calibration check** (particularly important for single channel instruments) – this will require removal of the instrument, and measurement of a sample of water of suitable quality spiked with nitrate. Prior to such measurement, the instrument must be rinsed thoroughly with optically pure water to ensure matrix effects are minimised. During measurement, ensure bubbles are absent from the windows and that stray light is minimised. Baseline checks must be done with uncontaminated water. If the baseline is corrected, take additional readings with optically pure water to ensure that a new blank falls within the specified criteria.

3.9 **Check response linearity** – where appropriate and necessary, the instrument may also be checked to ensure a suitably linear response to nitrate concentration. This would be done using a series of nitrate standards prepared in optically suitable water. Where linearity is not as expected, spiked matrix samples could be used, but these would generally be measured in the laboratory.

4.5 Data processing

Existing council water quality monitoring procedures probably could be expanded to include the evaluation and processing of data derived from nitrate-N sensors, including additional steps where

necessary. Experience gained from processing data derived from continuous DO and turbidity sensors should be instructive. Where staff lack experience, the processes documented by Wagner et al. (2006) are likely to be informative.

Two key activities are:

- **Fouling and drift correction** (to account for step changes etc., arising from cleaning sensors after a period of gradual deposition or fouling by biological materials).
- **Bias correction** – likely to arise from interferences in natural waters. Several criteria guide appropriateness of bias correction:
  - The error must be systematic (i.e., in one direction, and not random).
  - Adequate numbers of results are available to allow meaningful comparisons.
  - The relationship between the two data sets must be strong (R^2>0.8).
  - The slope of the regression line should be close to 1 (0.9-1.0), or the variation across the range of nitrate-N concentrations may be accounted for.

Pellerin et al. (2013) provide examples of data sets where the assumptions underlying bias correction are broken. In these circumstances, other measures may be required to improve the quality of data.

4.6 Reporting codes

The water quality variable or parameter code or description should be explicit in several areas:

- Whether the value is nitrate-N or nitrate- plus nitrite-N (this will be determined by the algorithm used).
- That the data were collected by in-situ measurement (i.e., a sensor deployed in the river, or supplied with a continuous flow of pumped river water).
- Whether the units are concentration of nitrate (NO_3^-), or nitrate-N (where nitrate-N = NO_3^-/4.42 mg/L)

4.7 Final data evaluation and review

The procedures followed by Pellerin et al. (2013) for nitrate sensors are based on general USGS methods (Wagner et al. 2006), and exceed those recommended in the NEMS for DO measurement (NEMS 2016). In particular, Pellerin et al. (2013) recognise that the trade-off between pathlength, accuracy and measurement range make it important to use instrument "accuracy ratings" to evaluate the performance of individual instruments, and when comparing data derived from various instruments. Accuracy ratings reflect the combined correction of bias, fouling and drift. Values suggested by Pellerin et al. (2013) are summarised in Table 4-2.

Table 4-2: Accuracy ratings derived from fouling, drift and bias correction applied to discrete samples. The sensor accuracy may be manufacturer specifications, or user-calculated values. After Pellerin et al. (2013).

Accuracy rating	Specification
Excellent	within sensor accuracy limits
Good	±1-3 times sensor accuracy
Fair	±3-4 times sensor accuracy
Poor	±4-6 times sensor accuracy

The reliability of data derived from continuous nitrate sensors is strongly dependent on several factors, some out of the user's control. These factors include: interferences (particulate and dissolved substances - many different materials may interfere, and their absolute and relative concentrations may vary over time), fouling, drift and bias. In addition, the light source is subject to deterioration over time. Acquiring accurate, fit-for-purpose data necessitates addressing all these factors, which in turn requires that adequate quality assurance procedures are put in place.

The NEMS approach to data collection and storage provides a template that may be modified to adequately address the requirements of continuous nitrate sensors. The quality coding approach could also be adopted, with suitable metrics identified to account for accuracy rating and other factors. It would be useful to have regard for materials such as Annex C of the DO NEMS, which relates data quality to calibration and quality assurance effort, making the point that the effort invested needs to relate the quality of data required.

5 Introduction to case studies – data and methods

This section briefly outlines the Otago Regional Council (ORC), Environment Southland (ES) and NIWA nitrate-N data that are evaluated in Sections 6, 7 and 8, respectively. Methods of data evaluation are also outlined.

5.1 Data used

The nitrate-N data evaluated later in this report are summarised in Table 5-1 and are drawn from continuous nitrate-N sensor deployments in Otago and Southland rivers.

ORC installed two TriOS OPUS nitrate-N sensors in September 2016 in the Kakanui River, North Otago, as part of an investigation into increasing nitrate-N concentrations observed in the river over time. Council staff collected manual grab samples for verification and calibration of the continuous data. Three TriOS NICO sensor were installed during July 2017 in the Shag River with continuous conductivity sensor; data will be used in the Shag River groundwater study. After these sensors serve their purpose in these two studies, there are plans underway to relocate them to various other SoE locations. Only data for the Kakanui River sites were considered in this report.

ES has invested in continuous water quality monitoring in several river catchments. Currently TriOS nitrate-N sensors are in place on the lower Aparima and Oreti rivers, with further installations planned for the Makarewa River, the middle reaches of the Oreti River and on the Mataura River at Mataura Island, which represents the lower reaches of the river upstream of tidal influence. The lower river reach sites are “key node” locations that have been identified for measurement to reduce uncertainty in estimation of contaminant loads to sensitive estuarine receiving environments, and to improve confidence when assessing the effectiveness of management actions and policy aimed at reducing contaminant load. Only data for the Aparima River site were considered in this report.

Under its Environmental Information Innovations Programme, NIWA runs two TriOS OPUS nitrate-N sensors on the Mataura River in Southland and a third TriOS sensor on the Hurunui River in Canterbury. The dual Mataura River deployment seeks to provide information on in-situ (i.e., deployed in the river channel) vs out-of-channel (deployed bankside, receiving water pumped from the river) sensor performance. Laboratory validation data derived from monthly grab samples and flow-proportional automatic samples are available for both sensors.

The Kakanui, Aparima and Mataura river data are used in a series of case studies in Sections 6 to 8 to demonstrate various procedures to which continuous nitrate-N data may be subject, and the uses to which the data may be put. Not all procedures were applied to all the data sets, but sufficient work was done to demonstrate the various processes and procedures discussed earlier in this report, as well as providing guidance on how these are carried out. Topics considered include:

- Sampling frequency – how much is enough?
- Sensor biofouling – how do sensor biofouling and cleaning affect nitrate-N measurements?
- Load estimation – what impact does measurement frequency have on load estimates?
- Trend detection – does trend detection benefit from increased sampling frequency?
- Spatial comparisons – what benefit does paired measurement provide?

- In-river vs out-of-channel (pumped) measurement – what are the relative benefits?
- Quality assurance – what do we learn from these case study data?

Table 5-1: Details of high frequency sensors, water quality data and flow measurement at sites in the Otago and Southland regions. Data type descriptions largely provided by contributing agencies.

Agency	Site	Frequency	Data type	Start	End	Comment
ORC	Kakanui at Mill Dam	C	Flow	7/09/2016	2/11/2017	Continuous data at 5 minute frequency
	Kakanui River at Gemmels	G	Nitrate nitrogen Nitrite nitrogen Nitrite/Nitrate nitrogen Suspended Solids (Lab) Turbidity	2/02/2016	20/12/2017	Event-related sampling
	Kakanui River at Gemmels Crossing Bridge	C	Nitrate TriOS Dissolved Organic Carbon TriOS Total Suspended Solids TriOS ABS360 TriOS	7/09/2016	2/11/2017	Continuous data at 5 minute frequency
		G	Nitrate nitrogen Nitrite nitrogen Nitrite/Nitrate nitrogen Suspended Solids (Lab) Turbidity	2/02/2016	20/12/2017	Event-related sampling
	Kakanui at McCones	C	Nitrate TriOS Dissolved Organic Carbon TriOS Total Suspended Solids TriOS ABS360 TriOS Flow	7/09/2016	6/04/2018	Continuous data at 5 minute frequency
		G	Nitrate nitrogen Nitrite/Nitrate nitrogen Suspended Solids (Lab) Turbidity	5/02/2016	18/01/2018	Event-related sampling

Agency	Site	Frequency	Data type	Start	End	Comment
ES	Aparima River at Thornbury	C	continuous flow	1/04/2015	19/04/2018	Continuous data at 10 minute frequency
		C	Nitrate-nitrogen (TriOS OPUS) Turbidity (WTW in-situ) Conductivity (WTW in-situ)	1/04/2015	12/03/2018	Continuous data at 10 minute frequency
		G	Nitrogen (Nitrate Nitrite) Nitrogen (Nitrate) Nitrogen (Nitrite) Turbidity (Lab FNU) Turbidity (Lab)			Event-related sampling
NIWA	Mataura River at Mataura Island	C	Flow Nitrate nitrogen (TriOS OPUS)	17/3/2016	20/3/2018	Continuous data at 5 minute frequency
			Nitrate nitrogen (TriOS OPUS)	17/3/2016	20/3/2018	Continuous data at 5 minute frequency
		G	Nitrate nitrogen Suspended sediment (Lab)	10/8/2016	9/1/2018	Event-related sampling

5.2 Data handling and processing

Data retrieval

For the assessments in Sections 6 and 7, data were retrieved from the Hilltop server at each organisation as an XML file, which was converted at the NIWA Christchurch office into CSV files.

The ES TriOS nitrate-N data were provided in two formats – as a continuous data set, together with flow data and other continuously measured water quality variables, as well as a field within the discrete or grab sample water quality record, matched using the date-time stamp. This facilitated further analysis.

The ORC data were provided as a continuously measured TriOS nitrate-N field within the continuously measured hydrology record. The grab or discrete water quality data were provided in a separate file, and it was necessary to append these data to the continuously measured hydrology data at the corresponding data and time stamp; in some cases manual adjustment of the time of collection was required.

For the assessment of the Mataura River data in Section 8 of this report, data were provided in CSV file format for further analysis. The data files include a NEMS-like quality code (200, non-verified), and approval rating (50).

Data were used “as received”, with one exception. The water quality data received from ORC for the Kakanui River sites were initially supplied without sample times. A second data set was supplied with sample collection times, as well as data for additional water quality monitoring site located a few hundred metres further downstream from one of the original sites.

Initial data processing was undertaken using MS Excel. Steps included:

1. Storing the data as-received from each council on a series of folders in a Raw Data folder.
2. Creating a duplicate data file on a series of folders in a Working folder.
3. In each file, altering the heading row content as required.
4. Creating uniform style and format date, time and date and time fields.
5. Where necessary (for grab samples) replacing censored values (below detection limit data) with half the detection value.
6. Creating additional date and time fields in numeric and text formats to meet other software requirements, and to ensure that importing and exporting data into and out of other software did not corrupt dates and times.
7. Selecting and matching specific data from the continuous flow file with the intermittent, more random frequency grab water quality sampling data using the VLOOKUP function within MS Excel.
8. Merging separate data files (grab sample water quality) with continuously measured data files using the facilities within Systat v13.

    8.1 In some cases, it was necessary to revise the sample time field to ensure the grab water quality result could be matched with a TriOS measurement. For example, the time of collection of the grab water quality sample from the Kakanui River at Gemmels Crossing Bridge on 6/5/2016 was 09:18. This value cannot be directly matched with a corresponding TriOS nitrate-N value – the nearest values were 09:15 or 09:20.

    8.2 In this specific instance the collection time was altered to 09:20 using an Excel rounding function, which then allowed the grab water quality record to be aligned with the TriOS nitrate-N and hydrology record.

    8.3 This was done for each water quality sample where required (fewer than five per site).

9. If necessary, exporting data back to Excel for use as input files to specialist modelling software. Microsoft Excel pivot tables were useful for two reasons:

    9.1 They allowed calculation of hourly average data “on the fly”.

    9.2 They provided a convenient method for eliminating duplicate rows that were generated either during retrieval from the data archive, or during conversion of the XML file to a CSV file. For example, the modelling tool used (LOADEST) is limited to hourly or less frequent data – to use this tool, a pivot table was

used to generate hourly average flow and water quality values (for continuous and grab sample data), which were then assessed.

10. Selecting specific files and repeating earlier actions to ensure that key steps led to repeatable outcomes.

11. Throughout all of the above processes, maintaining a record of actions.

One of the challenges of dealing with high frequency time series data is the size of data file. Data were collected at five-minute intervals. For the Kakanui River at McCones site for example, a fifteen-month period comprised more than 240,000 rows of data. For most purposes, hourly average or even daily average data appeared adequate. For much of this assessment (Section 6.1), hourly average data were used.

Care was required when merging grab water quality data files with the hydrology and TriOS time series data. Use of a date-time value field of the form YYYYMMDDhhmm was a useful check to ensure that dates and times aligned correctly during the merge process.

YYYYMMDD and hhmm fields are also required for LOADEST load calculations, described briefly in Section 5.4.

Data gaps were not filled – this is a task that is associated with standard hydrological practice. In some cases, techniques may have to be developed for this requirement. For the purposes of this report, these gaps had negligible impact on the outcomes, or were retained to indicate why they should be repaired.

5.3 Graphical and statistical summaries

All figures and summary statistics were prepared using Systat for Windows, v13.

5.4 Load estimation

Three basic methods were used for load estimation:

- For grab samples, instantaneous load was calculated as the product of concentration in the sample and the streamflow at the time of sampling, expressed as mass/unit of time; for this report, all load estimates were reported as kg/d.

- A similar process was followed for TriOS nitrate-N concentration values, which were multiplied by the corresponding flow value to provide instantaneous, hourly or daily load estimates (the latter using Excel pivot table functionality).

- LOADEST, an open source modelling tool produced and maintained by the USGS (Runkel et al. 2004):

"LOAD ESTimator (LOADEST) is a FORTRAN program for estimating constituent loads in streams and rivers.

Given a time series of streamflow, additional data variables, and constituent concentration, LOADEST assists the user in developing a regression model for the estimation of constituent load (calibration). Explanatory variables within the regression model include various functions of streamflow, decimal time, and additional user-specified data variables. The formulated regression model then is used to estimate loads over a user-specified time interval (estimation). Mean load estimates, standard errors, and 95 percent confidence intervals are developed on a monthly and(or) seasonal basis. The calibration and

estimation procedures within LOADEST are based on three statistical estimation methods. LOADEST output includes diagnostic tests and warnings to assist the user in determining the appropriate estimation method and in interpreting the estimated loads.

In specific cases, simple regression techniques were used to provide yield estimates to cross-check the results derived from the other techniques.

The load estimates were provided as a time-series for the extent of the flow record. These data were used to assess the seasonal characteristics of nitrate-N loads, and the relationship between contaminant load and flow during specific hydrological conditions, such as during base-flow, during seasonal flood events, and over discrete 'flood' events.

No attempt was made to fill in any missing data.

6 Case study 1: ORC Kakanui River data

As outlined in Section 5, the Otago Regional Council (ORC) deployed TriOS nitrate-N sensors in the Kakanui River at Gemmels Crossing Road and (downstream) at McCones in 2016. The deployments were made to investigate the influence of nitrogen-rich groundwater entering the river downstream of Gemmels Crossing, with groundwater considered the likely reason for increasing trends observed at a long-term SoE site at McCones. This SoE site has been sampled at monthly intervals for many years. A time series of grab nitrate-N concentrations for the McCones site, and grab sample concentrations from two other sites, are shown in Figure 6-1. Although the record is discontinuous for two of the three sites, a general increase in nitrate-N concentrations over time is evident. The record also indicates periodic high concentration episodes, such as in the mid-1990s and in the early 2000s.

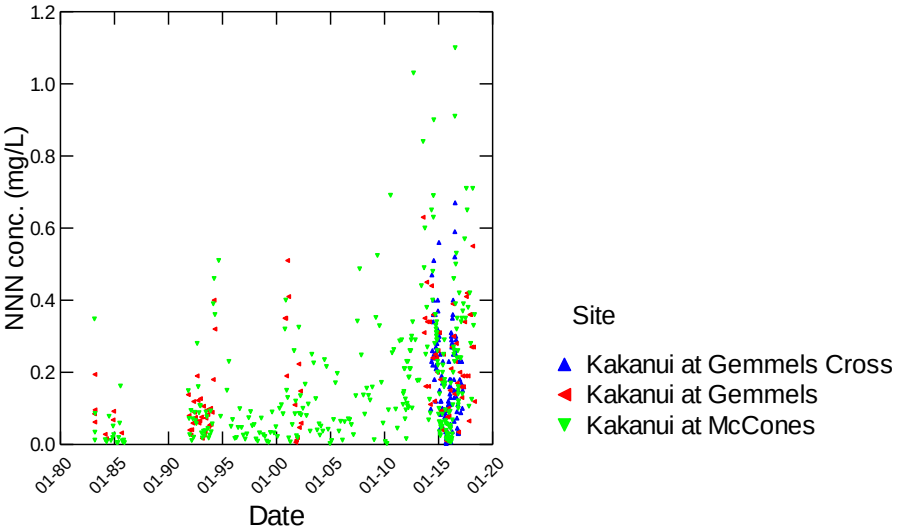


Figure 6-1: Time-series of NNN concentration at three SoE sites on the Kakanui River. Additional details associated with these data are shown in Table 5-1.

Figure 6-2 shows the annual median nitrate-N concentration over the entire data period, where the increasing concentration is still evident (note the *y*-axis has a $\log_{10}$ scale). The right-hand figure suggests an increase in nitrate-N concentrations during the period the TriOS devices were deployed as well.

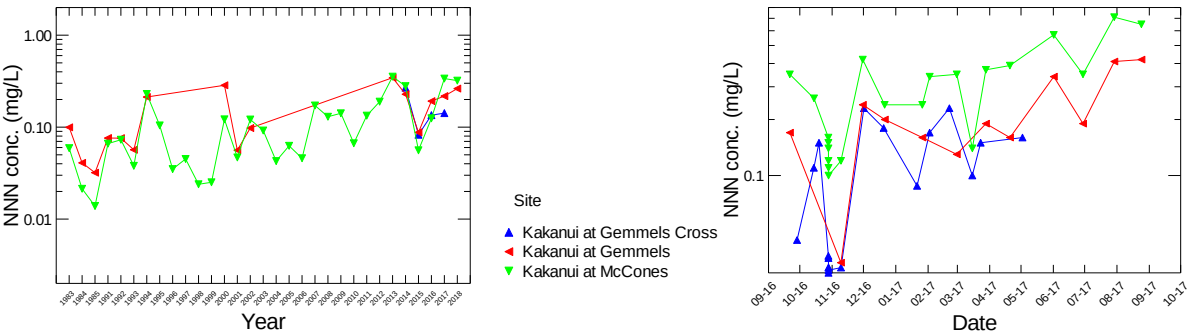
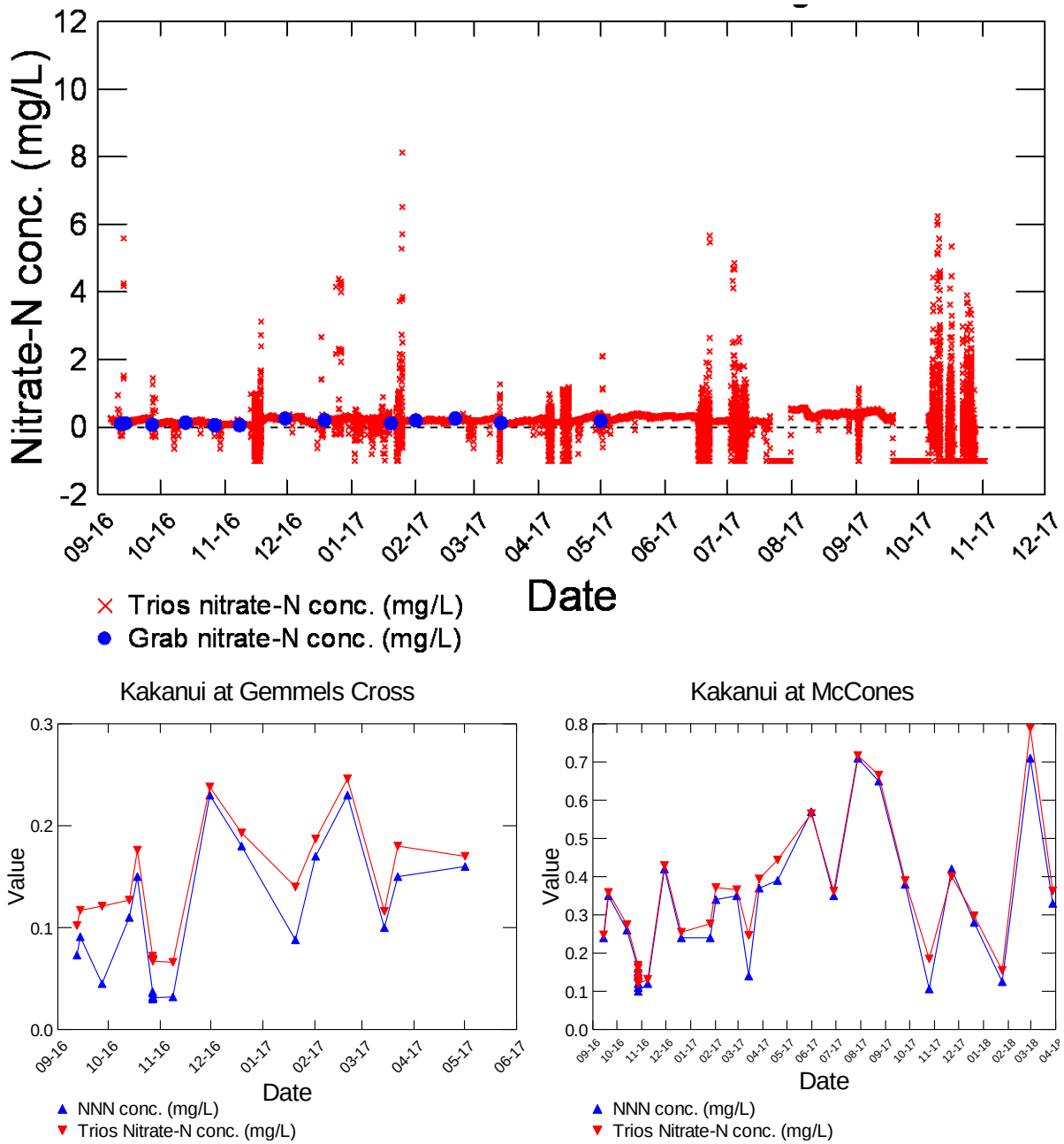


Figure 6-2: Nitrate-N concentration at three sites on the Kakanui River. Left: Annual median values, Right: Grab sample concentrations for the more recent period corresponding to the TriOS deployment period. Note *y*-axis has $\log_{10}$ scale.

In Figure 6-3 the grab sample concentration is compared with the TriOS concentration recorded at the corresponding time for each site. In general, the grab sample record corresponds tolerably with that of the TriOS estimates. Poorer relationship is evident during periods of low nitrate-N concentration, particularly at the Gemmels Crossing Road site between September to November 2016. The later period of the Gemmels Crossing record also indicates deterioration in the TriOS data quality with increasing periods of values less than 0 mg/L. Fewer negative values are observed for the McCones site, suggesting a site-specific issue at the upstream Gemmels Crossing site.

The relationship between grab sample results and TriOS estimates are explored further in Figure 6-4.



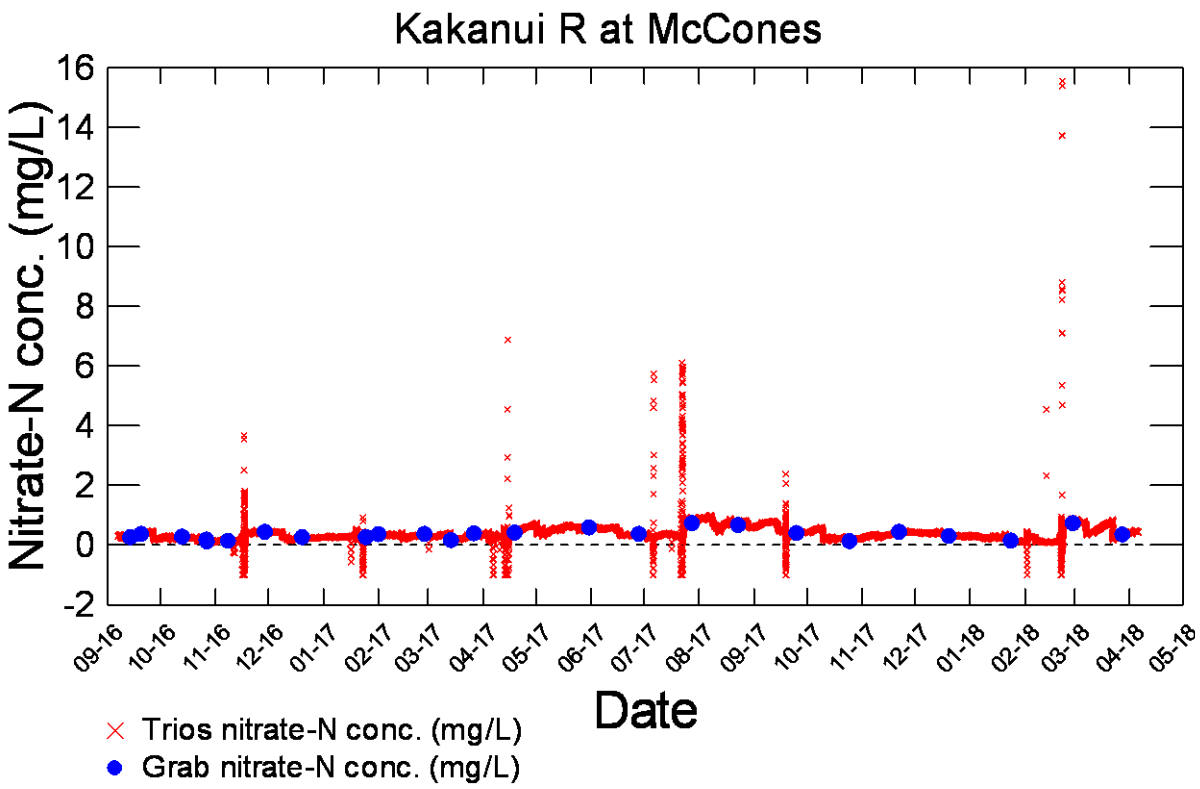


Figure 6-3: Relationship between grab sample nitrate-N concentration and TriOS sensor results over time (left), and difference between measurements and grab sample concentration (right). Note *y*-axis has $\log_{10}$ scale.

The data summarised in Figure 6-4 indicate that the TriOS sensor tends to over-predict nitrate-N concentrations at both sites. Non-parametric models (Appendix A) applied to these data indicate a high adjusted-R^2 value for both sites (0.994 and 0.997 for the Gemmels Crossing and McCones sites, respectively). The residuals plots show few outliers, and reasonably random and even distribution of residuals, indicating a robust relationship.

Figure 6-4 A) indicates the difference between the two measurement techniques. At both sites the difference between the two measurements tends to be greatest at lowest grab sample concentration. At the McCones site the difference ranged from approximately 15% to almost 43%, and the median difference was 6%, whereas at the Gemmels Crossing site the difference ranged from approximately 4% to almost 63%, and the median difference was 25%. However, the two data sets are quite different because:

- All grab sample nitrate-N concentrations at the Gemmels Crossing site were <0.25 mg/L, whereas for the McCones site, 0.25 mg/L represented the 40th percentile (i.e., 60% of data exceeded 0.25 mg/L).
- For the Gemmels Crossing data that exceeded 0.1 mg/L (the lowest grab sample concentration reported for the McCones site), the difference between grab and TriOS values was less than 20% – very similar to the differences observed at the McCones site.

The above results suggest that the practical limit of quantification requires consideration.

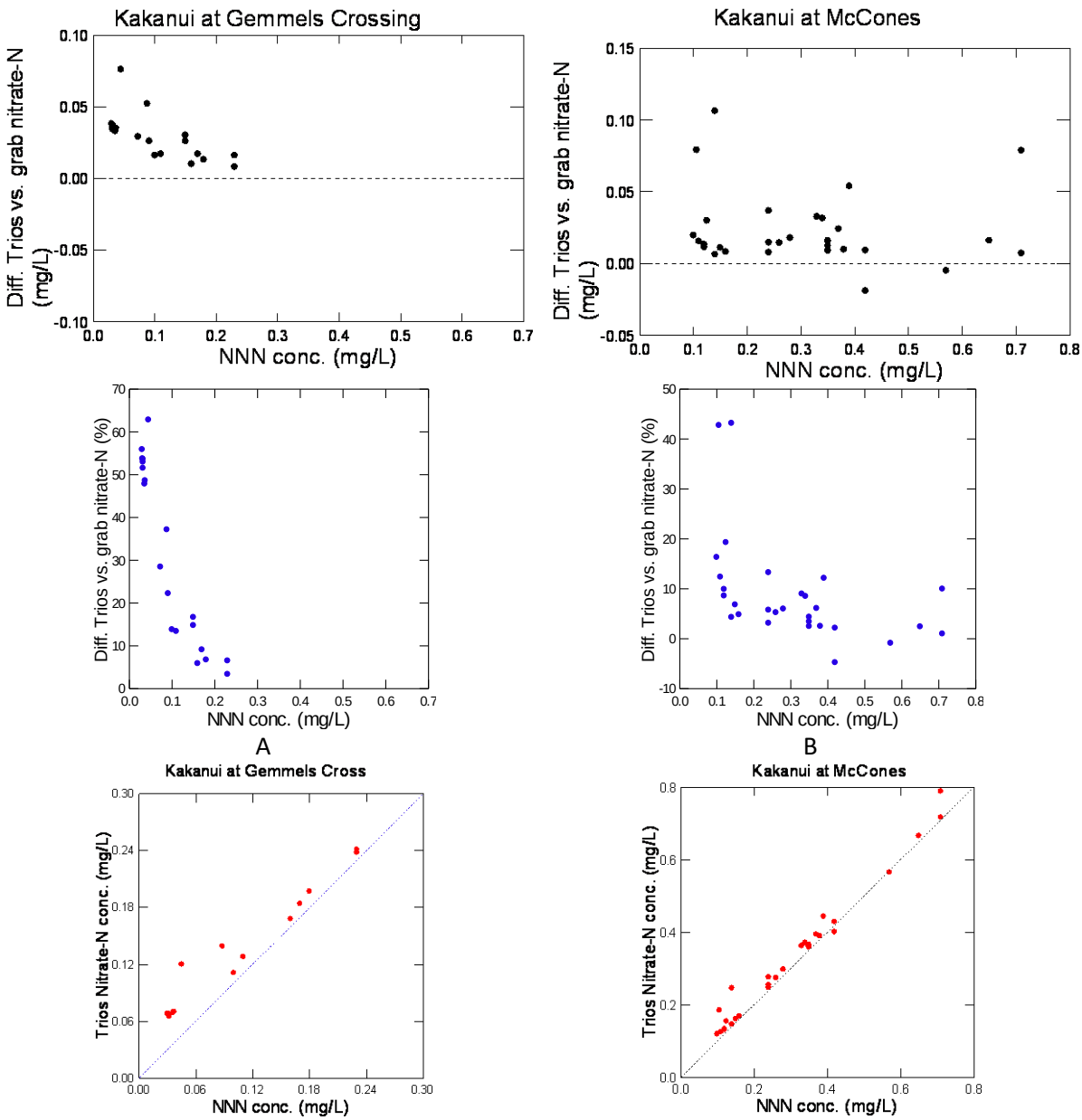


Figure 6-4: Relationship between grab sample and TriOS sensor nitrate-N concentrations for two sites. The top row indicates the absolute difference between TriOS estimates and grab sample results, the second row show the difference between TriOS estimates and grab sample results as a proportion of the grab sample estimate, and the third row shows a regression of TriOS estimates against grab sample results, where the black dotted line indicates the 1:1 relationship.

6.1 Kakanui River at McCones site

Data for the McCones site were selected for more detailed assessment. The time series of flow, grab sample nitrate-N concentrations and TriOS measured nitrate-N concentrations for the period September 2016 to April 2018 are summarised in Figure 6-5. There are several features to note:

- The period of record contains several periods of flood- and stable flow.
- There are several transient spikes in the TriOS nitrate-N data (both positive and negative).
- There are several events where an apparent step-change in TriOS sensor response occurred – some step changes appear to be related to flow events (e.g., November 2016, April 2017), but others of similar magnitude (June 2017, July 2017, February 2018) occur in periods of stable flow.
- Several manual sensor-cleaning events occurred.

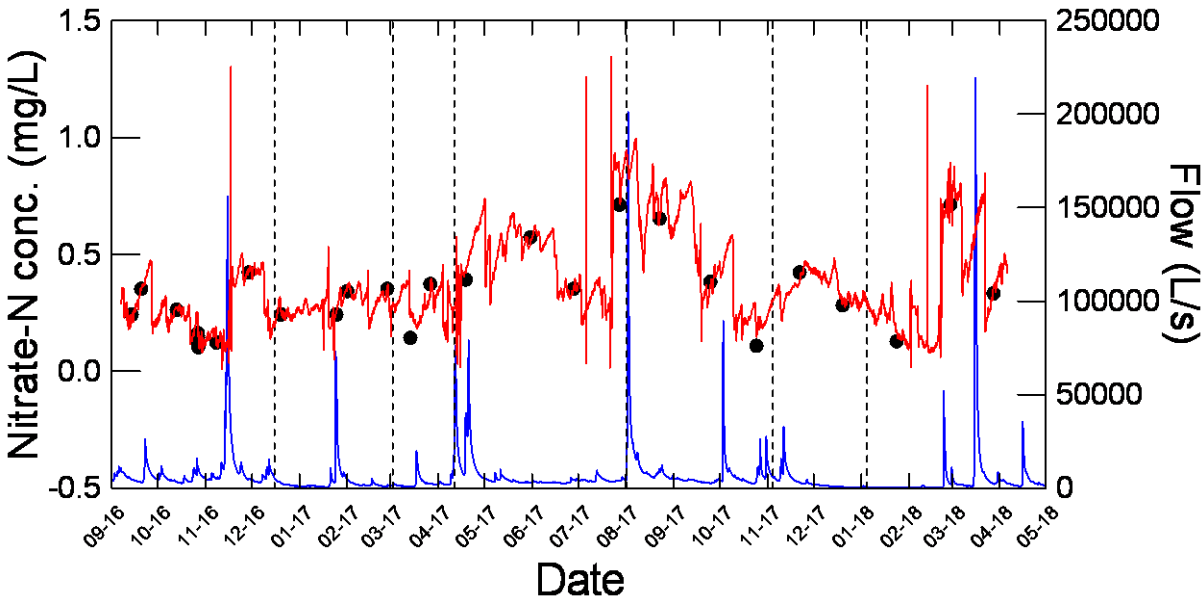


Figure 6-5: Time series of grab sample nitrate-N (black dots), hourly average TriOS sensor concentrations (red line) and river flow (blue line). The vertical broken lines indicate sensor cleaning events.

6.1.1 Flow-concentration relationship

Figure 6-6 highlights the very large difference between the number of grab samples and TriOS sensor estimates of nitrate-N concentration. It is difficult to determine the nature of the discharge-concentration relationship from the limited number of grab samples available (concentrations vary by an order of magnitude, whereas discharge varies by approximately three orders of magnitude). The tenuous relationship between concentration and discharge is also evident in the TriOS sensor results. These results confirm however that nitrate concentrations generally fall within a range from 0.1 – 1.0 mg/L unless flow exceeds approximately 80-100,000 L/s. Load estimation using a model that regresses available grab sample concentration values against flow is likely to have considerable uncertainty because of the poor correlation.

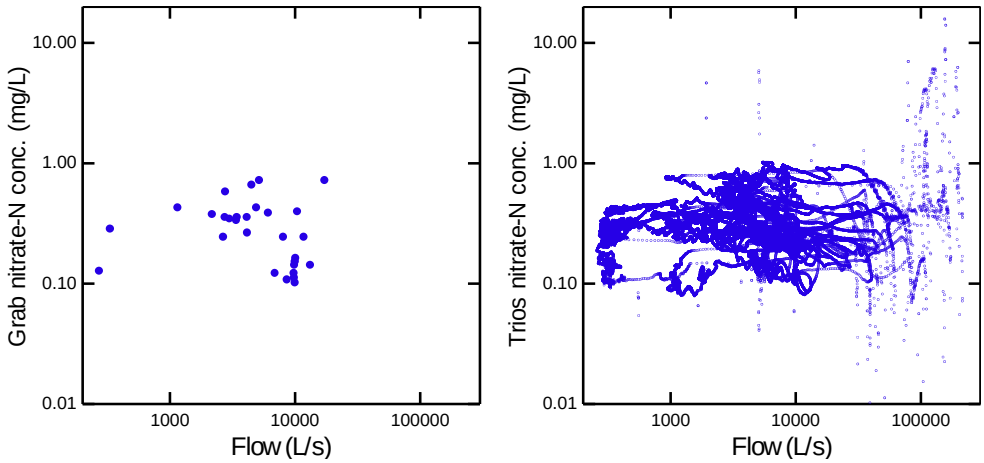


Figure 6-6: Relationship between grab sample concentration and flow (left), and TriOS sensor estimate and flow (right).

6.1.2 Effects of manual cleaning

Manual cleaning of the sensor (indicated by the vertical broken lines in Figure 6-5, as well as in detail for two cleaning events in Figure 6-7) suggest that cleaning had minimal effect on the quality of the data, i.e., the automatic cleaning of the device prevented build-up of material that could attenuate light, degrade the optics and impair measurement. Physical obstruction of the light path or change in the matrix during cleaning (i.e., removal of the device from the water column) caused transient spikes at the time of cleaning, but there is no sign of an offset or discontinuity in the record arising from the cleaning activity itself.

Comparison of the five-minute and hourly average data in Figure 6-7 also suggests that there is little visual difference in the measured values as a consequence of averaging; the transient spike caused by the cleaning itself is still evident in the hourly average data.

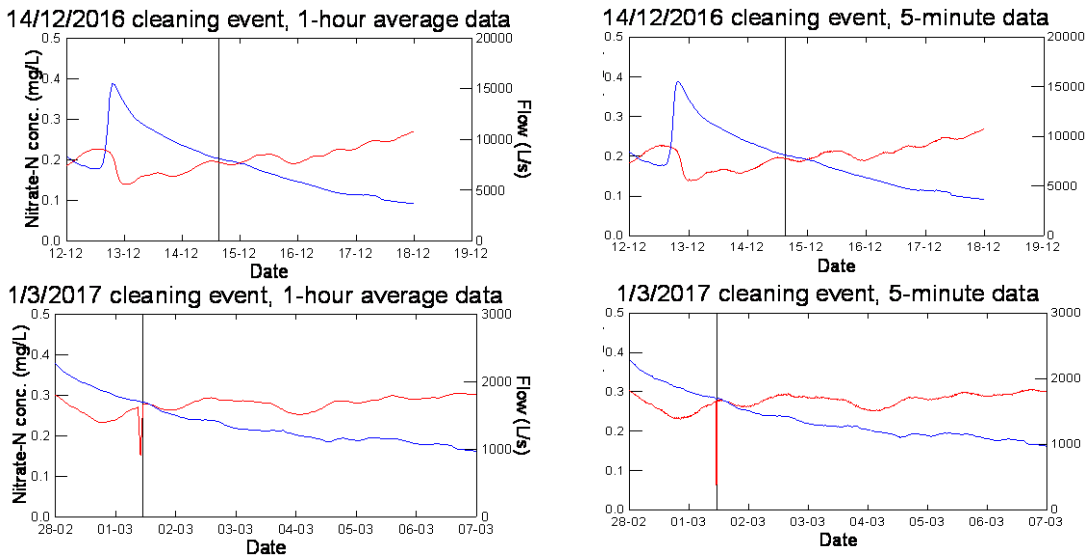


Figure 6-7: Time series of grab sample and TriOS sensor nitrate-N concentrations and river flow (blue line) for two representative cleaning events. The vertical broken lines indicate sensor cleaning events. The left-hand graphs use one-hour average data, and the right-hand graphs show the original data collected at five-minute intervals.

6.1.3 Transient spikes

Figure 6-5 shows several positive spikes in TriOS nitrate-N concentration, and more negative spikes. Most of the latter are less obvious because this figure uses hourly average data. Figure 6-8 shows the relationship between instantaneous nitrate-N and flow, for nitrate-N concentrations >1 mg/L or <0 mg/L, respectively. Although "spikes" may occur over the entire concentration range, there is a greater tendency for these to occur under higher flow conditions. Most TriOS values >1.0 mg/L occur above a flow threshold of approximately 80,000 L/s, whereas TriOS nitrate-N values <0 mg/L tend to occur during flows <30,000 L/s.

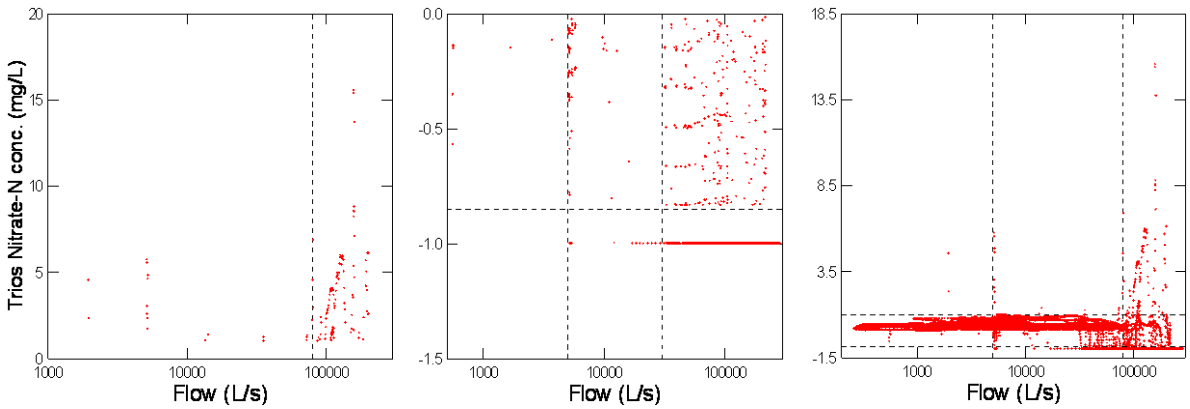


Figure 6-8: Relationship between TriOS sensor nitrate-N concentrations and river flow for categorised data. The panel on the left presents nitrate-N concentration >1 mg/L and the dashed vertical line indicates 80,000 L/s., The middle panel presents nitrate-N concentrations <0 mg/, where the dashed horizontal line indicates -0.85 mg/L and the vertical dashed line indicates 5,000 and 30,000 L/s respectively. In the right panel, all data are presented and the vertical dashed lines indicate 5,000 L/s and 80,000 L/s respectively.

As Figure 6-8 indicates, the overwhelming bulk of measurements do not comprise apparent "spikes". From Figure 6-5 it appears that nitrate-N concentrations greater than approximately 1 mg/L could potentially be regarded as spikes. There are 138 five-minute time periods in the record where the 1 mg/L threshold is exceeded (0.08% of the record). As indicated in Figure 6-9, these values occur in seven discrete "events", extending over periods between 10 min and approximately 10 hours. It is not clear whether the spikes are a consequence of material partially obscuring the sensor's light path, or over-ranging of the sensor (exposure to nitrate-N concentrations that exceed the measurement range of the sensor/path length combination), or a combination of these and other factors.

Values <0 mg/L represent 0.98% of all measurements, and as Figure 6-9 demonstrates, these values occur within approximately 14 events. Figure 6-9 indicates that these transient events occur infrequently, have common characteristics and are therefore likely to be manageable – either during data collection, or post collection, using conventional quality assurance/data cleaning procedures. Following data cleaning, these data are unlikely to have significant impact on subsequent water quality assessment activities.

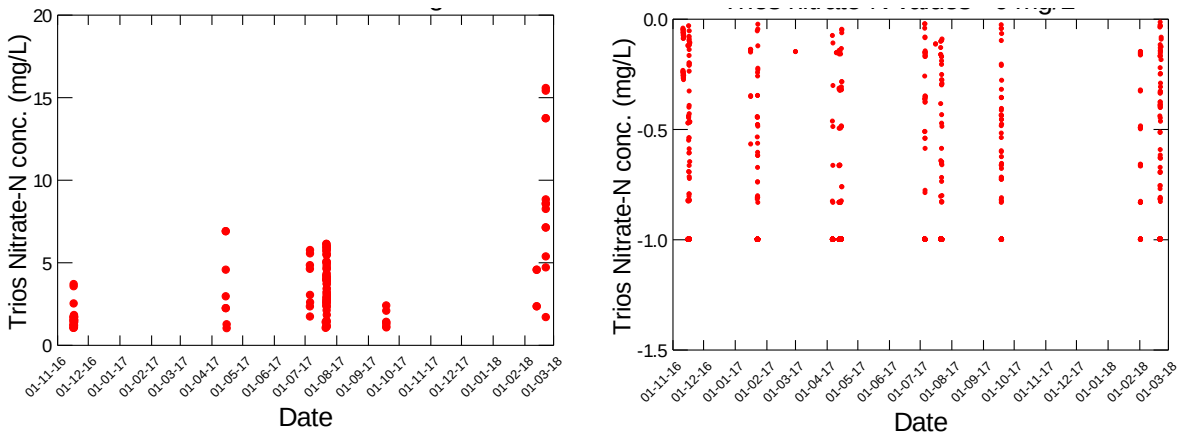
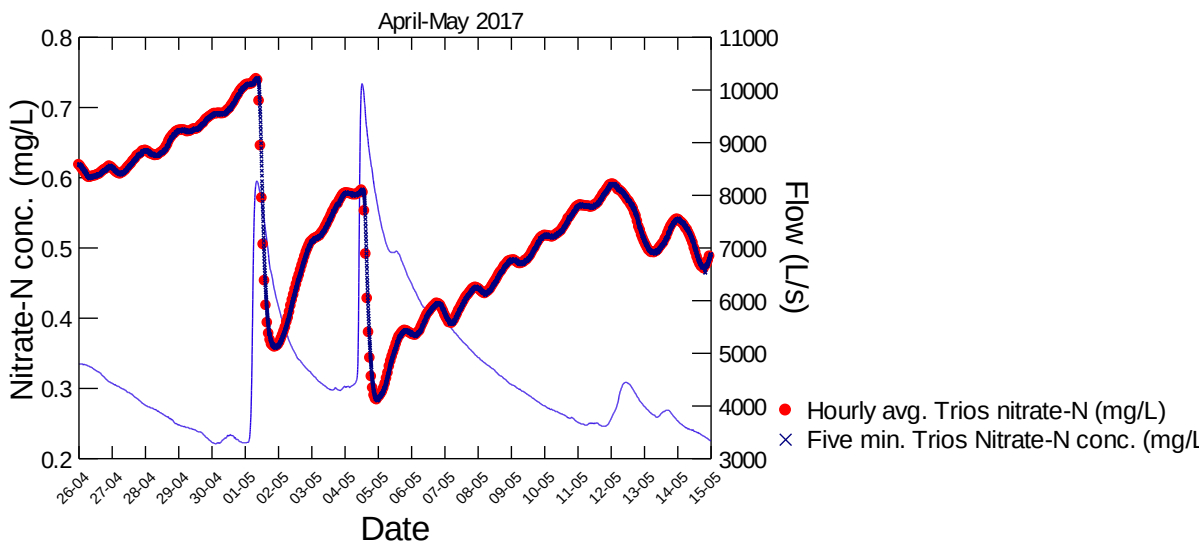


Figure 6-9: Time series of TriOS sensor nitrate-N concentrations ≥1 mg/L (left) or <0 mg/L (right).

6.1.4 Frequency of data collection/reporting/analysis

The data from the Kakanui River at McCones site were collected at five-minute frequency. A reasonable question arises: "Is this frequency or intensity of data collection desirable or necessary?" Figure 6-10 present data for a 19-day period, and thereafter for a one-week, one-day and one-hour subset of this period. This figure demonstrates that for a river of the size of the Kakanui River, one-hour average data are able to represent transient changes in nitrate-N concentration adequately for periods greater than one-hour in extent. Unless information for extremely transient events or very rapid changes is required, there appears to be little benefit in collecting data at five-minute intervals.



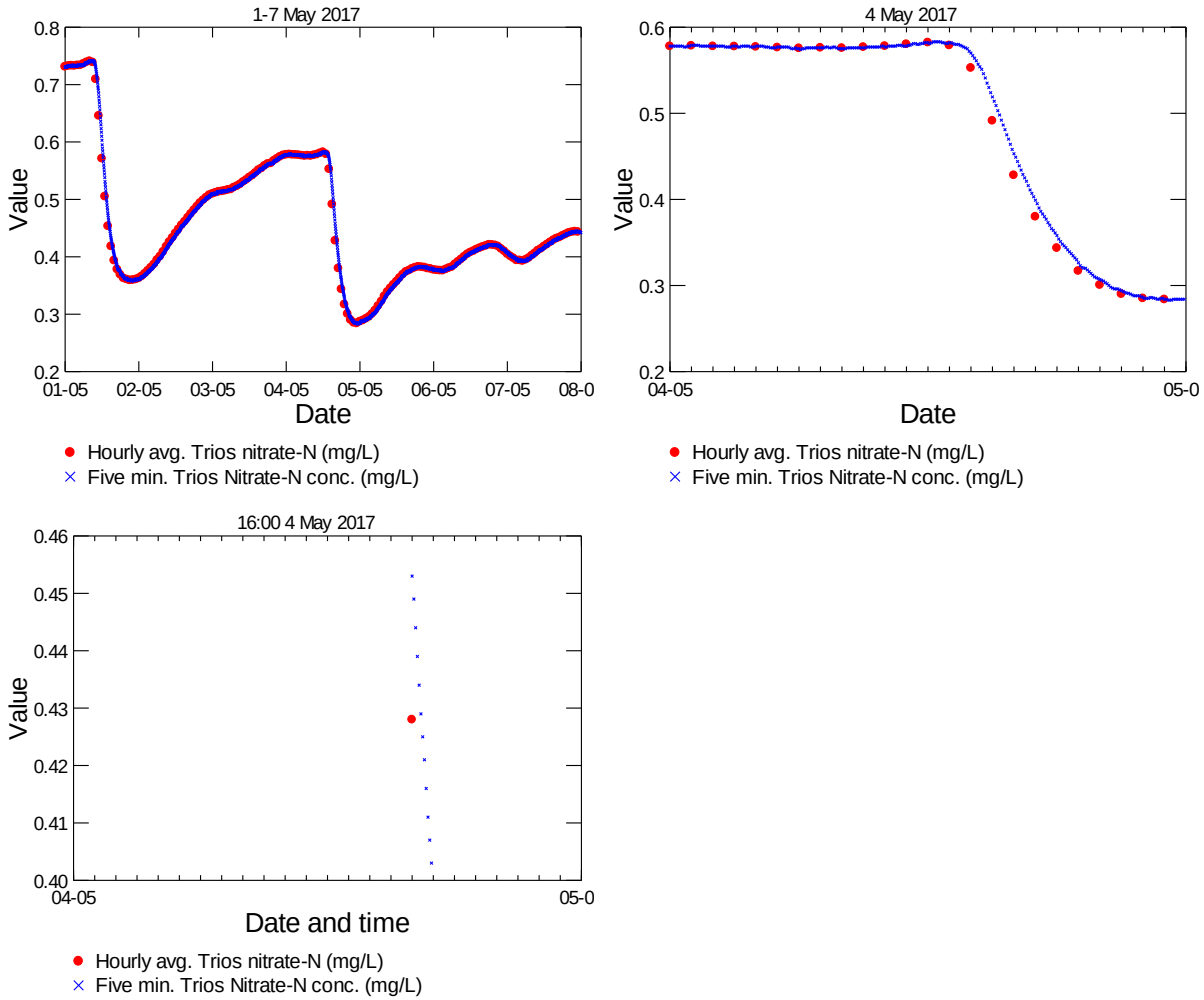


Figure 6-10: Time series of TriOS sensor nitrate-N concentrations, April-May 2017. The small blue crosses represent the raw data collected at five-minute intervals, while the red dots are hourly average data. The three lower figures represent a seven-day, one-day and one-hour period, respectively.

Figure 6-11 presents data for a (61-day) period that incorporates (limited) grab samples, with the TriOS data presented as both hourly average and five-minute data. The two-month time period was selected to include a transient negative spike, a period of persistent negative values, and a large flow event. None of the grab samples coincide with the flood event, and during the flood event the frequency of TriOS nitrate-N measurement is not able to improve our understanding of the discharge-concentration relationship during a period of anomalous (negative) measurements. It is not clear whether measurement failed, or if the time-series actually represent changes in nitrate concentration. It is possible that the transient downward spike and period of low nitrate-N concentrations reflects dilution of nitrate-N – concentrations summarised in Figure 6-10 (May 2017) were higher than those presented in Figure 6-11 (November 2016). The data demonstrate that additional information may be required to interpret the observed concentration data. Collecting data at higher frequency may not improve our understanding of nutrient mobilisation or catchment processes on its own.

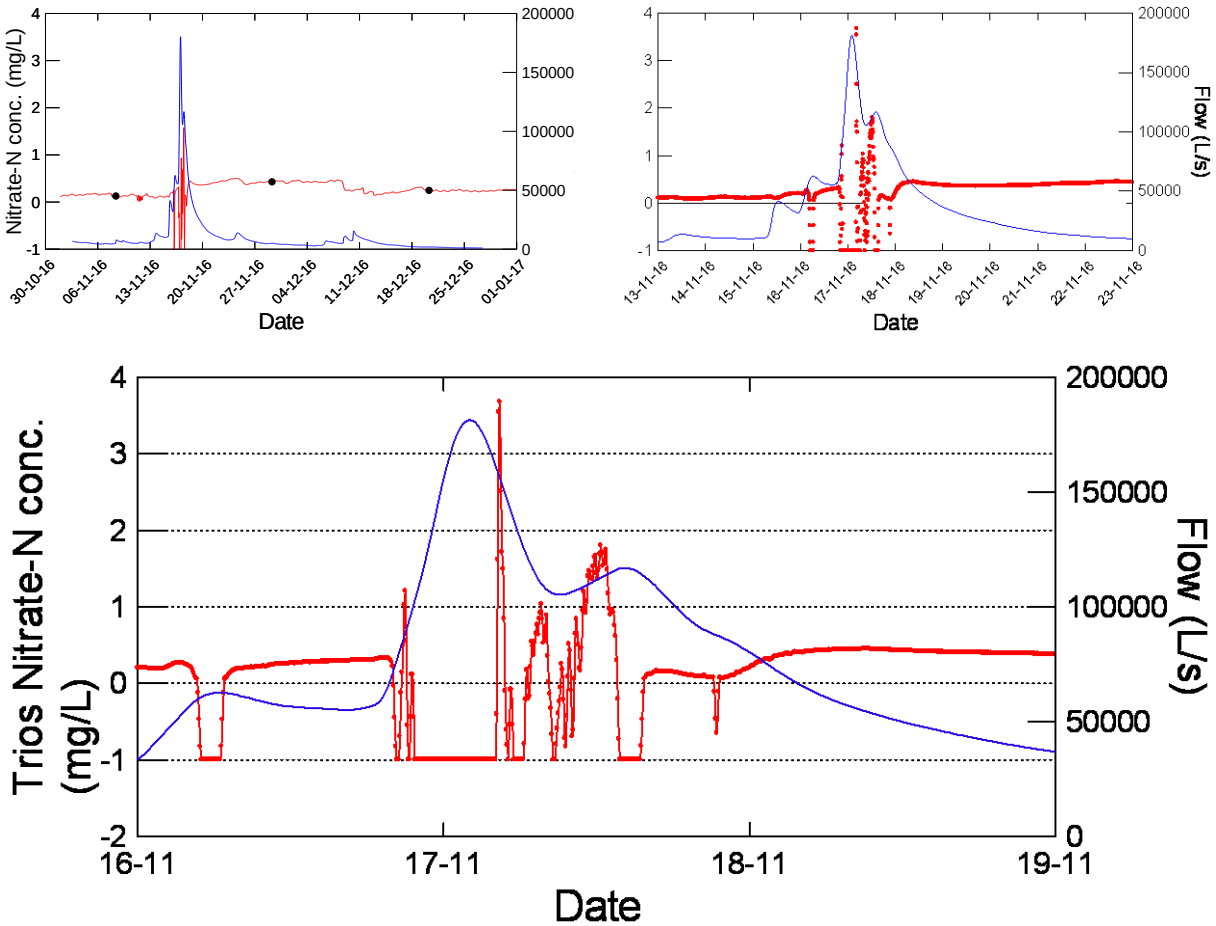


Figure 6-11: Time series of TriOS sensor nitrate-N concentrations, November 2016. Top left panel – hourly average values, plus grab samples (black dots) for the selected 61-day period. Top right panel – five-minute data collected over a ten-day period. Bottom panel – five-minute data over a three-day period.

6.1.5 Understanding flow and contaminant dynamics

The dynamic relationship between flow (Q) and contaminant (C) concentrations and loads has been long-established. One of the first formal examination of these relationships was undertaken by Williams (1989), who identified five principal classes of C–Q relationship, one with three subclasses. Williams identified several metrics which may be used to help characterise the C–Q relationship. More complex approaches have followed, including assessment of the shape and size of hysteresis loops, calculation of the area inside the hysteresis loop, along with several metrics (Lawler et al. 2006; Lloyd et al. 2016a; Lloyd et al. 2016b). Both Lawler et al. and Lloyd et al. (op cit.) provide examples of hydrographs and associated hysteresis curves. The shape of hysteresis curves identified by Williams (1989) are summarised in Table 6-1. The C/Q criteria relate to ratios calculated on the rising and falling limbs of the hydrograph at similar values of Q.

Table 6-1: Classes of C-Q relationships. Derived from Williams (1989), who also provides references to earlier work. C and Q denote concentration and discharge, and the subscripts r and f denote rising and falling limbs of the hydrograph, respectively.

Class	Subclass	Relationship	C/Q criteria
I	A	Straight line	$(C/Q)_r \approx (C/Q)_f$
	B	Curve, with slope increasing with increasing Q	Slope becomes steeper as Q increases
	C	Curve, with slope decreasing with increasing Q	Slope becomes flatter as Q increases
II		Clockwise loop	$(C/Q)_r > (C/Q)_f$ for all values of Q
III		Anticlockwise loop	$(C/Q)_r < (C/Q)_f$ for all values of Q
IV		Single line plus loop	$(C/Q)_r \cong (C/Q)_f$ for one range of Q values $(C/Q)_r <$ or $> (C/Q)_f$ for other range of Q values
V		Figure eight	$(C/Q)_r > (C/Q)_f$ for one range of Q values $(C/Q)_r < (C/Q)_f$ for other range of Q values

These general relationships between concentration and discharge may be used practically in several ways:

- it is generally assumed that clockwise hysteresis, caused by concentration increasing more rapidly than discharge during the rising limb, suggests a contaminant source close to the monitoring point, and
- anticlockwise hysteresis generally signifies a longer lag between the discharge and concentration peak, suggesting that the contaminant source was located further from the monitoring point.

This general behaviour is influenced by many factors presented by each unique river/catchment/land use combinations. Figure 6-10 presents data for a period that contained two minor flood events. This period can be examined to illustrate how high frequency data may be used to better understand discharge-concentration relationships, and practical uses for this information.

Figure 6-12 (left) presents data for the first flood event (1/05/2017). The discharge concentration relationship is equally well defined using either the five-minute or hourly average data. During this event, discharge increased without any change in nitrate concentration on the rising limb of the hydrograph. Shortly after the flood peak occurred, substantial (and rapid) dilution of nitrate-N occurred, followed by a slower increase in nitrate-N. Plotting nitrate-N against discharge (right hand figure) demonstrates a distinct clockwise relationship.

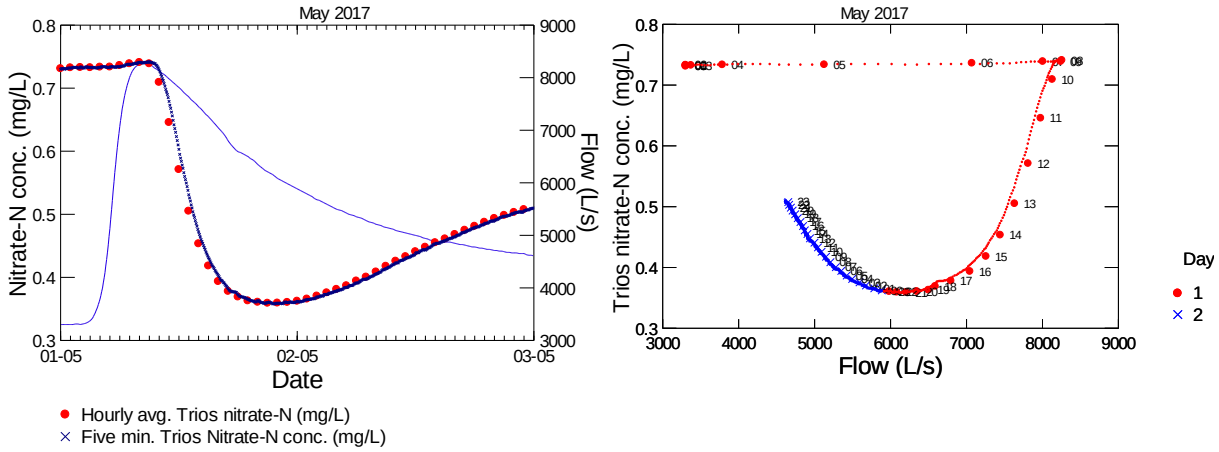


Figure 6-12: Time series of TriOS sensor nitrate-N concentrations and discharge 1-2 May 2017 (left), and concentration-discharge relationship (right).

Figure 6-13 extends the discharge-concentration data for a seven-day period presented as a time series in Figure 6-10, which includes the minor flood event of 1 May 2017, and a second one event on 4 May 2017. There appears to be little information loss in using hourly average data; both data sets demonstrate the dilution that occurred once flow had peaked, followed by concentration increase on the recession limb of the hydrograph.

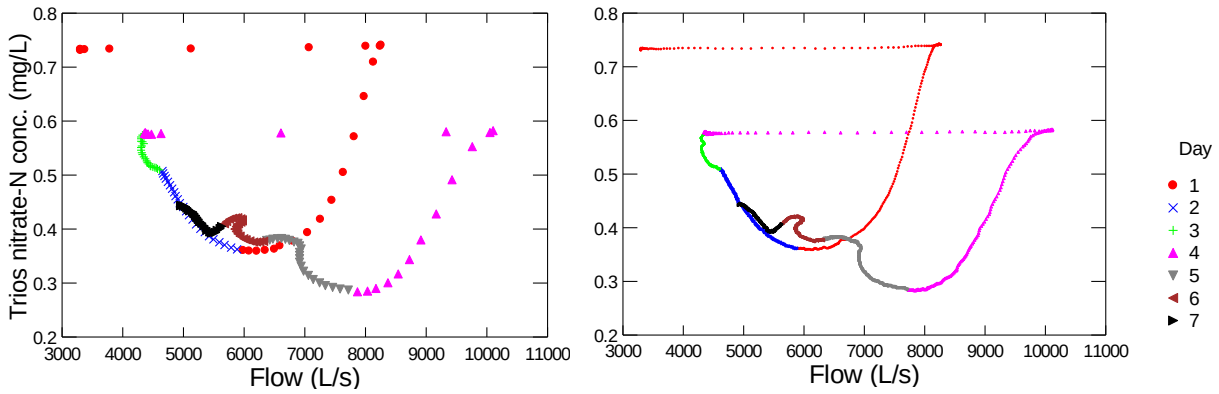


Figure 6-13: TriOS nitrate-N concentration-discharge relationship – hourly average data (left), and five-minute data (right). Data for period 1-7 May 2017, inclusive.

6.1.6 Diurnal concentration changes

Data for two periods of similar, relatively stable flow where diurnal fluctuation in nitrate-N concentration occur are presented in Figure 6-14 and Figure 6-15. In February 2017, the diurnal fluctuation (as hourly median) was relatively small (~0.03 mg/L), whereas in December 2017 it was approximately 0.15 mg/L. In February 2017, the maximum and minimum concentrations occurred at approximately 13:00 and midnight, whereas in December 2017 maximum concentration values occurred at approximately 07:00, and minima occurred at 19:00. In December the diurnal variation was also very distinct.

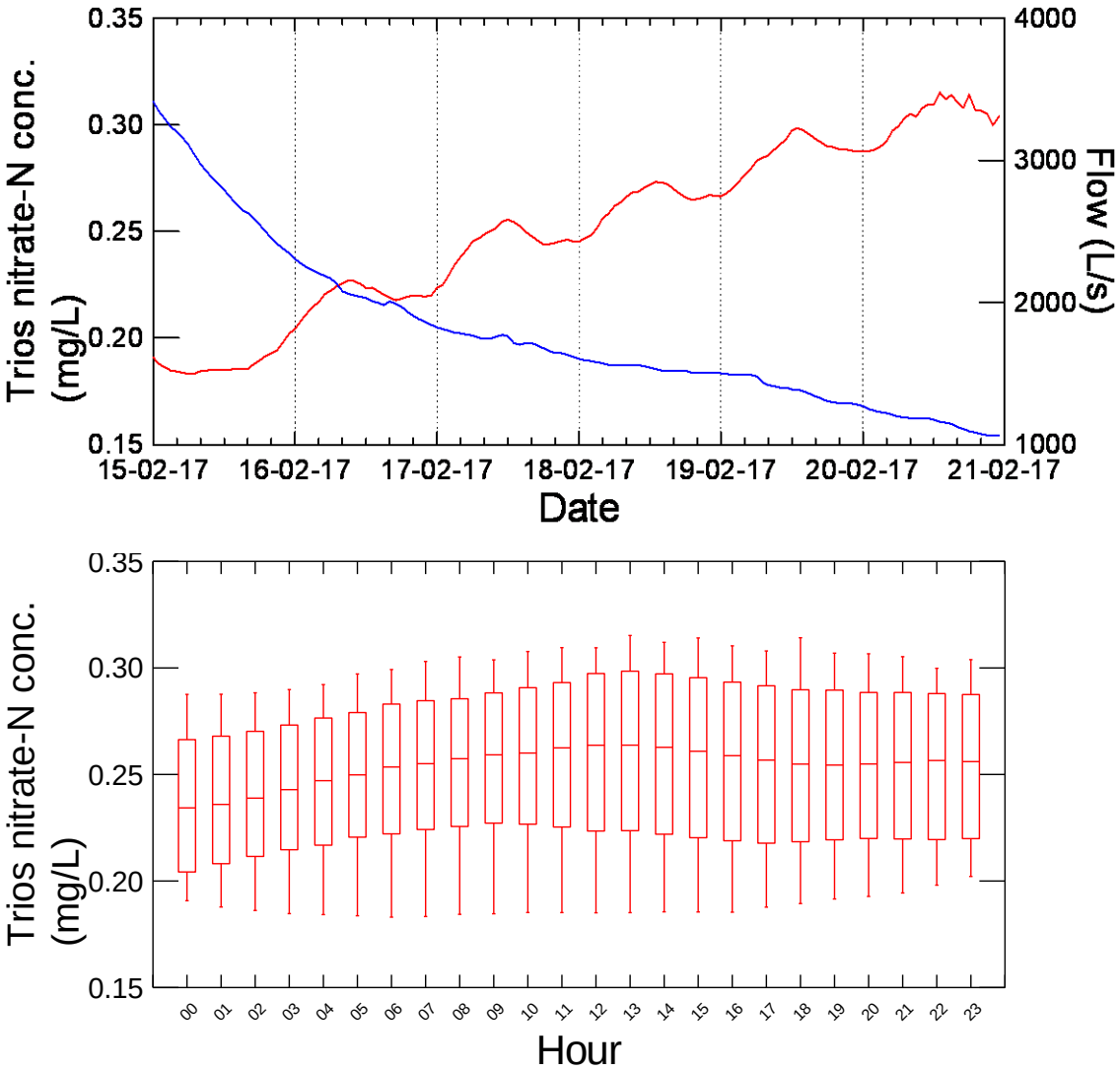


Figure 6-14: Change in TriOS nitrate-N concentration with time, 15-20 February 2017. Time-series (top), where the blue line denotes river flow, and variation in nitrate -N concentration by time of day (bottom), presented as box-and-whisker plots – where the horizontal line in each box denotes the median hourly concentration. An explanation of a box and whisker plots produced by Systat is included in Appendix B.

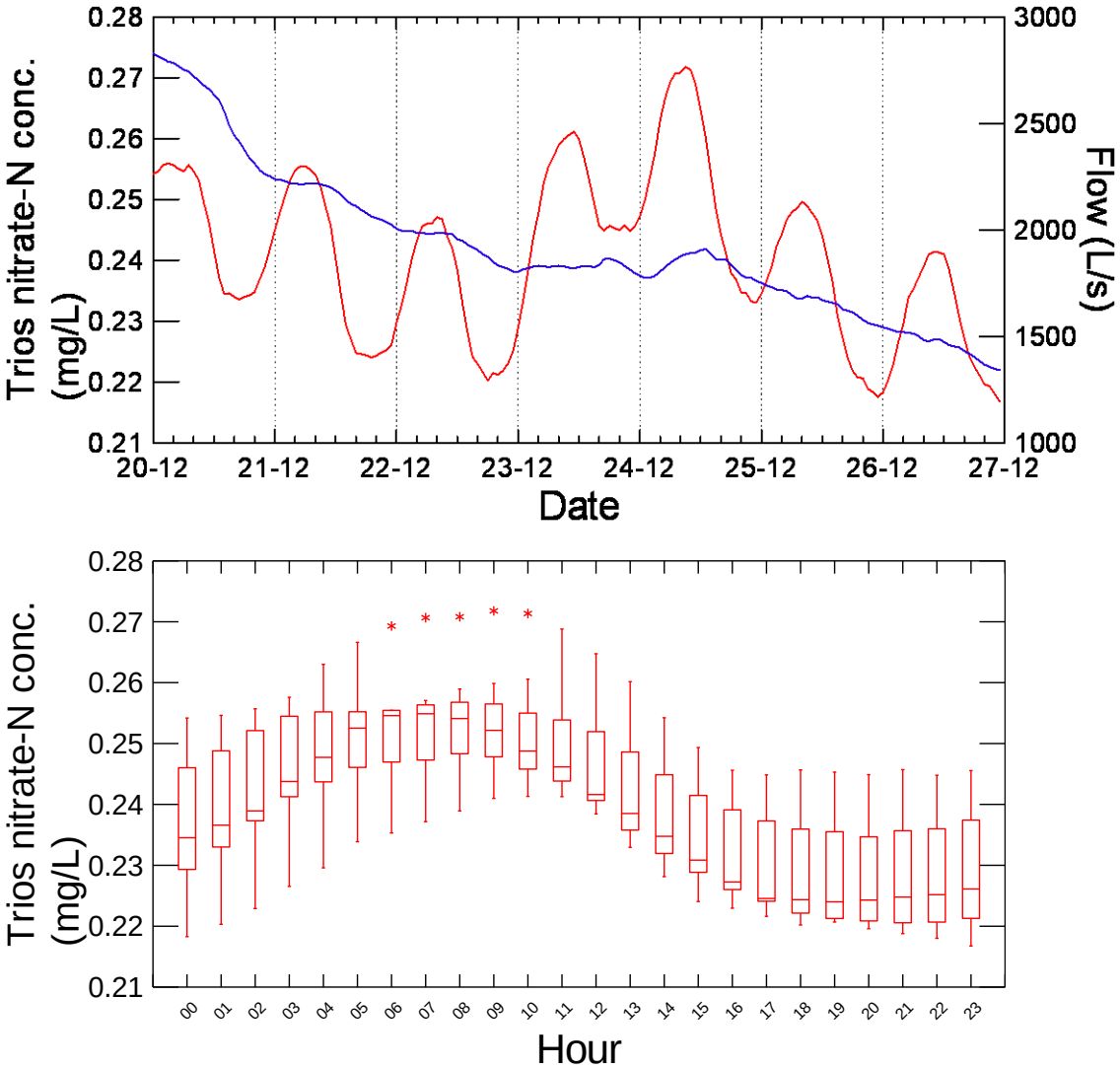


Figure 6-15: Change in TriOS nitrate-N concentration with time, 20-26 December 2017. Time-series (top), and variation in nitrate-N concentration by time of day (bottom), presented as box-and-whisker plots. An explanation of the symbols used in box and whisker plots is included in Appendix B. The blue line denotes river flow.

Cyclical diurnal changes in nitrate-N concentrations were also observed in the Manawatu River during 2016 and 2017 (Burkitt 2013). Data were presented for several days during two seasons, which indicated that the magnitude of change was larger (0.06 mg/L and 0.16 mg/L for February 2016 and March 2017, respectively). The pattern in diurnal change in nitrate-N concentration was quite different between these two periods as well, but were not dissimilar to those observed in the Kakanui River.

In the Manawatu River in summer 2016, concentrations increased during daylight hours and peaked at 17:00, whereas in autumn 2017, concentrations peaked at approximately 09:00, and lowest concentrations occurred at about 18:00. These changes were related to periphyton processing of nutrients, wastewater discharges and construction activities (Burkitt 2013).

More recent publications (Hensley et al. 2014; Hensley and Cohen 2016; Rode et al. 2016) have identified similar seasonal changes in diurnal nitrate-N concentrations. Aubert and Breuer (2016) related these seasonal changes to varying contributions arising from hydrological conditions, (specifically evapotranspiration and water limitation), and energy inputs. Examples presented for a data set identified as "Cluster G" by Aubert and Breuer (2016) were similar to those seen in the Kakanui River in January 2018, with maximum concentrations around midnight, and daily minima in the late afternoon (Aubert and Breuer 2016). Concentrations then declined gradually, but recovered rapidly each day. This is clearly evident in the Kakanui River during December 2017.

6.1.7 Load estimation

Load estimation is considered in detail in the next case study (Section 7.1.3), but a summary of load estimates derived from grab samples and TriOS data is provided here. Figure 6-16 demonstrates a strong linear relationship between grab sample instantaneous load and the instantaneous load estimated from the paired TriOS concentration. This is not surprising, because earlier a strong relationship was demonstrated for the paired concentration data. The positive bias in load estimates is related to the positive bias previously noted for nitrate-N concentrations (introductory part of Section 6.1).

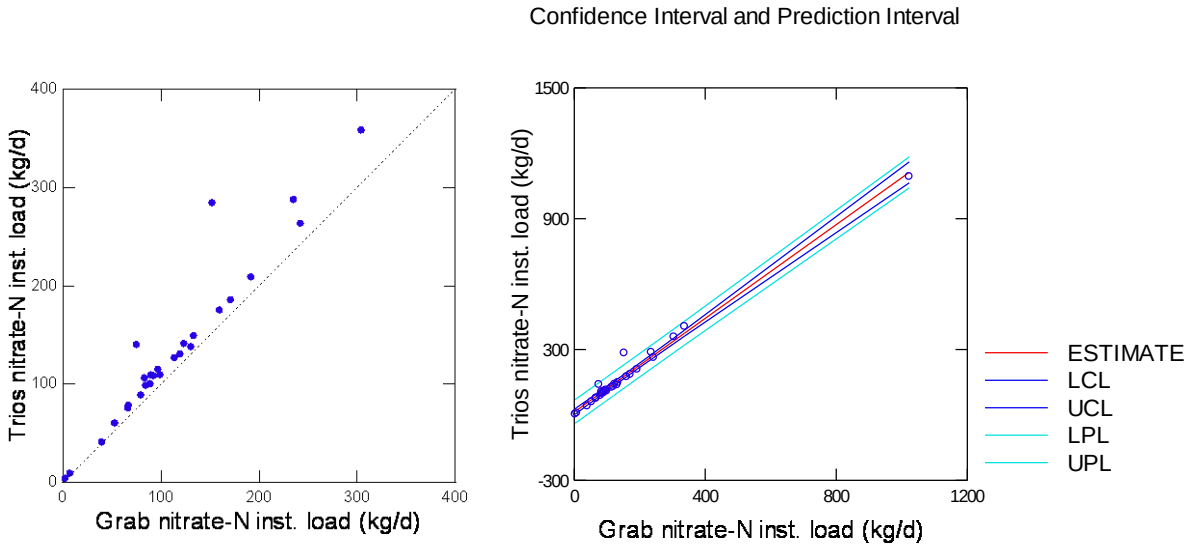


Figure 6-16: Comparison of instantaneous nitrate-N load estimates derived from TriOS sensor measurements and grab sample concentrations. The figure on the left indicates the relationship between these load estimates with the dashed line showing the 1:1 relationship, and the right-hand figure shows the predicted estimate, and upper and lower confidence intervals and prediction intervals, derived from a least square regression model.

Figure 6-17 shows a time series of instantaneous load estimates derived from two unrelated methods. There is a reasonable relationship between the two model results under low flow conditions, but the two estimates appear to diverge quite strongly during periods of elevated flow (which correspond to periods of elevated instantaneous load – see Figure 6-5). The grab sample regression model does not adequately represent the peak instantaneous loads. This is possibly a reflection of the relatively limited number of samples representing periods of elevated flow. By contrast, the TriOS estimates indicate a considerable number of events during which nitrate-N loads are elevated. The consequence of the grab sample regression model failing to predict peak nitrate-N loads becomes evident when these data are considered as seasonal average values. This is demonstrated in Figure 6-18 which indicates very large differences in daily average loads predicted

for November 2016, April 2017, July 2017 and February 2018. The loads estimated from the TriOS data in July 2017 and February 2018 are questionable, because they contain two periods where spikes occurred. As a consequence, these estimates have high uncertainty. The confidence intervals related to the other TriOS monthly estimates are generally much smaller than those associated with the grab sample regression model.

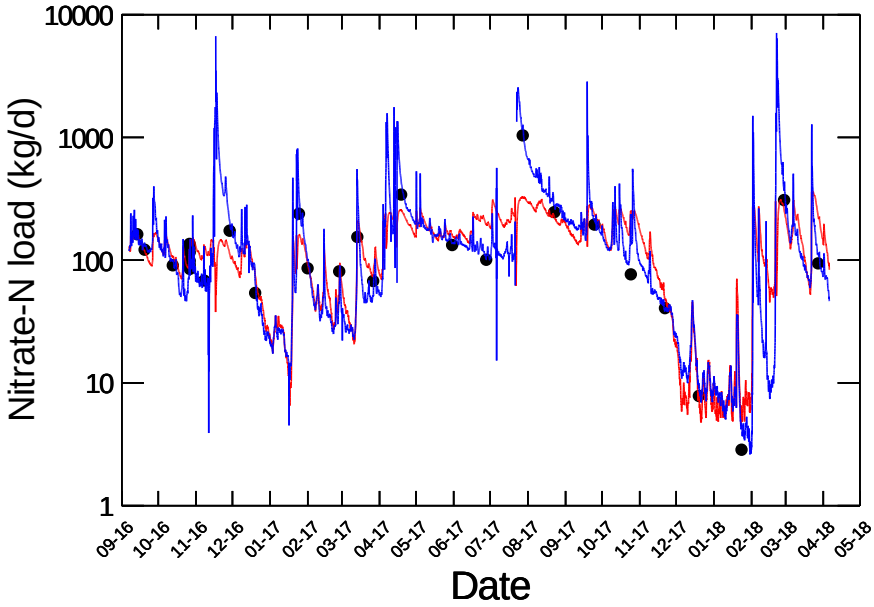


Figure 6-17: Comparison of instantaneous nitrate-N load estimates derived from hourly average TriOS sensor measurements and grab sample concentrations, using a regression model. The black dots are the grab sample instantaneous load estimates while the red and blue lines denote the TriOS sensor and river flow, respectively. Note y-axis has a $\log_{10}$ scale.

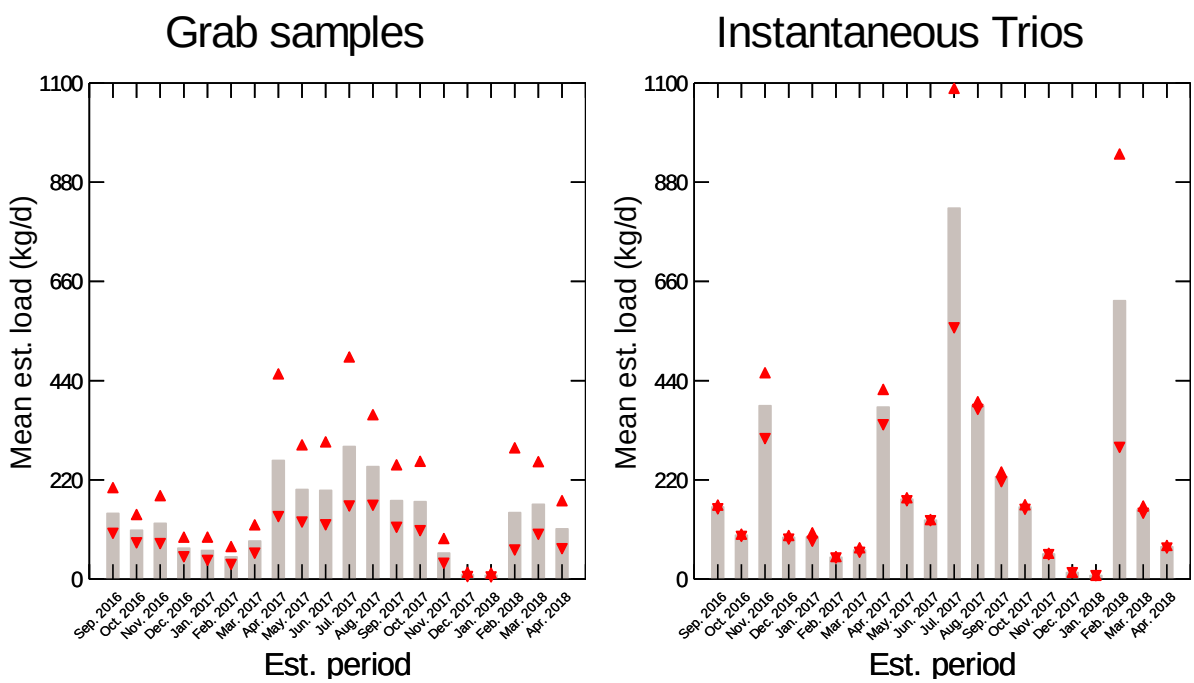


Figure 6-18: Comparison of monthly instantaneous nitrate-N load estimates derived from hourly average TriOS sensor measurements and grab sample concentrations, using a regression model. The red symbols represent the 95th percent upper and lower confidence intervals.

The difference between the two estimation techniques is also evident at a seasonal scale, as shown in Figure 6-19.

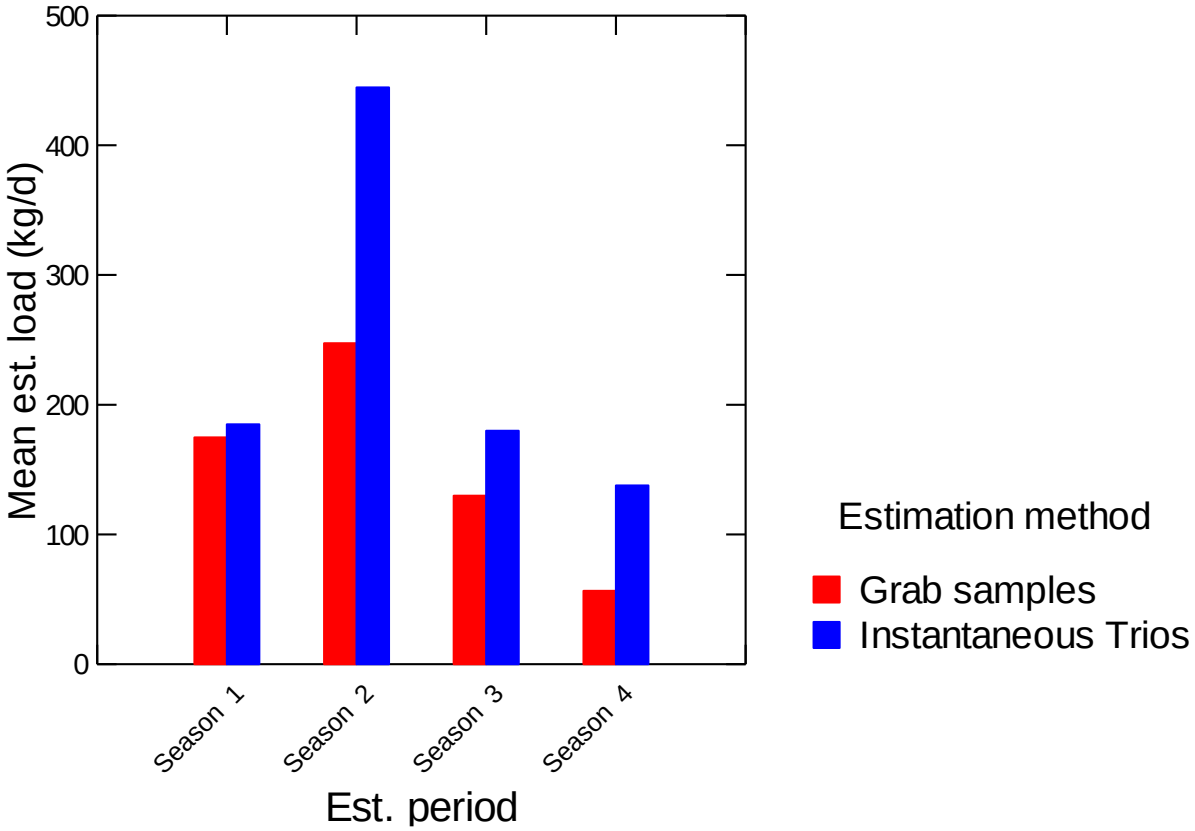


Figure 6-19: Comparison of seasonal instantaneous nitrate-N load estimates derived from hourly average TriOS sensor measurements and grab sample concentrations, using a regression model. Season 1= March-May, Season 2 = June-August, Season 3 = September- November, and Season 4 = December- February.

Estimation of contaminant loads should always be undertaken having regard for the representativeness of the data. When grab samples are used to estimate contaminant loads, there are generally far fewer concentration results than river discharge (flow) values. In the exercise illustrated in Figure 6-17, the regression model did not appear to adequately capture high flow loads. Although the load estimates could be improved by refining the regression model, the limited number of grab sample data is likely to be the factor that limits the usefulness of the model estimates. Figure 6-16 indicates caution is required in assuming that the larger number of TriOS estimates will automatically improve load estimates. Prior to estimating the load of nitrate-N, the data should be reviewed carefully and decisions made regarding high concentration results – are these real data? Do the estimated load or flux values look plausible? Are load or flux estimates improved by using five-minute vs one-hour or daily average concentration data?

6.1.8 Trend assessment

The data for the Kakanui River at McCones site was selected to investigate whether high frequency nitrate measurement has the potential to improve temporal trend detection. Several subsets of data were prepared for the assessment (Table 6-2). Each data set was analysed using the "Seasonally

adjusted trend test", included in the TimeTrends statistical package (vX), which is widely used in New Zealand for this purpose.[13]

Table 6-2: Summary of data sets selected for trend assessment. The trend analysis results are summarised in Appendix D. A + indicates increasing nitrate-N concentrations.

Data source	Description of data set	Number of data	Result of test at 5% significance level	
			Direction of trend	Rate of change (%/year)
Grab samples	1983-2018	308	+	3.84
Grab samples	Grab samples that coincide with period of TriOS data 2016-2018	28	Not significant	-
TriOS instantaneous with spikes removed	Data where concentration fell in range 0.0 to 2.0 mg/L, inclusive	237,923	+	19.8
TriOS hourly average with spikes	Average hourly value for each hour	13,646	+	22.5
TriOS hourly average	Average hourly value for each hour for data where concentration fell in range 0.0 to 2.0 mg/L, inclusive	13,506	+	19.8
TriOS daily	Single hourly average record selected for 10:00-11:00 for each day	564	+	19.1
TriOS daily	Single record selected for 10:30 each day	564	+	19.1
TriOS weekly	Single record selected for 10:30 for 1st, 8th, 15th, 22nd day of each month	91	+	25.3
TriOS fortnightly	Single record selected for 10:30 for 1st and 15th day of each month	36	+	28.1
TriOS monthly	Single record chosen for each of 10th and 15th of each month	16 and 17	Not significant	-

The results of assessment are summarised in Table 6-2 and included in full in Appendix D. Appendix D also includes an assessment to determine trend in variance over time using the output from the TriOS daily subset of data. Points to note from this assessment:

- The long-term grab sample record indicates a trend over the period 1983-2018, whereas the limited grab data available for the 2016-2018 period (n=28) do not indicate a statistically significant trend.
- For the TriOS data set, inclusion of the spikes increases the slope of the trend, which is misleading, and confirms the requirement to screen and remove questionable data.
- Very similar estimates of slope are provided by the TriOS instantaneous, hourly average and single daily data (19.1-19.8 %/year).
- As the TriOS measurement interval increases to weekly and fortnightly frequency, the slope of the trend increases, and for the fortnightly data, the probability of incorrectly detecting trend begins to increase.

[13] http://www.jowettconsulting.co.nz/home/time-1

- Monthly data are clearly unsuited to the task of reliably detecting trend over a relatively short period.
- The assessment of trend in variance in TriOS estimates over time could potentially be used to validate instrument performance and ensure high quality data are being collected.
  - Hyperspectral analysers rely on a high intensity light source, which is subject to deterioration.
  - Biofouling or deposition of minerals on optical windows may not be detected during maintenance visits if it is difficult or unsafe to retrieve the device.

The results of the trend assessments and similar analyses of high frequency data could be used to more rigorously determine the optimal sampling frequency to detect and reliably quantify water quality trend (i.e., assist with refining monitoring programme design). However, caution is required because improvement (or further degradation) in water quality often occurs over a long period of time. The data analysed were collected over a relatively short period of time – while the direction and magnitude of trend may be determined with accuracy and confidence, the results could not be extrapolated or hind-cast.

7 Case study 2: ES Aparima River data

As outlined in Section 5, Environment Southland (ES) has deployed a TriOS nitrate-N sensor in Aparima River at Thornbury to assist with nutrient load measurement and management. This section compares TriOS vs. grab sample data, and looks at range of uses of the data such as temporal trend assessment and nitrate-N load calculation.

7.1 Comparison of grab sample and TriOS nitrate-N concentrations

The time series of river discharge, grab sample nitrate-N and TriOS estimated nitrate-N concentration data are summarised in Figure 7-1.

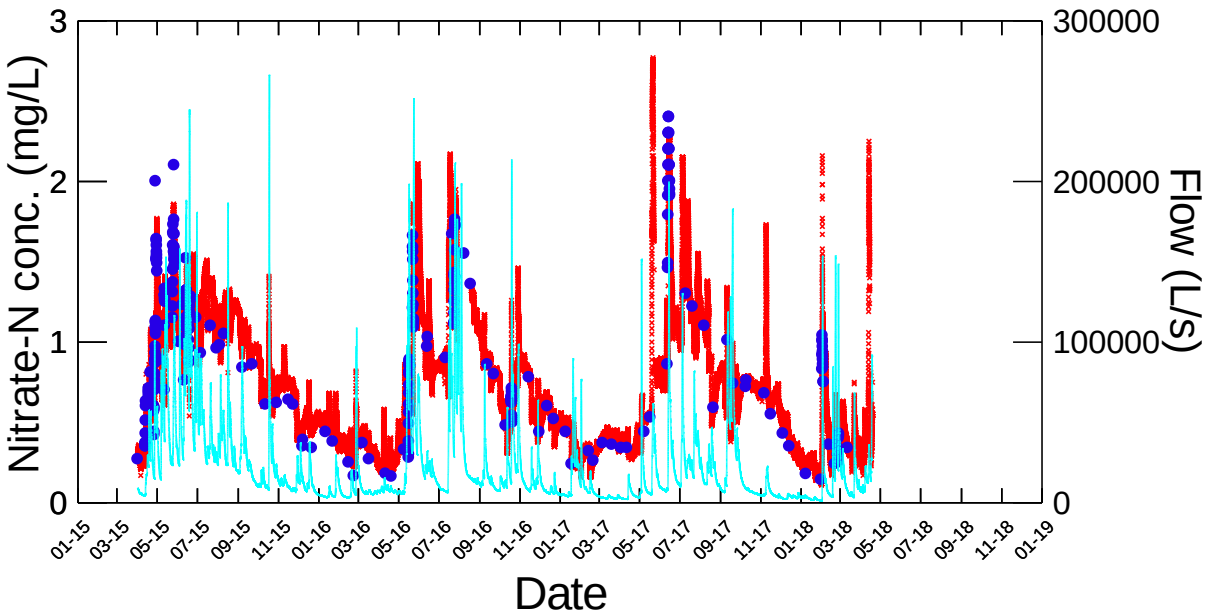


Figure 7-1: Time series of discharge, grab and 10-minute TriOS nitrate-N concentration data. Small red crosses = TriOS sensor estimates, blue dots = grab samples, cyan = discharge (flow) data.

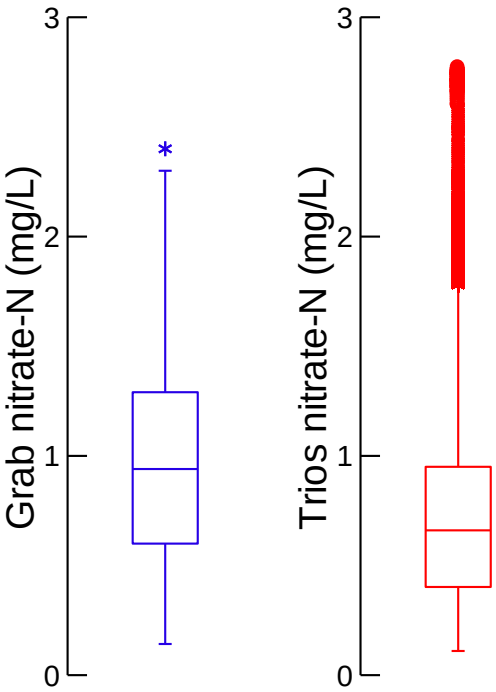
Summary statistics for these data are provided in Table 7-1, which includes a graphical summary of the two data sets. Points to note:

- median and mean grab sample nitrate-N concentrations are larger than those derived from the TriOS sensor
- minimum values estimated by the TriOS sensor are 22% smaller than those derived from grab samples
- maximum values estimated by the TriOS sensor are 15% larger than those derived from grab samples, and
- although the concentration range derived from the TriOS sensor is larger than that indicated by grab samples, the interquartile range is smaller.

Provided a robust relationship between the two techniques over the observed concentration range can be demonstrated, it is highly likely that the TriOS sensor will provide better estimates of minimum and maximum nitrate concentrations because of the better representation of all flow, season, and time of day conditions.

Table 7-1: Summary statistics for nitrate-N concentrations derived from grab water samples and continuous TriOS sensor measurements. Data selected for the period 1/4/2015-31/3/2018. These data are shown as part of a time series in Figure 7-1. An explanation of a box and whisker plot is provided in Appendix B. "Cleveland percentiles" are calculated using the method of Cleveland, an option in the Systat software.

Statistic	Nitrate-N concentration (mg/L)	
	Grab	TriOS
N	322	149523
Minimum	0.142	0.110
Maximum	2.400	2.770
Range	2.258	2.660
Interquartile range	0.700	0.548
Median	0.965	0.660
Mean	1.008	0.714
Standard Error of Mean	0.029	0.001
Mode	-	0.380
95.0% LCL of Mean	0.952	0.712
95.0% UCL of Mean	1.064	0.716
Standard Deviation	0.513	0.380
Variance	0.264	0.144
Cleveland percentiles		
1.0%	0.174	0.190
5.0%	0.300	0.250
10.0%	0.357	0.290
20.0%	0.529	0.370
25.0%	0.610	0.402
30.0%	0.650	0.450
40.0%	0.833	0.530
50.0%	0.965	0.660
60.0%	1.120	0.750
70.0%	1.269	0.860
75.0%	1.310	0.950
80.0%	1.451	1.060
90.0%	1.692	1.230
95.0%	2.000	1.390
99.0%	2.300	1.850



Box and whisker plot showing the distribution of all grab and TriOS sensor concentration data

The time series for grab and TriOS nitrate-N concentrations is shown in Figure 7-2, and the relationship between paired grab sample and TriOS nitrate-N concentrations are shown in Figure 7-3. Summary statistics for the pairs of data are provided in Table 7-2.

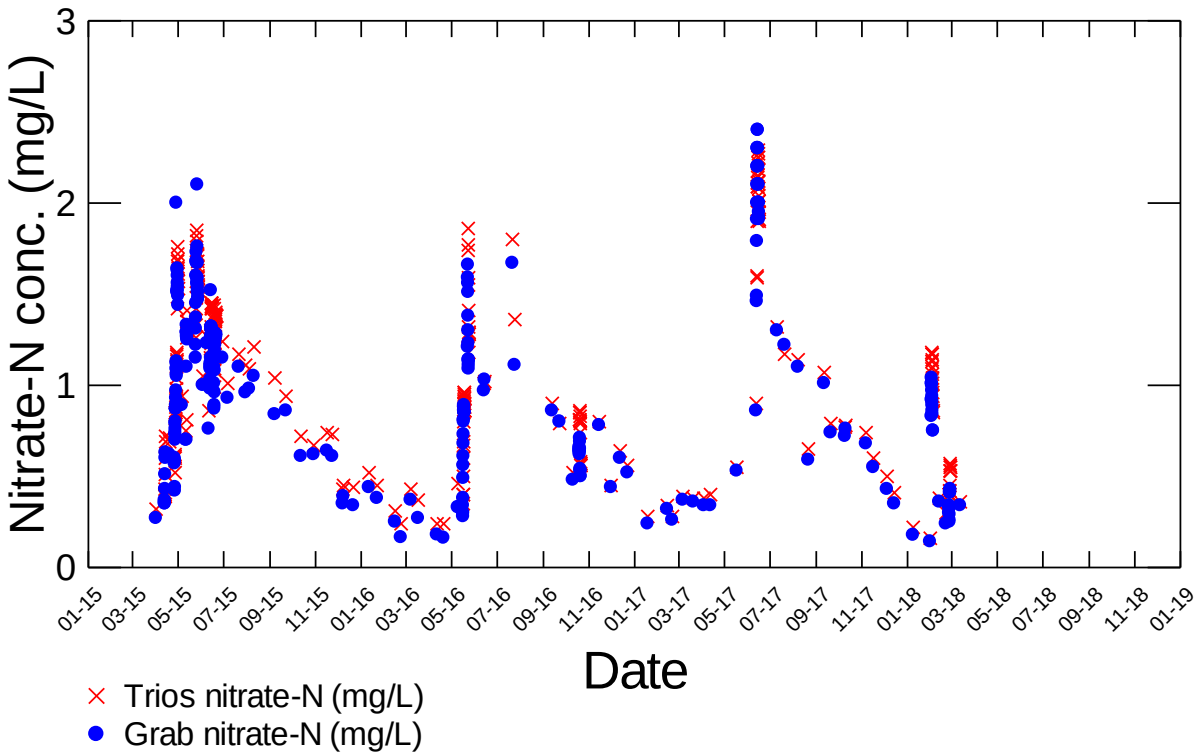


Figure 7-2: Time series of paired grab sample and TriOS sensor nitrate-N concentration data. Grab samples represent a combination of manual and automatic sampling.

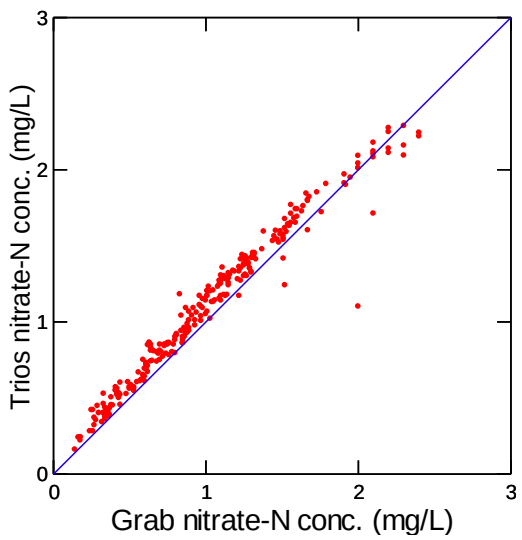
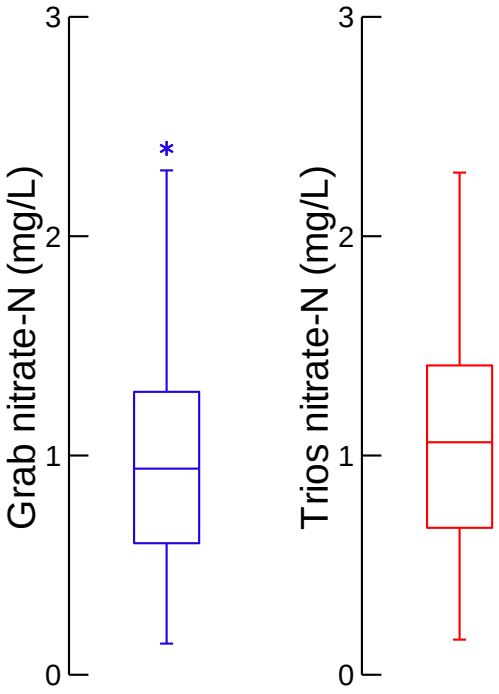


Figure 7-3: Relationship between paired grab sample- and TriOS sensor nitrate-N concentration data. The blue line is the 1:1 relationship line.

Table 7-2: Summary statistics for nitrate-N concentrations derived from paired grab water samples and continuous TriOS sensor measurements. Only data for paired samples where both grab nitrate-N >0 mg/L and TriOS nitrate-N >0 mg/L are included. These data are shown as a time series in Figure 7-2. An explanation of a box and whisker plot is provided in Appendix B. "Cleveland percentiles" are calculated using the method of Cleveland, an option in the Systat software.

Statistic	Nitrate-N concentration (mg/L)	
	Grab	TriOS
N	285	285
Minimum	0.142	0.160
Maximum	2.400	2.290
Range	2.258	2.130
Interquartile Range	0.693	0.740
Median	0.940	1.060
Mean	0.997	1.079
Standard Error of Mean	0.031	0.030
95.0% LCL of Mean	0.936	1.020
95.0% UCL of Mean	1.058	1.138
Standard Deviation	0.521	0.504
Variance	0.271	0.254
Cleveland percentiles		
1.0%	0.170	0.240
5.0%	0.287	0.378
10.0%	0.350	0.410
20.0%	0.500	0.565
25.0%	0.600	0.670
30.0%	0.640	0.780
40.0%	0.835	0.900
50.0%	0.940	1.060
60.0%	1.100	1.230
70.0%	1.250	1.350
75.0%	1.293	1.410
80.0%	1.445	1.465
90.0%	1.670	1.760
95.0%	2.025	2.050
99.0%	2.300	2.250



Box and whisker plot showing the distribution of grab and TriOS estimated concentration data where pairs of data exist

Assuming that the lab-analysed grab samples accurately represent stream nitrate-N concentrations, the key points to note from assessment of the paired data are:

- The TriOS sensor generally overestimated minimum, median and mean nitrate (12%, 12% and 8%, respectively).
- The TriOS sensor tended to underestimate maximum nitrate concentrations slightly (approximately 4%).
- The ranges and interquartile ranges for the two measurement techniques were more similar than for the entire data set, varying by approximately 5% and 7%, respectively.

There is a robust relationship between the TriOS and grab nitrate-N data sets (shown in detail in Appendix E). The difference between measurements made with these two estimation techniques is summarised in Figure 7-4(A and B). Figure 7-4(A) indicates that the difference between the two measurements is reasonably consistent across the entire concentration range, but with an increasing tendency for grab sample results to exceed TriOS estimates at the higher grab sample values. Figure 7-4(B) indicates that the differences between the two measurements are approximately normally distributed.

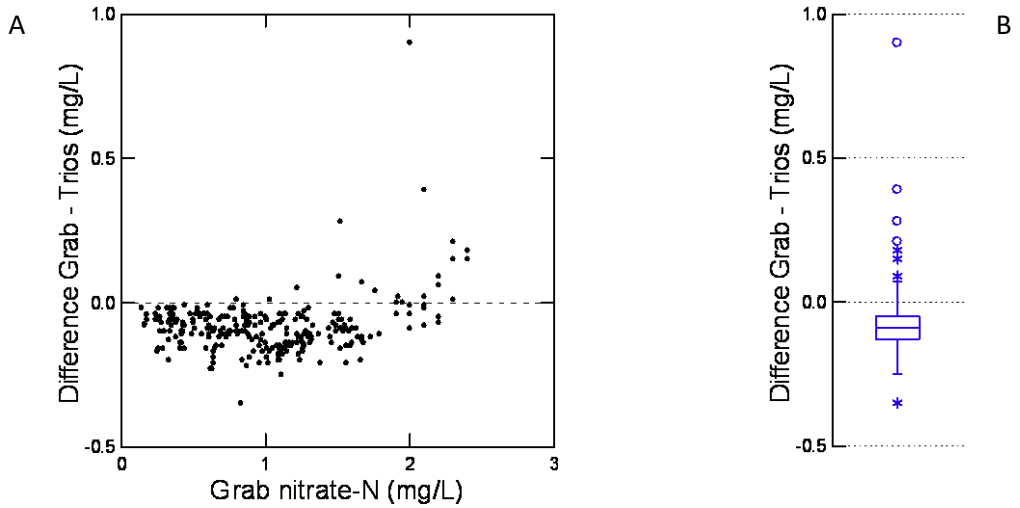


Figure 7-4: Difference between grab sample and TriOS sensor nitrate-N concentrations for paired data. Values in A) are the differences plotted as a function of grab sample nitrate-N concentration, and B) shows the distribution of the differences in concentration data.

A non-parametric Kolmogorov-Smirnoff test indicates that the nitrate-N values derived from the two measurement techniques are significantly different (maximum difference is 0.105, critical D = 0.086) at the 95% confidence level. The distribution of paired data is shown in Figure 7-5, which confirms that the TriOS sensor provides slightly larger estimates of nitrate-N across the concentration range.

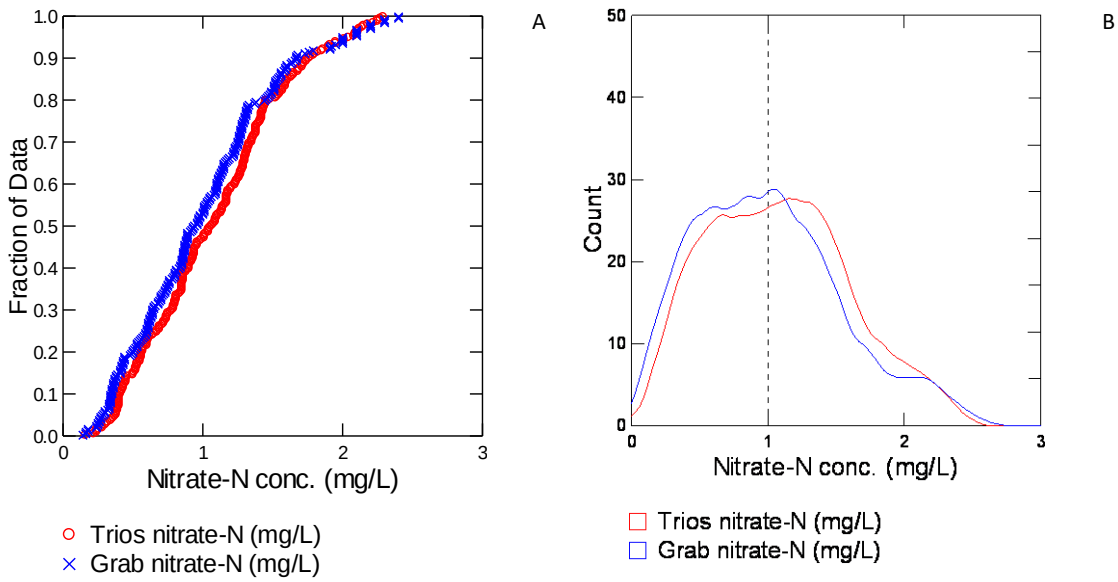


Figure 7-5: Distribution of grab sample (blue) and TriOS sensor (red) nitrate-N concentrations for paired data. The dashed vertical line in b) is for reference purposes only.

Although the differences in nitrate-N concentrations derived from the two measurement techniques are not large, the potential for bias should be considered carefully before these data are used for resource management purposes. If the measurement technique and/or the frequency of sampling can be demonstrated to alter the outcomes of the assessment, it may be necessary to review how nitrate-N concentrations are determined at key times. This approach is analogous to measurement of dissolved oxygen concentrations – there is no point in measuring dissolved oxygen concentrations at midday in winter, if dissolved oxygen minima information is required.

7.1.1 Use of continuous nitrate-N measurement for nutrient processing assessment

Two subsets of the continuous data record were selected to demonstrate information related to diurnal processes for the Aparima River during two seasons. The time periods were selected to capture relatively stable river flows in autumn and late spring 2017 (Figure 7-6).

During the spring period, nitrate-N concentrations varied by approximately 0.035 mg/L (~5.5%), whereas in autumn the concentration varied by approximately 0.045 mg/L, a change of approximately 12%.

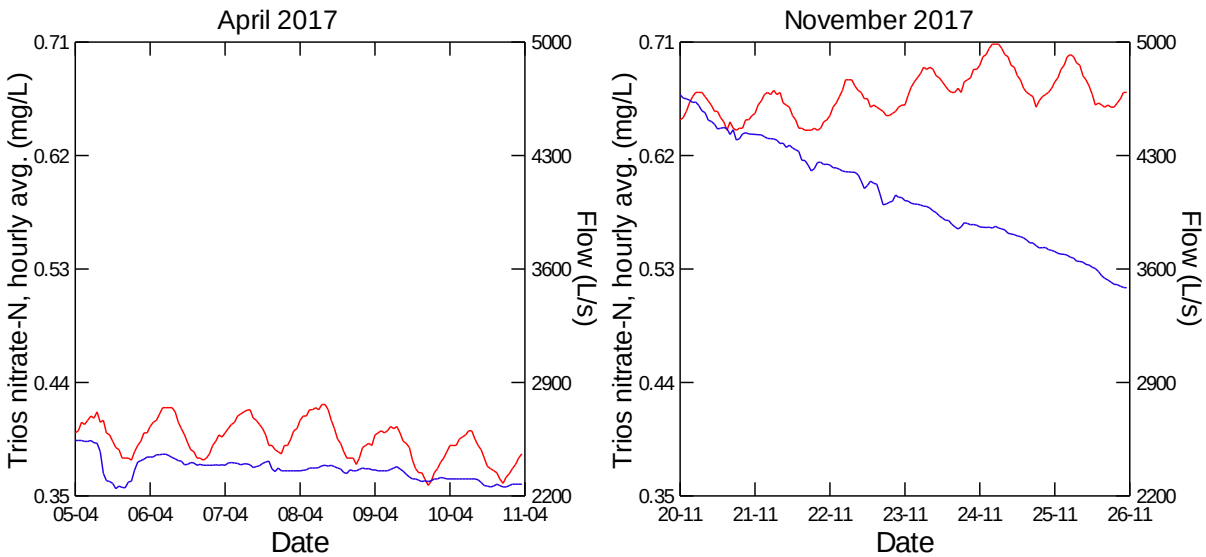


Figure 7-6: Time series of TriOS sensor nitrate-N concentrations for two seasonal periods. Discharge (flow) is indicated by the blue line.

The approximate timing of daily minima and maxima was similar during both seasonal periods (Figure 7-6). This is different to what has been reported in the other reported study undertaken in New Zealand. In the Manawatu River, very marked differences in the timing of minimum and maximum concentrations were observed, and the difference between minima and maxima was also much larger (Burkitt et al. 2017). The flows in the Manawatu River were probably larger (ca. 10,000 L/s) than those recorded in the Aparima River, although it is difficult to accurately estimate this from the figure provided. The timing of nitrate-N minima and maxima also differ from those identified in two periods in the Kakanui River (Section 6). In addition to flow, concentration differences probably arise from latitude and climate differences, as well as other catchment-specific factors, such as the importance of groundwater in delivering nitrate-N to the Kakanui River. Although these differences cannot be explained fully at this time, obtaining a better understanding of nutrient processing is likely to be an important factor when developing policy for management of land uses and water resources at the catchment or Freshwater Management Unit scale. These considerations are likely to

be particularly key for annual periods, when toxicity issues may occur, or where reduction of nuisance periphyton growth requires specific management action.

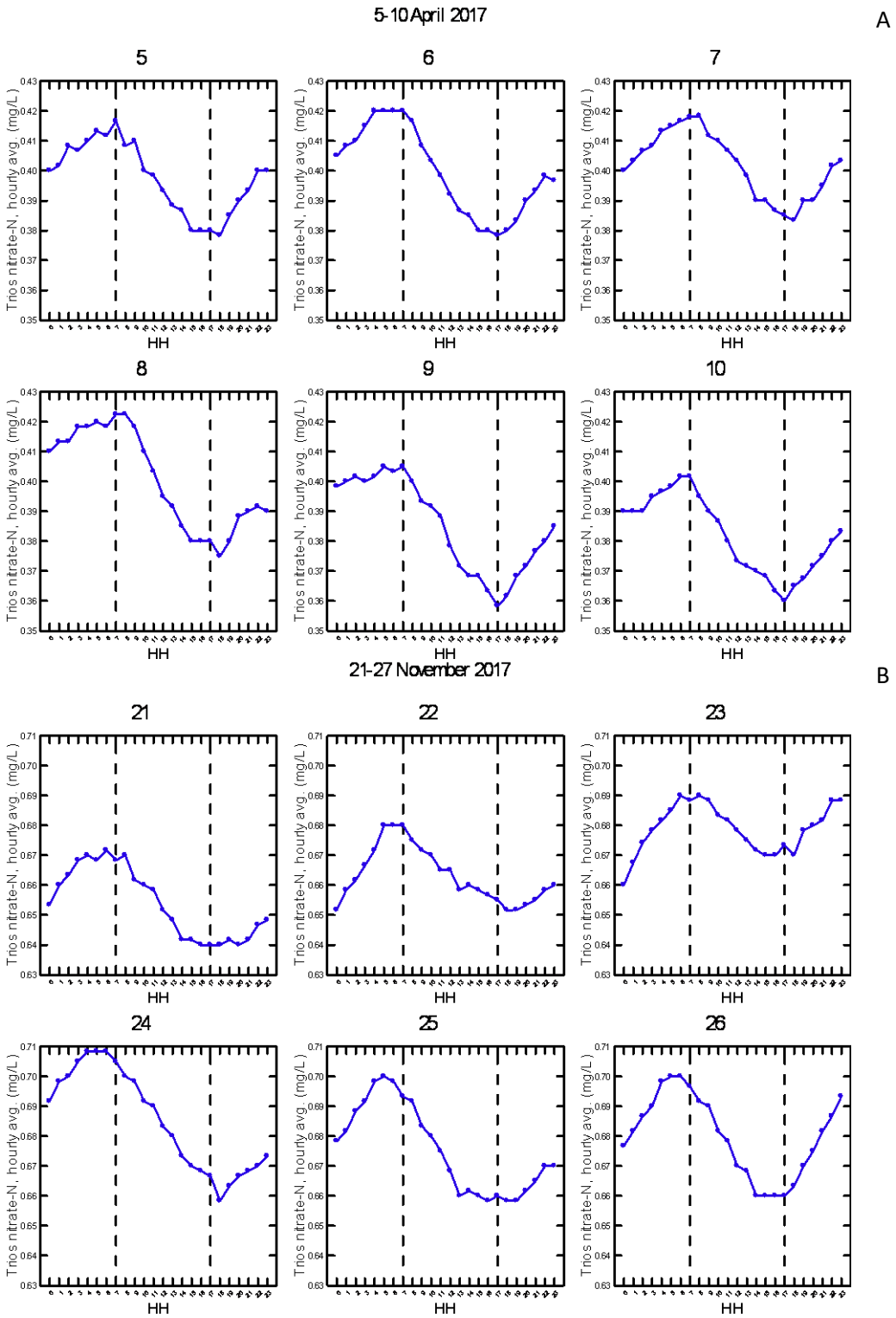


Figure 7-7: Diurnal variations of TriOS sensor nitrate-N concentrations during two different seasonal periods. A) Autumn 2017, B) late Spring 2017. Title numbers refer to the day of the month, vertical lines 07:00 and 17:00 respectively, included for reference purposes only. Note that the y-axis scales are different.

7.1.2 Flow and contaminant dynamics

High frequency measurement of nitrate-N concentrations can assist with understanding river flow and concentration relationships, as well as flow and instantaneous yield (flux). Figure 7-8 summarises relationships between flow and concentration, and flow and load over a six-day hydrological event. Key points to note:

- The magnitude of load is (as expected) more strongly influenced by changes in flow than by changes in concentration, and the timing of load transport closely reflects the hydrograph shape.
- Nitrate-N concentrations increase on the rising limb of the hydrograph, but some dilution occurs soon thereafter.
- As a consequence of this dependence, nitrate-N concentrations increased approximately three-fold, whereas the flux increased at least 20-fold.

The contaminant-flow (C-Q) relationship is complex. Using the broad descriptors provided by Williams (1989), summarised in Table 6-1, a general clockwise loop exists, complicated with a figure eight. These relationships suggest an immediate response characteristic of a nearby contaminant source, as well as more complex C-Q relationship on rising and falling limbs of the hydrograph.

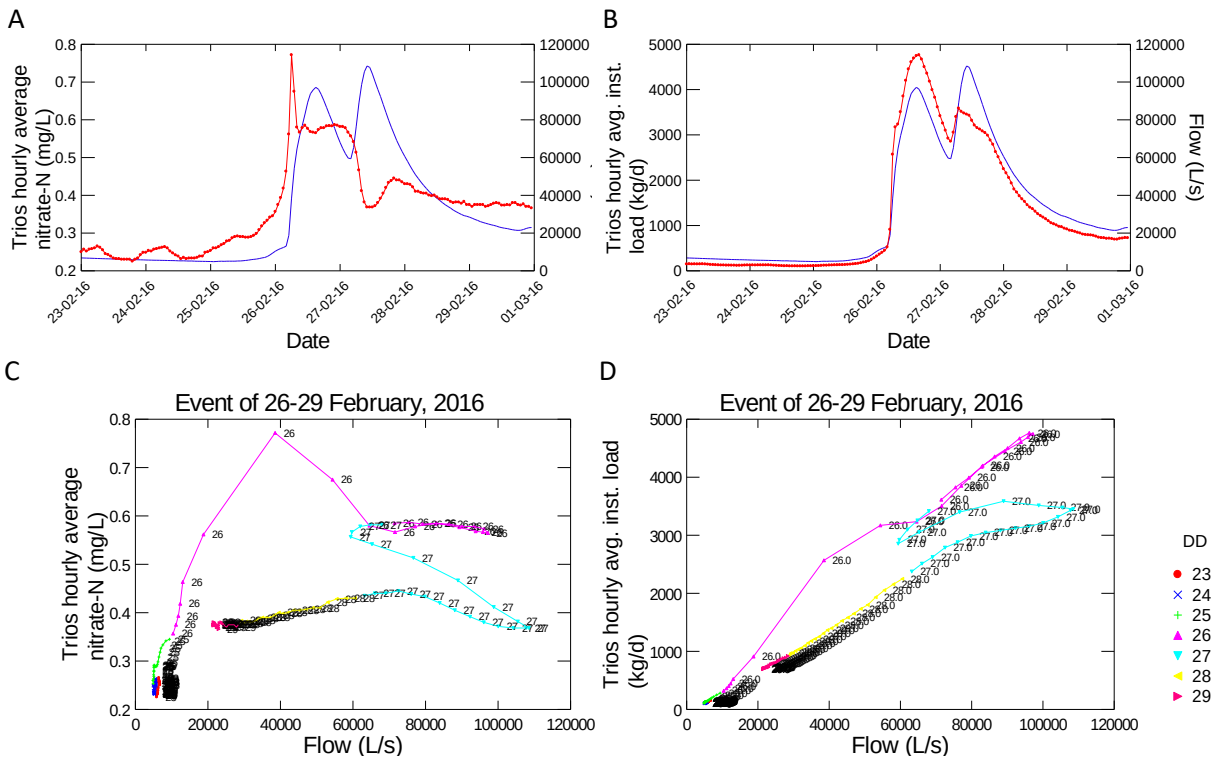


Figure 7-8: Variations of TriOS sensor nitrate-N concentrations and instantaneous load (flux) over a short-duration hydrological event. A) and C) variation in concentration, B) and D) variation in flux.

A further example is provided in Figure 7-9 where an eight-hour break in the TriOS concentration record exists around 23 May 2017. The break in the record is also associated with a step change in apparent concentration.

An elongated, clockwise C-Q relationship exists, which translates into a steep increase and decrease in instantaneous load. The break in the concentration record translated into the load estimate as well. Although a seven-hour break in the record is unlikely to alter an annual load estimate, it is important at the daily time scale. Ideally quality assurance procedures would detect the gap in the record, and a process would be followed to fill the data gap, and if appropriate, apply a correction to connect the data sets more smoothly before and after the gap. Such processes exist for some other continuous data (e.g., rainfall and flow data are often used to address gaps in continuous turbidity records). The apparently invariant concentration after the break in the record also warrants investigation.

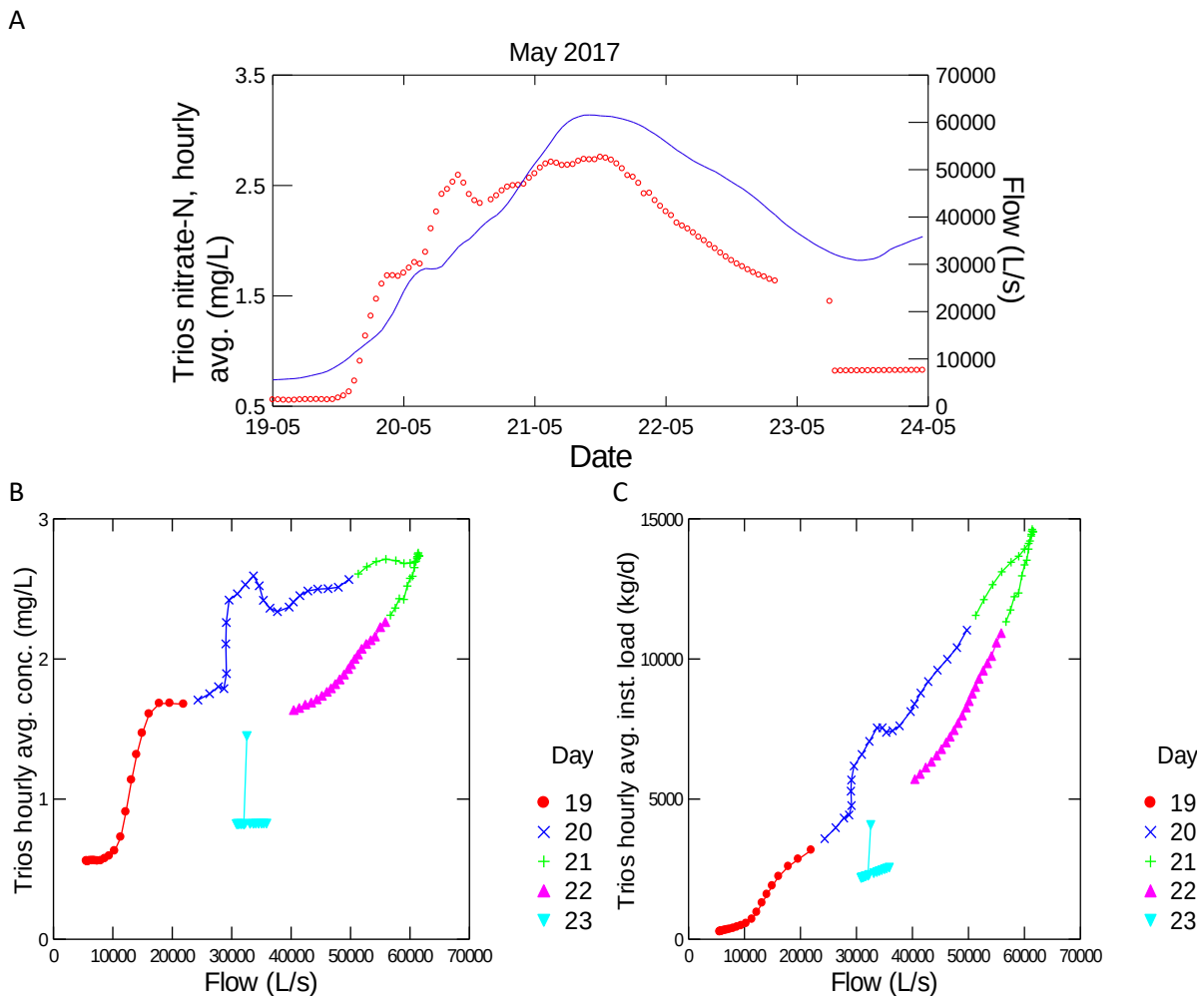


Figure 7-9: Variations of TriOS sensor nitrate-N concentrations and instantaneous load (flux) over a short-duration hydrological event. A) and B) variation in concentration, C) variation in flux.

7.1.3 Load estimation

As outlined in Section 5.4, many techiques exist to calculate the load of a contaminants transported in a stream or river. More than 300 nitrate-N concentration values with a matching discharge estimate are available for the Aparima River over the period 1 April 2015 to 31 March 2018, from which an instantaneous load may be calculated. The relationship between grab sample concentration data and flow and TriOS sensor estimates and flow are summarised in Figure 7-10. The grab sample collection strategy has provided a good distribution of concentration data over the entire flow range, and the seasonal distribtion of data are also adequate. The distribution of grab

and TriOS sensor concentrations by flow conditions and season is summarised in Table 7-3 and Table 7-4, respectively. A higher proportion of grab samples were collected under high flow and winter conditions – this ensures that the conditions during which the greatest nitrate-N load is generated and transported have been well-characterised. As a consequence, there is likely to be a good relationship between regression model estimates and estimates derived from the TriOS sensor data, after accounting for missing records.

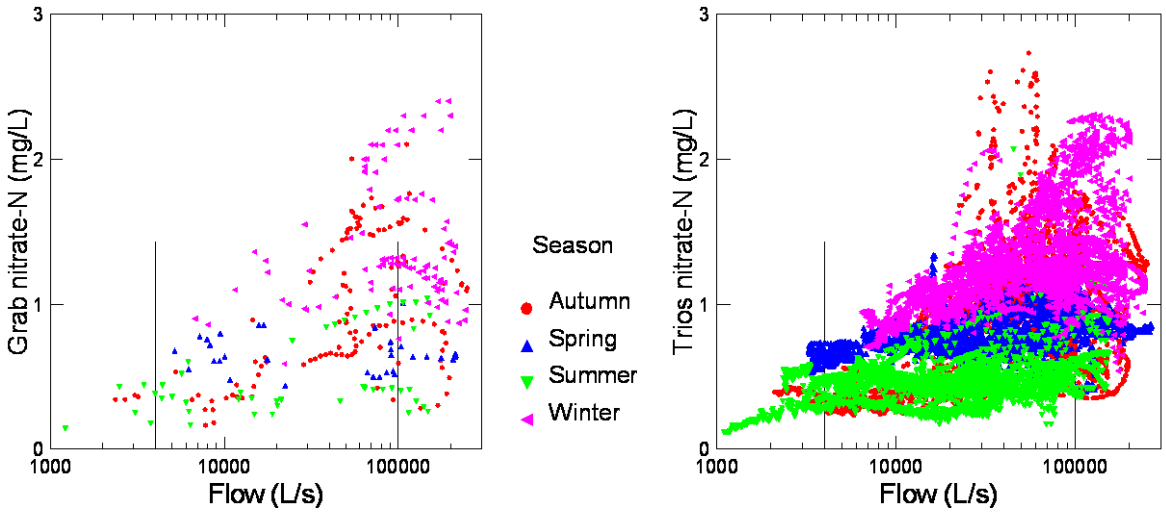


Figure 7-10: Relationship between grab and 10-minute TriOS nitrate-N concentrations and discharge (flow). The dashed vertical lines indicate 4,000 L/s and 100,000 L/s respectively. The number of grab samples collected per season was Autumn 134, Winter 107, Spring 33, and Summer 48, respectively.

Table 7-3: The number of nitrate-N concentration measurements according to three broad flow categories. These data and the two flow thresholds are shown in Figure 7-10.

Flow value (L/s)	Grab		TriOS	
	No. concentration estimates	Proportion of total (%)	No concentration estimates	Proportion of total (%)
All flow conditions	322	100	149,523	100
<4,000	10	3.1	18,760	12.5
4,000-100,000	199	61.8	126,897	84.9
>100,000	113	35.1	3,862	2.6

Table 7-4: The number of nitrate-N concentration measurements by season. These data are summarised in Figure 7-10.

Season	Grab		TriOS	
	No. concentration estimates	Proportion of total (%)	No concentration estimates	Proportion of total (%)
Autumn	134	41.6	37,040	24.8
Winter	107	33.2	34,982	23.4
Spring	33	10.3	38,794	25.9
Summer	48	14.9	38,707	25.9

Grab sample and TriOS sensor ten-minute nitrate-N load estimates agree well, as shown in the time series in Figure 7-11. This is not surprising given the good relationship observed between grab sample and TriOS sensor concentrations (e.g., Figure 7-3).

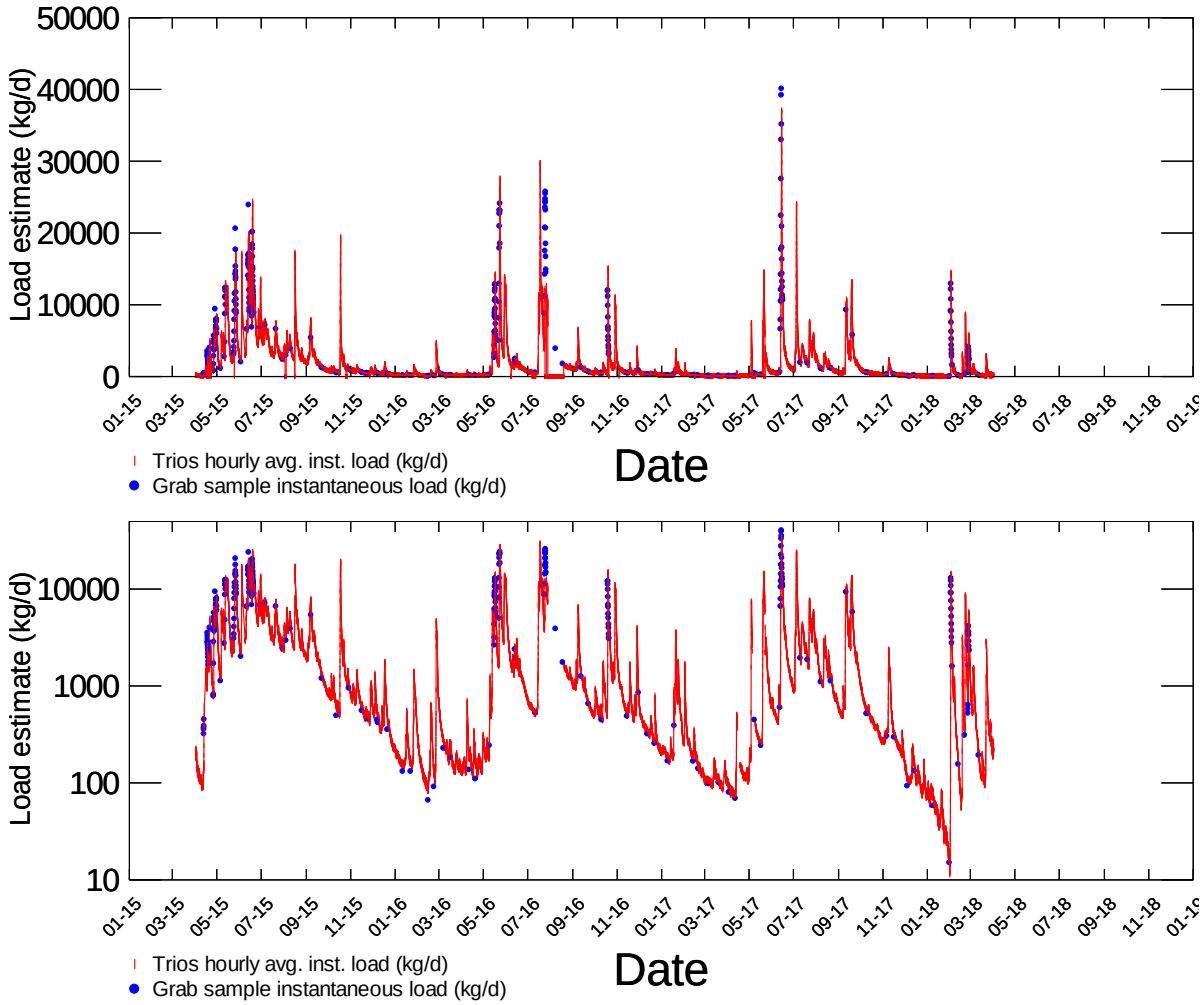


Figure 7-11: Comparison of nitrate-N load estimates derived from grab sample and TriOS sensor concentrations and discharge (flow). The lower figure has a $\log_{10}$ y-axis scale to better demonstrate small values of mass load.

Figure 7-12 demonstrates the good correspondence between instantaneous load estimated from grab samples and that estimated using the TriOS sensor measurements for a period containing a period of low flow, a major flood event and several minor flood events. The TriOS estimates represent the maximum and minimum loads well, and fill the gaps between grab sample estimates in a plausible manner.

It is clear however that two of the three minor peaks during the period 11-28 February 2018, would not have been detected if just grab samples were available. With regard to grab sample flux estimates, none of the short-term variation in flux evident during most of January 2018 would be revealed. This short-term variation in nitrate flux arises from diurnal variation in nitrate concentrations, discussed in Section 7.1.1.

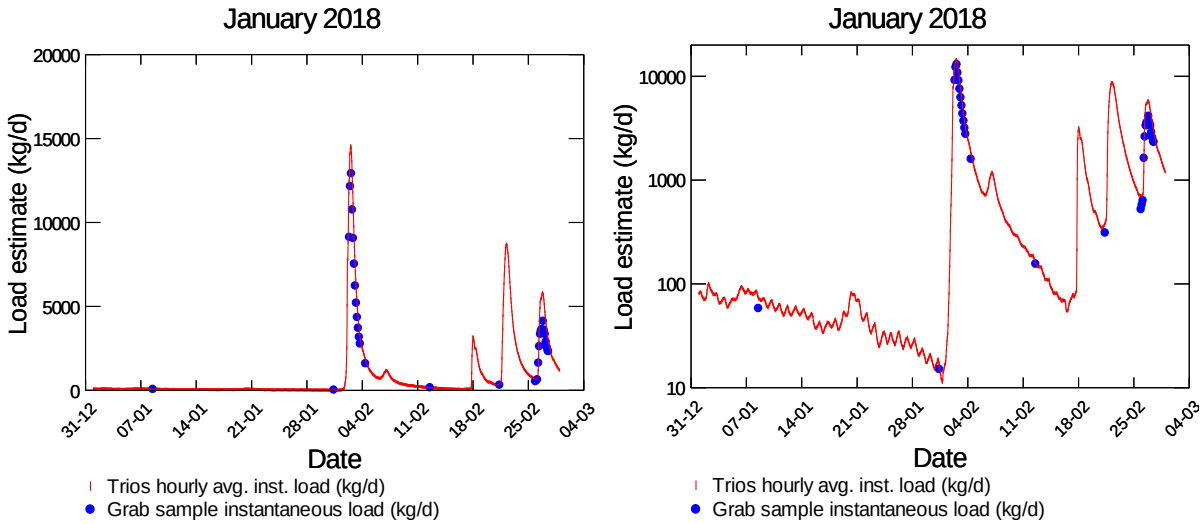


Figure 7-12: Comparison of nitrate-N load estimates derived from grab sample and TriOS sensor concentrations and discharge for a rain event following a period of low flow. The figure on the right has a $\log_{10}$ y-axis scale to better demonstrate small mass load values.

Relatively few periods exist between April 2015 and March 2018 where TriOS sensor estimates are not available. Where gaps in the concentration record exist, these will either have to be filled with concentration estimates, or some other modelling technique is required to create a continuous estimate of load. Figure 7-13 provides a period of almost three weeks during which TriOS sensor concentration estimates were not recorded. This creates a gap in the load estimate record as well.

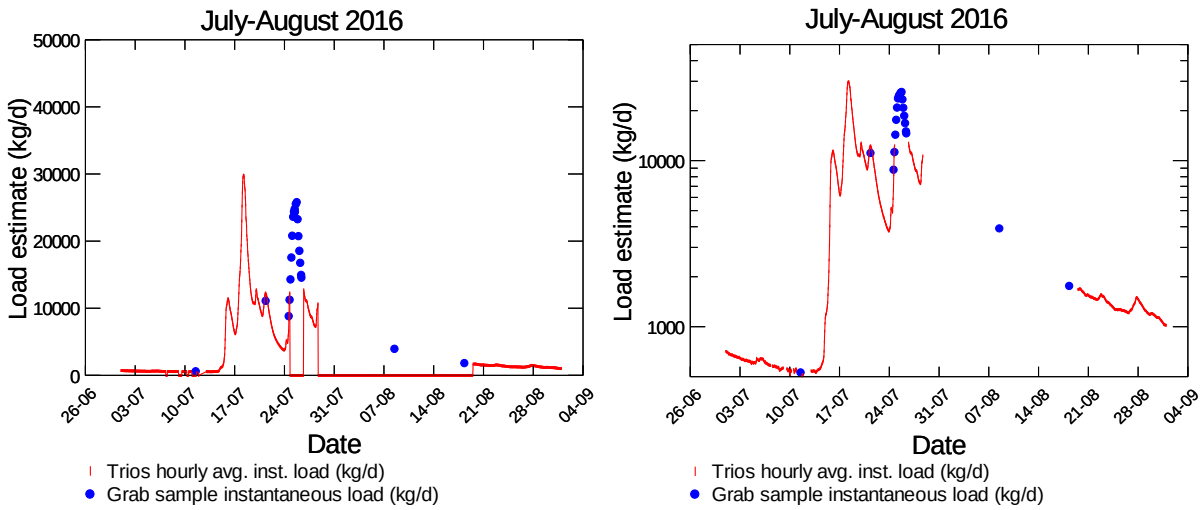


Figure 7-13: Comparison of nitrate-N load estimates derived from grab sample and TriOS sensor concentrations and discharge (flow) during a period of missing record. The figure on the right has a $\log_{10}$ y-axis scale to better demonstrate small values of mass load.

Several sets of load estimation data were generated to explore the effect that the number of concentration samples has on the estimation of catchment loads, as well as to demonstrate the requirement for different load estimation techniques for specific periods. The series of subsets of

data that were generated are described in Table 7-5. The load estimates derived from these subsets of data were then compared with the loads estimated using the ten-minute TriOS data.

Table 7-5: Number of concentration values used to estimate nitrate-N loads per data set. TriOS ten-minute concentration values were multiplied by the corresponding instantaneous flow value, TriOS hourly average values were multiplied by the corresponding hourly averaged flow value, and all other data sets were associated with an hourly average flow value using the LOADEST modelling suite. Selection of data for the period 10:00-11:00 each day was arbitrary – it was intended to replicate a daily grab sample.

Data set	Derivation of data	Load calculation method	Number of concentration records
Grab sample	Data used as hourly average on day collected (if multiple samples collected within an hour), otherwise at time collected, on day of collection	Regression model using LOADEST suite, grab sample estimate and hourly average discharge values	313
TriOS instantaneous data (10 min frequency)	Data used at frequency collected	Product of concentration and flow at time of concentration measurement	151,541
TriOS hourly average data	Hourly average value calculated	Product of hourly average concentration and hourly average flow	26,345
TriOS daily	Hourly average for period 10:00-11:00 each day used	Regression model using LOADEST suite, daily TriOS estimate and hourly average discharge values	1,065
TriOS weekly	Hourly average for period 10:00-11:00 on 1st, 8th, 15th, 22nd and 28th day of each month used	Regression model using LOADEST suite, weekly TriOS estimate and hourly average discharge values	173
TriOS monthly	Hourly average for period 10:00-11:00 on 10th day of each month used	Regression model using LOADEST suite, monthly TriOS estimate and hourly average discharge values	34

Regression models were used to generate a time series of estimates via the LOADEST modelling package. Details of one of the model outputs are included in Appendix D. Additional information is also provided for this model output, and load estimates at various time scales, in Appendix D.

A. Time series plots: Figure E-1 - Figure E-2

B. Bar graphs of average load over the entire assessment period, seasonal and monthly load estimates, with associated error estimates: Figure E-3 - Figure E-7

C. Tables of summary statistics: Table E-1 - Table E-5

The model results are plotted and tabulated with load estimates derived from the ten-minute TriOS data, or hourly average TriOS data. The hourly average and instantaneous TriOS estimates provide very similar nitrate-N load estimates for all time scales (entire period, seasonal and monthly). As a consequence, the hourly average TriOS data were used to create a series of subsets of data for regression modelling. The principal reason for this was to determine and where possible, quantify

the benefits derived from, more intensive measurement of stream concentrations when determining contaminant load estimates.

a) Data gaps and using regression modelling to fill these

In Figure 7-14 the grab sample instantaneous load, TriOS sensor load and the load predicted using a regression model based on grab sample concentrations and flow are shown together. The two figures indicate that the regression model provides nitrate-N load estimates that match both grab sample and TriOS estimated loads. The figure on the left also indicates how a regression model may be used to estimate loads for the periods of missing TriOS concentration record.

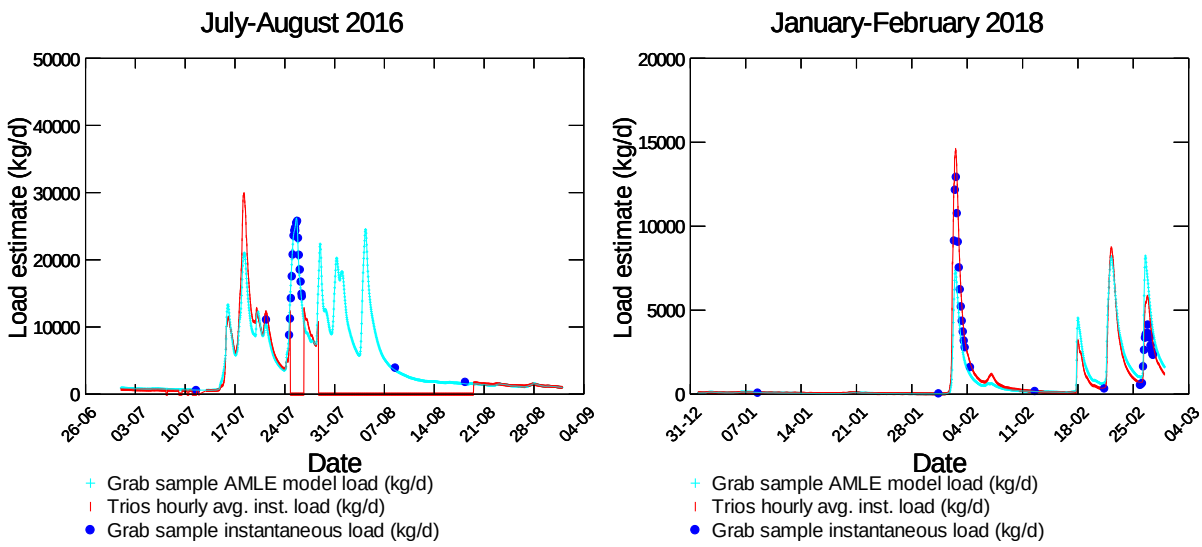


Figure 7-14: Comparison of nitrate-N load estimates derived from grab samples (instantaneous load), grab samples (as LOADEST model estimate) and TriOS sensor concentrations and discharge. The figure on the left includes a period containing a minor flood event and periods of missing TriOS data. The figure on the right includes a major flood event and several smaller flood events.

Figure 7-15 compares the results from various load estimation techniques for the period January-February 2018. A $\log_{10}$ scale is used to better represent the data over the full flux estimate range. The regression model provides reasonable estimates of elevated and very low loads, but cannot easily define valleys that occur on "shoulders" or periods of persistently elevated loads (e.g., as occur during the second half of February). The model is also unable to indicate the diurnal fluctuations in nitrate-N load that occurred during January 2018. These diurnal fluctuations arise from biological processes occurring in the river (e.g., nutrient uptake by periphyton and vascular plants, and loss of nitrate-N following denitrification). The latter processes could potentially be included in a more sophisticated process-based model if additional data were available.

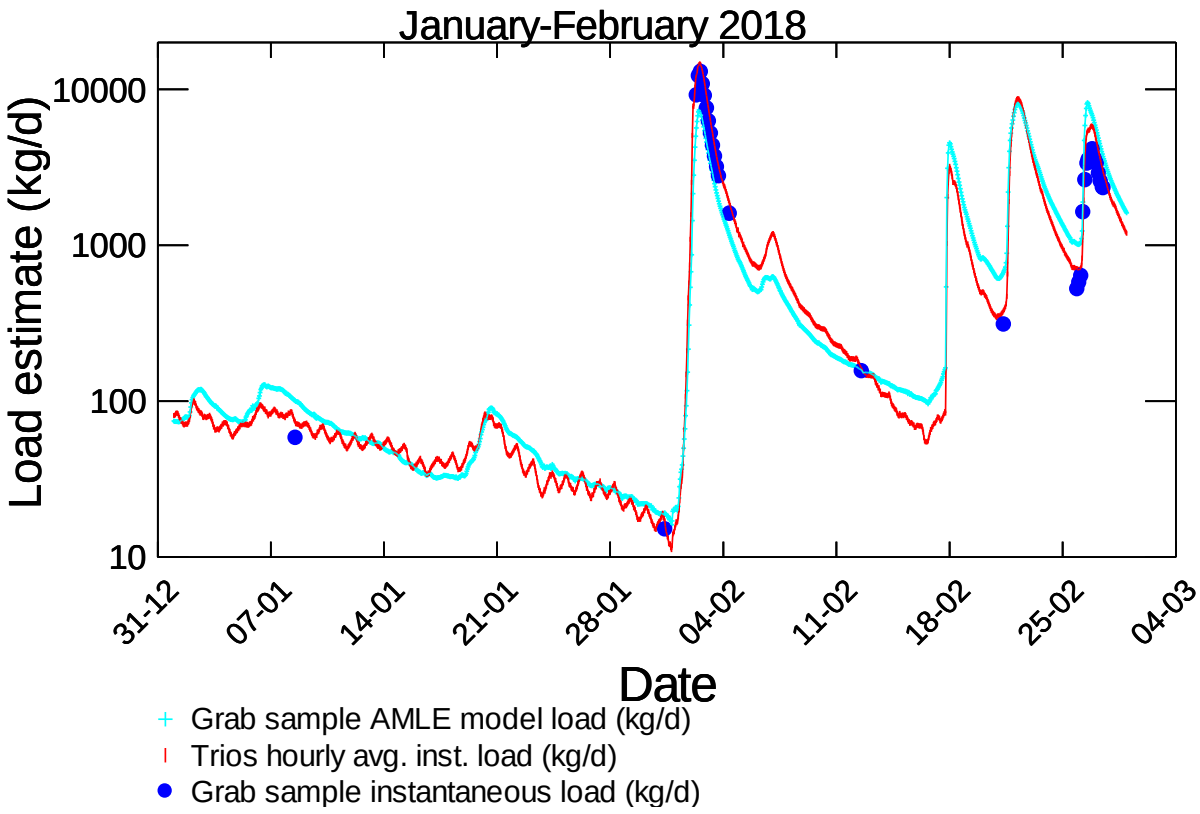


Figure 7-15: Comparison of nitrate-N load estimates derived from grab samples (instantaneous load), grab samples (as LOADEST model estimate) and TriOS sensor concentrations and discharge. The figure includes a major flood event and several smaller flood events.

Earlier the question was asked "How frequently should TriOS sensor measurements be recorded?" Figure 7-15 indicates that if detailed information regarding short duration, biological processes is required, high frequency sensor measurement is necessary. From the Kakanui River case study (Section 6.1.4), hourly frequency appears adequate to characterise most short-term events in rivers of this magnitude. Figure 7-15 also indicates that a relatively simple regression model using relatively few grab sample estimates is able to provide similar load estimates to those derived from high frequency measurements.

(b) Comparison of various model outputs

The results of the six estimation techniques outlined in Table 7-5 are summarised in Figure 7-16 and Figure 7-18 for the entire monitoring period, and at seasonal and monthly scales, respectively. Monthly data are summarised graphically in Figure E-1 through Figure E-7, and the summary statistics for loads estimated using each estimation technique are provided in Table E-1 through Table E-5 in Appendix E. In the discussion that follows it is assumed that the most accurate estimate of load is provided by the ten-minute TriOS data. Reasons supporting this assumption include:

- the very large number of concentration estimates that can represent all flow, time of day and seasonal conditions, and
- the large number of "correct" estimates are able to compensate for the relatively few incorrect values (i.e., produced as spikes or periods of missing data).

Data are expressed in terms of difference from the TriOS instantaneous estimate in Figure 7-19 (entire estimation period) and Figure 7-20 (seasonal and monthly periods).

The TriOS instantaneous and hourly average load estimates are almost identical at entire data set and seasonal scales. The error estimates are also very similar.

The grab sample/AMLE regression model provide the largest load estimates for the entire assessment period. The seasonal estimates (Figure 8-17) indicate that most of the over-estimation arises in the winter season, and in a few months in the winter-spring period. The confidence intervals are similar to those of the TriOS weekly estimates, and smaller than those of the TriOS monthly subsample estimates.

The TriOS monthly subsample provide the lowest average load estimates for the entire monitoring period – this under estimation occurs primarily during the autumn and winter periods. The model over-estimates the average load slightly relative to the daily and weekly subsamples of TriOS data, but provides largest estimates of loads for the summer season. In all periods, the error associated with the monthly subsample estimate is largest.

Several of the larger discrepancies between grab sample estimates and TriOS ten-minute nitrate-N load estimates relate to missing data. Table 7-6 lists months where more than 144 records are missing – the large difference between estimates in the July and August 2016 period probably relate to these periods of missing data. The difference between nitrate-N load estimates relative to TriOS sensor instantaneous concentrations for each month in the assessment period are shown in Figure 7-19, where these differences are shown as a proportion.

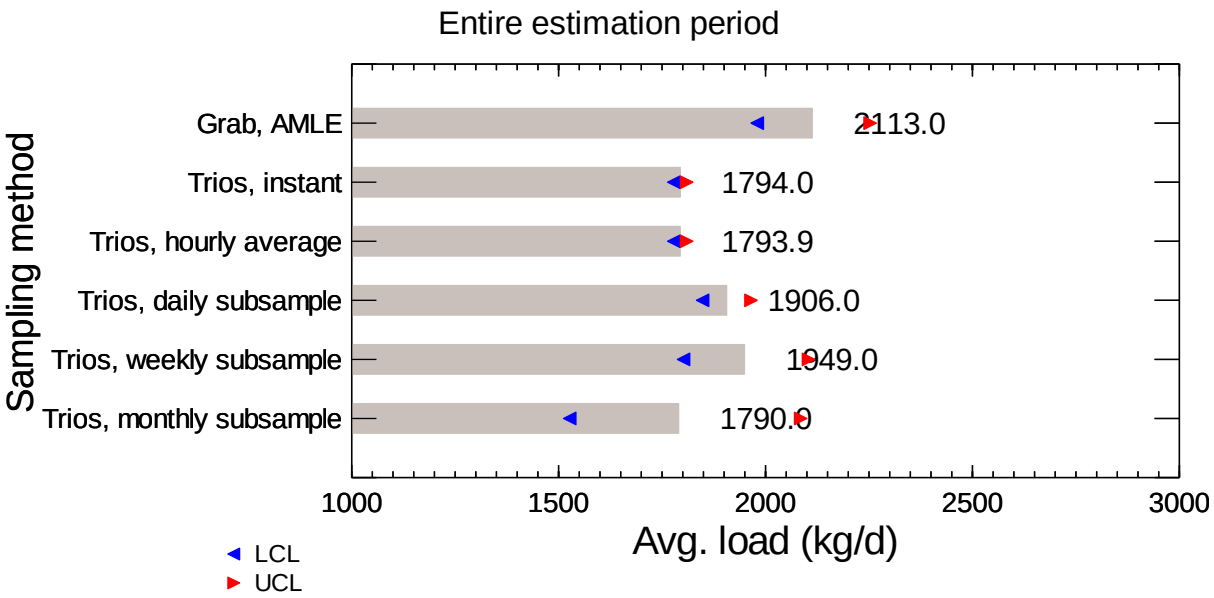


Figure 7-16: Comparison of nitrate-N load estimates derived from grab samples (as LOADEST AMLE model estimate) and TriOS sensor concentrations and discharge for the full monitoring period, April 2015-March 2018. The blue and red symbols indicate the 95th% lower and upper confidence intervals, respectively. The TriOS estimates are derived from instantaneous measurements, monthly and weekly subsamples. The daily TriOS samples represent the hourly average concentration measured each day between 10:00 and 11:00. The weekly TriOS samples represent the hourly average concentration measured each day between 10:00 and 11:00 on the 10th day of each of the 1st, 8th, 15th 22nd and 28th day of each month. The monthly TriOS samples represent the hourly average concentration measured each day between 10:00 and 11:00 on the 10th day of each month.

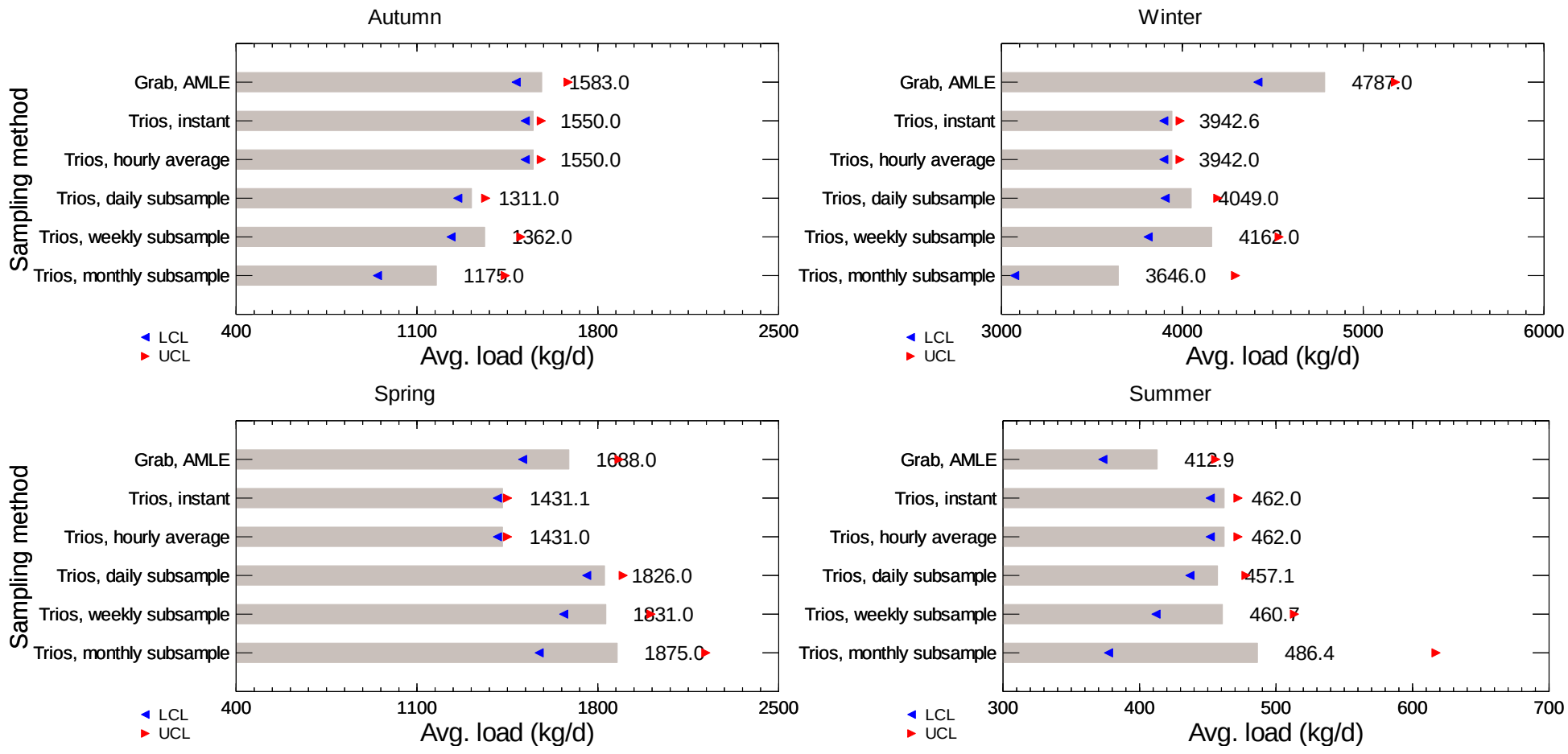


Figure 7-17: Comparison of nitrate-N load estimates derived from grab samples (as LOADEST AMLE model estimate) and TriOS sensor concentrations and discharge for the full monitoring period, April 2015-March 2018, expressed as seasonal values. The blue and red symbols indicate the 95th% lower and upper confidence intervals, respectively. Autumn= March- May, Winter= June- August, Spring= September - November, Summer = December- February. The TriOS estimates are derived from instantaneous measurements, monthly and weekly subsamples. The daily TriOS samples represent the hourly average concentration measured each day between 10:00 and 11:00. The weekly TriOS samples represent the hourly average concentration measured each day between 10:00 and 11:00 on the 10th day of each of the 1st, 8th, 15th 22nd and 28th day of each month. The monthly TriOS samples represent the hourly average concentration measured each day between 10:00 and 11:00 on the 10th day of each month.

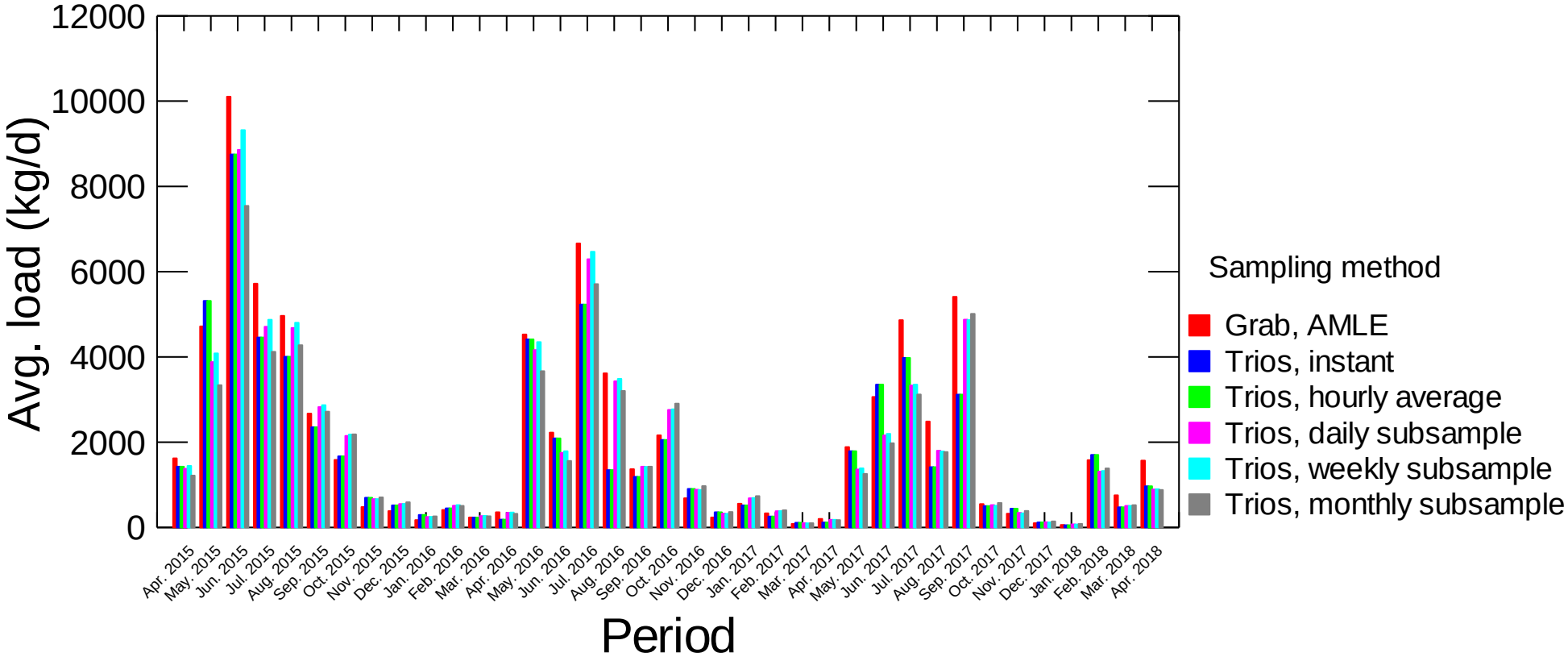


Figure 7-18: Comparison of nitrate-N load estimates derived from grab samples (as LOADEST AMLE model estimate) and TriOS sensor concentrations and discharge for the full monitoring period, April 2015-March 2018, expressed as monthly values. The TriOS estimates are derived from instantaneous measurements, monthly and weekly subsamples. The daily TriOS samples represent the hourly average concentration measured each day between 10:00 and 11:00. The weekly TriOS samples represent the hourly average concentration measured each day between 10:00 and 11:00 on the 10th day of each of the 1st, 8th, 15th 22nd and 28th day of each month. The monthly TriOS samples represent the hourly average concentration measured each day between 10:00 and 11:00 on the 10th day of each month.

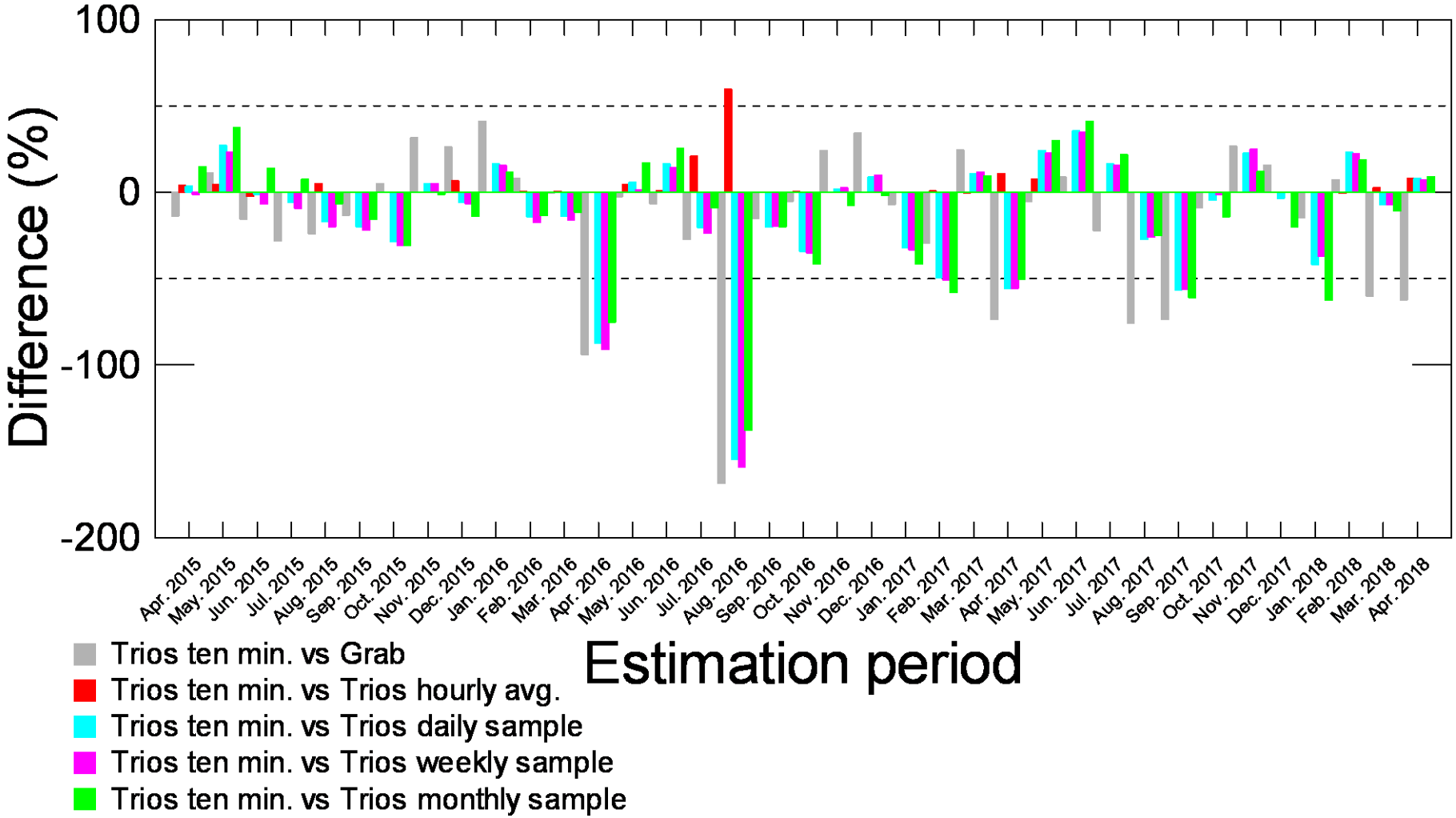


Figure 7-19: Difference between nitrate-N load estimates relative to TriOS sensor instantaneous concentrations for each month in the assessment period expressed as percent difference. The dashed lines indicate ±50%. The TriOS estimates are derived from instantaneous measurements, monthly, weekly and daily subsamples. The daily TriOS samples represent the hourly average concentration measured each day between 10:00 and 11:00. The weekly TriOS samples represent the hourly average concentration measured each day between 10:00 and 11:00 on the 10th day of each of the 1st, 8th, 15th 22nd and 28th day of each month. The monthly TriOS samples represent the hourly average concentration measured each day between 10:00 and 11:00 on the 10th day of each month.

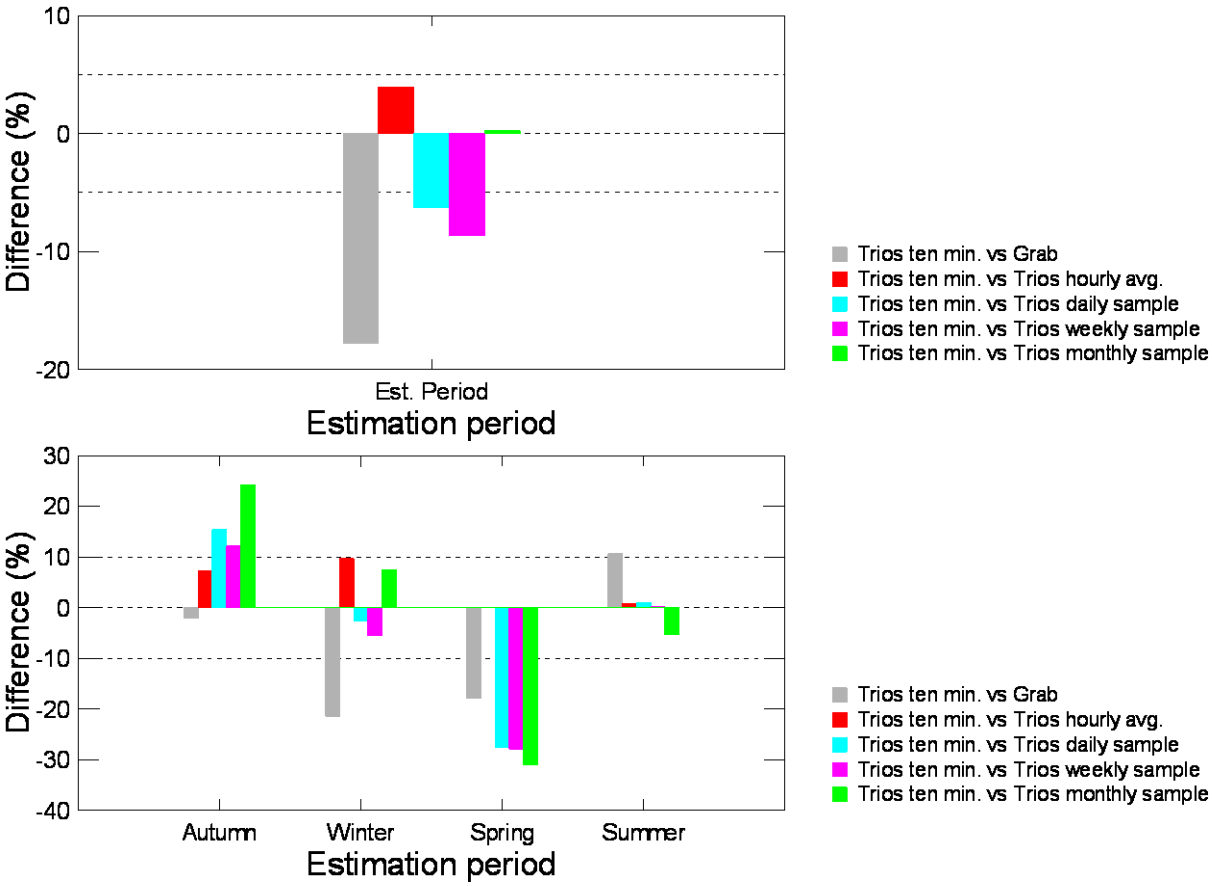


Figure 7-20: Difference between nitrate-N load estimates relative to TriOS sensor instantaneous concentrations for the entire monitoring period (top) and by season (bottom) expressed as percent difference. The dashed lines indicate ±5% in the upper figure and ±10% in the lower figure. The TriOS estimates are derived from instantaneous measurements, monthly, weekly and daily subsamples. The daily TriOS samples represent the hourly average concentration measured each day between 10:00 and 11:00. The weekly TriOS samples represent the hourly average concentration measured each day between 10:00 and 11:00 on the 10th day of each of the 1st, 8th, 15th 22nd and 28th day of each month. The monthly TriOS samples represent the hourly average concentration measured each day between 10:00 and 11:00 on the 10th day of each month.

Table 7-6: Number of missing 10-minute TriOS sensor records per month. Only months where 144 values or more were missing (representing a 24-hour period or more) have been selected.

Month	No missing values	Days of missing record
Apr-15	467	3.2
Aug-15	362	2.5
Oct-15	276	1.9
Jul-16	1,126	7.8
Aug-16	2,675	18.5
Apr-17	613	4.2
May-17	767	5.3
Mar-18	225	1.5
Apr-18	459	3.1

Another reason for the discrepancy between sensor-derived load estimates and estimates derived from regression models is illustrated in Figure 7-21, where 24 grab samples cover the four day period of a flood event. There is good general correspondence between the two estimation methods, with three areas of difference worth noting:

- the grab samples do not capture the steep increase in nitrate-N concentration on the rising limb of the hydrograph
- the TriOS sensor possibly overestimates nitrate-N concentrations on the rising limb, and
- the TriOS sensor possibly underestimates the nitrate-N concentration under peak flow conditions.

None of these areas of difference are cause for concern, but they do confirm the requirement to fully understand the spectral absorbance technique, particularly the effect of interferences and the efficacy of the algorithms used to correct for these interferences. Specific investigation would be required to confirm whether the potential effects noted above require specific correction.

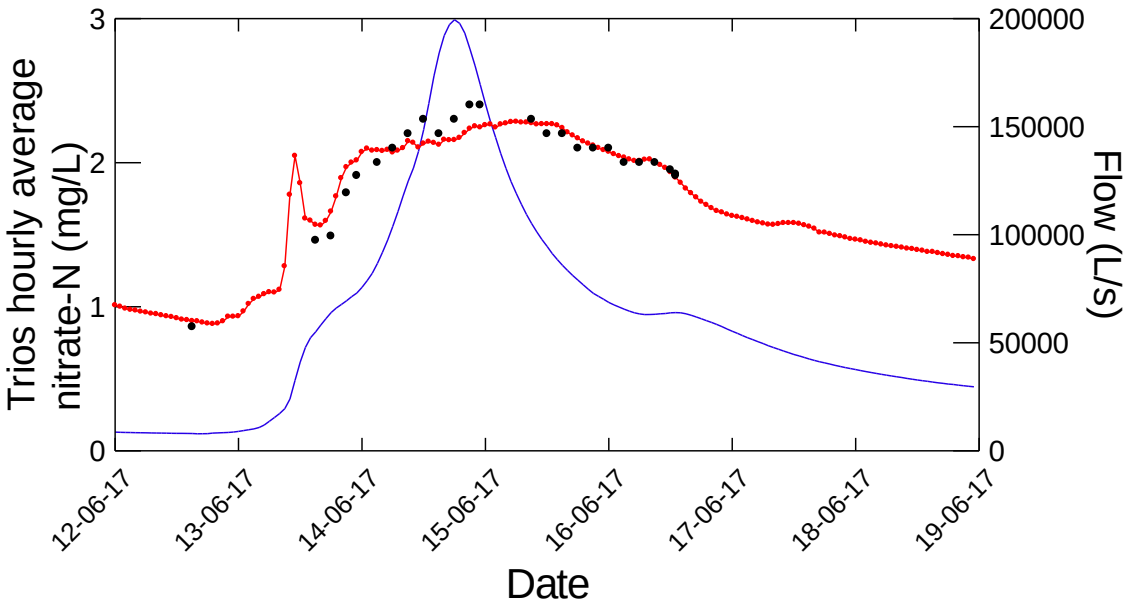


Figure 7-21: Comparison of grab sample and TriOS instantaneous nitrate-N concentrations for a flood event in June 2017.

8 Case study 3: NIWA Mataura River data

As outlined in Section 5, NIWA runs two TriOS OPUS nitrate-N sensors on the Mataura River at Mataura Island in Southland. The Mataura River is much larger than the Kakanui and Aparima rivers and NIWA has been using two monitoring approaches in parallel. The deployment of both instruments is illustrated in Appendix I:

- an in-river deployment, with one TriOS sensor installed in the river channel (protected from physical damage using suitable sheathing), and
- an out-of-channel deployment, where river water is pumped to a TriOS sensor installed in an enclosure on the bank, with measurement made in flow chamber sleeve at atmospheric pressure.

NIWA operates this site as a benchmark site, to trial new or emerging techniques. The dual sensor deployment strategy allows the relative benefits and weaknesses of in-river vs. out of channel measurement to be compared.

8.1 Time series data

Time series data for the two TriOS sensors are shown in Figure 8-1 through Figure 8-3 for various timescales. General agreement between the grab sample concentrations and the bulk of the measurements from either the TriOS River or TriOS Pumped sensors is evident. However, a considerable number of TriOS River sensor values are substantially greater than those of the grab samples. As Figure 8-1 indicates, values less than zero are also reported. The grab samples indicate that nitrate-N concentrations are typically within a range from approximately 0.1 to 3 mg/L (discussed further below).

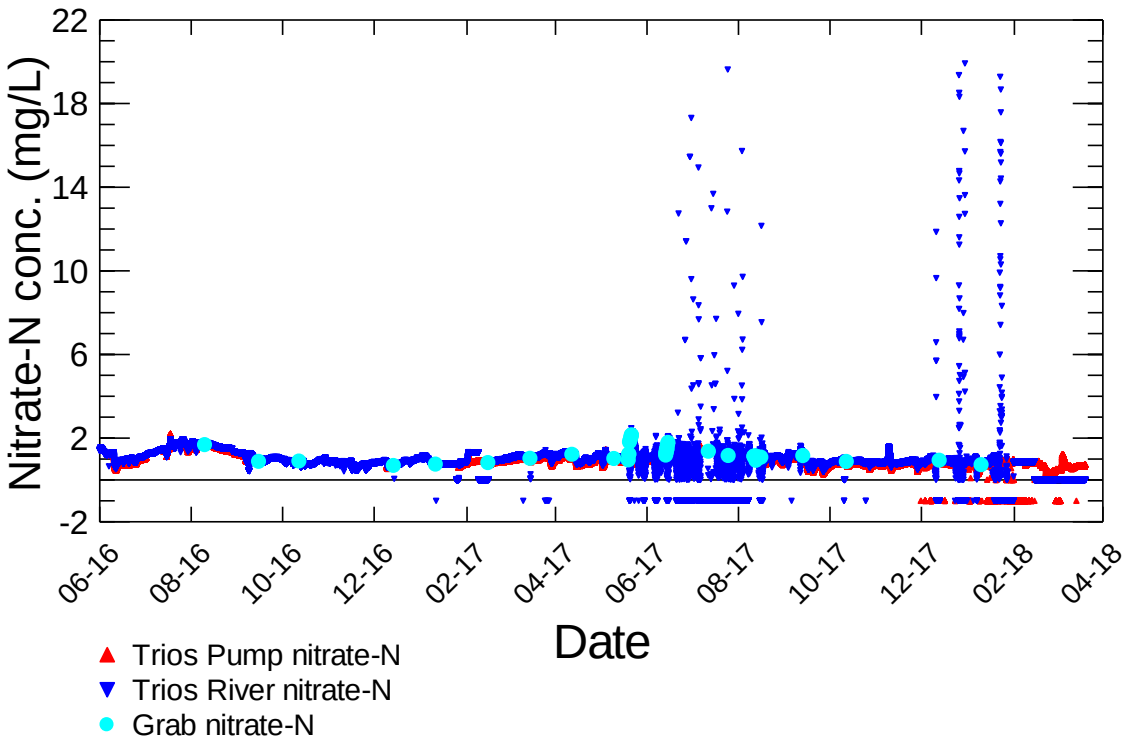


Figure 8-1: Comparison of grab sample and TriOS sensor nitrate-N concentrations, from June 2016 to March 2018 (full available record).

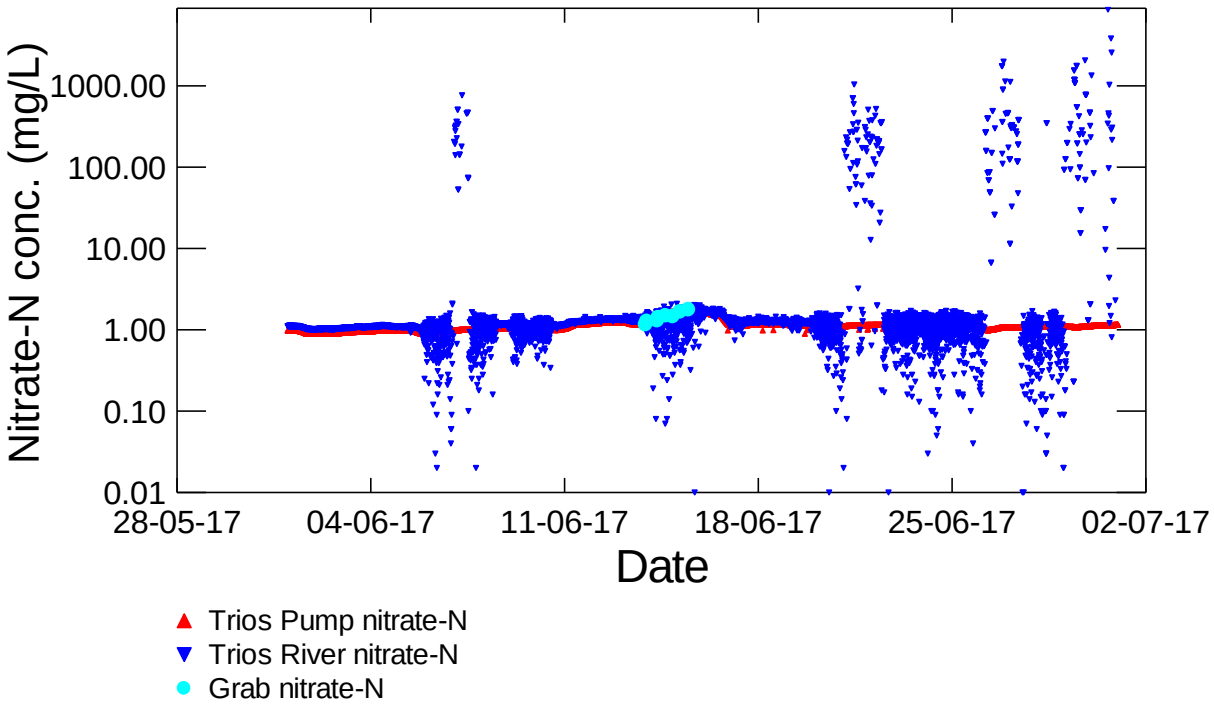


Figure 8-2: Comparison of grab sample and TriOS sensor nitrate-N concentrations, June 2017.

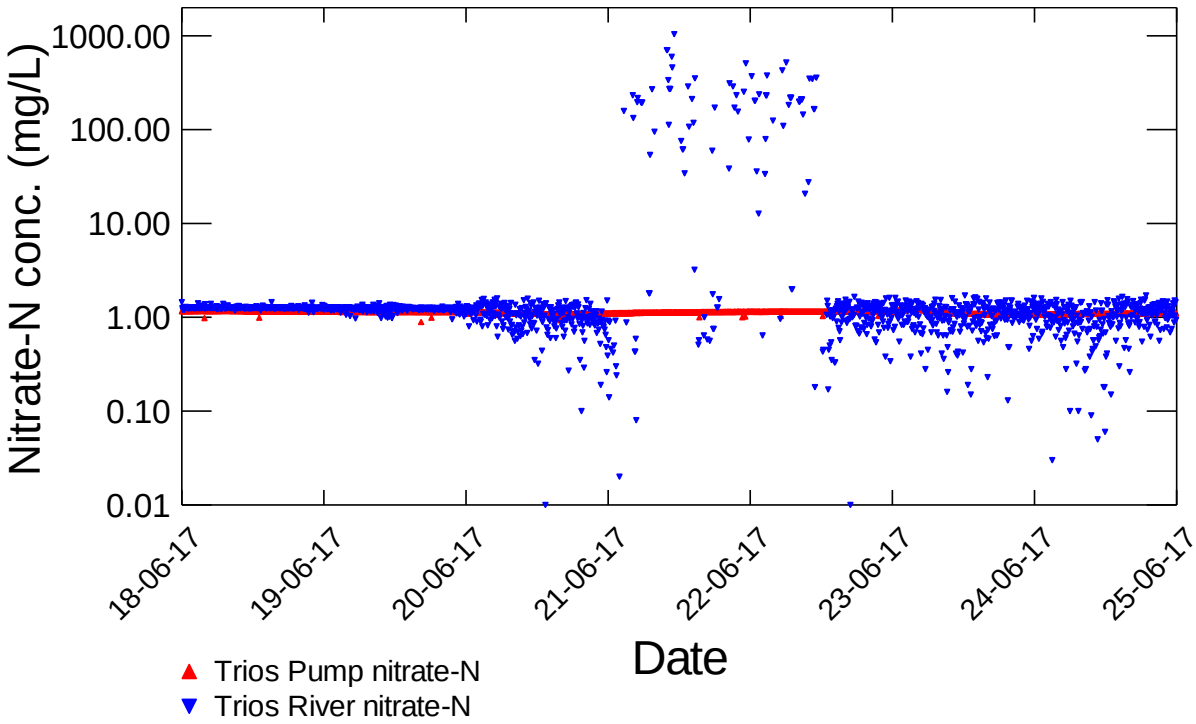


Figure 8-3: Comparison of grab sample and TriOS sensor nitrate-N concentrations, 18-25 June 2017.

As Figure 8-4 shows, TriOS sensor deployed in the river recorded many nitrate-N concentrations outside the range 0.1 – 3.0 mg/L, and these occurred under all flow conditions. There are a larger number of extremely high (and non-sensical) nitrate concentrations under higher flow conditions. The cause of these high readings is unknown.

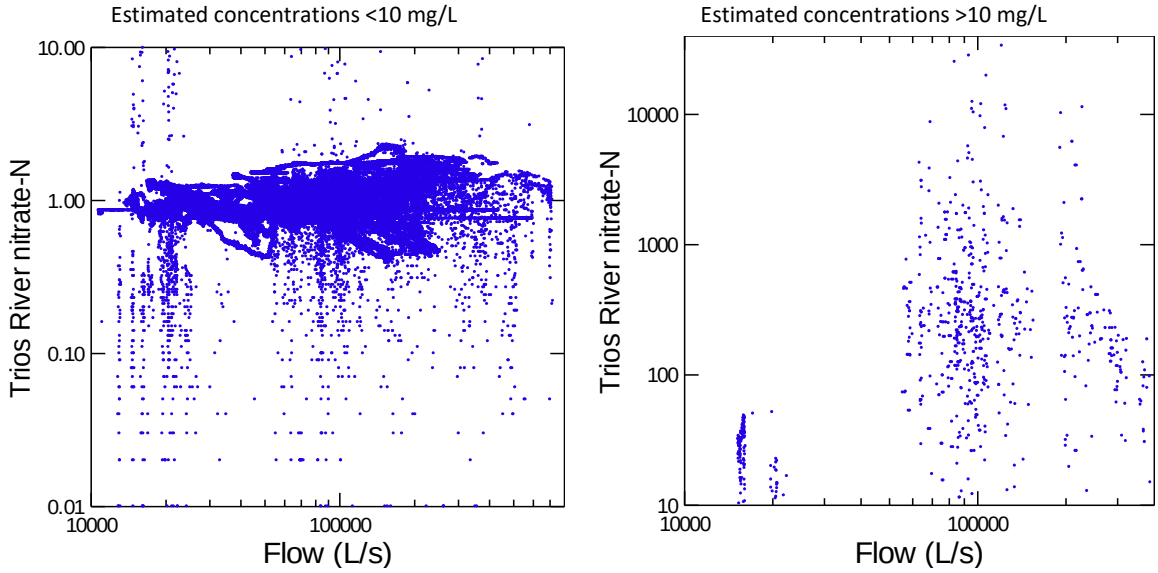


Figure 8-4: Relationship between TriOS River instantaneous nitrate-N concentrations and discharge (flow) for two ranges of concentration values. The data in the righthand plot are all considered erroneous.

8.2 Concentration characteristics

The summary statistics in Table 8-1 indicate that the wide range of values observed in the both the TriOS River and TriOS Pump data influence the median and mean values, even when apparent outlier data are excluded. If an identified management target for the Mataura River was "median nitrate-N concentrations are not to exceed 1 mg/L", either of the subsamples of TriOS sensor data sets in Table 8-1 would indicate compliance, whereas the grab samples would not.

Table 8-1: Summary statistics for nitrate-N measurements, Mataura River. Data were selected from the entire monitoring records where nitrate-N concentrations were > 0 mg/L and < 3 mg/L. The box-and-whisker plot represent the selected data only.

Statistic	Grab	River	Pump
N	45	178182	148370
Minimum	0.66	0.01	0.01
Maximum	2.11	2.89	2.2
Median	1.096	0.95	0.89
Mean	1.206	1.009	0.934
SE of Mean	0.055	0.001	0.001
Mode	-	0.86	0.77
95.0% LCL of Mean	1.096	1.008	0.933
95.0% UCL of Mean	1.317	1.011	0.936
Percentiles:			
10th	0.845	0.74	0.62
90th	1.78	1.37	1.35

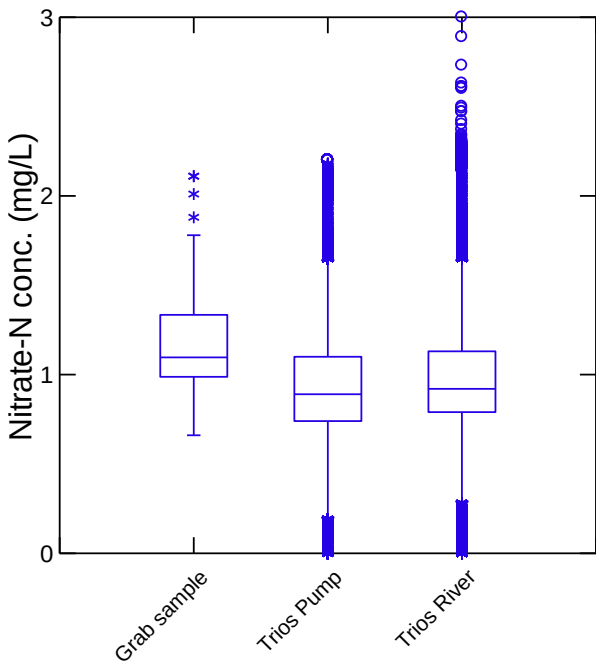


Figure 8-5 illustrates the relationship between grab sample concentration and discharge in the Mataura River for the period 2012-2017 inclusive. These data were sourced from the LAWA website for the nearby ES monitoring site "Mataura at Seaward Downs". The graph on the right presents data for the 2016-2018 period for which TriOS data exist. The grab sample concentration data represent the range of flow conditions and concentration range indicated by the longer data set reasonably well. The longer-term data set indicate that nitrate-N concentrations are unlikely to be less than 0.2 mg/L or greater than 2.5 mg/L.

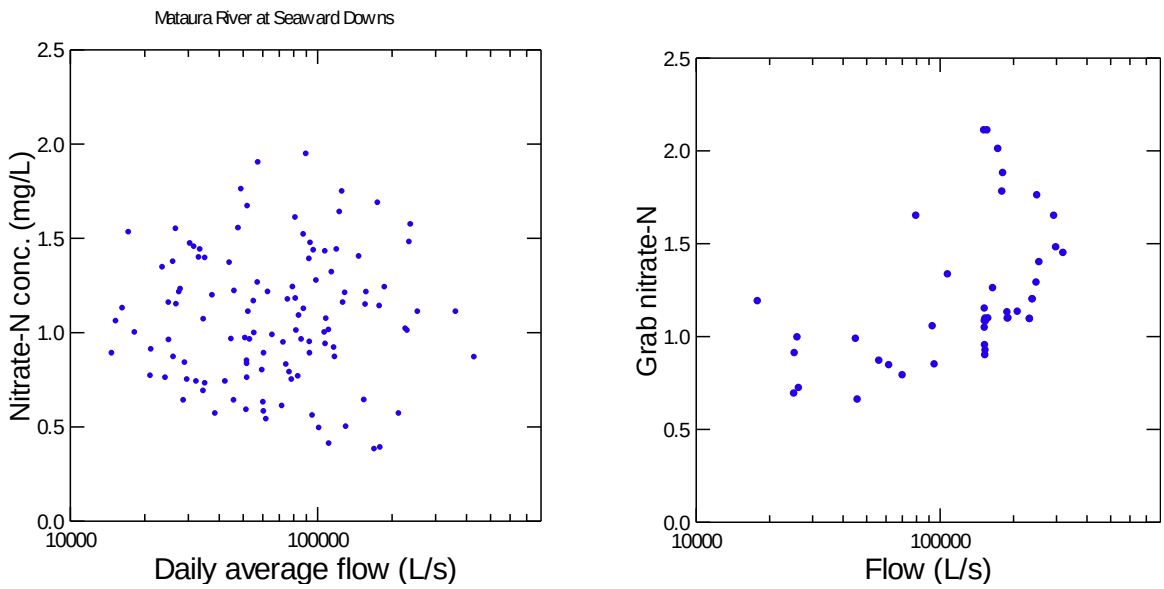


Figure 8-5: Relationship between grab sample nitrate-N concentration and discharge (flow). Note x-axis has $\log_{10}$ scale.

The relationship between the two TriOS data sets sharing grab sample data is shown in Figure 8-6. Only data points that have paired grab samples are included in the figure.

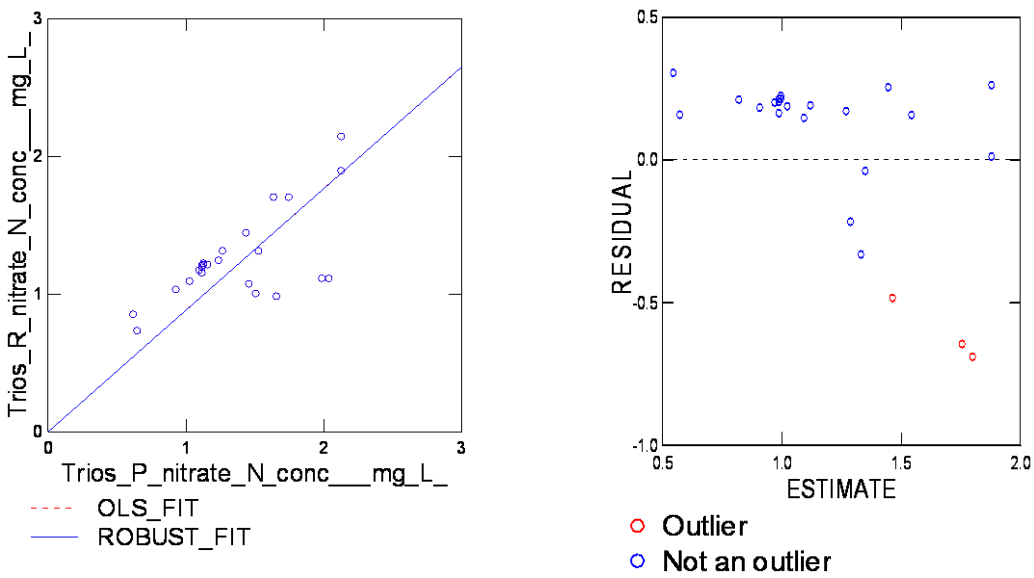


Figure 8-6: Comparison of nitrate-N concentrations from pumped vs river TriOS sensors. The figure on the left includes an Ordinary Least Squares (OLS) and Least Absolute Deviation model fit, and the figure on the right indicates three identified outliers.

With the three outliers included, the model explains less than half the variance (R^2 = 0.435) – with the three outliers removed, the R^2 increase to 0.98. The residuals are reasonably evenly distributed across the concentration range, but indicate positive bias in the river measurements. The slope of the line is ~1 (0.971), indicating that the in-river TriOS sensor slightly underestimates nitrate-N concentration relative to the TriOS sensor installed out of the river channel.

The relationship between TriOS sensor and grab sample nitrate-N concentrations is shown in Figure 8-7. A strong correlation exists for the pumped TriOS estimates and the grab sample concentrations (R^2 = 0.95); the relationship between the in-river TriOS sensor and the grab sample is relatively weak (R^2 = 0.43), but increases to 0.84 if the three outlies are removed.

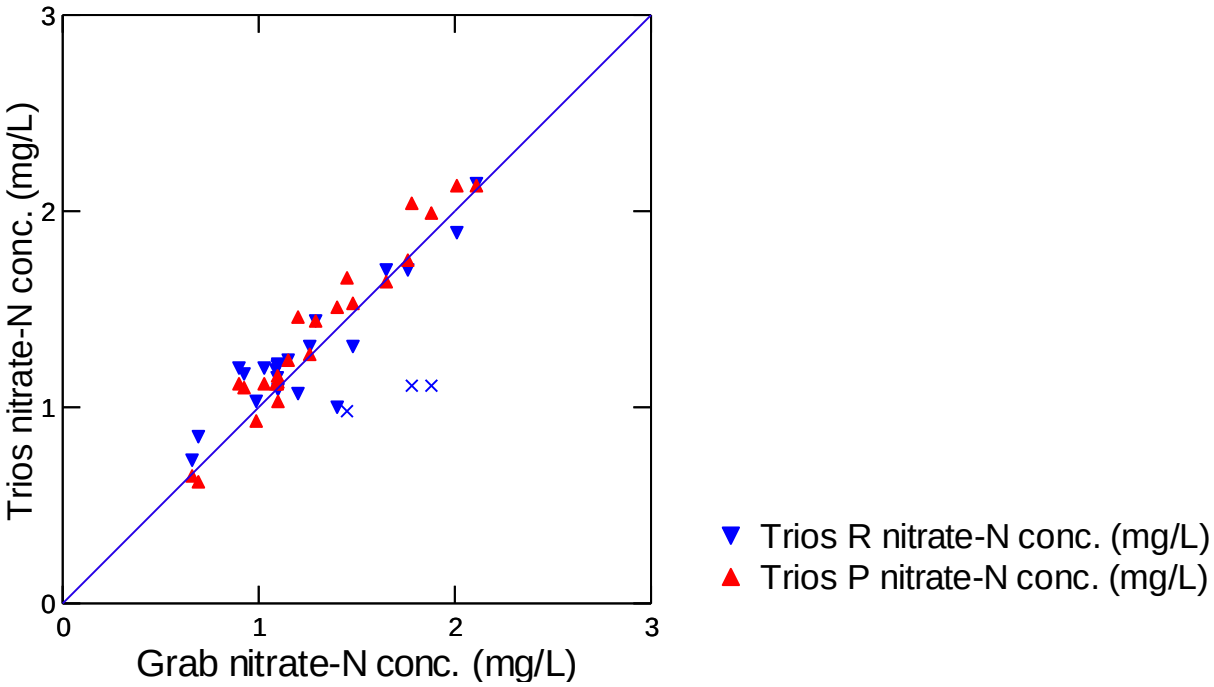


Figure 8-7: Comparison of TriOS sensor with grab sample nitrate-N concentrations. Three outlier values previously identified are shown as crosses. The 1:1 line is indicated by the blue line.

In Figure 8-8, the relationship between the difference between the TriOS sensor and grab sample nitrate-N concentrations are shown. For the pumped sensor, there is little suggestion of a trend associated with nitrate-N concentration, suggesting little measurement bias. A weak correlation between sensor response and grab sample concentration is evident (R^2 = 0.35), suggesting an increasing difference between sensor estimates and grab sample concentration. There was no obvious explanation for this behaviour, although there was a weak positive relationship with river discharge, and a slightly stronger but negative relationship with suspended sediment concentrations. However, similar relationships were observed between pumped TriOS nitrate-N data and these variables, indicating that they did not affect one or other measurement method substantially.

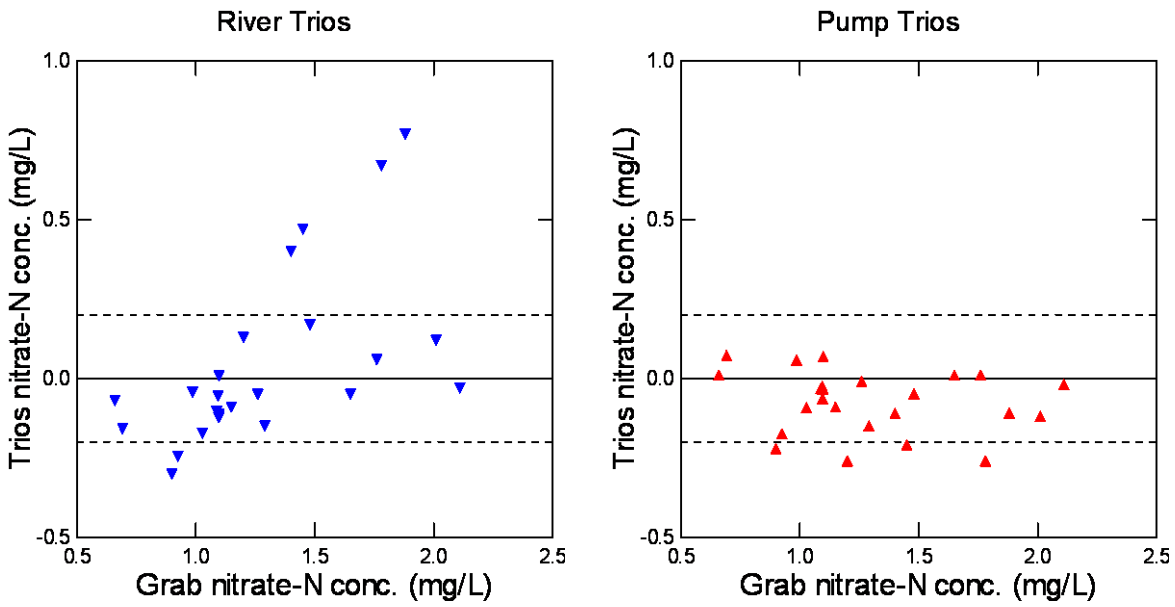


Figure 8-8: Difference between TriOS sensor and grab sample nitrate-N concentrations according to sensor location. The horizontal dashed lines indicate ±0.2 mg/L.

Figure 8-9 presents three subsets of data selected to demonstrate the effect that outlier data may have on determining water quality characteristics. The three subsets include all available grab sample concentrations as TriOS sensor estimates are excluded because they are either missing or fall outside of the range defined by the long-term concentration record. Taking into account that the confidence intervals overlap, the TriOS River values underestimate the mean concentration, and failure to exclude outlier data may lead to incorrect management decisions. The median concentration values derived from these subsets are summarised in Table 8-2, which indicates that compliance with the fictional "management target" may be biased according to the data selection method.

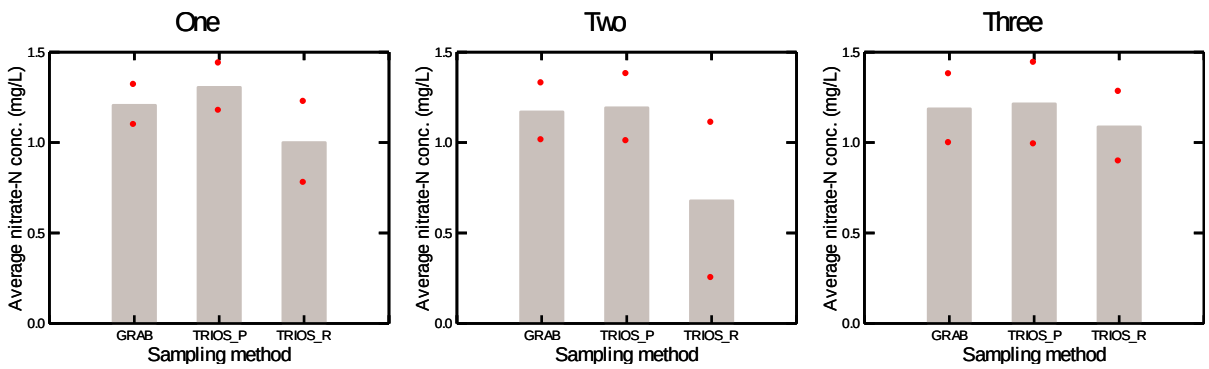


Figure 8-9: Grab sample and TriOS sensor instantaneous nitrate-N concentrations for three subsets of data. The red dots indicate the 95th% lower and upper confidence intervals. The criteria for data selection are summarised in the caption to Table 8-2.

Table 8-2: Median nitrate-N concentrations derived from subsets of data. One = all TriOS values corresponding to a grab sample (includes missing values), Two = all TriOS data corresponding to a grab sample where both a TriOS River and TriOS Pump value exist, Three = all TriOS data corresponding to a grab sample where both a TriOS River and TriOS Pump value exists and where TriOS River and TriOS Pump estimates lie within the range 0.2 to 2.5 mg/L. Values in parentheses indicate number of results in each subset for each measurement technique.

Selected subset of data	Median nitrate-N conc. (mg/L)		
	Grab nitrate-N	TriOS River	TriOS Pump
One	1.096 (45)	1.17 (45)	1.13 (40)
Two	1.097 (35)	0.895 (35)	1.23 (35)
Three	1.17 (14)	0.985 (14)	1.23 (14)

The above example highlights the importance of collecting high quality data, and for having sound methods in place for excluding outlier data prior to undertaking a detailed assessment. ”More is not necessarily better” if poor quality data are not excluded.

Various statistical methods exist to evaluate the quality of data following various data screening, subsampling or replacement actions. Two examples are provided in Appendix F, where two regression techniques are used to assess the relationship between the TriOS river data and the TriOS pumped data sets. In the first example, the entire data set is used, and the model identifies and omits outlier data. In the second example, an a priori selection is applied, and the number of spurious data are reduced before the assessment occurs. Although the rigour of the relationship between the two data sets is improved, there is obviously high autocorrelation in both sets of data. This may have other unwanted effects when undertaking regression analysis. In this exercise that was not an important consideration, but it does highlight another effect of collecting “too much” data. The volume of available data makes manipulation and analysis cumbersome, and an excessive volume of data may hide – rather than reveal – important information.

8.3 Sampling frequency

The two Mataura River TriOS sensors collected data at a five-minute frequency over the period March 2016 to March 2018. More than 150,000 and 200,00 data exist for the TriOS pumped and river sensors, respectively. Figure 8-10 indicates that there is little benefit in collecting data at higher than daily frequency for general resource management purposes, and probably for most modelling applications. Should a daily value be required, it would however be prudent to collect several measurements and report the median (or mean) to minimise potential for bias arising from transient spikes.

Should highly precise data be required over short timescales, then as demonstrated in Figure 8-11 it might be necessary to collect high frequency data. Provided large transient spikes are removed from these data, it is possible to estimate variability at sub-hourly intervals with high precision and accuracy. It would require considerable effort to ensure that this level of precision and accuracy is maintained throughout a long duration sensor deployment.

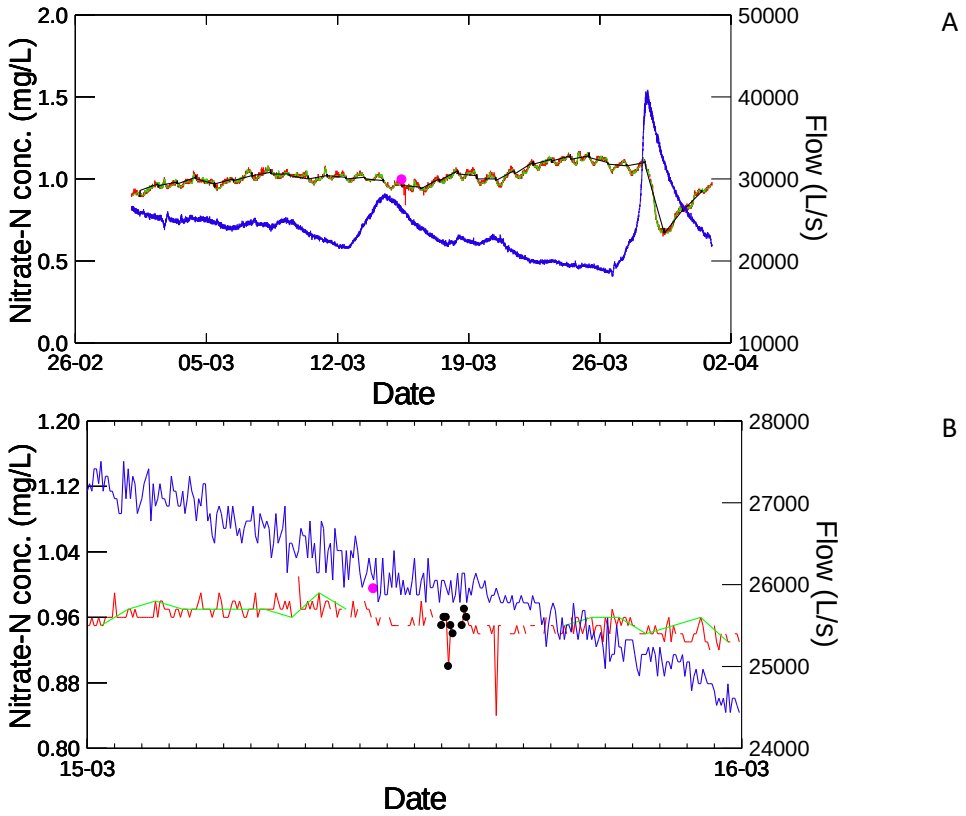


Figure 8-10: Time series of TriOS pump sensor nitrate-N concentrations for three subsets of data. The red line represents five-minute data, the green line represents one-hour data (the 30-minute value of each hour) and the black dots represent a one-hour sample of five minute TriOS data (the 12 values measured between 13:00 – 14:00). The magenta dot is a grab sample concentration value.

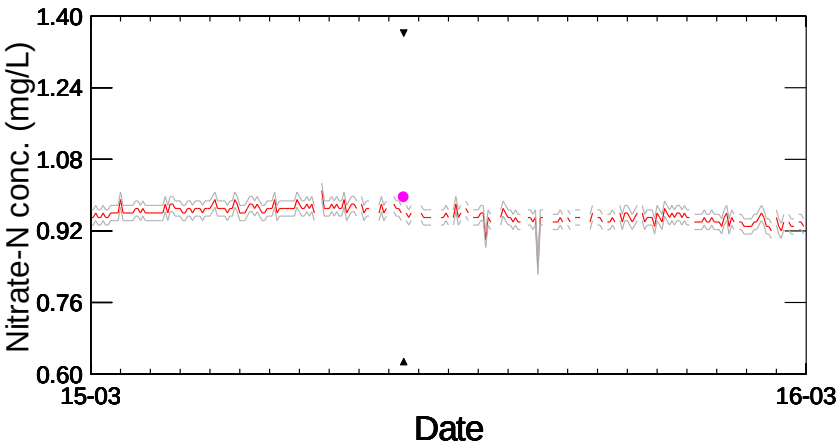


Figure 8-11: One-day time series of TriOS pump sensor nitrate-N concentrations and grab sample result, showing standard deviations. The red line represents five-minute data, the grey lines represents the lower and upper standard deviation (calculated for that day). The gaps in the red line indicate missing data. The magenta dot and black triangles represent a grab sample and the standard deviation for all grab samples available.

9 Time-series data management

The increasing use of in-situ sensors to continuously measure different water quality properties in rivers brings with it a requirement for robust data processing and management procedures. While regional councils are very experienced with hydrological data, hyperspectral water quality brings different challenges and may require different software (and procedures) to handle the multiple data files and greater number of data fields. Several NEMS exist for continuous water quality data, including dissolved oxygen, temperature and turbidity. These Standards should be consulted as an initial reference to guide some aspects of nitrate-N data processing and management.

In this section, the data derived from two nitrate-N sensors in use in New Zealand – the TriOS OPUS and Specta::lyser – are described. Current NIWA data storage practices are also outlined.

9.1 Data output files

9.1.1 Spectra::lyser instrument

Two output files are generated:

1. A PAR (parameter) file, which is a time-series data set of derived water quality variables ("concentration data"), and quality control information, including:
    - a date-time field (in non-standard format – yyyy.mm.dd hh:mm:ss)
    - an instrument status value and variable-specific status fields, and
    - depending on the capability of the specific instrument, a range of concentration values, including "Nitrate-N", "TOC", "DOC"[14], a turbidity estimate, and several status and Spectral Absorption Coefficient values (e.g., SAC_{254})[15].
2. A FP (fingerprint file), which is a time series of absorbance values for a series of spectral bandwidths.

A date-time field identical to that of the PAR file, and up to 221 spectral slices (2.5 nm bandwidth), ranging from 200 nm to 750 nm. A file holding two-minute frequency data collected for 24 hours is 1.1 MB in size. The FP file would be used for quality assurance purposes, to alter the standard calibration, to develop generate relationships for other variables not included in the standard suite of parameters, or to develop algorithms that improve nitrate-N quantification in different sample matrices .

For the Spectra::lyser devices in use at NIWA, 12 fields are included in the data files. A file containing 24 hours' of data collected at two minute frequency is 63 kB in size. These are the data that would generally be used for water quality assessment and reporting.

9.1.2 TriOS OPUS instrument

The TriOS OPUS instrument produces multiple output files; for the instruments in use at NIWA, these include:

- A "water quality" data file, comprising 15 fields, including:

[14] TOC = total organic carbon, DOC = dissolved organic carbon

[15] These data provide information regarding likely efficacy of UV irradiation for sterilising potable or treated wastewater

- A date-time field, a descriptor field, and several comment fields, as well as a quality assessment metric (these are the data that would generally be used for water quality assessment and reporting).
- Specific water quality variable concentration data, including "nitrate-N, nitrite-N, DOC, total suspended sediment", three specific absorbance measurements, and SAC_{254},

- raw light and dark absorption measurements (190 – 393 nm, 0.8 nm bandwidth) – 277 fields, and
- a calibrated set of absorption measurements, creating 277 spectral slices (200 nm - 360 nm, 0.8 nm bandwidth), each of which becomes a discrete data field.

Each file contains instrument-specific information regarding instrument and lamp performance, and calibration and quality assurance data, including statistical summaries of key performance metrics. The raw data files contain three averaged readings at each time step, used to create the water quality variable file. The 24-hour duration raw and calibrated spectral files range from 1.6 MB to 3.7 MB in size, while the "water quality" data file is 153 kB in size.

9.2 Data storage and exchange

9.2.1 Spectra::lyser data

Currently at NIWA the FP and PAR files derived from the Spectra::lyser instruments are retrieved from the instrument each day, and both are stored on a secure server. The relatively small size of these files makes transfer over the cellular network possible at reasonable cost. Data retrieval is controlled by bespoke software, which compares available data against data on the instrument, and retrieves new data only each day. If the data retrieval fails on one day, the process is retried several times, and then suspended until the next day. Capacity on the instrument and local storage allows several days of information to be stored, overwriting the oldest data first. On retrieval, the data are stored on a secure network server as a series of discrete files.

Data may be used "as-is" (using the standard PAR file), or the information in the standard PAR file may be revised if necessary using the FP file and alternate calibration files; the proprietary software supplied by the manufacturer may be used for this purpose. Alternately, "data mining" or modelling procedures involving discrete calibration data may be used with the FP data to generate alternate data files or new relationships for other variables. To enable immediate and post-collection processing, both sets of data (the PAR and FP files) must be stored.

The Spectra::lyser instruments are currently used for specific water quality investigations, which tend to be of short duration (days to weeks to months). The data are currently not stored on a specific database or time-series manager as a compiled data set. As a consequence, the raw data derived from the instrument is stored on a server (if retrieved remotely), as well as in specific project drives. When cell phone connectivity is poor, it is necessary to store the data on-site for later retrieval. The data must then be stored to the server as well as on the relevant project "Raw Data" folder.

Before the data may be analysed as a complete data set or part of a larger data set, it is necessary to join the individual data files to create a single file. At NIWA, scripts have been written in Python programming language to allow multiple files to be joined in a batch process. The Python script also checks the data file, strips out header information and other extraneous data within the data file.

Currently the output file is in CSV format, facilitating subsequent use in a wide range of software, or storage in an appropriate database or time-series manager. The Python script could also be used generate specific file formats. Software other than Python may also be used for data processing. Storage of the data using MS Access was recently explored at NIWA.

9.2.2 TriOS data

Two TriOS OPUS sensors are currently deployed at NIWA's Mataura Island site on the Mataura River and a further TriOS sensor is in place on the Hurunui River. For both sites, only data for the derived water quality variables are currently retrieved via a NEON logger interface. These data are secured on the NEON telemetry server, but are not currently stored along with the hydrological data on the AQUARIUS time-series manager. Flow and continuous water quality data may however be retrieved directly from the NEON server in csv file format.

9.2.3 Which data should be stored?

The answer to this question is determined by the intended data use.

- If the data are to be as-is, using the concentration data derived from the standard algorithms included with the instruments and software, it will be adequate to store just the discrete derived water quality concentration or unit values. The data should probably be regarded as of unknown data quality until compared against grab sample calibration data, at which time a quality code may be applied.
- If the data are to be subject to detailed analysis and additional calibration applied, or used as input to more detailed data mining or modelling, then store the hyperspectral data as well. This will considerably increase the volume of data requiring storage and management, although as indicated in the three case studies, the measurement frequency may be reduced substantially without loss of information.
- Should a user wish to undertake specific investigation in a 'problem' river, or a short duration trial, the full data suite should be collected and stored (hyperspectral data as well as the concentration of the derived water quality variable). The hyperspectral data could then be used to refine the data, recalibrate the sensor response, or derive measurements for other variables for which standard output does not exist.
- It may be necessary to consider existing practice regarding grab sample collection – the time of collection must match that of a sensor measurement if the data are to be directly compared. Several options exist:
  - the time of collection is standardised so that the recorded value will match a value in the high frequency data record (preferred), or
  - the sample collection time is adjusted during the data analysis process.
- Manual, post-collection collection time adjustment is tedious and a potential source of error, so unless it is possible to round the sample collection time during retrieval from the time series manager, it is advisable to standardise the collection time. This would be consistent with the draft (NEMS 2017) which recommends "the timing of field

measurements and sample collection shall be recorded as a single visit time to the nearest 5 minutes….", expressed as NZ standard time.[16]

The storage and future use of data should be considered when designing monitoring programmes. Presumably the hyperspectral analysers are primarily deployed to measure nitrate-N concentrations at high frequency. It would be better to ensure that the quality of data derived directly from the sensor is as high as possible at the time of collection, rather than relying on extensive and complex post-measurement manipulation to "improve" the quality of the data.

9.2.4 Managing time series data

The Hilltop software suite, which currently has widespread use across regional councils, is able to accommodate high frequency water quality data. The database has facility to include comments and quality description fields. Data may also be visualised and summarised within the software.

It is important to take care with date and time fields when exporting databases to other software for analysis to ensure that discontinuities arising from leap years, and apparent date and time values (ones that may appear to be date(s) and time(s), but are actually text or non-date/time numbers) have not arisen.

[16] http://www.nems.org.nz/assets/Documents/NEMS-60/NEMS-Discrete-WQ-Part-2-Rivers.pdf page xix and Section 2.6.2 page 15.

10 Summary

This report has touched on uses of high frequency nitrate-N monitoring data for purposes such as water quality characterisation, trend detection and quantification, load estimation, and to a lesser extent, better understanding of ecological processes and nutrient cycling. Aspects not directly covered in this report include spatial surveys, which could be used to assess the efficacy of mitigation strategies. The detailed assessment of high frequency nitrate-N data reported here indicate how these data may be used. Whether specific councils require this type of information is a decision that they will have to make and highlights the importance of identifying the purpose of monitoring at the outset.

The modelling exercises have demonstrated that reasonable estimates of nitrate loads are available using grab samples derived from conventional monitoring programmes. The model estimates are enhanced by collection of data during several hydrological events. While it might be assumed that the additional data required to characterise flow-concentration relationships during flood events may be obtained from hyperspectral data, several case study examples demonstrate that the quality of hyperspectral data may be degraded during floods because of interferences. It is important to support the collection of hyperspectral data using conventional grab samples, particularly when the grab samples are collected on a flow proportional basis. Results from these samples may also be used to validate the hyperspectral data and assure the quality of the data.

Having decided that high frequency nitrate data are required, the requirements for high quality data need to be satisfied. There is no point in collecting data where spectral or optical interferences, physical obstruction of the light path and other factors downgrade much of the data. It might be tempting to rely on the large volume of data to overcome the gaps in information arising from intermittent loss of data. This strategy may be flawed because loss of data may occur, particularly during those periods when the information is required (e.g., during flood events), and necessitates collection of larger volumes of data to ensure redundancy. Once again, the decision to collect hyperspectral data needs to be based on information requirements, and be supported by investment in equipment management, maintenance, calibration and validation, data processing and management.

Several documents exist to guide councils in best practice operation of hyperspectral analysers. Information from several of these well-established, tried and tested procedures have been summarised. We recommend that the principles and steps identified in Sections 3 and 4 be used to guide individual councils until such time that procedures for operation of hyperspectral analysers have been documented. The process used in creating the various NEMS are suggested as appropriate for this purpose. This will ensure that the experience and expertise of chemists, hydrologists, water quality scientists and monitoring officers are adequately reflected in the guidance document.

Deployment of high frequency, hyperspectral water quality analysers creates a complex set of measurement and operational challenges. These challenges relate to the basic measurement principle and the relationship between sample matrix, pathlength and nitrate-N concentrations, coupled with the challenges arising from deployment of any measurement device in the harsh and changeable riverine environment. Pathlength determines sensitivity, but also limits measurement accuracy and sensitivity to interferences. In some cases, achieving sensitivity over a wide concentration range may require use of two instruments, with each optimised for part of the overall concentration range.

This report has demonstrated that UV-visible spectroscopy is a well-established procedure for measuring nitrate-N in water. The limitations of the procedure have also been well-documented. Coupling miniaturised spectrophotometers with data algorithms has overcome some of these challenges for specific classes of water, allowing routine unattended collection of in-situ data.

Routine use of these instruments over several years by several agencies has provided information suitable for development of a best practice guidance document or a standard operating procedure. Factors likely to influence performance include interferences, the algorithms used to convert spectral data into nitrate concentration values, the trade-off between pathlength, accuracy and detection limit, and evaluation of instrument precision and accuracy. Quality assurance requirements include the local calibration (optimising calibration to account for specific water matrix effects), use of calibration standards, and the requirement for routine inspection and cleaning. Data management and handling procedures are also important. The large volume of data potentially derived from hyperspectral instruments provide several challenges that may not be encountered when dealing with hydrometric data, or discrete water quality data.

The logical next step is development of a formal procedures document, most likely in the form of a NEMS. The information in this document will assist in this process.

Several case studies presented covering the Kakanui, Aparima and Mataura rivers described data handling procedures in detail, and the effects of several routine operation procedures (e.g., cleaning events, location of deployment within-channel or adjacent to channel), and the effects of transient spikes. Specific uses of continuous data presented, included:

- Evaluating the relationship between discrete grab sample and continuous data.
- Understanding flow and concentration dynamics, and how this knowledge may be used to identify contaminant mobilisation processes within catchments.
- Understanding short-term variability and potential drivers of this variability.
- Trend assessment.
- Nitrate-N load estimation.

A recurring theme is measurement frequency. In several case study examples, subsets of data derived from five and ten- minute frequency data were generated, and these were used to repeat several assessments, including load estimation and trend assessment. In some cases, comparison of the results derived from the subsets help identify “suitable” measurement frequency. It is apparent that unless very high frequency information requirements exist, it is difficult to justify measurement in larger rivers at frequencies greater than one hour. The case study results suggest that daily measurements appear adequate for most purposes.

Implementation of continuous nitrate-N sensors will benefit from follow up work. For example, research within NIWA is exploring the interplay between suspended sediment, dissolved organic material and measurement accuracy. This is being undertaken at both laboratory and field-scale, and is likely to contribute further to the development of standard procedures for deployment and operation, and in data interpretation and use.

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Appendix A Kakanui River - Gemmels Crossing Site

Relationship between grab and continuous measurement for the Kakanui at Gemmels Crossing Bridge site

▼Robust Regression

107 case(s) deleted due to missing data.

Dependent Variable	TriOS Nitrate-N conc. (mg/L)
No. of cases	20
No. of Regressors	1

Least Trimmed Squares (LTS) Regression

Size of Subset	20
Number of C-Steps	2
Maximum Number of Replications	500
Number of Solutions for Final C-Steps	10
Intercept Adjustment	NO
Number of Squared Residuals Minimized (h)	12
Breakdown Value	40%

LTS Parameter Estimates

Effect	Coefficient
CONSTANT	0.040
NNN conc. (mg/L)	0.857

Scale Estimates

Scale (LTS)	0.003
Scale (Weighted)	0.004

Cutoff Point	3.000
Number of Outliers Detected	3

Robust R-square	0.997

Ordinary Least Squares (OLS) Regression for Outlier Free Data

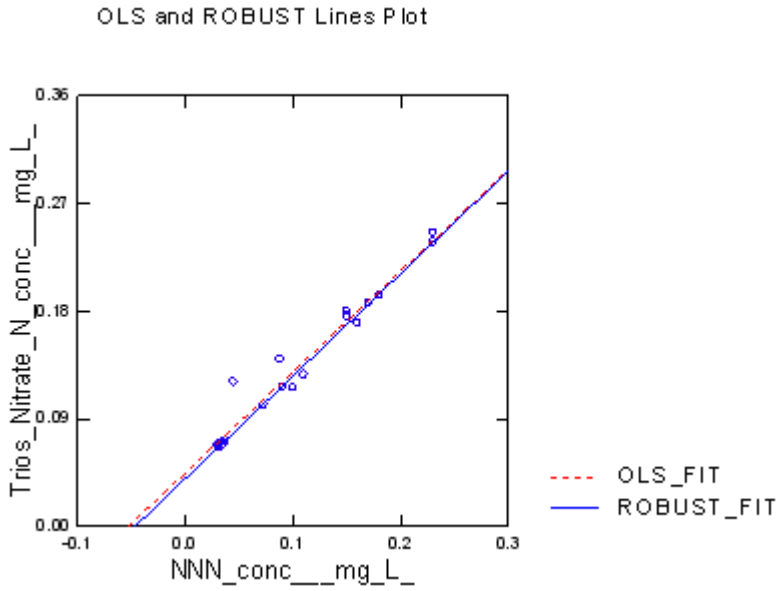
Multiple R	0.997
Squared Multiple R	0.995
Adjusted Squared Multiple R	0.994
Standard Error	0.005

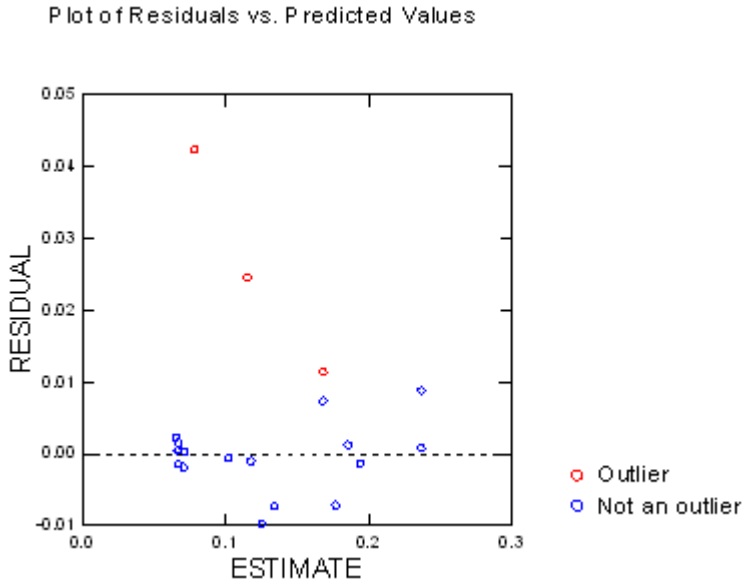
OLS Parameter Estimates

Effect	Coefficient	Standard Error	95.00% Confidence Interval	
			Lower	Upper
CONSTANT	0.038	0.002	0.034	0.043
NNN conc. (mg/L)	0.869	0.016	0.834	0.904

Analysis of Variance					
Source	SS	df	Mean Squares	F-Ratio	p-Value
Regression	0.063	1	0.063	2820.742	0.000
Residual	0.000	15	0.000		

Durbin-Watson D Statistic	1.936
First Order Autocorrelation	-0.051





Data for the following results were selected according to
SELECT TRIOS_NITRATE>0

Eigenvalues of Unit Scaled X'X	
1	2
1.832	0.168

Condition Indices	
1	2
1.000	3.305

Variance Proportions		
	1	2
CONSTANT	0.084	0.916
NNN conc. (mg/L)	0.084	0.916

Dependent Variable	TriOS Nitrate-N conc. (mg/L)
N	20
Multiple R	0.980
Squared Multiple R	0.961
Adjusted Squared Multiple R	0.958
Standard Error of Estimate	0.012

Regression Coefficients B = $(X'X)^{-1}X'Y$						
Effect	Coefficient	Standard Error	Std. Coefficient	Tolerance	t	p-Value
CONSTANT	0.045	0.005	0.000	.	9.213	0.000
NNN conc. (mg/L)	0.845	0.040	0.980	1.000	20.959	0.000

Confidence Interval for Regression Coefficients				
Effect	Coefficient	95.0% Confidence Interval		VIF
		Lower	Upper	
CONSTANT	0.045	0.035	0.055	.
NNN conc. (mg/L)	0.845	0.760	0.930	1.000

Correlation Matrix of Regression Coefficients		
	CONSTANT	NNN conc. (mg/L)
CONSTANT	1.000	
NNN conc. (mg/L)	-0.832	1.000

Analysis of Variance					
Source	Type III SS	df	Mean Squares	F-Ratio	p-Value
Regression	0.064	1	0.064	439.265	0.000
Residual	0.003	18	0.000		

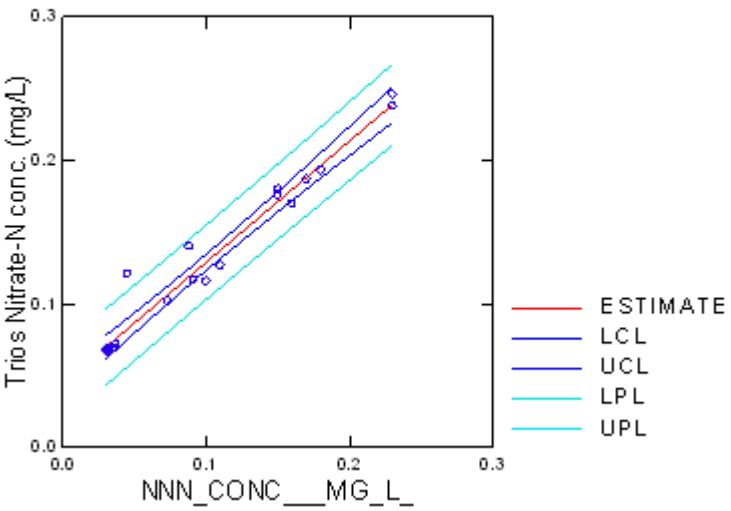
WARNING

Case 110 is an Outlier (Studentized Residual : 5.140)

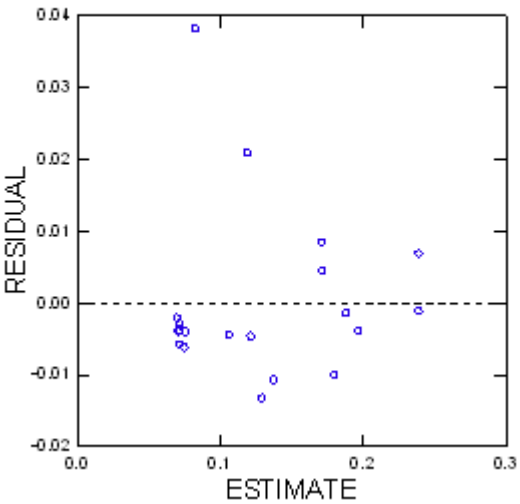
Durbin-Watson D-Statistic	2.671
First Order Autocorrelation	-0.358

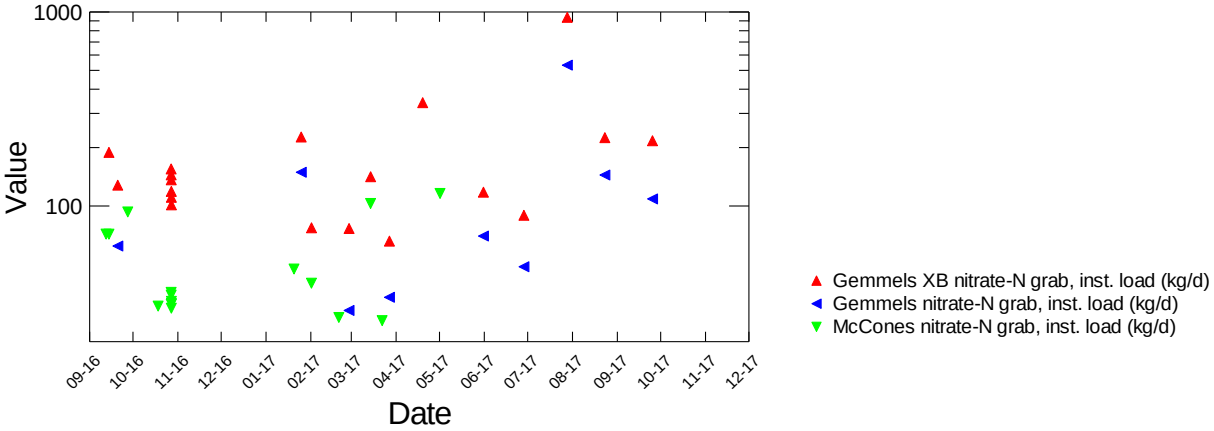
Information Criteria	
AIC	-116.081
AIC (Corrected)	-114.581
Schwarz's BIC	-113.094

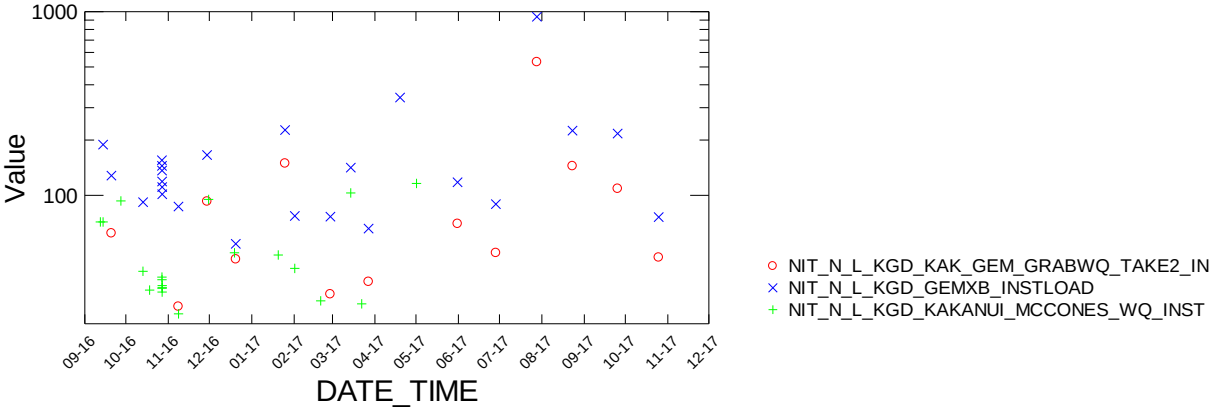
Confidence Interval and Prediction Interval



Plot of Residuals vs. Predicted Values

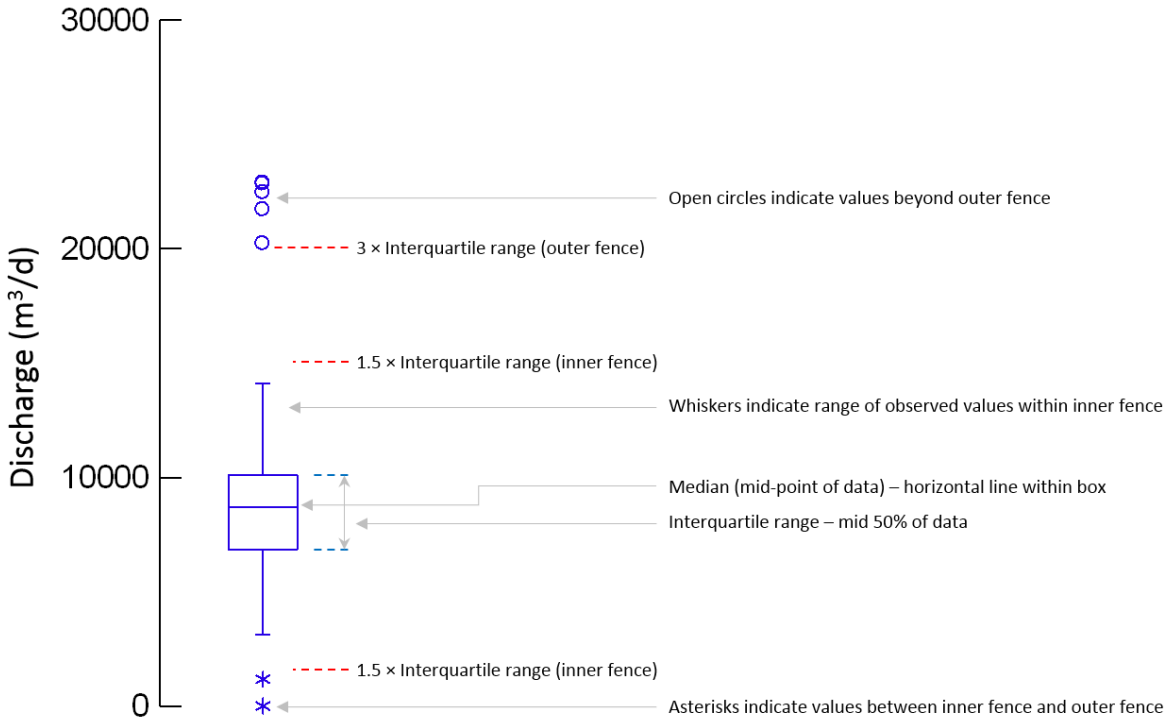



1000
100
Value
09-16
10-16
11-16
12-16
01-17
02-17
03-17
04-17
05-17
06-17
07-17
08-17
09-17
10-17
11-17
12-17
Date
Gemmels XB nitrate-N grab, inst. load (kg/d)
Gemmels nitrate-N grab, inst. load (kg/d)
McCones nitrate-N grab, inst. load (kg/d)


1000
100
Value
09-16
10-16
11-16
12-16
01-17
02-17
03-17
04-17
05-17
06-17
07-17
08-17
09-17
10-17
11-17
12-17
DATE_TIME
NIT_N_L_KGD_KAK_GEM_GRABWQ_TAKE2_IN
NIT_N_L_KGD_GEMXB_INSTLOAD
NIT_N_L_KGD_KAKANUI_MCCONES_WQ_INST

Appendix B Explanation of box and whisker plot conventions

It should be noted that these conventions apply to box and whisker plots generated by the Systat software package - they may be quite different to plots, symbols and names applied to elements in graphs generated by other software, particularly with regard to the whiskers, and “outliers”.



Appendix C Kakanui River - McCones site

Relationship between grab and continuous concentration measurement

Number of Variables : 21
Number of Cases : 13832

SYSTAT Rectangular file O:\ELF18203\Working\From ORC\Neale\McCones\Processed\Kakanui_McCones_GrabWQ_TriOS_G_InstLoad_Take2.syz, Created data file Wed Jun 27 23:02:36 2018 containing variables:

YYYYMMDDHH	HH$	YYYYMMDD$	HHMM$	FLOW_CFS	FLOW_LS
NITRATE_TRIOS_M-CC	NITRATE_INST_LO-AD	YYYY	MM	DD	HH
MIN	SEC	DATE	TIME	DATE_TIME	NITRATE_H_MGL
NITRATE_H_L_KGD	LINEX	LINEY			

▼Robust Regression

13803 case(s) deleted due to missing data.

Dependent Variable	TriOS Nitrate-N conc. (mg/L)
No. of cases	29
No. of Regressors	1

Least Trimmed Squares (LTS) Regression

Size of Subset	29
Number of C-Steps	2
Maximum Number of Replications	500
Number of Solutions for Final C-Steps	10
Intercept Adjustment	NO
Number of Squared Residuals Minimized (h)	14
Breakdown Value	49.99%

LTS Parameter Estimates

Effect	Coefficient
CONSTANT	0.014
NNN conc. (mg/L)	0.992

Scale Estimates

Scale (LTS)	0.007
Scale (Weighted)	0.009

Cutoff Point	3.000
Number of Outliers Detected	5

Robust R-square	0.998

Ordinary Least Squares (OLS) Regression for Outlier Free Data

Multiple R	0.998
Squared Multiple R	0.997
Adjusted Squared Multiple R	0.997
Standard Error	0.010

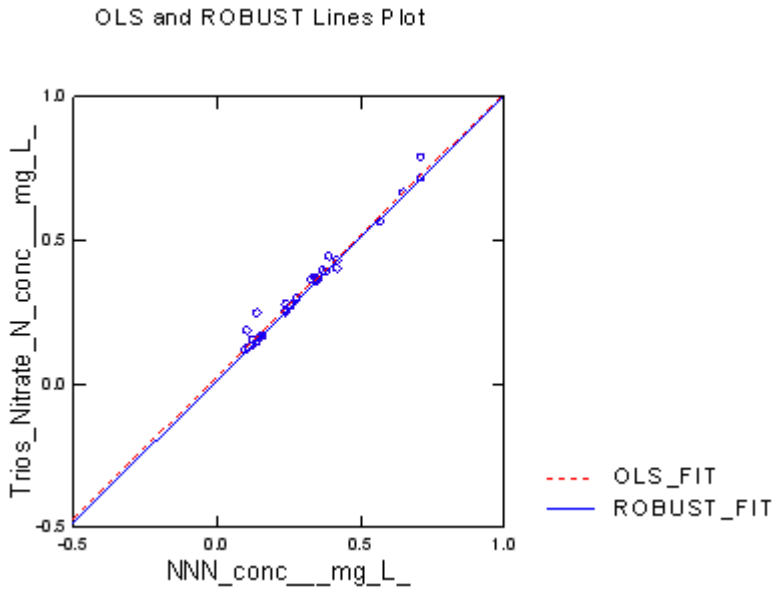
OLS Parameter Estimates

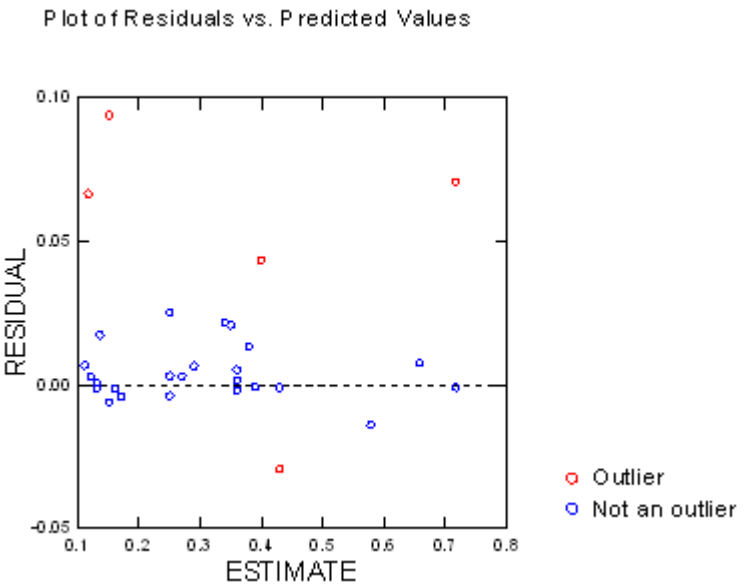
Effect	Coefficient	Standard Error	95.00% Confidence Interval	
			Lower	Upper
CONSTANT	0.019	0.004	0.011	0.028
NNN conc. (mg/L)	0.987	0.012	0.962	1.012

Analysis of Variance

Source	SS	df	Mean Squares	F-Ratio	p-Value
Regression	0.634	1	0.634	6803.695	0.000
Residual	0.002	22	0.000		

Durbin-Watson D Statistic	1.124
First Order Autocorrelation	0.345





Data for the following results were selected according to
SELECT NITRATE_TRIOS_MCC >0 AND INST_TRIOS_LOAD_KGD >0

13662 case(s) are deleted due to missing data.

Eigenvalues of Unit Scaled X'X	
1	2
1.866	0.134

Condition Indices	
1	2
1.000	3.733

Variance Proportions		
	1	2
CONSTANT	0.067	0.933
Grab nitrate-N (mg/L)	0.067	0.933

Dependent Variable	TriOS nitrate-N conc. (mg/L)
N	29
Multiple R	0.989
Squared Multiple R	0.979
Adjusted Squared Multiple R	0.978
Standard Error of Estimate	0.027

Regression Coefficients B = $(X'X)^{-1}X'Y$						
Effect	Coefficient	Standard Error	Std. Coefficient	Tolerance	t	p-Value
CONSTANT	0.027	0.010	0.000	.	2.702	0.012
Grab nitrate-N (mg/L)	0.987	0.028	0.989	1.000	35.075	0.000

Confidence Interval for Regression Coefficients				
Effect	Coefficient	95.0% Confidence Interval		VIF
		Lower	Upper	
CONSTANT	0.027	0.006	0.047	.
Grab nitrate-N (mg/L)	0.987	0.930	1.045	1.000

Correlation Matrix of Regression Coefficients		
	CONSTANT	Grab nitrate-N (mg/L)
CONSTANT	1.000	
Grab nitrate-N (mg/L)	-0.866	1.000

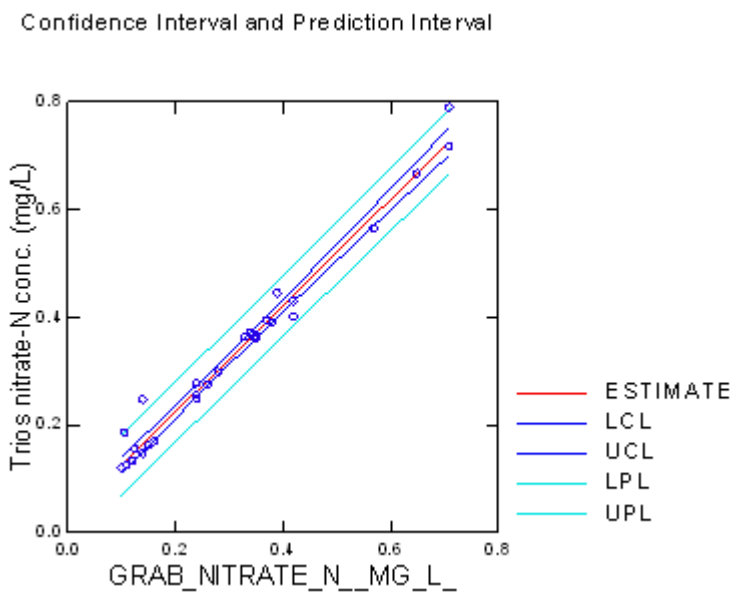
Analysis of Variance					
Source	SS	df	Mean Squares	F-Ratio	p-Value
Regression	0.881	1	0.881	1230.257	0.000
Residual	0.019	27	0.001		

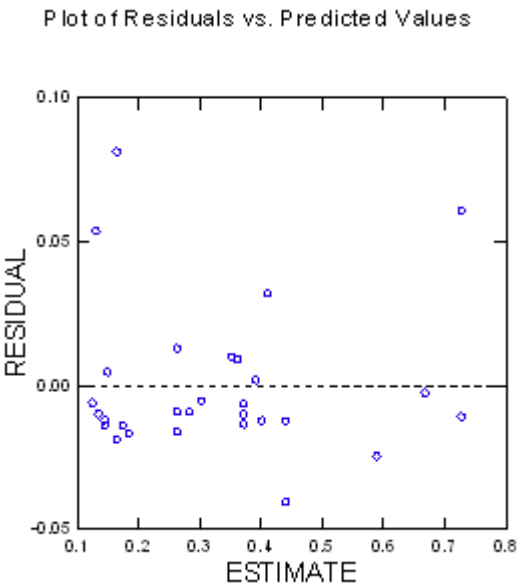
WARNING

Case 4527 is an Outlier (Studentized Residual : 3.865)
Case 12950 is an Outlier (Studentized Residual : 2.891)

Durbin-Watson D-Statistic	2.058
First Order Autocorrelation	-0.038

Information Criteria	
AIC	-123.775
AIC (Corrected)	-122.815
Schwarz's BIC	-119.674





▼General Linear Model

Data for the following results were selected according to
SELECT NITRATE_TRIOS_MCC >0 AND INST_TRIOS_LOAD_KGD >0

13662 case(s) are deleted due to missing data.

Eigenvalues of Unit Scaled X'X	
1	2
1.866	0.134

Condition Indices	
1	2
1.000	3.733

Variance Proportions		
	1	2
CONSTANT	0.067	0.933
Grab nitrate-N (mg/L)	0.067	0.933

Dependent Variable	TriOS nitrate-N conc. (mg/L)
N	29
Multiple R	0.989
Squared Multiple R	0.979
Adjusted Squared Multiple R	0.978
Standard Error of Estimate	0.027

Regression Coefficients B = $(X'X)^{-1}X'Y$						
Effect	Coefficient	Standard Error	Std. Coefficient	Tolerance	t	p-Value
CONSTANT	0.027	0.010	0.000	.	2.702	0.012
Grab nitrate-N (mg/L)	0.987	0.028	0.989	1.000	35.075	0.000

Confidence Interval for Regression Coefficients				
Effect	Coefficient	95.0% Confidence Interval		VIF
		Lower	Upper	
CONSTANT	0.027	0.006	0.047	.
Grab nitrate-N (mg/L)	0.987	0.930	1.045	1.000

Correlation Matrix of Regression Coefficients		
	CONSTANT	Grab nitrate-N (mg/L)
CONSTANT	1.000	
Grab nitrate-N (mg/L)	-0.866	1.000

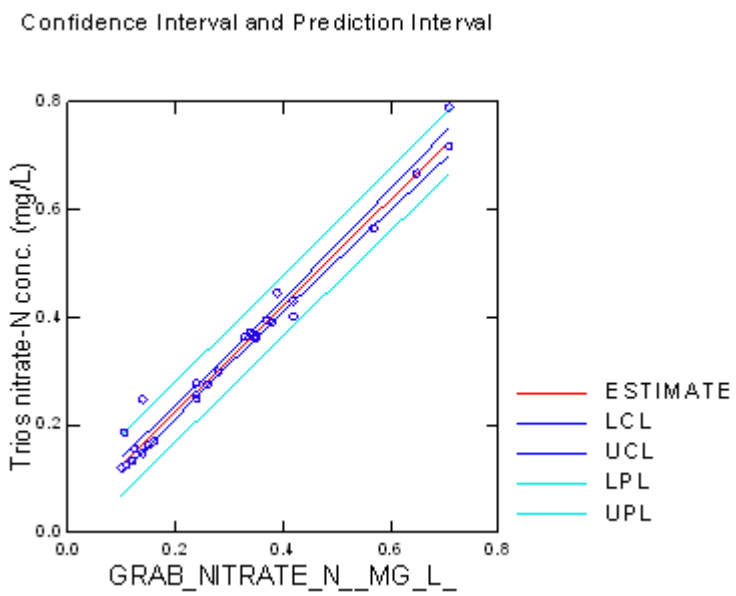
Analysis of Variance					
Source	Type III SS	df	Mean Squares	F-Ratio	p-Value
Regression	0.881	1	0.881	1230.257	0.000
Residual	0.019	27	0.001		

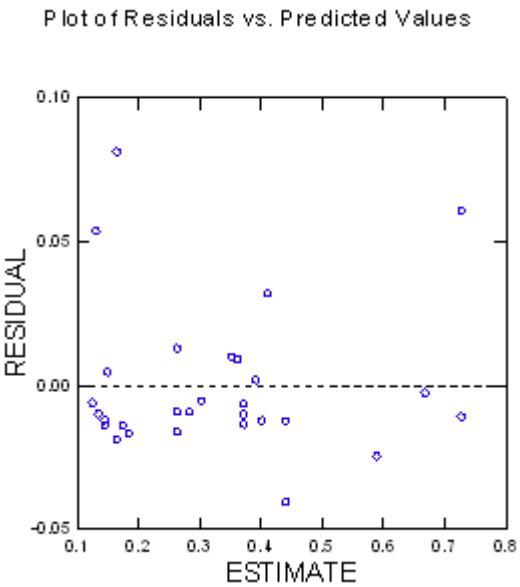
WARNING

Case 4527 is an Outlier (Studentized Residual : 3.865)
Case 12950 is an Outlier (Studentized Residual : 2.891)

Durbin-Watson D-Statistic	2.058
First Order Autocorrelation	-0.038

Information Criteria	
AIC	-123.775
AIC (Corrected)	-122.815
Schwarz's BIC	-119.674





Load values

▼General Linear Model

13800 case(s) are deleted due to missing data.

Eigenvalues of Unit Scaled X'X	
1	2
1.648	0.352

Condition Indices	
1	2
1.000	2.163

Variance Proportions		
	1	2
CONSTANT	0.176	0.824
Grab nitrate-N inst. load (kg/d)	0.176	0.824

Dependent Variable	TriOS nitrate-N inst. load (kg/d)
N	29
Multiple R	0.992
Squared Multiple R	0.984
Adjusted Squared Multiple R	0.983
Standard Error of Estimate	25.711

Regression Coefficients B = $(X'X)^{-1}X'Y$						
Effect	Coefficient	Standard Error	Std. Coefficient	Tolerance	t	p-Value
CONSTANT	12.860	6.266	0.000	.	2.052	0.050
Grab nitrate-N inst. load (kg/d)	1.075	0.026	0.992	1.000	40.837	0.000

Confidence Interval for Regression Coefficients				
Effect	Coefficient	95.0% Confidence Interval		VIF
		Lower	Upper	
CONSTANT	12.860	0.002	25.718	.
Grab nitrate-N inst. load (kg/d)	1.075	1.021	1.129	1.000

Correlation Matrix of Regression Coefficients		
	CONSTANT	Grab nitrate-N inst. load (kg/d)
CONSTANT	1.000	
Grab nitrate-N inst. load (kg/d)	-0.648	1.000

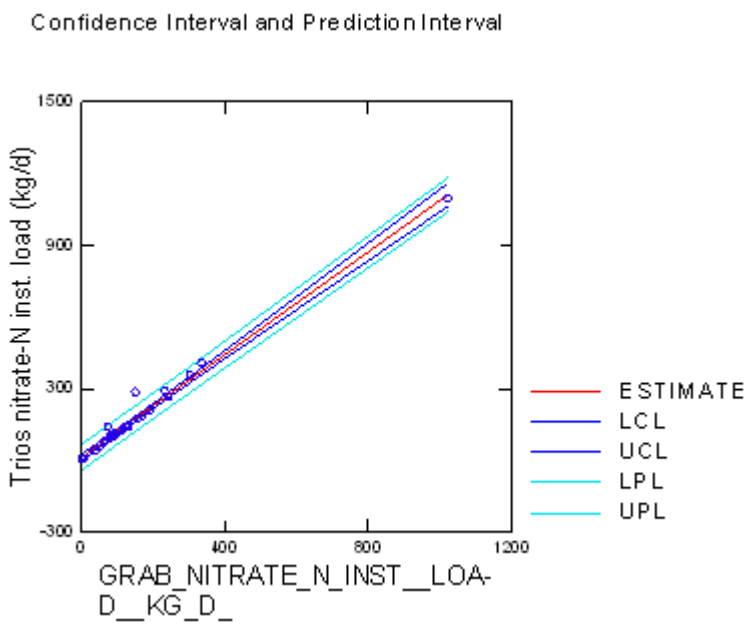
Analysis of Variance					
Source	Type III SS	df	Mean Squares	F-Ratio	p-Value
Regression	1102396.590	1	1102396.590	1667.645	0.000
Residual	17848.345	27	661.050		

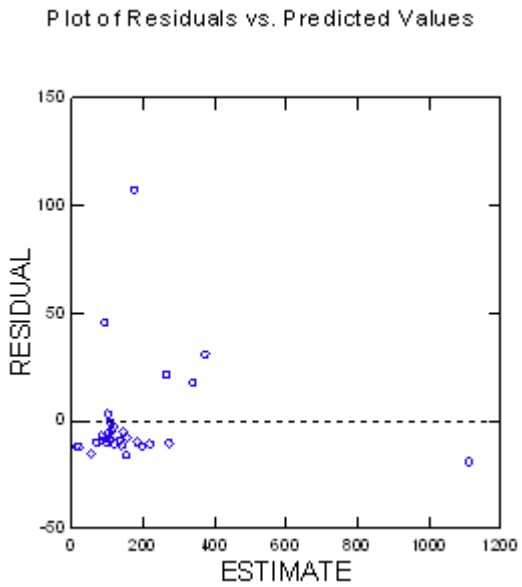
WARNING

Case 4527 is an Outlier (Studentized Residual : 7.196)
Case 7791 has large Leverage (Leverage : 0.826)

Durbin-Watson D-Statistic	2.333
First Order Autocorrelation	-0.170

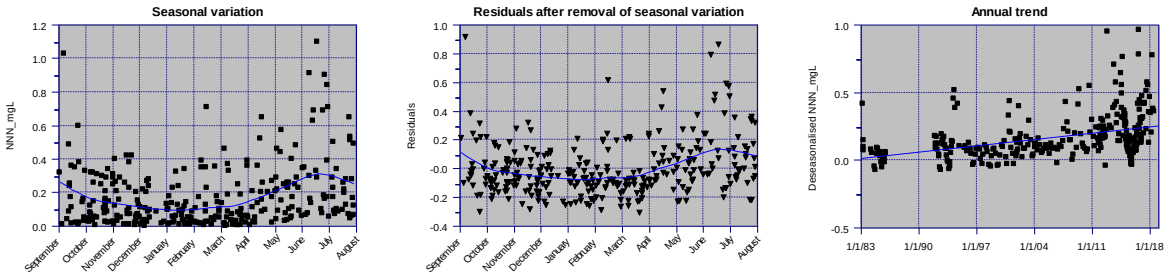
Information Criteria	
AIC	274.547
AIC (Corrected)	275.507
Schwarz's BIC	278.649




Plot of Residuals vs. Predicted Values
RESIDUAL
ESTIMATE
150
100
50
0
-50
0
200
400
600
800
1000
1200

Appendix D Deseasonalised trend analysis of grab and TriOS data

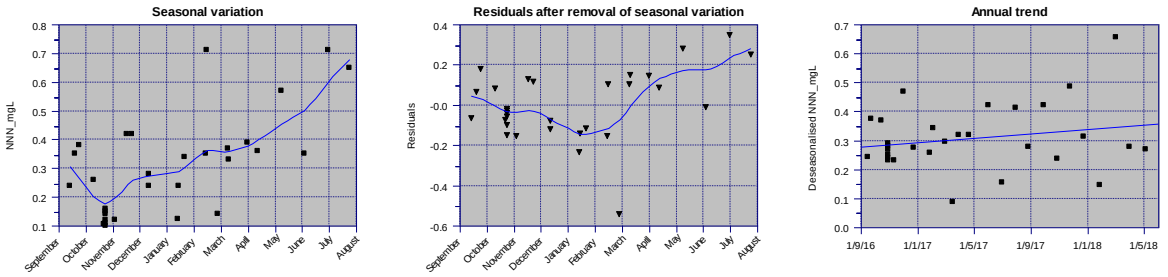
Grab sample, entire record, 1983-2018



Trend removed by subtracting seasonal variation derived by fitting a generalised additive model with 7 degrees of freedom to seasonal data for NNN_mgL
Significance level is 0.05
The slope of the trend line fitted to deseasonalised data is 0.00 per day (0.01 per year or **3.84% per year)**
Slope is positive

t, df	7.44, 308
H0: no slope	Reject, P = 0.00

Grab sample, September 2016-April 2018

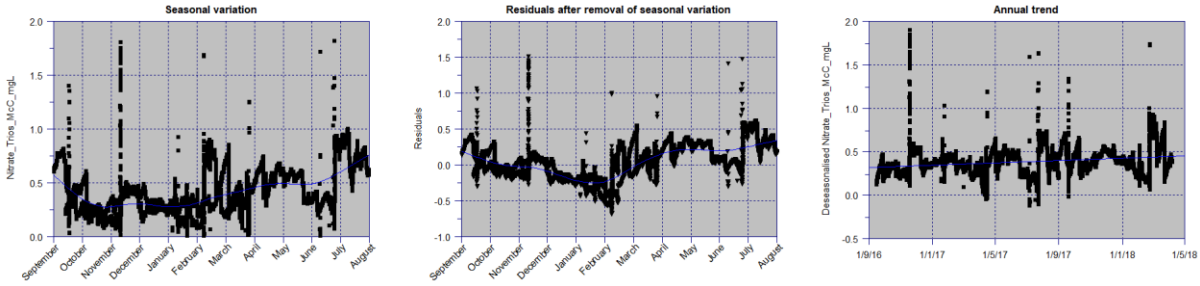


Trend removed by subtracting seasonal variation derived by fitting a generalised additive model with 7 degrees of freedom to seasonal data for NNN_mgL
Significance level is 0.05
The slope of the trend line fitted to deseasonalised data is 0.00 per day (**0.05 per year or 14.75% per year)**

Null hypothesis - unable to detect trend:

t,df	1.13,28
H0: no slope	Fail to reject, P = 0.27

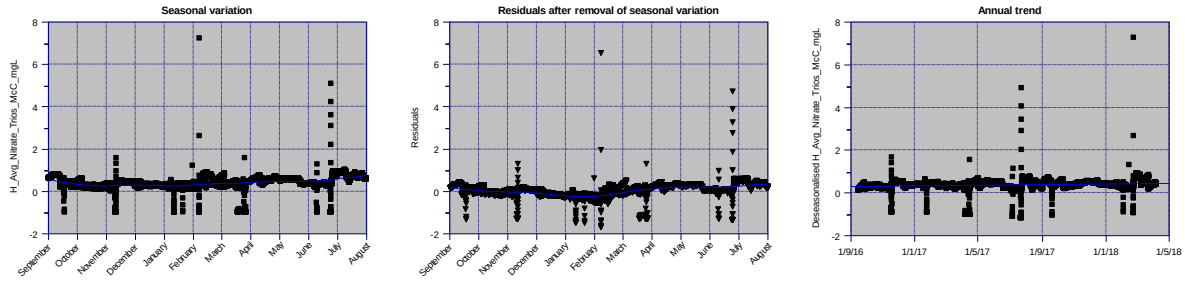
TriOS instantaneous – Trimmed (excludes data not in range from 0.00 to 2.00 mg/L inclusive)



Trend removed by subtracting seasonal variation derived by fitting a generalised additive model with 7 degrees of freedom to seasonal data for Nitrate_TriOS_McC_mgL
Significance level is 0.05
The slope of the trend line fitted to deseasonalised data is 0.00 per day **(0.08 per year or 19.78% per year)**
Slope is positive

t,df	122.63,237923
H0: no slope	Reject, P = 0.00

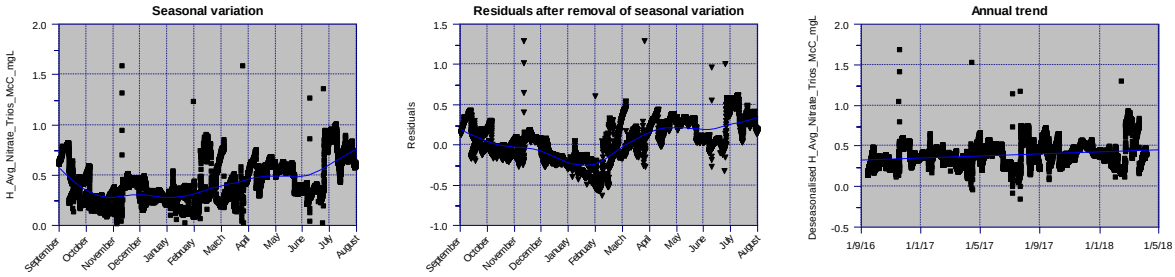
TriOS hourly average, with spikes



Trend removed by subtracting seasonal variation derived by fitting a generalised additive model with 7 degrees of freedom to seasonal data for H_Avg_Nitrate_TriOS_McC_mgL
Significance level is 0.05
The slope of the trend line fitted to deseasonalised data is 0.00 per day **(0.08 per year or 22.52% per year)**
Slope is positive

t,df	21.68,13646
H0: no slope	Reject, P = 0.00

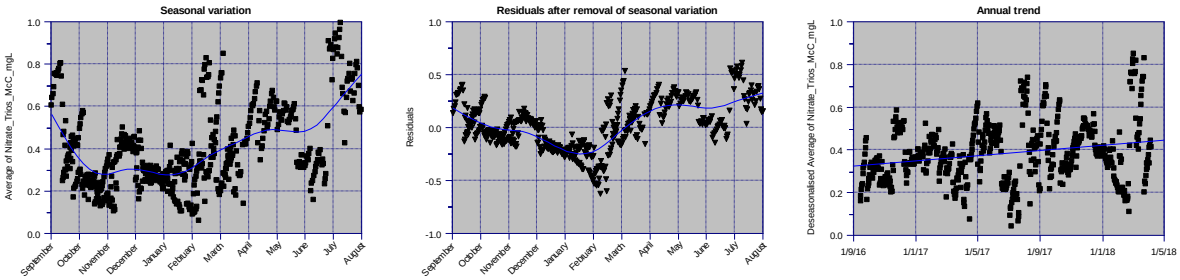
TriOS hourly average – Trimmed (excludes data not in range from 0.00 to 2.00 mg/L inclusive)



Trend removed by subtracting seasonal variation derived by fitting a generalised additive model with 7 degrees of freedom to seasonal data for H_Avg_Nitrate_TriOS_McC_mgL
Significance level is 0.05
The slope of the trend line fitted to deseasonalised data is 0.00 per day **(0.08 per year or 19.80% per year)**
Slope is positive

t,df	29.13,13506
H0: no slope	Reject, P = 0.00

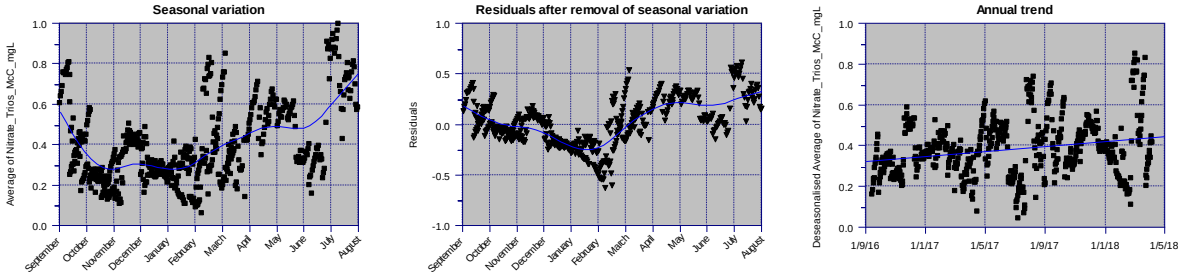
TriOS instantaneous, daily 10:00-11:00 average value



Trend removed by subtracting seasonal variation derived by fitting a generalised additive model with 7 degrees of freedom to seasonal data for Average of Nitrate_TriOS_McC_mgL
Significance level is 0.05
The slope of the trend line fitted to deseasonalised data is 0.00 per day **(0.07 per year or 19.08% per year)**
Slope is positive

t,df	5.77,564
H0: no slope	Reject, P = 0.00

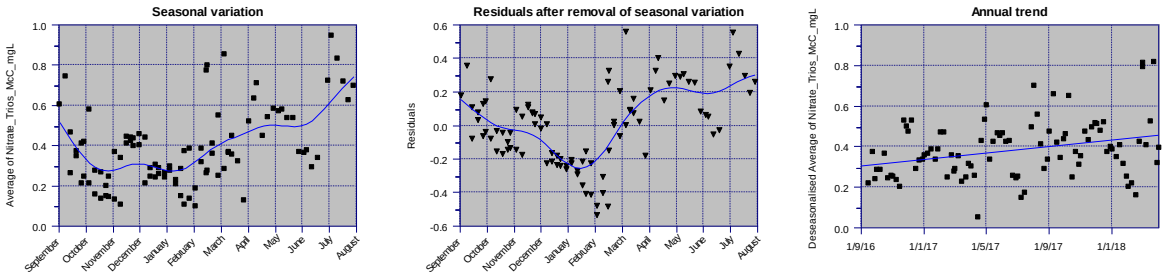
TriOS instantaneous, trimmed, daily 10:00 reading (i.e., single value)



Trend removed by subtracting seasonal variation derived by fitting a generalised additive model with 7 degrees of freedom to seasonal data for Average of Nitrate_TriOS_McC_mgL
Significance level is 0.05
The slope of the trend line fitted to deseasonalised data is 0.00 per day **(0.07 per year or 19.08% per year)**
Slope is positive

t,df	5.77,564
H0: no slope	Reject, P = 0.00

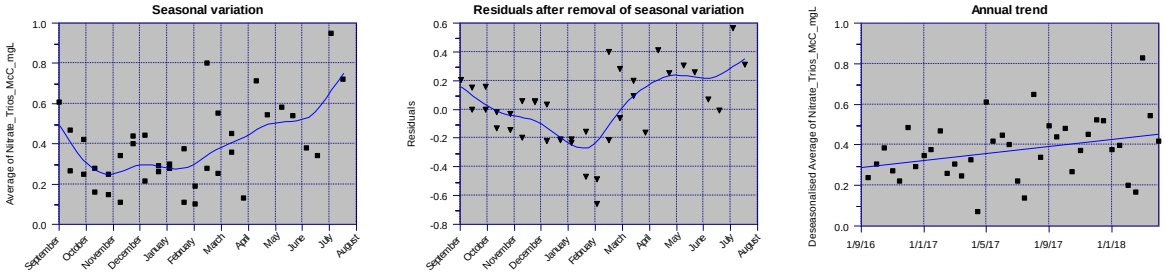
TriOS instantaneous, trimmed, weekly 10:30 reading on 1st, 8th, 15th, 22nd and 28th of each month



Trend removed by subtracting seasonal variation derived by fitting a generalised additive model with 7 degrees of freedom to seasonal data for Average of Nitrate_TriOS_McC_mgL
Significance level is 0.05
The slope of the trend line fitted to deseasonalised data is 0.00 per day **(0.10 per year or 25.33% per year)**
Slope is positive

t,df	3.12,91
H0: no slope	Reject, P = 0.00

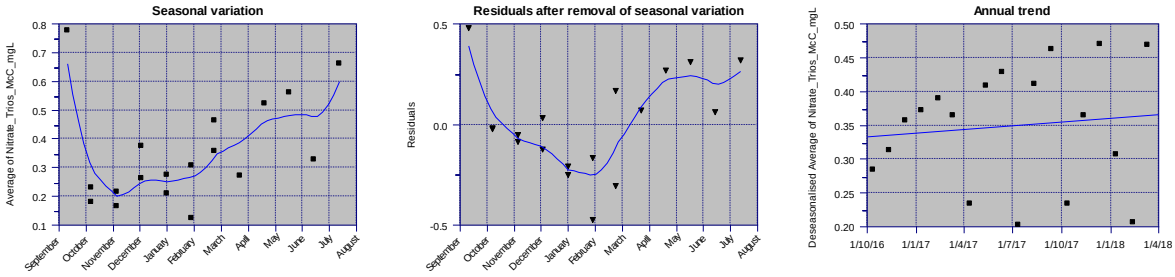
TriOS instantaneous, trimmed, fortnightly 10:30 reading on 1st and 15th of each month



Trend removed by subtracting seasonal variation derived by fitting a generalised additive model with 7 degrees of freedom to seasonal data for Average of Nitrate_TriOS_McC_mgL
Significance level is 0.05
The slope of the trend line fitted to deseasonalised data is 0.00 per day **(0.10 per year or 28.12% per year)**
Slope is positive

t,df	2.05,36
H0: no slope	Reject, P = 0.05

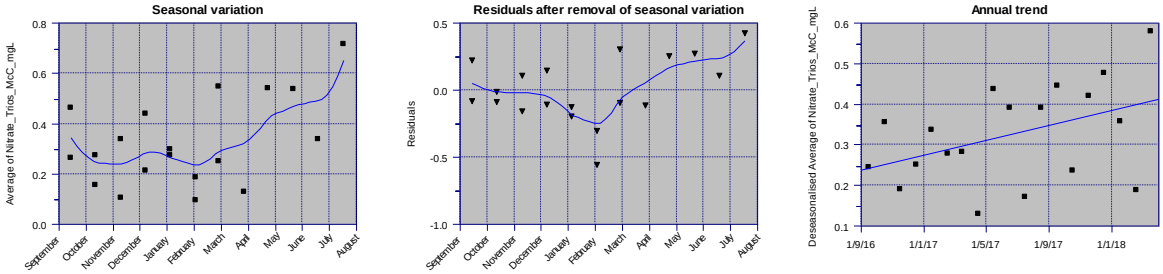
TriOS instantaneous, trimmed, monthly 10:30 reading on 10th of each month



Trend removed by subtracting seasonal variation derived by fitting a generalised additive model with 7 degrees of freedom to seasonal data for Average of Nitrate_TriOS_McC_mgL
Significance level is 0.05
The slope of the trend line fitted to deseasonalised data is 0.00 per **day (0.02 per year or 6.15% per year)**
Null hypothesis - unable to detect trend:

t,df	0.43,16
H0: no slope	Fail to reject, P = 0.67

TriOS instantaneous, trimmed, monthly 10:30 reading on 15th of each month

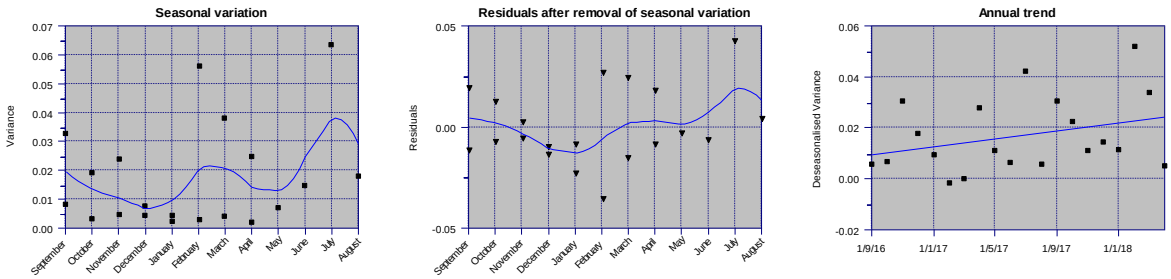


Trend removed by subtracting seasonal variation derived by fitting a generalised additive model with 7 degrees of freedom to seasonal data for Average of Nitrate_TriOS_McC_mgL
Significance level is 0.05
The slope of the trend line fitted to deseasonalised data is 0.00 per day **(0.11 per year or 33.83% per year)**
Null hypothesis - unable to detect trend:

t,df	1.96,17
H0: no slope	Fail to reject, P = 0.07

Test for trend in variance over time

The "TriOS instantaneous, trimmed, daily 10:30 reading (i.e., single value)" subset of data was selected for this assessment.



DeSeasonalised trend analysis of Variance
Trend removed by subtracting seasonal variation derived by fitting a generalised additive model with 7 degrees of freedom to seasonal data for Variance
Significance level is 0.05
The slope of the trend line fitted to deseasonalised data is 0.00 per day **(0.01 per year or 56.32% per year)**
Null hypothesis - unable to detect trend:

t,df	1.43,18
H0: no slope	Fail to reject, P = 0.17

Appendix E Aparima River

Summary statistics for discharge data

	Flow (L/s)
N of Cases	159652
Minimum	1094.000
Maximum	266445.000
Median	11808.000
Arithmetic Mean	22594.653
Standard Error of Arithmetic Mean	73.095
95.0% LCL of Arithmetic Mean	22451.389
95.0% UCL of Arithmetic Mean	22737.916
Standard Deviation	29206.096
Coefficient of Variation	1.293
Method = CLEVELAND	
1.000%	1900.000
5.000%	3008.000
10.000%	3711.000
20.000%	5292.000
25.000%	6089.000
30.000%	6968.000
40.000%	8829.000
50.000%	11808.000
60.000%	15662.000
70.000%	22107.000
75.000%	26028.000
80.000%	31671.400
90.000%	55564.000
95.000%	82099.700
99.000%	151600.680

Results for Measurement technique = Grab nitrate-N (mg/L)

	Nitrate-N conc. (mg/L)	Nitrate-N conc. (mg/L)
	Grab	TriOS
N of Cases	327	282
Minimum	0.142	0.160
Maximum	2.400	2.287
Arithmetic Mean	1.008	1.086
Standard Deviation	0.512	0.500
Shapiro-Wilk Statistic	0.967	0.972
Shapiro-Wilk p-Value	0.000	0.000
Method = CLEVELAND		
1.000%	0.175	0.240
5.000%	0.300	0.386
10.000%	0.360	0.420
20.000%	0.529	0.570
25.000%	0.613	0.692

	Nitrate-N conc. (mg/L)	Nitrate-N conc. (mg/L)
30.000%	0.650	0.795
40.000%	0.833	0.900
50.000%	0.960	1.063
60.000%	1.120	1.230
70.000%	1.264	1.349
75.000%	1.310	1.410
80.000%	1.451	1.481
90.000%	1.712	1.762
95.000%	2.000	2.056
99.000%	2.300	2.245

Wilcoxon Signed-Rank Test Results

Data for the following results were selected according to
SELECT NITRATE_MGL >0 AND GRAB_NITRATE_N <>.

Counts of Differences (row variable greater than column)

	TriOS nitrate-N (mg/L)	Grab nitrate-N (mg/L)
TriOS nitrate-N (mg/L)	0.000	265.000
Grab nitrate-N (mg/L)	18.000	0.000

Z = (Sum of signed ranks)/Square root (sum of squared ranks)

	TriOS nitrate-N (mg/L)	Grab nitrate-N (mg/L)
TriOS nitrate-N (mg/L)	0.000	
Grab nitrate-N (mg/L)	-12.792	0.000

Two-Sided Probabilities using Normal Approximation

	TriOS nitrate-N (mg/L)	Grab nitrate-N (mg/L)
TriOS nitrate-N (mg/L)	1.000	
Grab nitrate-N (mg/L)	0.000	1.000

> end

▼Robust Regression

Dependent Variable	TRIOS_NITRATE_M-GL
No. of cases	282
No. of Regressors	1

Least Absolute Deviations (LAD) Regression

Method of Estimation	IRLS

Raw R-square (1-Residual/Total)	0.994
R-square(Observed vs. Predicted)	0.965

LAD Parameter Estimates

Effect	Coefficient
CONSTANT	0.133
GRAB_NNN_MGL	0.949

Scale Estimates	0.092

Cutoff Point	3.000
Number of Outliers Detected	3

Ordinary Least Squares (OLS) Regression for Outlier Free Data

Multiple R	0.991
Squared Multiple R	0.982
Adjusted Squared Multiple R	0.982
Standard Error	0.067

OLS Parameter Estimates

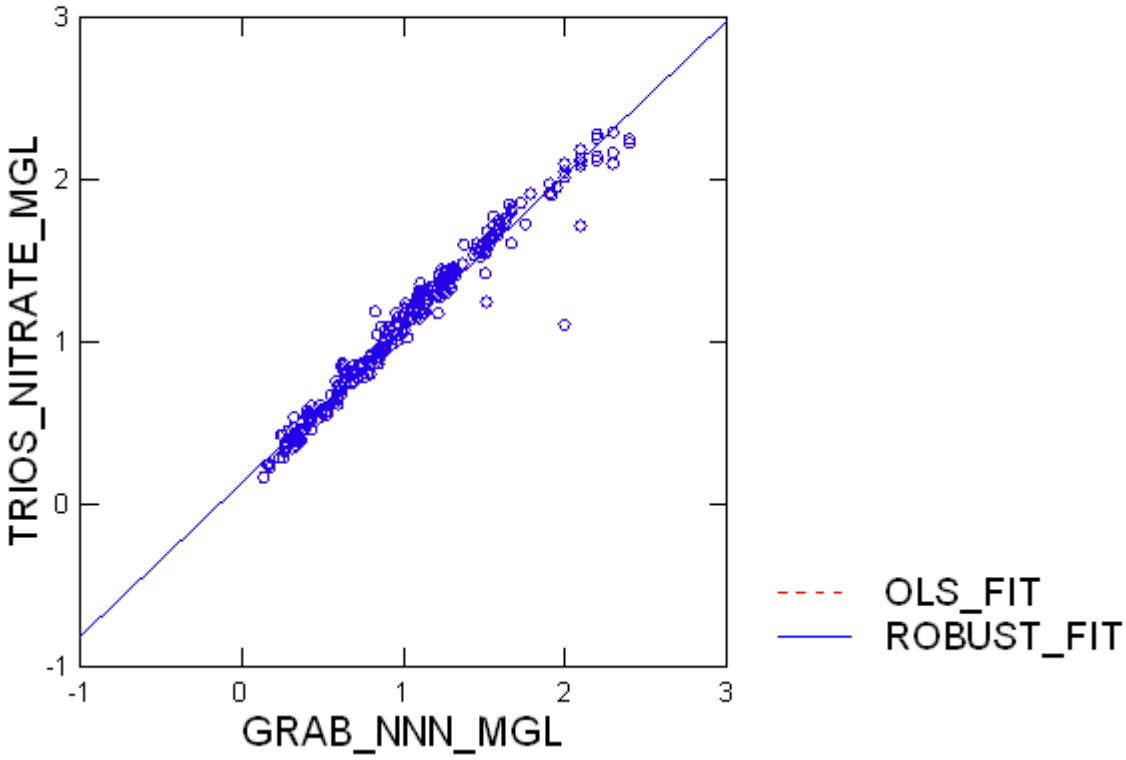
Effect	Coefficient	Standard Error	95.00% Confidence Interval	
			Lower	Upper
CONSTANT	0.117	0.009	0.100	0.134
GRAB_NNN_MGL	0.971	0.008	0.955	0.986

Analysis of Variance

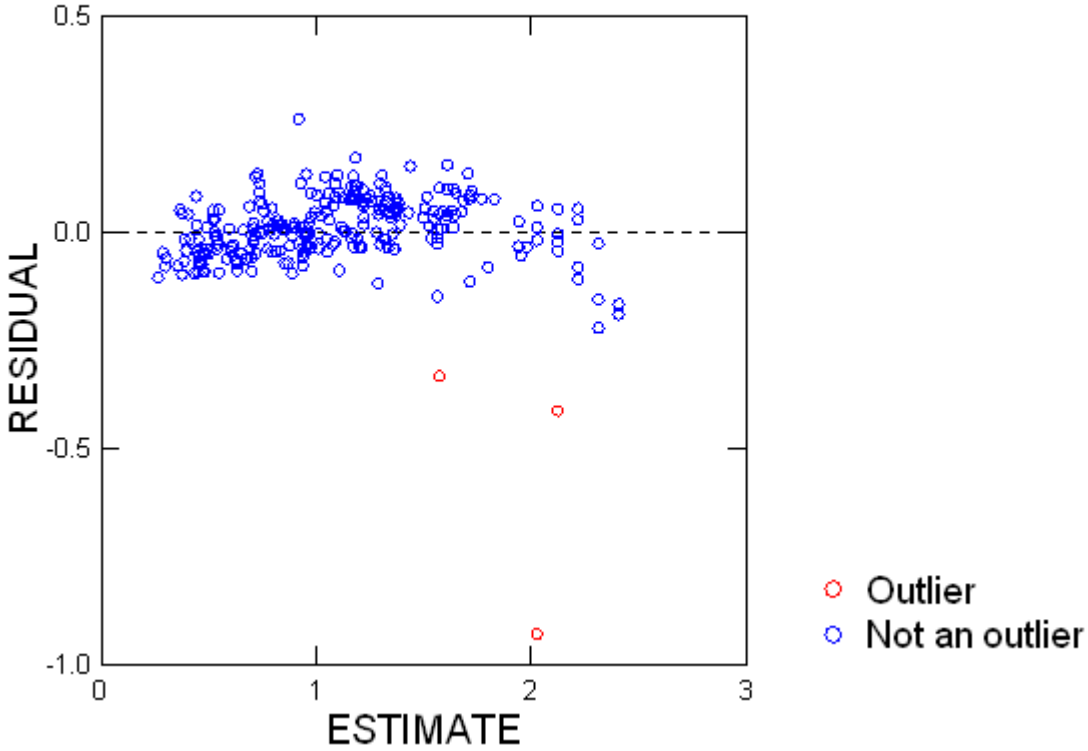
Source	SS	df	Mean Squares	F-Ratio	p-Value
Regression	68.476	1	68.476	15327.534	0.000
Residual	1.238	277	0.004		

Durbin-Watson D Statistic	0.809
First Order Autocorrelation	0.591

OLS and ROBUST Lines Plot



Plot of Residuals vs. Predicted Values



▼General Linear Model

26371 case(s) are deleted due to missing data.

Eigenvalues of Unit Scaled X'X	
1	2
1.889	0.111

Condition Indices	
1	2
1.000	4.132

Variance Proportions		
	1	2
CONSTANT	0.055	0.945
GRAB_NNN_MGL	0.055	0.945

Dependent Variable	TRIOS_NITRATE_M-GL
N	282
Multiple R	0.983
Squared Multiple R	0.965
Adjusted Squared Multiple R	0.965
Standard Error of Estimate	0.093

Regression Coefficients B = $(X'X)^{-1}X'Y$						
Effect	Coefficient	Standard Error	Std. Coefficient	Tolerance	t	p-Value
CONSTANT	0.133	0.012	0.000	.	10.925	0.000
GRAB_NNN_MGL	0.949	0.011	0.983	1.000	88.271	0.000

Confidence Interval for Regression Coefficients				
Effect	Coefficient	95.0% Confidence Interval		VIF
		Lower	Upper	
CONSTANT	0.133	0.109	0.157	.
GRAB_NNN_MGL	0.949	0.928	0.970	1.000

Correlation Matrix of Regression Coefficients		
	CONSTANT	GRAB_NNN_MGL
CONSTANT	1.000	
GRAB_NNN_MGL	-0.889	1.000

Analysis of Variance					
Source	Type III SS	df	Mean Squares	F-Ratio	p-Value
Regression	67.698	1	67.698	7791.710	0.000
Residual	2.433	280	0.009		

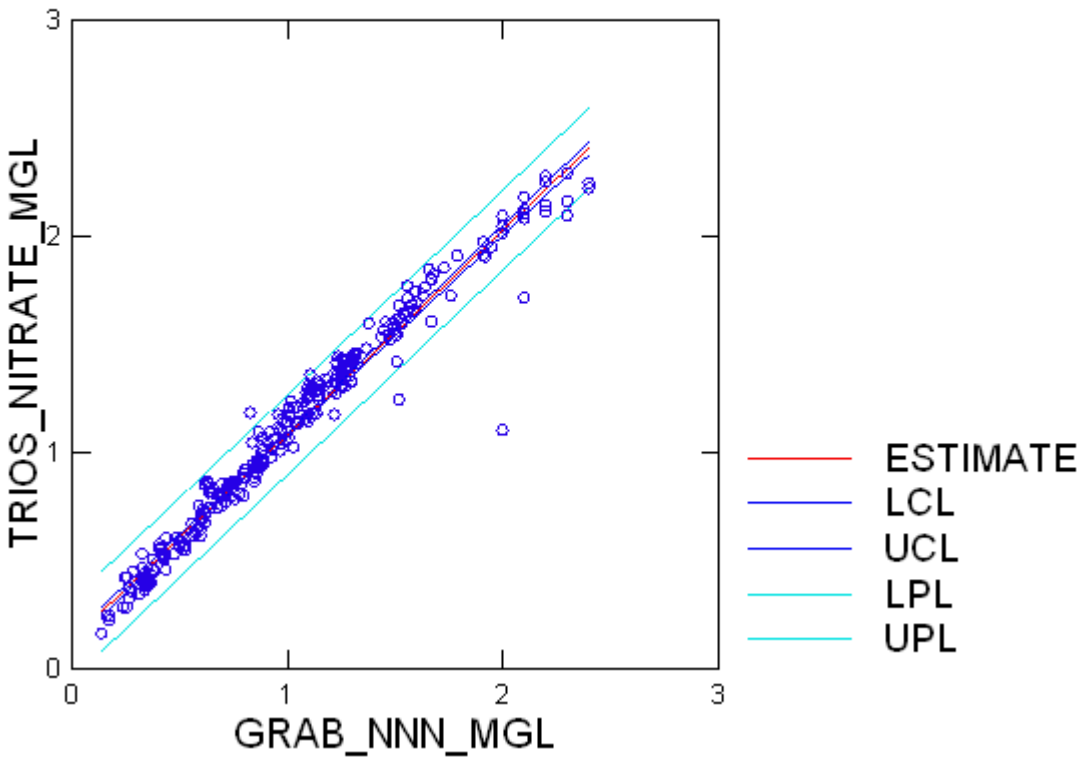
WARNING

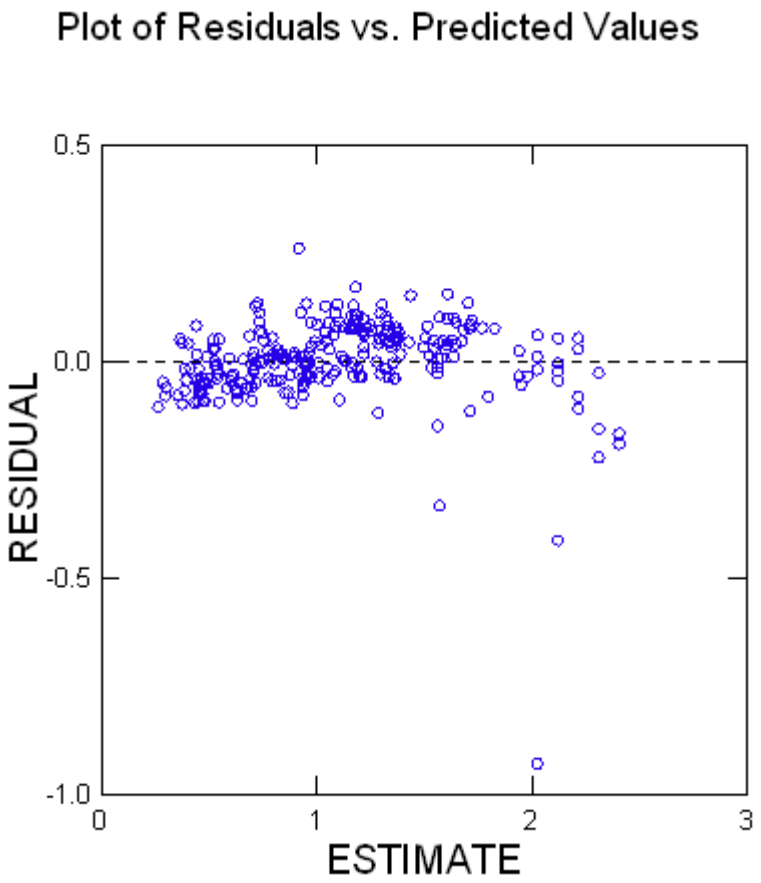
Case 649 is an Outlier (Studentized Residual : -12.590)
Case 1297 is an Outlier (Studentized Residual : -4.658)

Durbin-Watson D-Statistic	1.412
First Order Autocorrelation	0.291

Information Criteria	
AIC	-534.030
AIC (Corrected)	-533.943
Schwarz's BIC	-523.104

Confidence Interval and Prediction Interval




Plot of Residuals vs. Predicted Values
0.5
0.0
-0.5
-1.0
RESIDUAL
0
1
2
3
ESTIMATE

Load estimates – grab samples

Details of LOADEST are provided in Runkel et al. (2004)

Ln(Load) = a0 + a1 LnQ + a2 LnQ^2 + a3 Sin(2 pi dtime) + a4 Cos(2 pi dtime) + a5 dtime + a6 dtime^2

where:

Load = constituent load [kg/d]
LnQ = Ln(Q) - center of Ln(Q)
dtime = decimal time - center of decimal time

Model Coefficients

	a0	a1	a2	a3	a4	a5	a6
AMLE	7.5322	1.1213	-0.0676	-0.1338	0.6599	0.0750	0.1039

AMLE Regression Statistics

R-Squared:	94.18
Residual:	0.1398
Serial Correlation of Residuals:	0.8164
Prob. Plot Corr. Coeff. (PPCC) :	0.9925
Significance Level of PPCC Test:	3.348E-03

Coeff.	**Std.Dev.**	**t-ratio**	**P Value**
a0	0.0572	131.71	5.502-278
a1	0.0224	50.09	4.559-153
a2	0.0163	-4.15	3.481E-05
a3	0.0416	-3.22	1.248E-03
a4	0.0494	13.36	3.926E-33
a5	0.0260	2.88	3.757E-03
a6	0.0354	2.94	3.183E-03

Correlation Between Explanatory Variables

Explanatory variable corresponding to:

	a1	a2	a3	a4	a5
a2	0.0000				
a3	-0.2615	0.1490			
a4	0.4738	0.0022	-0.0998		
a5	-0.1549	0.2174	0.4553	-0.3148	
a6	-0.0774	-0.2998	-0.2380	-0.4744	0.0000

Additional Regression Statistics

MLE Residual Variance: 0.1398

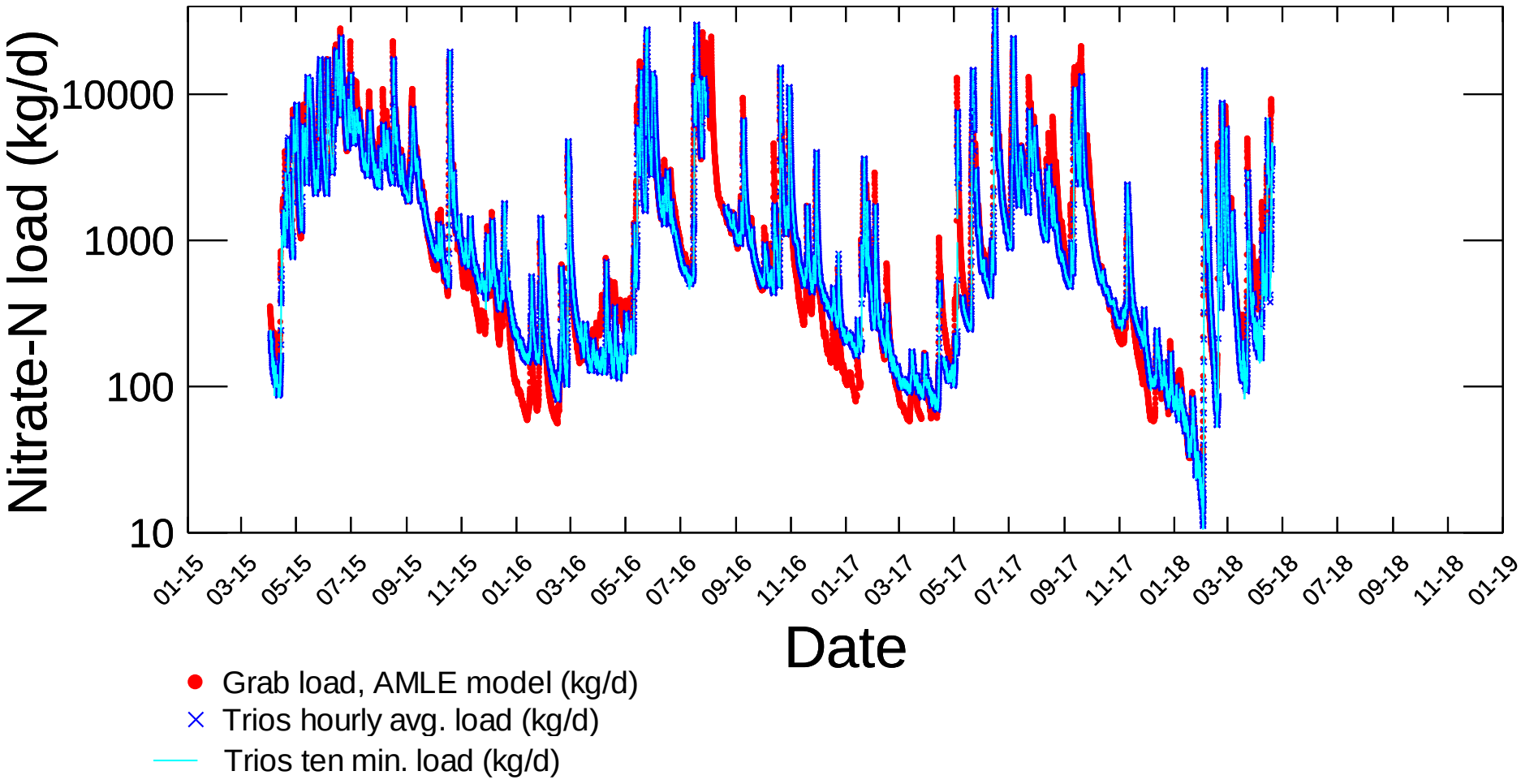


Figure E-1: Comparison of nitrate-N load estimated using grab sample results (using a regression model), and hourly average TriOS concentration data for the period April 2015 to March 2018. Note $\log_{10}$ scale for y-axis.

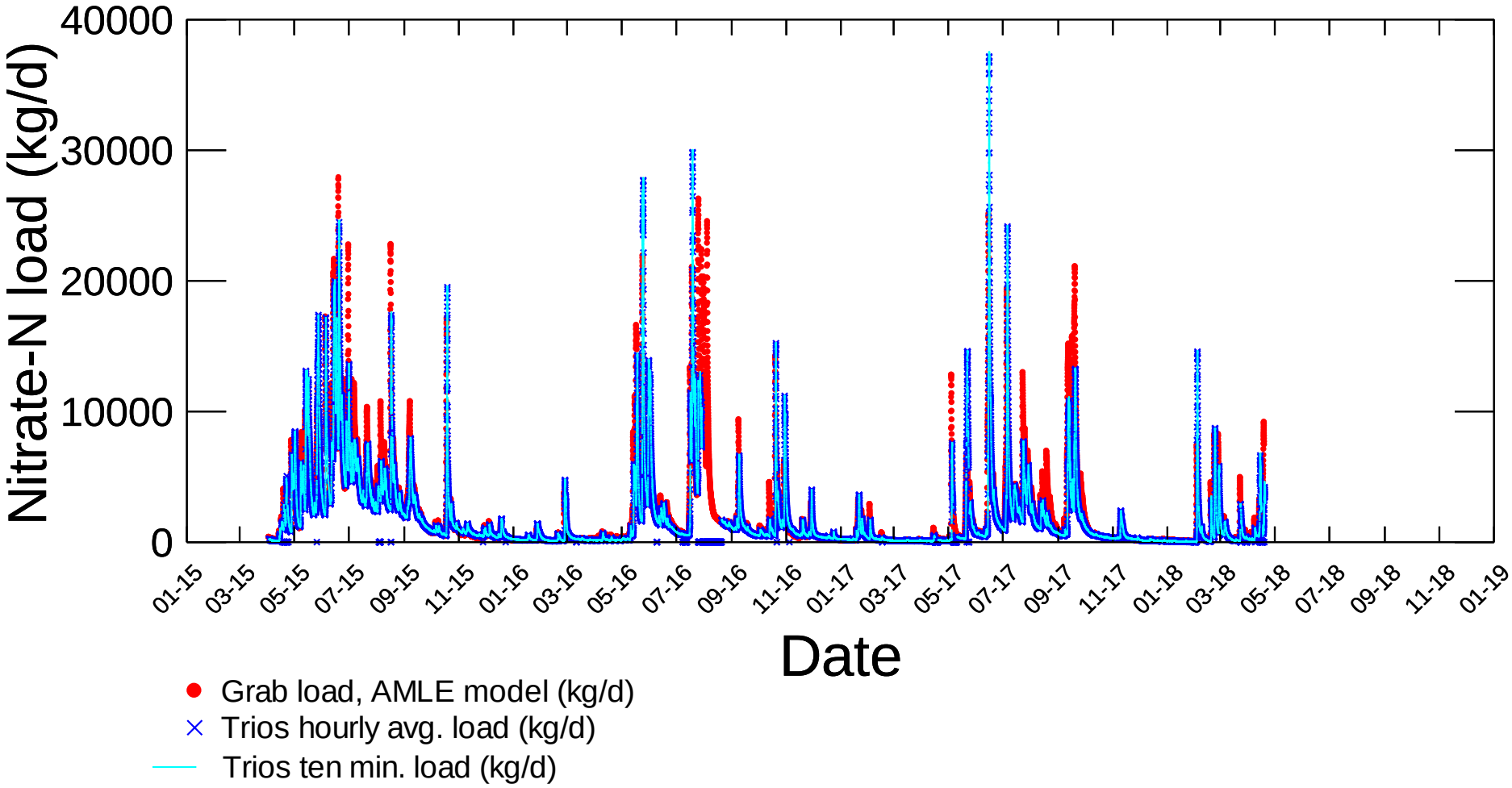


Figure E-2: Comparison of nitrate-N load estimated using grab sample results (using a regression model), and hourly average TriOS concentration data for the period April 2015 to March 2018.

Model results for part of 2015 calendar year

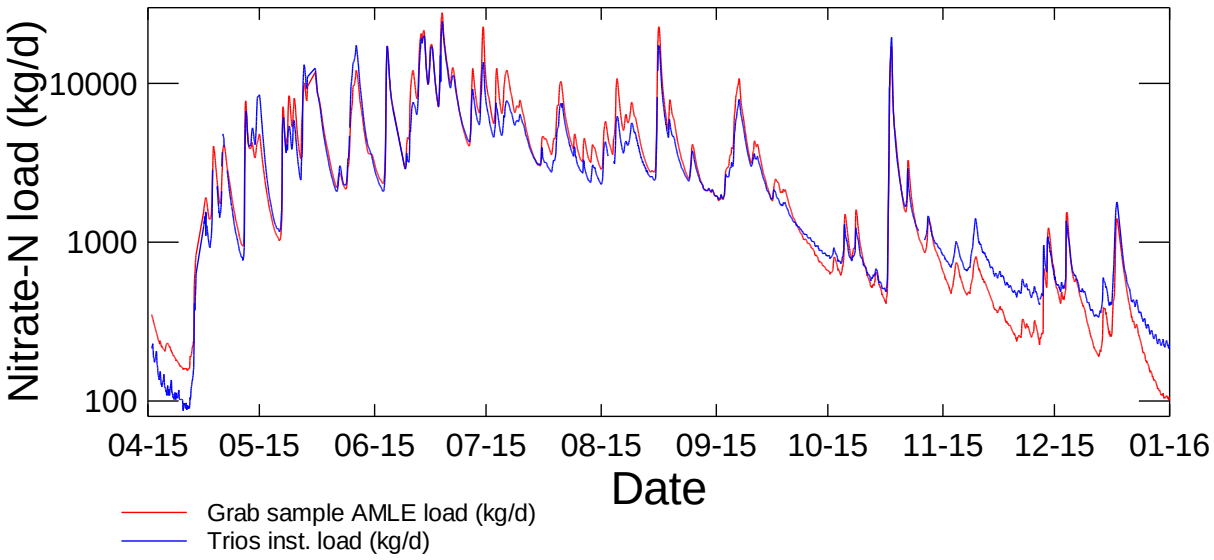


Figure E-3: Comparison of nitrate-N load estimated using grab sample results(using a regression model), and hourly average TriOS concentration data for part of the 2015 calendar year. Note $\log_{10}$ scale for y-axis.

Model results for 2016 calendar year

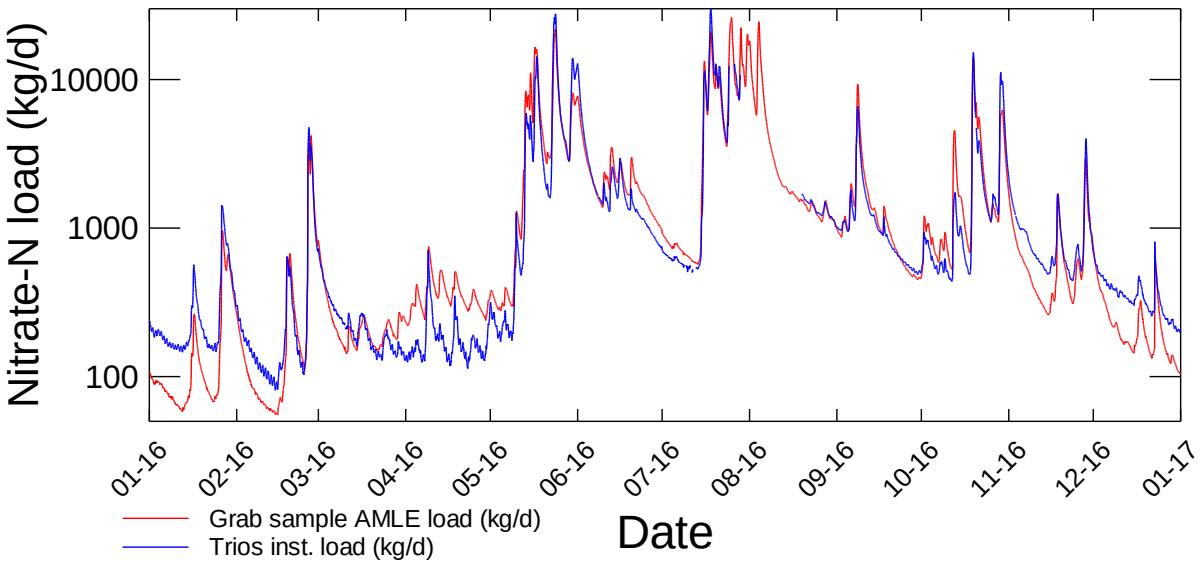


Figure E-4: Comparison of nitrate-N load estimated using grab sample results(using a regression model), and hourly average TriOS concentration data for the 2016 calendar year. Note $\log_{10}$ scale for y-axis.

Model results for 2017 calendar year

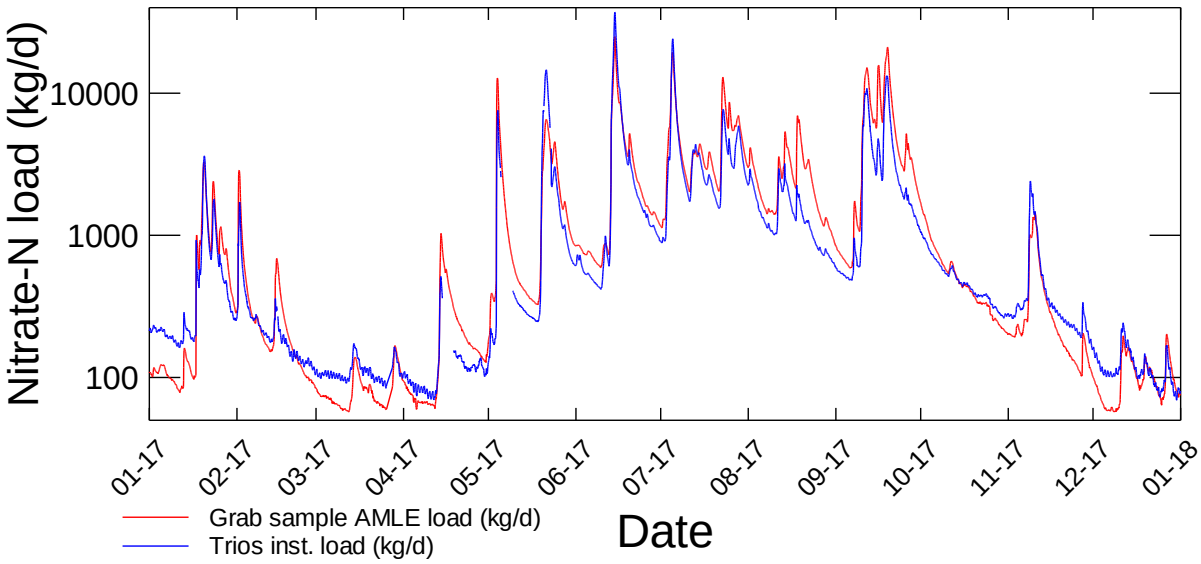


Figure E-5: Comparison of nitrate-N load estimated using grab sample results(using a regression model), and hourly average TriOS concentration data for the 2017 calendar year. Note $\log_{10}$ scale for y-axis.

Model results for part of 2018 calendar year

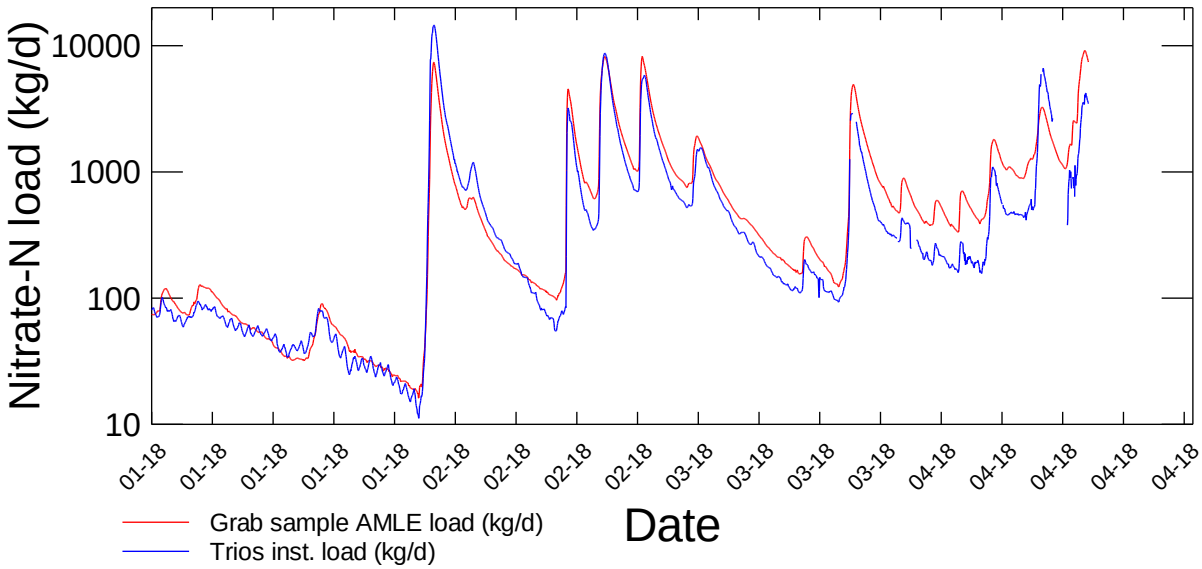
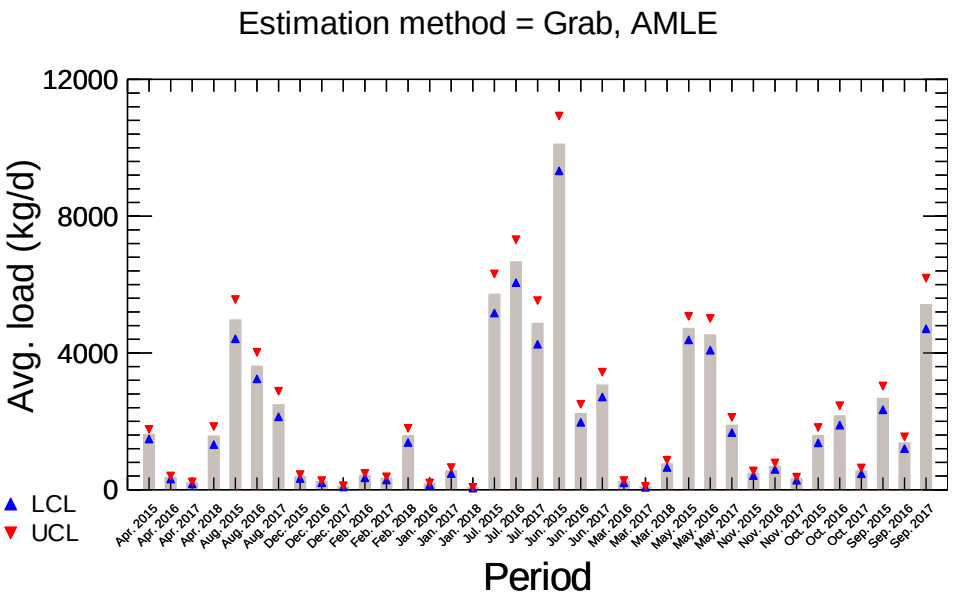
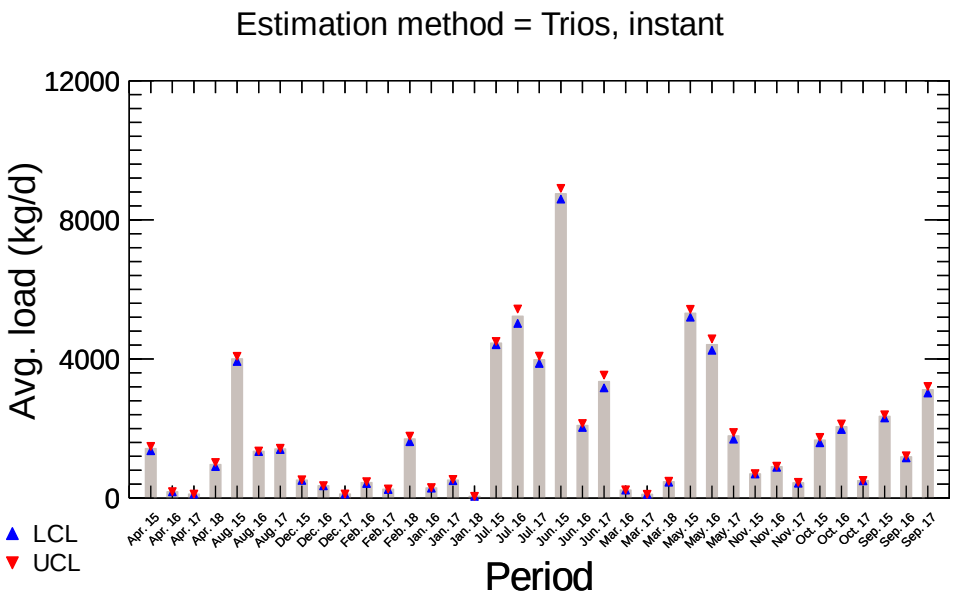
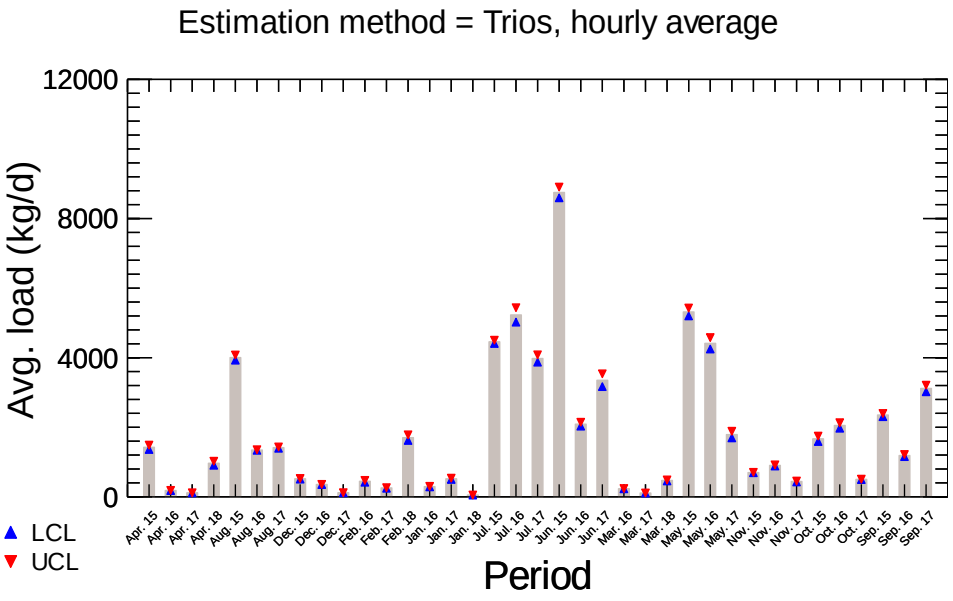
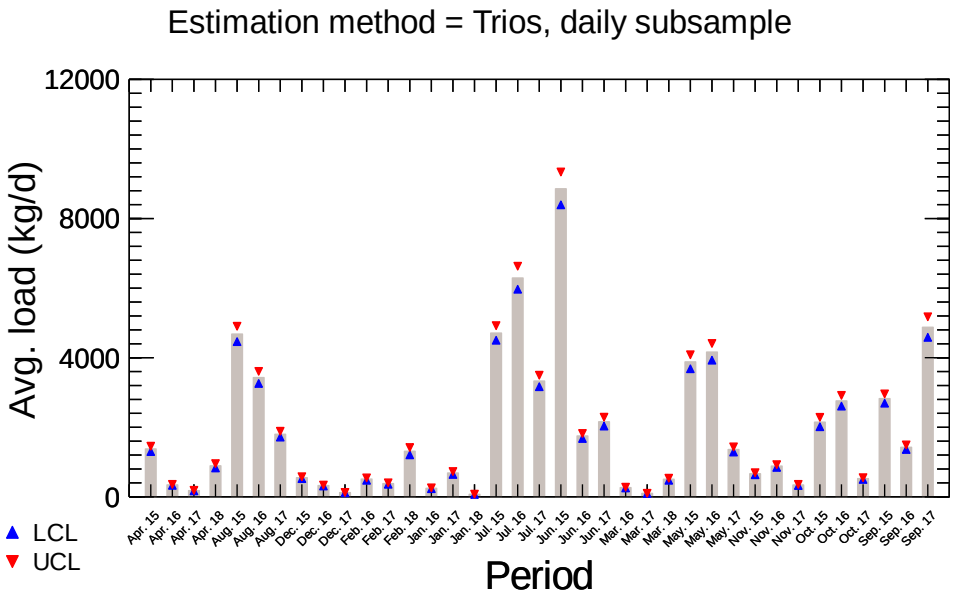


Figure E-6: Comparison of nitrate-N load estimated using grab sample results(using a regression model), and hourly average TriOS concentration data for part of the 2018 calendar year. Note $\log_{10}$ scale for y-axis.


Estimation method = Grab, AMLE
Avg. load (kg/d)
12000
8000
4000
0
LCL
UCL
Period


Estimation method = Trios, instant
Avg. load (kg/d)
12000
8000
4000
0
LCL
UCL
Period


Estimation method = Trios, hourly average
Avg. load (kg/d)
12000
8000
4000
0
LCL
UCL
Period


Estimation method = Trios, daily subsample
Avg. load (kg/d)
12000
8000
4000
0
LCL
UCL
Period

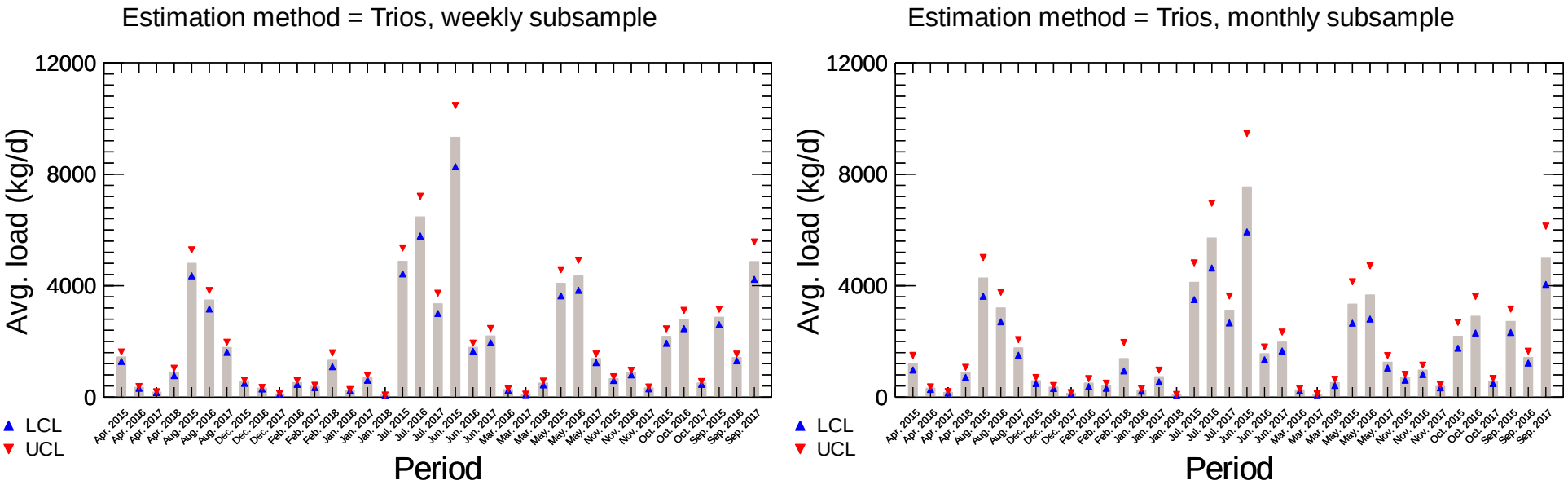


Figure E-7: Comparison of load estimates derived from grab samples (as LOADEST AMLE model estimate) and TriOS estimated nitrate-N concentrations and discharge for the period April 2015-March 2018, expressed as monthly values in each year. The TriOS estimates are derived from instantaneous measurements, monthly and weekly subsamples. The monthly TriOS samples represent the hourly average concentration measured on the 10th day of each month between 10:00 and 11:00. The weekly TriOS samples represent the hourly average concentration measured on the 10th day of each of the 1st, 8th, 15th 22nd and 28th day of each month.

Table E-1: Summary statistics for load estimates derived from grab samples using an AMLE model using the LOADEST modelling package. Details of LOADEST are provided in Runkel et al. (2004).

Period	No conc. vals./ measurement period	Mean load (kg/d)	LCL	UCL	Std. Error of Prediction	Std. Error
Est. Period	313	2113	1980	2253	70	69
Autumn	132	1583	1484	1685	51	49
Winter	103	4787	4418	5178	194	191
Spring	31	1688	1509	1882	95	94
Summer	47	412.95	373.16	455.79	21.09	20.57
Apr. 2015	53	1620	1483	1766	72	63
May. 2015	35	4716	4381	5069	176	156
Jun. 2015	46	10103	9324	10929	410	370
Jul. 2015	3	5717	5167	6310	292	278
Aug. 2015	2	4963	4413	5562	293	281
Sep. 2015	2	2669	2337	3034	178	171
Oct. 2015	2	1585	1372	1821	115	107
Nov. 2015	2	477.44	412.81	549.28	34.83	34.02
Dec. 2015	3	382.51	328.45	442.89	29.21	28.41
Jan. 2016	2	172.63	148.39	199.69	13.1	12.58
Feb. 2016	2	410.18	348.69	479.34	33.35	30.75
Mar. 2016	2	234.39	203.7	268.37	16.51	16.09
Apr. 2016	2	355.02	310.41	404.2	23.94	23.34
May. 2016	33	4527	4079	5009	237	217
Jun. 2016	2	2224	1971	2499	135	130
Jul. 2016	20	6662	6056	7312	321	290
Aug. 2016	2	3614	3242	4017	198	180
Sep. 2016	2	1366	1202	1547	88	83
Oct. 2016	15	2159	1888	2457	145	138
Nov. 2016	2	683.75	593.67	783.57	48.47	46.93
Dec. 2016	2	233.99	204.16	266.94	16.02	15.57
Jan. 2017	2	555.57	473.41	647.84	44.53	42.75
Feb. 2017	2	329.37	284.4	379.41	24.25	22.86
Mar. 2017	2	82.86	69.6	97.89	7.22	7.11
Apr. 2017	2	199.25	172.19	229.33	14.59	14.04
May. 2017	2	1885	1671	2118	114	106
Jun. 2017	24	3059	2712	3439	185	170
Jul. 2017	2	4862	4254	5531	326	315
Aug. 2017	2	2485	2131	2880	191	187
Sep. 2017	2	5409	4707	6186	378	362
Oct. 2017	2	546.7	466.93	636.14	43.2	42.23
Nov. 2017	2	321.97	278.29	370.53	23.54	22.65
Dec. 2017	2	98.83	82.65	117.23	8.83	8.7
Jan. 2018	2	58.3	47.37	71	6.03	5.96
Feb. 2018	30	1579	1381	1796	106	99
Mar. 2018	1	753.61	653.57	864.55	53.85	51.55
Apr. 2018	-	1568	1320	1848	135	127

Table E-2: Summary statistics for load estimates derived as the product of ten-minute interval TriOS sensor measurement and corresponding discharge values.

Period	No conc. vals./ measurement period	Mean load (kg/d)	LCL	UCL	Std. Error	Standard Deviation
Est. Period	151541	1793.9	1778.4	1809.6	7.9	3098
Autumn	6864	1550	1519	1581	15.8	3122
Winter	6528	3942	3897.5	3987.3	23	4301
Spring	6552	1431	1411.569	1450.574	10	1960
Summer	6480	462	451.847	472.148	5.2	1019
Apr. 15	3662	1423.4	1360.8	1486.0	31.9	1931.7
May. 15	4251	5313.3	5200.1	5426.5	57.7	3764.6
Jun. 15	4016	8748.3	8594.0	8902.6	78.7	4987.5
Jul. 15	4357	4455.8	4409.2	4502.3	23.7	1566.8
Aug. 15	4101	4002.9	3928.5	4077.2	37.9	2428.8
Sep. 15	4258	2350.2	2304.4	2396.1	23.4	1525.8
Oct. 15	4189	1667.6	1589.5	1745.8	39.9	2580.2
Nov. 15	4253	697.5	691.5	703.6	3.1	201.1
Dec. 15	4391	517.6	508.6	526.6	4.6	303.6
Jan. 16	4398	293.1	285.8	300.5	3.8	248.8
Feb. 16	4124	446.0	420.2	471.8	13.2	845.5
Mar. 16	4357	233.2	229.9	236.5	1.7	111.3
Apr. 16	4258	183.0	180.6	185.4	1.2	80.5
May. 16	4388	4412.1	4247.7	4576.5	83.8	5554.3
Jun. 16	4193	2087.8	2032.0	2143.7	28.5	1844.1
Jul. 16	3326	5228.5	5021.4	5435.7	105.7	6093.1
Aug. 16	1781	1345.8	1338.1	1353.6	3.9	166.5
Sep. 16	4302	1186.3	1156.2	1216.4	15.4	1007.6
Oct. 16	4435	2050.6	1970.7	2130.4	40.7	2712.1
Nov. 16	4298	902.6	886.2	919.0	8.3	547.2
Dec. 16	4436	355.2	352.1	358.2	1.6	104.3
Jan. 17	4441	518.7	500.4	536.9	9.3	621.5
Feb. 17	3978	254.5	247.3	261.8	3.7	233.1
Mar. 17	4344	109.9	109.3	110.4	0.3	18.2
Apr. 17	3709	114.7	112.9	116.6	1.0	58.2
May. 17	3689	1789.4	1694.0	1884.8	48.7	2955.6
Jun. 17	4291	3352.0	3168.7	3535.3	93.5	6125.0
Jul. 17	4458	3976.3	3872.0	4080.7	53.2	3552.9
Aug. 17	4459	1414.3	1396.5	1432.1	9.1	605.6
Sep. 17	4284	3114.6	3020.5	3208.7	48.0	3142.0
Oct. 17	4460	502.0	496.3	507.7	2.9	193.3
Nov. 17	4315	440.0	427.1	452.9	6.6	431.8
Dec. 17	4462	117.3	116.3	118.3	0.5	34.0
Jan. 18	4458	50.9	50.3	51.6	0.3	21.7
Feb. 18	4019	1701.8	1622.0	1781.5	40.7	2579.5
Mar. 18	4239	470.9	457.3	484.6	6.9	451.7
Apr. 18	2620	965.3	907.9	1022.8	29.3	1361.8

Table E-3: Summary statistics for load estimates derived as the product of TriOS one-hour sensor measurement and corresponding discharge values.

Period	No conc. vals./ measurement period	Mean load (kg/d)	LCL	UCL	Std. Error	Standard Deviation
Est. Period	26345	1722.8	1685.9	1759.6	18.8	3050.2
Autumn	6861	1438.6	1509.3	1367.9	36.1	2988.6
Winter	6524	3561.6	3665.1	3458.1	52.8	4265.1
Spring	6513	1431.6	1479.1	1384.1	24.2	1956.4
Summer	6447	458.5	483.6	433.5	12.8	1025.6
Apr.15	647	1364.3	1215.4	1513.3	75.9	1929.4
May.15	696	5084.3	4814.5	5354.1	137.4	3625.8
Jun.15	648	8965.5	8578.9	9352.2	196.9	5012.3
Jul.15	744	4449.8	4337.2	4562.4	57.4	1564.9
Aug.15	744	3800.5	3618.9	3982.0	92.5	2522.1
Sep.15	720	2350.7	2239.1	2462.4	56.9	1525.7
Oct.15	706	1664.7	1474.6	1854.8	96.8	2572.4
Nov.15	720	696.5	681.7	711.4	7.6	202.7
Dec.15	688	483.5	463.5	503.6	10.2	267.2
Jan.16	744	293.1	275.2	311.0	9.1	248.6
Feb.16	696	444.2	381.5	506.9	32.0	842.9
Mar.16	744	232.2	224.1	240.3	4.1	112.4
Apr.16	720	182.9	177.0	188.8	3.0	80.3
May.16	720	4223.5	3820.6	4626.4	205.2	5506.5
Jun.16	720	2071.1	1936.6	2205.7	68.5	1838.6
Jul.16	719	4139.7	3709.0	4570.4	219.4	5882.3
Aug.16	743	542.1	493.9	590.3	24.6	669.5
Sep.16	720	1185.4	1111.7	1259.0	37.5	1006.2
Oct.16	744	2045.9	1851.0	2240.9	99.3	2708.9
Nov.16	720	901.4	861.3	941.5	20.4	547.5
Dec.16	744	355.0	347.5	362.5	3.8	104.2
Jan.17	744	517.7	473.1	562.4	22.7	620.5
Feb.17	671	252.8	235.2	270.5	9.0	233.0
Mar.17	696	110.5	109.1	111.8	0.7	18.3
Apr.17	720	102.3	96.9	107.7	2.8	73.9
May.17	742	1654.0	1440.5	1867.6	108.8	2963.5
Jun.17	719	3352.5	2904.8	3800.2	228.0	6114.8
Jul.17	743	3976.7	3720.7	4232.7	130.4	3554.2
Aug.17	744	1414.2	1370.5	1457.8	22.2	605.9
Sep.17	719	3115.2	2885.8	3344.6	116.8	3133.0
Oct.17	744	502.1	488.1	516.0	7.1	193.4
Nov.17	720	439.8	408.2	471.4	16.1	431.8
Dec.17	744	117.3	114.9	119.8	1.2	34.0
Jan.18	744	50.9	49.4	52.5	0.8	21.7
Feb.18	672	1714.2	1517.4	1911.0	100.2	2598.3
Mar.18	744	459.2	425.6	492.7	17.1	466.0
Apr.18	432	888.9	760.8	1017.1	65.2	1355.3

Table E-4: Summary statistics for load estimates derived from weekly subsample values derived from ten-minute interval TriOS sensor measurements. Sub-sample values are the hourly average values for the period 10:00-11:00 on the 1st, 8th, 15th, 22nd and 28th day of each month. An AMLE model from the LOADEST modelling package was used.

Period	No conc. vals./ measurement period	Mean load (kg/d)	LCL	UCL	Std. Error of Prediction	Std. Error
Est. Period	173	1949	1802	2104	77	77
Autumn	43	1362	1232	1502	69	68
Winter	41	4162	3811	4535	185	183
Spring	45	1831	1668	2006	86	85
Summer	44	460.72	412.07	513.5	25.88	25.63
Apr. 2015	3	1443	1281	1621	87	83
May. 2015	5	4082	3633	4570	239	232
Jun. 2015	5	9319	8269	10463	560	544
Jul. 2015	5	4871	4421	5354	238	230
Aug. 2015	5	4802	4352	5285	238	228
Sep. 2015	5	2867	2600	3153	141	135
Oct. 2015	5	2180	1933	2450	132	122
Nov. 2015	5	662.88	600.38	730.06	33.09	32.08
Dec. 2015	5	551.72	497.35	610.36	28.84	27.81
Jan. 2016	5	247.53	223.95	272.9	12.49	11.88
Feb. 2016	5	524.26	460.51	594.3	34.14	31.58
Mar. 2016	5	270.18	246.92	295.02	12.27	11.81
Apr. 2016	5	349.13	319.08	381.22	15.85	15.32
May. 2016	5	4346	3832	4911	275	264
Jun. 2016	4	1787	1644	1938	75	71
Jul. 2016	5	6465	5783	7206	363	346
Aug. 2016	2	3484	3164	3827	169	156
Sep. 2016	5	1420	1305	1543	61	56
Oct. 2016	5	2770	2458	3112	167	160
Nov. 2016	5	878.98	801.61	961.74	40.86	38.96
Dec. 2016	5	320.36	295.19	347.08	13.24	12.62
Jan. 2017	5	691.34	606.32	784.88	45.57	43.87
Feb. 2017	4	383.84	344.54	426.35	20.88	19.43
Mar. 2017	5	97.19	88.38	106.63	4.66	4.51
Apr. 2017	4	178.61	162.41	195.96	8.56	8.16
May. 2017	4	1387	1241	1546	78	73
Jun. 2017	5	2195	1949	2462	131	123
Jul. 2017	5	3350	3002	3728	185	179
Aug. 2017	5	1782	1610	1969	92	89
Sep. 2017	5	4864	4227	5569	343	333
Oct. 2017	5	509.13	461.77	560	25.07	24.23
Nov. 2017	5	330.56	300.16	363.18	16.08	15.32
Dec. 2017	5	117.11	106.5	128.48	5.61	5.44
Jan. 2018	5	69.81	63.27	76.84	3.46	3.36
Feb. 2018	5	1324	1093	1589	127	124
Mar. 2018	5	505.16	442.18	574.54	33.78	32.79
Apr. 2018	1	896	773	1034	66	63

Table E-5: Summary statistics for load estimates derived from monthly subsample values derived from ten-minute interval TriOS sensor measurements. Sub-sample values are the hourly average values for the period 10:00-11:00 for the 10th day of each month. An AMLE model from the LOADEST modelling package was used.

Period	N/Measurement period	Mean load (kg/d)	LCL	UCL	Std. Error of Prediction	Std. Error
Est. Period	34	1790	1527	2085	142	142
Autumn	9	1175	947	1442	126	126
Winter	8	3646	3073	4294	312	311
Spring	9	1875	1573	2218	165	164
Summer	9	486.41	377.32	617.22	61.31	61.23
Apr. 2015	1	1215	974	1497	134	133
May. 2015	1	3336	2654	4140	380	378
Jun. 2015	1	7543	5932	9456	900	896
Jul. 2015	1	4120	3500	4817	336	334
Aug. 2015	1	4273	3619	5010	355	352
Sep. 2015	1	2716	2321	3160	214	212
Oct. 2015	1	2183	1756	2682	237	233
Nov. 2015	1	706.12	608.39	815.02	52.74	52.29
Dec. 2015	1	589.91	489.76	704.44	54.82	54.43
Jan. 2016	1	258.93	216.61	307.08	23.1	22.88
Feb. 2016	1	506.02	378.26	663.18	72.85	72.19
Mar. 2016	1	260.75	224.79	300.81	19.4	19.23
Apr. 2016	1	320.6	278.5	367.23	22.65	22.45
May. 2016	1	3666	2803	4712	488	485
Jun. 2016	1	1559	1344	1798	116	115
Jul. 2016	1	5707	4633	6955	593	588
Aug. 2016	1	3201	2705	3761	269	265
Sep. 2016	1	1424	1223	1648	109	107
Oct. 2016	1	2903	2303	3611	334	332
Nov. 2016	1	970	814	1148	85	85
Dec. 2016	1	361.95	310.87	419	27.6	27.36
Jan. 2017	1	734.63	545.3	968.66	108.26	107.76
Feb. 2017	1	402.5	319.04	501.12	46.52	46.08
Mar. 2017	1	99.63	85	116.04	7.92	7.87
Apr. 2017	1	172.27	147.47	200.04	13.42	13.27
May. 2017	1	1255	1047	1492	114	112
Jun. 2017	1	1973	1657	2332	172	169
Jul. 2017	1	3117	2663	3627	246	244
Aug. 2017	1	1767	1503	2063	143	142
Sep. 2017	1	5010	4046	6135	533	529
Oct. 2017	1	573.07	487.31	669.5	46.51	46.15
Nov. 2017	1	387.31	335.88	444.34	27.69	27.3
Dec. 2017	1	140.7	120.87	162.85	10.71	10.63
Jan. 2018	1	82.75	70.81	96.1	6.45	6.4
Feb. 2018	1	1384	943	1960	260	260
Mar. 2018	1	521.88	422.2	637.98	55.11	54.71
Apr. 2018	1	878	712	1071	92	91

Appendix F Mataura River

Regression techniques to improve prediction

Number of Variables : 11
Number of Cases : 152000

SYSTAT Rectangular file
O:\ELF18203\Working\Mataura\Neale\Mataura_Hourly_Q_TriOSN_P_R_Grab2_select3.syz,
Created data file Sat Oct 13 11:33:32 2018 containing variables:

NITRATE_MGL	YYYY	MM	DD	HH	MI
TRIOSRIVER_NITRATE_MGL	TRIOSPUMP_NITRATE_MGL	DATE	TIME	DATE_TIME	

> REM -- Following commands were produced by the LTSREG dialog:
> ROBREG
> MODEL TRIOSRIVER_NITRATE_MGL = CONSTANT + TRIOSPUMP_NITRATE_MGL
> LTS / NCSTEP = 2 NREP = 500 NBSOL = 10
> ESTIMATE / CUTOFF = 3 CONFI = 0.95 TOL = 1e-012 ITER = 100

▼ Robust Regression

Dependent Variable	TRIOSRIVER_NITRATE_MGL
No. of cases	152000
No. of Regressors	1

Least Trimmed Squares (LTS) Regression

Size of Subset	300
Number of C-Steps	2
Maximum Number of Replications	500
Number of Solutions for Final C-Steps	10
Intercept Adjustment	NO
Number of Squared Residuals Minimized (h)	114000
Breakdown Value	25%

LTS Parameter Estimates

Effect	Coefficient
CONSTANT	0.162
TRIOSPUMP_NITRATE_MGL	0.917

Scale Estimates

Scale (LTS)	0.120
Scale (Weighted)	0.091

Cutoff Point	3.000
Number of Outliers Detected	38499

Robust R-square	0.867

Ordinary Least Squares (OLS) Regression for Outlier Free Data

Multiple R	0.969
Squared Multiple R	0.939
Adjusted Squared Multiple R	0.939
Standard Error	0.071

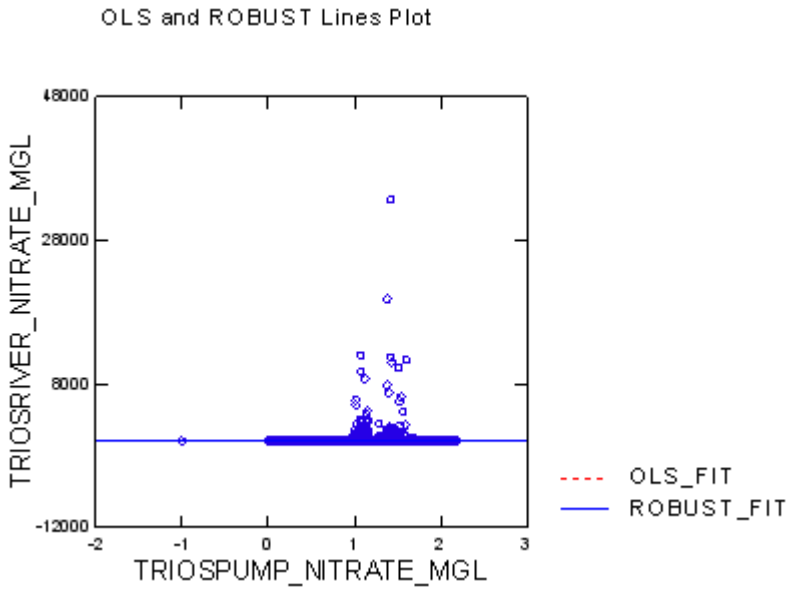
OLS Parameter Estimates

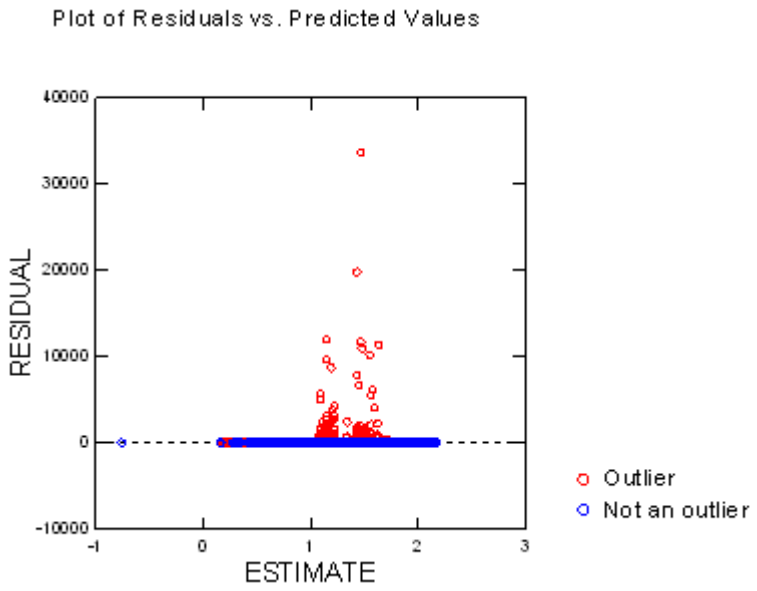
Effect	Coefficient	Standard Error	95.00% Confidence Interval	
			Lower	Upper
CONSTANT	0.161	0.001	0.159	0.162
TRIOSPUMP_NITRATE_MGL	0.919	0.001	0.918	0.921

Analysis of Variance

Source	SS	df	Mean Squares	F-Ratio	p-Value
Regression	8801.380	1	8801.380	1753349.476	0.000
Residual	569.737	113499	0.005		

Durbin-Watson D Statistic	0.352
First Order Autocorrelation	0.824




Plot of Residuals vs. Predicted Values
RESIDUAL
ESTIMATE
40000
30000
20000
10000
0
-10000
-1
0
1
2
3
Outlier
Not an outlier

Subset of data selected

Data for the following results were selected according to
SELECT TRIOSRIVER_NITRATE_MGL >0.1 AND TRIOSRIVER_NITRATE_MGL <5 AND TRIOSPUMP_NITRATE_MGL >0.1

Dependent Variable	TriOS R nitrate-N conc. (mg/L)
No. of cases	120197
No. of Regressors	1

Least Absolute Deviations (LAD) Regression

Method of Estimation	IRLS

Raw R-square (1-Residual/Total)	0.982
R-square(Observed vs. Predicted)	0.737

LAD Parameter Estimates

Effect	Coefficient
CONSTANT	0.234
TriOS P nitrate-N conc. (mg/L)	0.833

Scale Estimates	0.048

Cutoff Point	3.000
Number of Outliers Detected	14150
Proportion of data	11.8%

Ordinary Least Squares (OLS) Regression for Outlier Free Data

Multiple R	0.984
Squared Multiple R	0.969
Adjusted Squared Multiple R	0.969
Standard Error	0.046

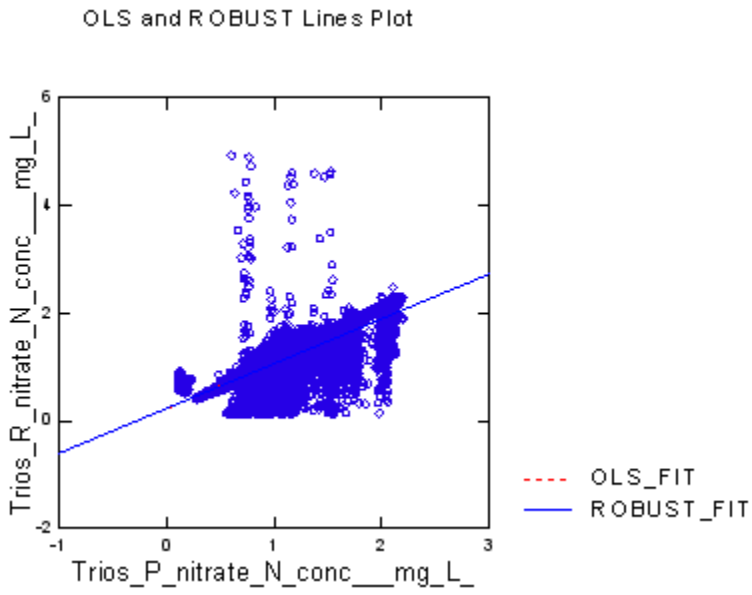
OLS Parameter Estimates

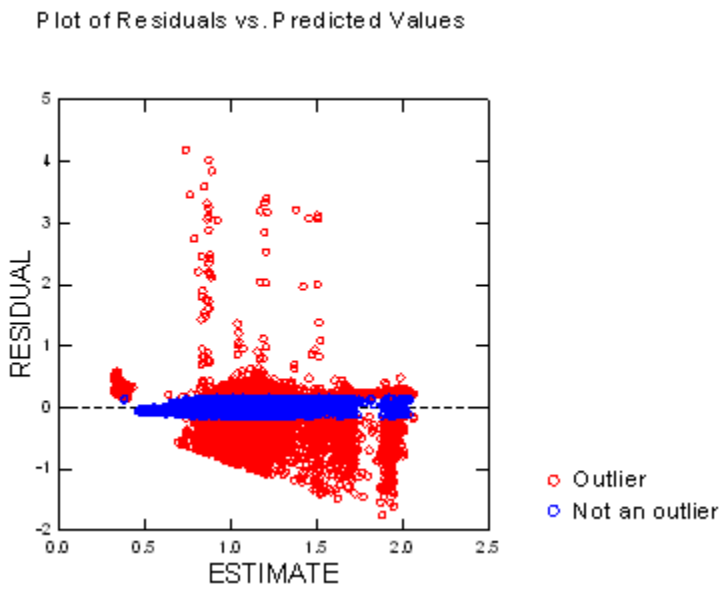
Effect	Coefficient	Standard Error	95.00% Confidence Interval	
			Lower	Upper
CONSTANT	0.161	0.001	0.160	0.162
TriOS P nitrate-N conc. (mg/L)	0.927	0.001	0.926	0.928

Analysis of Variance

Source	SS	df	Mean Squares	F-Ratio	p-Value
Regression	7054.532	1	7054.532	3284219.732	0.000
Residual	227.786	106045	0.002		

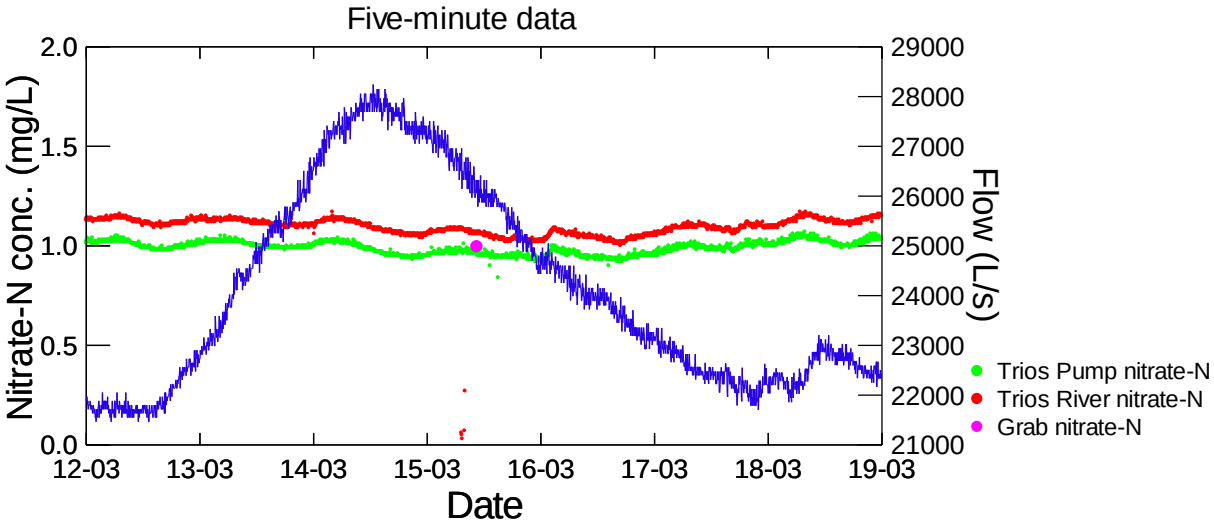
Durbin-Watson D Statistic	0.280
First Order Autocorrelation	0.860

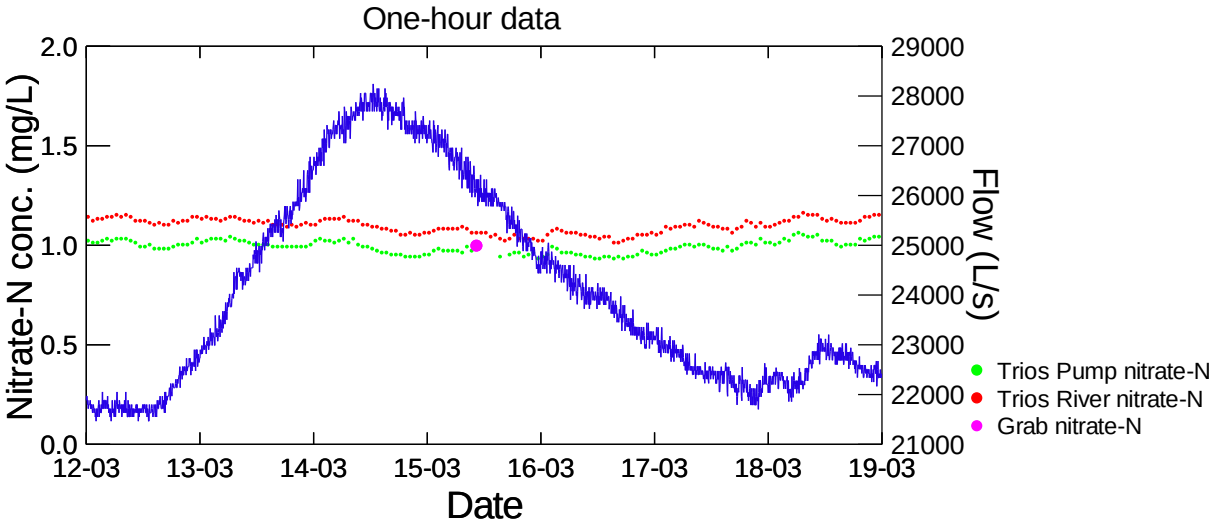


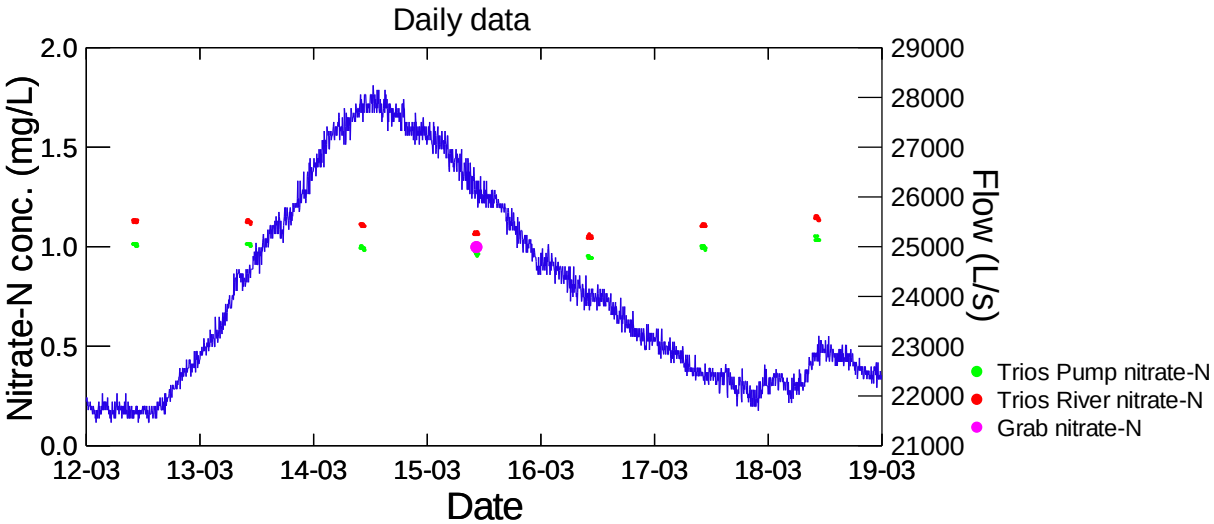


> REM -- End of commands from the LADREG dialog

Comparison of time series data collected at varying frequency







Appendix G Draft procedure for use of continuous nitrate sensors

Examples of some of the effects of some of the procedures identified below are illustrated graphically in XXX to YYYY. This material was originally presented and discussed in the October 2018 workshop hosted by NIWA.

Disclaimer

The three agencies that contributed data for the case studies were canvassed to obtain information regarding current procedures in use. These have been incorporated in the material that follow, which are largely based on published USGS procedures. This should not be regarded as a recommendation for exclusive use of USGS procedures, or an endorsement of these procedures – rather, it has been used as a starting point.

The Standard – nitrate-N sensors

For data to meet the Standard, the following shall be achieved:

Nitrate-N Measurement Accuracy	Deviation from primary reference	• Instrument specific • Concentration range dependent • Minimum accuracy specification to be defined
Stationarity	Stationarity of record shall be maintained.	

Requirements

As a means of achieving the Standard (QC 600), the following requirements apply:

Units of Measurement		Nitrate-nitrogen, expressed as N (mg/L or g/m^3)
Resolution		• Instrument specific • Concentration range dependent • To be recorded for each instrument type
Precision		• Instrument specific • Concentration range dependent • To be recorded for each instrument type
Timing of Measurements	Maximum recording interval	Record nitrate-N (eq) concentration at the logging time
	Measurement	A single value is reported at logging time. Any statistical function undertaken (i.e., estimation of average or median value derived from several discrete measurements) shall utilise a sample period smaller than or equal to the recording interval. The number of discrete values and time period over which these data are collected to be reported.
	Resolution	• Instrument specific
	Accuracy	± 90 s/month
	Time zone	Record time as New Zealand Standard Time (NZST) only.

Supplementary measurements	If instantaneous load or flux estimates are required…	• Flow or discharge • Discrete or grab water samples for laboratory analysis of nitrate-N concentration • Date and time of grab sample to be related to time series
	Measurement statistics	Details regarding method and derivation of statistics to be defined in the metadata.
Laboratory validation tests	Minimum test requirements	Minimum required pre-deployment tests: • Record nitrate concentration of clean instrument in air. • Record nitrate concentration of clean instrument in high spectral purity water. • Follow manufacturer recommendations to apply baseline correction (zero the instrument) using high spectral purity water.
	Accuracy, precision and linearity checks	Using natural waters (i.e., river water) spiked with known amounts on nitrate-N: • Perform accuracy, precision and linearity checks. • Estimate the recovery of added nitrate-N (i.e., account for nitrate-N in the river water). • Ensure the recovery is within accuracy specification of the sensor type. • Ensure that spiked samples are utilised immediately. • Ensure that particulate material is maintained in suspension. • When necessary, add organic matter and/or particulate material derived from suitable standard materials.
	Accuracy	**Theoretical concentration estimation** $$C_c = \frac{C_{std} \times V_{std}}{V_{sample}}$$ Where C_c = calculated concentration of spiked sample (mg/L) C_{std} = concentration of nitrate spike standard (mg/L) V_{std} = volume of nitrate spike added (L) V_{sample} = total volume of solution after addition of spike (L)
		Recovery estimation $$Recovery\ (\%) = R(\%) = \frac{C_s \times C_u}{C_c} \times 100 \text{ perc.}$$ Where C_s = measured conc. of spiked sample or nitrate standard C_u = measured conc. of unspiked sample or high spectral purity water C_c = calculated conc. of nitrate standard or matrix spike spectral purity water $Recovery\ (conc) = (C_s - C_u) - C_c$

		Measured accuracy may be compared with manufacturer reported values. Bias (persistent under- or over estimation) may also be estimated and remedial action taken (e.g., baseline correction).
	Precision	Precision is determined from repeated measures of a nitrate standard solution, or a spiked matrix solution. A standard deviation and relative standard deviation may be calculated. These values may be compared with manufacturer specification. Manufacturer specifications are generally determined on high spectral purity water and may therefore better represent analytical precision – care is required to ensure that the difference between sample or analytical precision is compared.
	Linearity checks	• Multiple point calibration curve check. • Nitrate standards and spike concentrations to span range typical for deployment site. • Fitting a linear relationship to the data ($y = ax + b$) is useful. The slope (*a*) should be near one, and the intercept (*b*) should be near zero, and the coefficient of determination (R^2) should exceed say 0.95.
Field validation methods	Primary sensor tests	Minimum required pre-deployment tests: • Record nitrate concentration of clean instrument in air. • Record nitrate concentration of clean instrument in high spectral purity water.
	Secondary sensor tests	• Using a second instrument of known performance, collect paired in situ measurements
	Primary reference measurement	• Annual zero-point validation: ± defined value, which may be instrument specific • Monthly validation samples/measurements – grab sample submitted for laboratory analysis. • Annual validation grab sample set collected during a runoff event in nitrate-N spans some pre-defined measurement range, which may be catchment and instrument specific. *Note: Validation samples are laboratory analysed.*
	Tolerance	• Instrument specific • Concentration range dependent • To be recorded for each instrument type • These values and ranges may be matrix dependent
Calibration	Frequency	• Calibration shall occur when validation confirms that the in situ sensor is not conforming to the accuracy of the

		Standard (QC 600) and/or as per the manufacturer's specifications. • In-situ calibration is unlikely to be achievable or practical. • The instrument should be swapped out and returned to base for calibration using suitable standards
	Method	• Multi-point calibration using primary standards
Metadata		Metadata to be recorded for all measurements.
Quality Assurance		Protocols to be developed
Processing of Data		All changes shall be documented. All data shall be quality coded as per a Quality Code flowchart, once one has been developed.

The following table summarises best practice and is not required for QC 600:

Validation Methods	Inspection of recording installations	Sufficient to ensure the data collected are free from error and bias, both in turbidity and time.
Archiving	Original and final records	File, archive indefinitely and back up regularly: • raw and processed records • primary reference data • supplementary measurements • validation checks • site inspections • verification results, and metadata.
Auditing		To be developed.

Mataura WQ Instrument Calibration and Cleaning Instructions

Note the recorded sensor values before and after cleaning on the inspection record. Either on site by connecting to the loggers, or afterwards from the telemetry record.

Cleaning:

Equipment: *Wipes, cotton buds, Acetone, and containers. These are stored in the shed.*

River TriOS:

Figure G-1: The instrument and mounting bracket as it is withdrawn from the PVC protection tube. (Evan Baddock, NIWA).

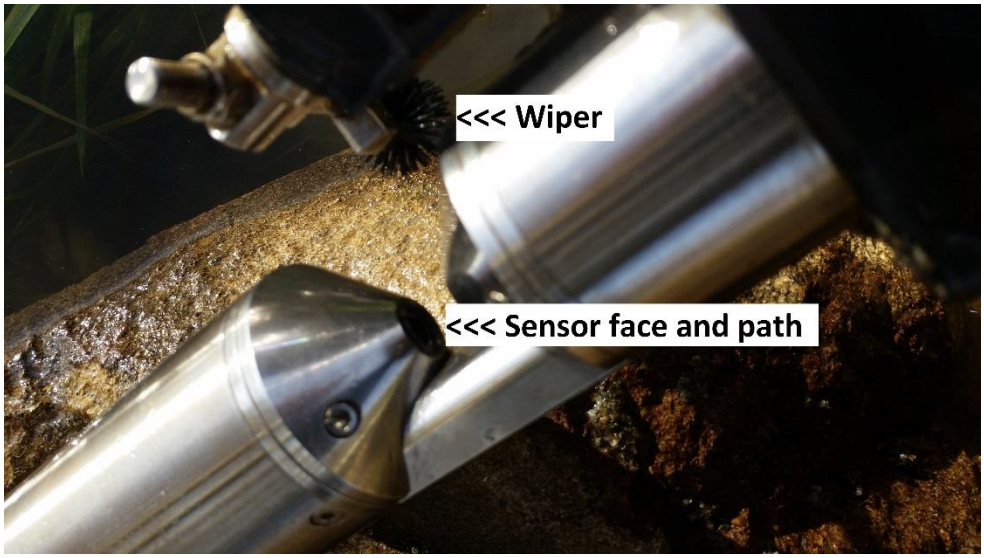


Figure G-2: Close up of the sensor windows and optical path with the automatic wiper at rest behind. (Evan Baddock, NIWA).

Figure G-3: Close up of the sensor after a two week deployment in the river (including major flood). Automatic wiper at rest behind. (Evan Baddock, NIWA).

The build-up on and between the two lens needs removed with care so they do not get scratched. Use the large cotton buds soaked in Acetone to wipe between the lenses. Acetone will remove any algae or silt film, and most mineral deposits. Also clean the wiper and probe body.

Pump TriOS: In the container under the bench.

Check that the pump is working. It comes on for 2 minutes of every 5 minute interval. Check that the water runs freely, and there is no build up on hose wall? Choose your time for checking this between pump cycles or removed the inlet clear hose into a bucket or this time.

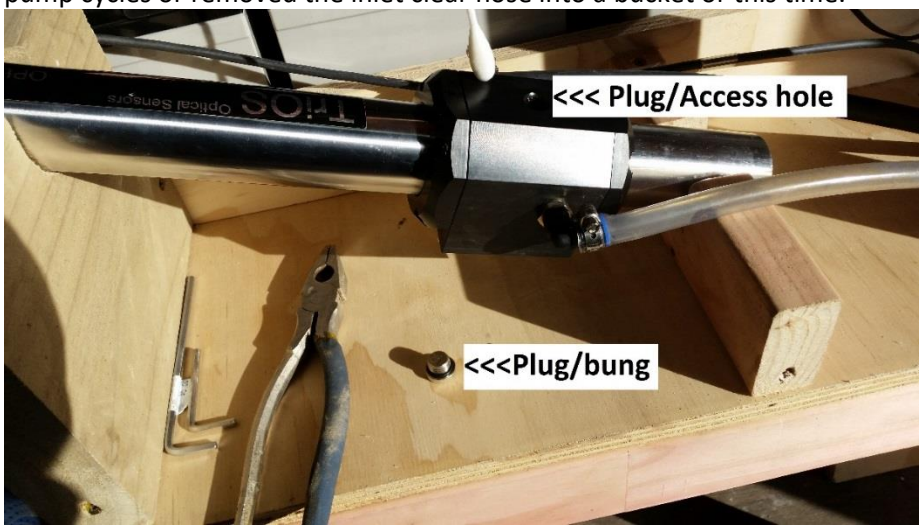


Figure G-4: Deployment of pump-fed TriOS sensor in instrument shed. (Evan Baddock, NIWA).

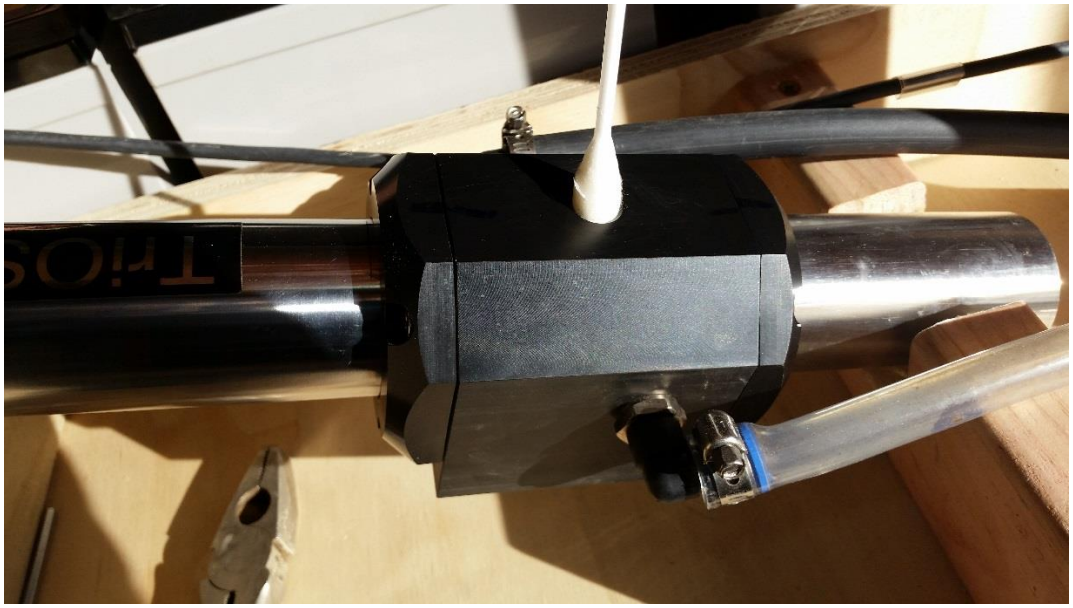


Figure G-5: Cleaning of optical surfaces with a large cotton bud soaked in acetone following removal of the upper screw to allow access to the lens faces. Full cleaning of the black measurement chamber/sleeve requires complete removal. Allan keys are left with the instrument for this purpose (Evan Baddock, NIWA).

Pump in the river for pump-fed TriOS instrument:

Remove and clean the intake mesh by unscrewing the black alkathene connector first, when this is loose the galvanised steel cap will turn, enabling easy removal of the pump and hose. Care is required to not kink the alkathene pipe as its withdrawn.

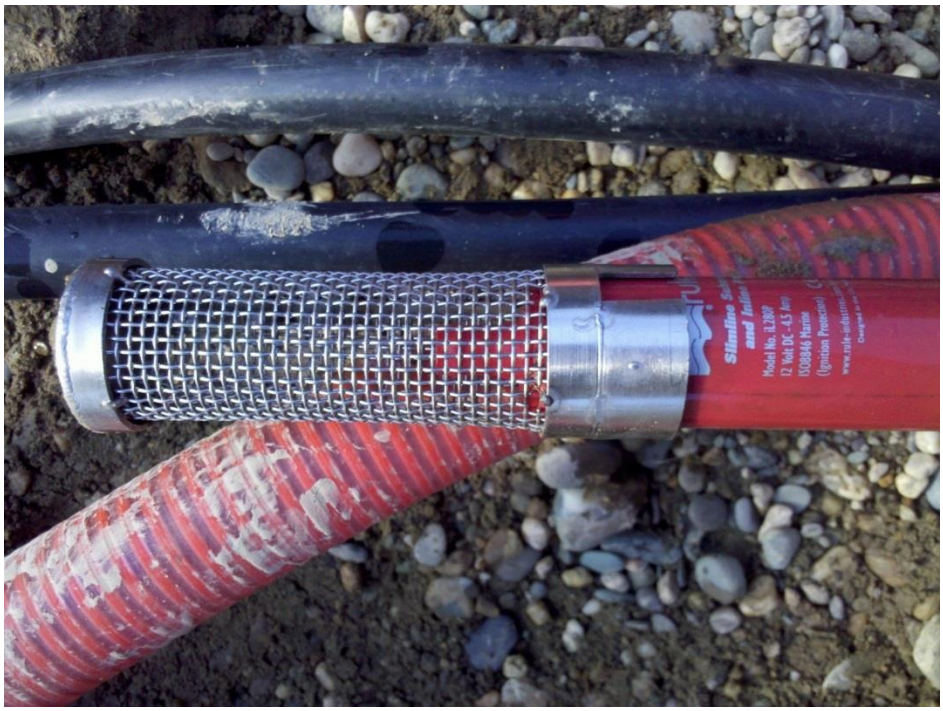


Figure G-6: Stainless steel mesh over pump intake for pump fed instrument. (Evan Baddock, NIWA).

The stainless steel mesh covering the pump intake can be removed. It is a tight friction fit to stop it falling off. The pump operates for 2 min every 5 min, but it can be run dry for a short period without damage.

Example of calibration worksheet/records:

Mataura BM Site - TriOS Calibration			**NO3 only**	
18th May 2016	**EB**			
		Pump TriOS	**River TriOS**	
Initial logger readings:				Comment
1100		0.137 locked	0.908	Chamber dry - pump blocked so no water for some time!
				Modbus problem shows channel data flat lining with these values!
Initial manual readings:		0.153 dry	0.93	Raw downloads: logger(3).tar = Pump 170mb, logger(4).tar = River 302mb.
1100				
Both in River Water:		0.862	0.93	Uncleaned - 7.3% Neon data shows around 10% - possible cal offsets missing?
Both in Solution				Cleaned.
1.3 mg/l		1.24 / 1.25 / 1.24	1.3 / 1.29 / 1.28 / 1.3	So 1.3 to 1.24 difference = 4.6%
Back in River				
1430		0.842	0.885	Cleaned - 4.8%
Pump Trios back in				
chamber - 1500		0.854 / 0.858	0.895	4.40%

Mataura BM Site - Instrument Spec's						
Instrument	**Model**	**Serial#**	**Parameter**	**Range**	**Accuracy**	**Resolution**
ISCO Samplers	6712		**Water**	0 - 30m line	N/A	N/A
	Avalanche		**Sample**			
DAA Bubbler	H-3553	16D102663	**Stage**	1 - 10m	0.02% of Full Scale Output	0.0001
					Drift = 0.05% FSO per year	
Turbidity	DTS - 12		**NTU**	0 - 1600 NTU	±2% of reading + 0.2 NTU (0-399 NTU)	0.01 NTU
					±4% of reading (400-1,600 NTU)	
TriOS	12S Photometer	River =	**NO2**	0 - 150 mg/l	+/- 5% +0.1	0.5
		Pump =	**NO3**	0 - 100 mg/l	+/- 5% +0.1	0.3
YSI Sonde	EXO2		**Temp**	-5 to 50°C	-5 to 35°C: ±0.01°C 35 to 50°C: ±0.05°C	0.001 °C
			Salinity	0 to 70 ppt	±1.0% of reading or 0.1 ppt	0.01 ppt
			EC	0-200 mS/cm	0 to 100: ±0.5% 100-200: ±1%	0.0001 to 0.01 mS/cm
			TSS	0 to 1500 mg/L	Not Specified	Variable
			Turb	0 to 4000 FNU	0 to 999 FNU: 2%, 1000 to 4000 ±5%	0 to 999 FNU: 0.01
						1000 to 4000 FNU: 0.1

Instrument	**Calibration recommendations**	**Cleaning recommendations**	**Other / Comment**
ISCO Samplers	When installed and when problems.	General check over - spilled water etc...	Volume calibrations both out when installed - 600ml give 900ml?
			Possibly long lines and draw height causing this - to be watched!
DAA Bubbler	Against ESG every visit	Purge gas line each month	Don't use offset function - problems with large offsets!
	In known standpipe (1, 2, 3m) yearly	Check orifice for fouling	
Turbidity	Accurate readings for up to 12 months	Each monthly visit	
	Check readings with HACH meter		
TriOS	24 months (manufacturer)	Each monthly visit - clean with Acetone	Will Calibrate more offen with slight discrepancy between units?
	25 months (manufacturer)	Periodically remove pump chamber and clean	
YSI Sonde	Complete calibration in less than 15 minutes	Each monthly visit - remove black outer cover.	Do we need to purchase or hire the calibration unit?
	using EXO's suite of smart sensors and		
	intuitive KOR interface software.		

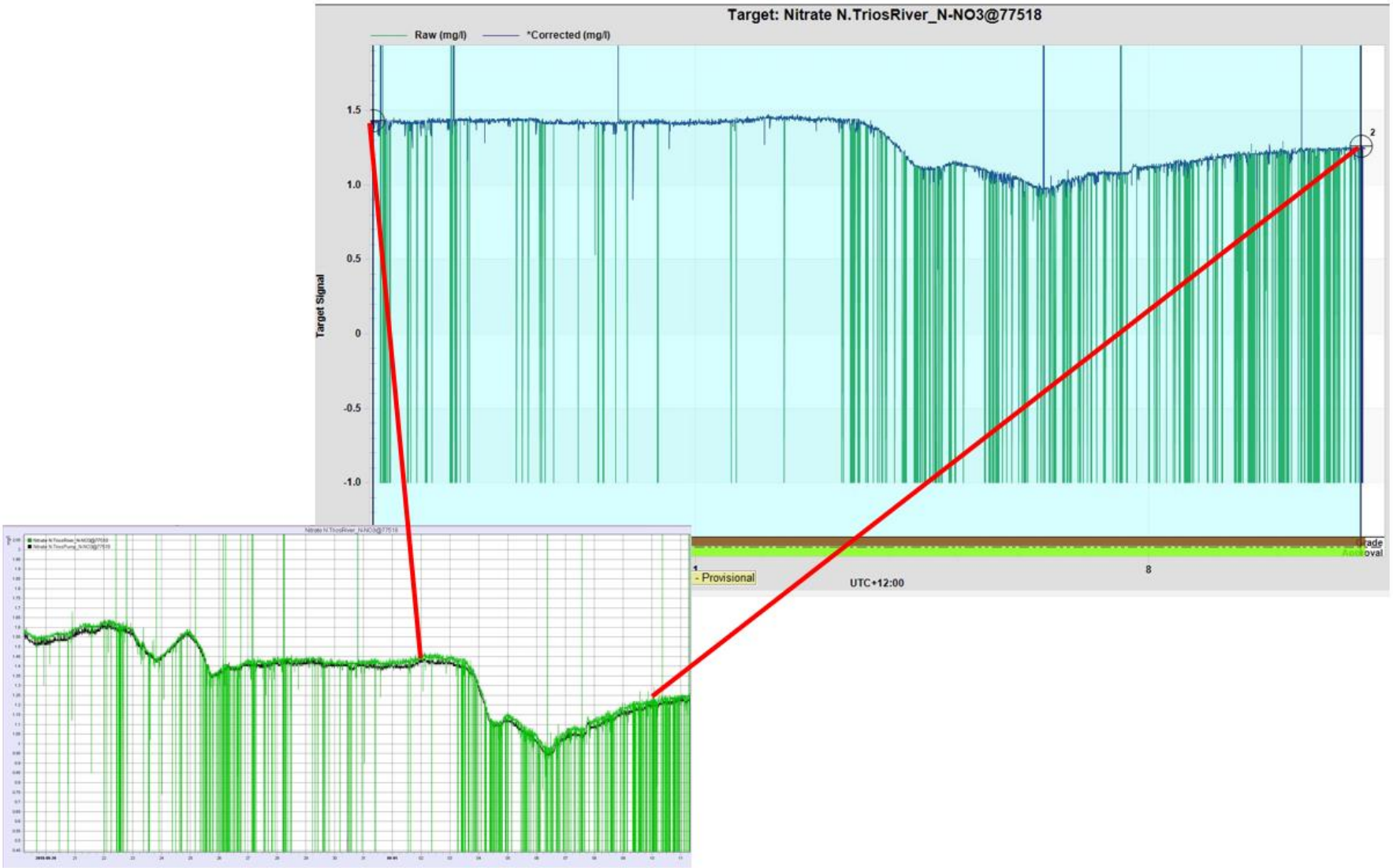


Figure G-7: Effect of data "cleaning" on quality of data. The lower left figure indicates the raw in-river (green) and pumped (black) data set. The upper right indicates the corrected data set (blue line). Note the removal of almost all spikes (Evan Baddock, NIWA).

Appendix H Installation of nitrate-sensors – ORC experience

This material was kindly made available by Paul Hannah, Senior Environmental Officer (Hydrology), Otago Regional Council, Dunedin.

Trios Nitrate draft 'draft how to Guide'

Pre-install Calibration:

The Trios nitrate probes are shipped pre-calibrated. No calibrations are required prior to installing in the field. Pre-determining the instream nitrate levels using grab samples are recommended. These results are used to determine the optimum optical path length (distance between lenses). For rivers with very low baseline levels of nitrate the optical path length may need to be increased. Refer to manufacturer's recommendations.

Note: It is worth determining the path length prior to ordering as this will affect the brush width if using an after-market brush wiper.

Installation (refer to Figure H-1 through Figure H-4)

There are two main field installation methods for continuous water qual sensors, 'in-river' and 'out-of-river' installations. An 'in-river' installation is self-explanatory, the sensor is installed submerged in a river. Out-of-river installations have higher power demands so are generally used where 240V is available. The sensor is located away from the river and a pump is used to deliver river water to the sensor housed inside a monitoring station hut.

To date ORC has only installed Trios probes using the in-river installation method. Two methods of 'in-river' mounting options have been used by ORC staff these are 'shielded' and 'non-shielded' mounting. There are pro's and con's to each in-river mounting technique as listed below:

Non-shielded:

- Pro's: Most cost-effective mounting option as it requires little fabrication prior to install. In clear water the probe and wiper brush can be visually checked without disturbing the sensor. As the probe is more exposed to the river currents fine filamentous algae tends to get sloughed off before it accumulates to problem levels. An exposed sensor also provides less refuge space for aquatic organisms such as snails which can congregate in larger numbers inside a shield (such as a perforated pipe). This technique is better suited to locations positioned just out of the main flow such as a small side eddy. This helps to avoid a build-up of water born debris. When conditions are right, this mounting option has provided the longest duration of hands-free operation.

- Con's: The probe is most exposed to impact damage from water-borne debris when mounted in-river and unshielded. Sticks, roots and leaves can build up around the sensor and wiper arm. Debris can wedge within the optical path length and damage wiper brush mechanisms. Sensor more visible to the public and exposed to vandalism. Sensor removal can be more time consuming and problematic to access during high flows (depending on the mounting.

Shielded:

- Pro's: Shields intercept water borne debris better when mounted in the main current. Less exposed to vandalism. May get better life out of wiper mechanisms. Sensors mounted within a shield on a sliding mechanism are generally easier to remove for inspection and cleaning.
- Con's: The probe needs to be removed from the shield/pipe more regularly to inspect and remove biofouling of the shield. As a shield decreases the water velocity passing over the sensor, long filaments of algae can form which clog the optics that brush and optics and require manual removal.

Installing the sensor in a pipe with slots rather than holes at the "Shag at Craig road" site appears to have provided two benefits:

- Less trapping of debris in the pipe that shields the sensor.
- Reduced noise in the data. This may be due to the pipe slowing the velocity of water passing through the optical path which may in turn reduce suspended particle size(?)

Field Cleaning

Compressed air or Wiper options. To date ORC have only used an aftermarket wiper (Zebratech hydro-wiper) with reasonable results. The wiper drive gears are prone to shearing in the event debris such as sticks or gravel gets caught in the wiper arms path. On occasions small stones can get imbedded in the wiper brush which can in-turn score the sensor's optical lense(s). If possible avoid areas where the sensor is likely to get buried during flood events as the brush will be unable to clear away small stones and damage do both the wiper mechanism and optics are likely. An alternative would be to disable the brush during high flows if practical. Additional sensor cleaning is recommended monthly using acetone and a non-abrasive cloth. The ABS-360 signal output is helpful as a surrogate measure of biofouling and/or the condition of the optical lenses. When this value is above 1, or if the ABS-360 value trends upwards over time (during settles stream/river flows) this may indicate the sensor needs additional cleaning.

Installing the sensor in the pipe at Shag at Craig road appears to have reduced data noise. This may be due to the pipe slowing the velocity of water passing through the optical path which may in turn reduce suspended particle size??

Recommended depth of installation (in-river installation)

The depth of water the sensor is installed at will vary depending on the depth of water available at each site. Any installation should have the ability to move the sensor up or down in the water column if it is to be deployed for any length of time. This will allow the technician to keep the sensor clear of any changes in the river bed level or adjust the sensor down if required during low river flows. To avoid damage to the sensors optics, avoid mounting the optics within 200mm of a mobile gravel river bed.

240V v's 12V systems

ORC has only used 12V solar powered systems to run a telemetered nitrate sensor and wiper. Most installations consist of 80W of solar capacity and a 12V 60Ah battery. This power supply has not given issue through the last 3 Otago winters.

Data validation and QC

ORC field hydrology staff currently quality assess and archive continuous nitrate data to a QC200 – non-verified standard. External checks are derived from lab analysed nitrate grab samples. Data irregularities and non-conformances are commented on, such as missing record and data affected by flood events.

Grab samples

Physical grab samples used to validate continuous nitrate data should be collected as close to the logged time period as possible and also as close to the Trios optics as practicable. This will help to ensure the grab sample 'check' value is representative.

Installation in direct sunlight:

Where possible avoid installation in direct sunlight (see manufacturer's instructions).

Wet-mateable connectors (cable plugs) are recommended for continuous water quality sensors and wipers. Being able to quickly un-plug a sensor head for maintenance or replacement is very beneficial.

Figure H-1: Example of a Trios probe mounting using scaffolding swivel clamps and 40GMP pipe. Probe is clamped in the water on the downstream side and is non-shielded. This non-shielded installation works when the probe is in the lee of willow trees, not in the direct current. When in the direct current too much debris will get caught around the sensor (Paul Hannah, ORC).

Figure H-2: Pipe installation at the Mill Creek at Lake Hayes Nitrate recording station. (Paul Hannah, ORC).

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Figure H-3: Example of mounting a Trios probe, wiper and conductivity probe to 'sliders' which keep the probes in position inside the 150mm PVC pressure pipe. These sliders are cut from a thinner gauge PVC pipe of the same external diameter as the outer pipe (Paul Hannah, ORC).

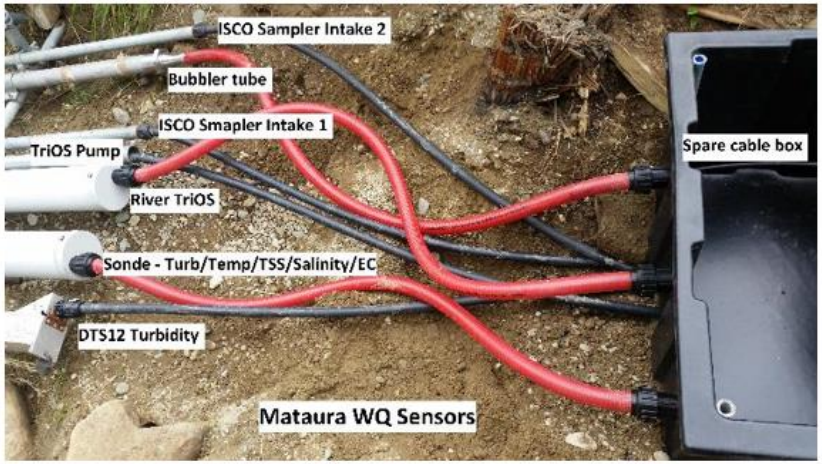
Figure H-4: Intake slots cut into thick-walled 150mm PVC pressure pipe to facilitate water flow and exchange. Slots are being trailed instead of holes to reduce the likelihood of sticks and other debris being caught in the holes (Paul Hannah, ORC).

Appendix I Installation of nitrate-sensors – NIWA experience

This material was originally shared at the NIWA workshop held in October 2018, and kindly made available by Evan Baddock, Principal Technician – Environmental Monitoring, NIWA South Island Field Teams, Dunedin.

The figures that follow are associated with the "Mataura at Mataura Island" benchmark site operated by NIWA.

- Earthworks/piles
- Container
- Mains power
- In river frame (driven galv. pipe/scaffold clamps)
- Rock armouring on bank
- Multiple sensor pipes
- Multiple large diameter conduits



- Neon loggers x2 – Sat & Cell.
- Wireless router for Side-looker.
- ISCO samplers x2
- Waterlog bubbler for stage record.
- Nitrate sensors – 2x TriOs, one in situ the other pumped into shed.
- Turbidity sensors – DTS-12, Exo2, Observator.
- Multi parameter Sonde – Turb, DO, Temp, Salinity, EC.
- Acoustic Doppler velocity meter (sidelooker) – TRDI Channelmaster.
- Pump for Nitrate sensor in shed.

- ISCO samplers
- Refrigerated (Nitrates)
- Sediment sampler
- Triggered >150m3/s

Trios OPUS sensor, measuring pumped river water supply
The black enclosure allows connection of water supply and drainage pipe, and out-of-river measurement.

Plumbing entering the housing, showing water supply and drainage pipe for out-of-river measurement.

Trios OPUS sensor, measuring pumped river water supply
The black enclosure allows connection of water supply and drainage pipe, and out-of-river measurement.

Appendix J Other TriOS deployment experiences

Biomass build-up and cleaning requirements in a small, nutrient-rich stream.

Figure J-1: TriOS deployment in Waikato region – left, detritus build-up within weeks of deployment, right wiper installed after cleaning. Unpublished work (Stan Lodge)

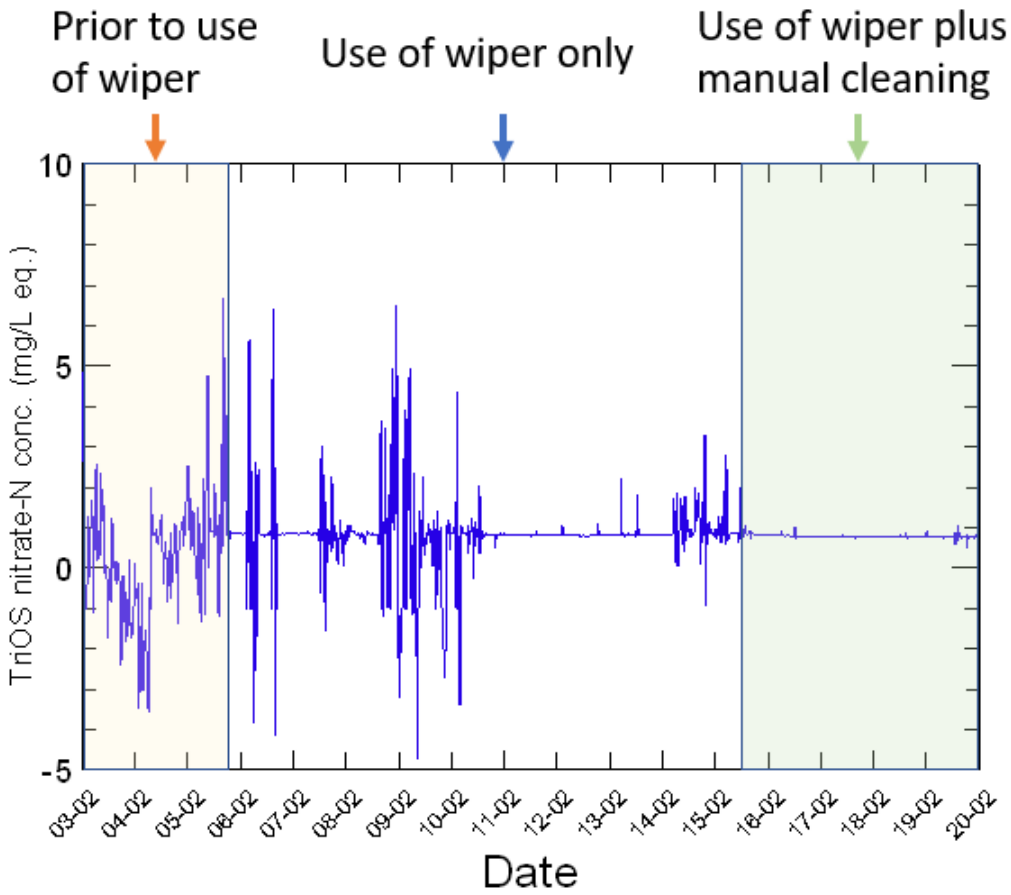


Figure J-2: Effect of detritus and biomass on nitrate-N measurement – before wiper installed (left), after wiper installed and automatic cleaning commenced (centre), and manual cleaning plus wiper cleaning (right). Unpublished work.