High Resolution Monitoring of Nitrate in Agricultural Catchments
– a case study on the Manawatu River, New Zealand

August 2017

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Prepared for:

Abby Matthews
Science & Innovation Manager

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Executive summary

Horizon Regional Council (HRC) requested Massey University's Fertilizer and Lime Research Centre (FLRC) to investigate and provide advice on the potential of using high-resolution monitoring of nitrate-N sensors to measure water quality in streams and rivers in their agricultural catchments. The objectives of this study were: (1) to test the performance of two commercially available high-resolution sensors (NITRATAX and OPUS) in monitoring nitrate-N concentrations, particularly under a low nitrate-N concentration environment, in a New Zealand river; and (2) to compare the nitrate-N loads calculated using the high-resolution sensor data, verses the standard monthly grab sampling method in the river. The study was undertaken in the Manawatu River at the Teachers College monitoring site, for a period of one year from Feb 2016 to Jan 2017.

At the study site, the NITRATAX sensor was deployed from Feb 2016 to Jan 2017, but the OPUS sensor was deployed for a shorter duration from Dec 2017 to Jan 2017. The self-cleaning NITRATAX sensor provided accurate and *precise* nitrate-N measurements over the entire range of nitrate-N concentrations, with raw values measured from 0.00 to 1.29 mg/L. The NITRATAX values, however, were slightly negatively *biased* in comparison to the standard laboratory analysis method, and a comprehensive calibration was used to apply a correction factor to achieve the final adjusted NITRATAX results. Interestingly, the NITRATAX *precisely* measured small changes in nitrate-N concentrations over a 24 hr period when nitrate-N concentrations were very low (<0.25 mg/L). These diurnal changes in nitrate-N measured by the NITRATAX were validated with the laboratory measurements, confirming the reliability and accuracy of this sensor's measurements.

The measurement of nitrate-N concentrations every 15 minutes using the NITRATAX sensor, allowed a detailed examination of the annual fluctuation of nitrate-N concentrations in the Manawatu River, revealing trends that have rarely been studied at a catchment scale in New Zealand. Elevated nitrate-N concentrations were consistently detected at the start of the drainage season (May, Jun, Jul), when the river flow rate increased. Nitrate-N concentrations decreased around Oct and generally remained low (<0.6 mg/L) for the remainder of the year. Although the monthly grab samples followed this general trend, the sample timing did not allow the detection of the first runoff/drainage event for the season (Mar) or some of the peak flow events, limiting our ability to understand or analyse nitrate-N loss processes at the catchment-scale. Further studies could use the high-resolution sensor data to examine the time lag between drainage/runoff events and elevated nitrate-N concentrations in more detail.

The OPUS nitrate-N sensor also performed with *precision* during low flow and low nitrate-N concentrations (<0.35 mg/L) from Dec 2017 to Jan 2017. Despite issues with fouling of the sensor lens, two discrete sets of OPUS sensor data results showed that the sensor measured nitrate-N concentrations that were slightly positively *biased* in comparison to the standard laboratory method. Although these concentrations were closer to the laboratory values (mean difference of 0.021 mg/L) compared to the NITRATAX (mean difference of -0.063 mg/L), a correction factor based on detailed calibration data is recommended if these sensors were to be used for routine water quality monitoring in streams and rivers in the region.

The high-resolution NITRATAX sensor data improved the quantification accuracy of the nitrate-N loads in the study river. There was a 14% difference between the annual nitrate-N load measured using the NITRATAX sensor data and monthly grab samples analysed in a laboratory (using the flow-weighted method), with higher annual nitrate-N load measured using the NITRATAX (1926 vs 1674 t/yr). The data analysis confirmed that the monthly grab sampling missed some of the highest flow events, resulting in an underestimation of annual nitrate-N loads in the Manawatu River.

Overall, the NITRATAX and OPUS high-resolution sensors appear promising, novel tools to allow detailed measurement of nitrate-N concentrations and loads in the Manawatu River, provided that extensive calibration and adjustment is undertaken, and a lens cleaning mechanism is installed. On this basis, these sensors' are recommended for further testing and evaluation, as a new tool to improve our understanding of nitrate-N loss processes from New Zealand catchments and to improve the accuracy of our nitrate-N load calculations.

Introduction

Leaching of nitrate-N (NO_3^--N) from grazed pastoral systems and other intensive land uses, has been implicated as a key water contaminant in the deterioration of surface and ground water quality in New Zealand's agricultural catchments. Regional Councils regularly monitor river flows and water quality in their streams and rivers to assess effects and trends in water quality. They are able to monitor river flow rates at a high-resolution (i.e. up to every 15 minutes), but commonly use a grab sampling method for monitoring water quality, at a monthly time step. A monthly grab sampling approach risks over- or underestimation of nitrate-N loads in rivers and streams. Monthly sampling also prevents the study of seasonal and diurnal fluctuations in nitrate-N concentrations and loadings, that could provide insights into the biogeochemical processes associated with transport and transformation of nitrate-N from farms to streams and rivers.

Horizon Regional Council (HRC) requested Massey University's Fertilizer and Lime Research Centre (FLRC) to investigate and provide advice on the potential of using high-resolution monitoring of nitrate-N sensors to measure water quality in streams and rivers in their agricultural catchments. Although high-resolution water quality sensors are commonly used in drinking and waste water plants in New Zealand, their broader use for monitoring nitrate-N in streams and rivers in New Zealand agricultural catchments is rare. Most of the nitrate sensors available on the market are manufactured in Europe and are designed to measure higher nitrate-N concentrations than are typical of New Zealand freshwater conditions. For this reason, it is important to thoroughly assess the precision and bias of nitrate sensors in order to make informed decisions about their use under New Zealand conditions.

As a case study, this study reviewed and analysed the effectiveness of high-resolution, automated nitrate-N monitoring strategies, using two commercially available nitrate sensors which were installed and tested at the Teachers College monitoring site on the Manawatu River in Palmerston North, from Feb 2016 to Jan 2017 (NITRATAX) and Dec 2017 to Jan 2017 (OPUS). The catchment area above the monitoring site is 391,397 ha, with the land use dominated by sheep and beef cattle grazing (63%), followed by native and exotic forest (23%) and dairy cattle grazing (13%) (Parfitt *et al.* 2013). This catchment is of particular interest, as total oxidised nitrogen concentrations generally fluctuate from 0 to ~1.25mg/L (Land and Water Aotearoa 2017) and concentrations regularly exceed the Australian and New Zealand Guidelines (< 0.444 mg/L) for lowland rivers (ANZECC 2000).

The objectives of the study were (1) to test the performance of two commercially available high-resolution sensors (NITRATAX and OPUS) to monitor nitrate-N concentrations, particularly under low nitrate-N concentrations in a New Zealand river and (2) to compare the nitrate-N loads calculated using the sensor data verses the standard monthly grab sampling method in the river. Based on these results, recommendations are made to HRC regarding the accuracy and robustness of these sensors to monitor water quality in the rivers and streams in their region.

Materials and Methods

Two commercially available high-resolution sensors, the NITRATAX and OPUS, were installed and tested to measure high-resolution nitrate-N concentrations in the Manawatu River at the Teachers College monitoring site in Palmerston North. The NITRATAX sensor was deployed from Feb 2016 to Jan 2017, but the OPUS sensor was deployed for a shorter duration from Dec 2017 to Jan 2017. The NITRATAX (Hach Lange GmbH, Germany) UV/VIS sensor with a flow path length of 5mm and self-cleaning (wiper) mechanism was deployed for a total period of 14 months, but the key data collection period was from 1 Feb 2016 to 31 Jan 2017. A pump malfunction resulted in the loss of the sensor data for the month of July 2017. The sensor was set up to monitor nitrate-N concentrations on a 15 minute interval. In addition, a total of 165 water quality samples were collected in synchronization with the NITRATAX readings, either using an auto-sampler (to enable samples to be collected 1-2 hourly over a 24 hr period) or by the grab sample method, hereby identified as ‘grab samples’. The collected water samples were analysed for nitrate-N concentration using the standard laboratory method at a commercial laboratory.

The laboratory measured nitrate-N concentrations were compared with the NITRATAX measured concentrations, to test the performance of the NITRATAX sensor. A linear relationship between the raw NITRATAX results and the laboratory nitrate-N concentrations was used to calculate a calibration factor and adjust the final NITRATAX concentrations (see Fig. 1). Additional calibration checks of the NITRATAX sensor were undertaken by reading the concentration of known standard solutions of nitrate-N (0, 1, 2.5 and 12.5 mg/L) every month (Appendix 1, Table 1 and see Fig. 2a). The concentrations of these standard solutions were checked on 3 occasions by analysing the nitrate-N concentration using Ion Chromatography (IC) in the Soil and Water Laboratory at Massey University (Appendix 1, Table 2). A linear relationship between the raw NITRATAX results and the IC adjusted standard solution concentrations was plotted over the range of standard solution concentrations typically measured in the Manawatu River (0-5 mg/L) (see Fig. 2a). Standard error around the mean NITRATAX nitrate-N values measured for each standard solution concentration was calculated to assess the *precision* of the sensor (see Fig. 2b). Using an auto-sampler installed at the study site, hourly water samples were collected over a 24 hr period in Mar 2017 and then analysed using the standard laboratory method. These laboratory results were compared with the sensor data to verify diurnal changes in nitrate-N concentrations measured by the sensor and further test the sensor’s *precision* (see Fig. 3).

During this study period, an OPUS UV spectral nitrate-N sensor (TriOS, Germany) with a path length of 10mm was loaned to the HRC for a performance trial in the Manawatu River. This sensor was installed alongside the NITRATAX sensor for a period of approximately 6 weeks from 20 Dec 2016 to 30 Jan 2017. The sensor readings from both devices were sampled within 2 minutes of each other, to allow a comparison of their data. It is important to note that the OPUS sensor was not provided with a lens cleaner, hence, its data collection was inhibited when the lens was fouled by high sediment concentration in the river water. This occurred twice during the 6-week period, resulting in only two sets of useable data collected from 20 Dec 2016 to 2 Jan 2017 and from 16 Jan to 23 Jan 2017 (see Fig. 9). Over this period, a total of 17 grab samples were collected and analysed for nitrate-N using the standard laboratory method, allowing a comparison (but with fewer data points) of the accuracy of the OPUS sensor (Appendix 2, Table 1).

The performance of high-resolution NITRATAX sensor was further evaluated by comparing the effects of high-resolution (every 15 minutes) or standard monthly grab sampling on estimates of annual nitrate-N loads in the river. The river flow was collected at the same site and calibrated using regular river gauging as per HRC protocols. The standard monthly grab sample data collected by HRC were used to calculate and compare annual nitrate-N loads to those calculated using the high-resolution NITRATAX sensor data, from Feb 2016 to Jan 2017. The river loads were calculated using the flow-weighed and flow-stratified methods (Elwan *et al.* 2014) and the effects of the sampling resolution and method of load calculation, were compared.

Results and Discussion

NITRATAX calibration checks

Assessing bias

Strong linear relationships ($R^2 > 0.94$) were observed between the NITRATAX nitrate-N concentrations and the manual grab sample laboratory checks (Fig. 1) and the standard solution calibrations (Fig. 2a). The data indicates that the nitrate-N concentrations measured by the NITRATAX sensor were slightly negatively *biased,* particularly at the low concentration range (<0.4 mg/L) monitored in this study (Fig. 1). The strong linear relationships however, allow the adjustment of the NITRATAX values using the equations given in Fig 1.

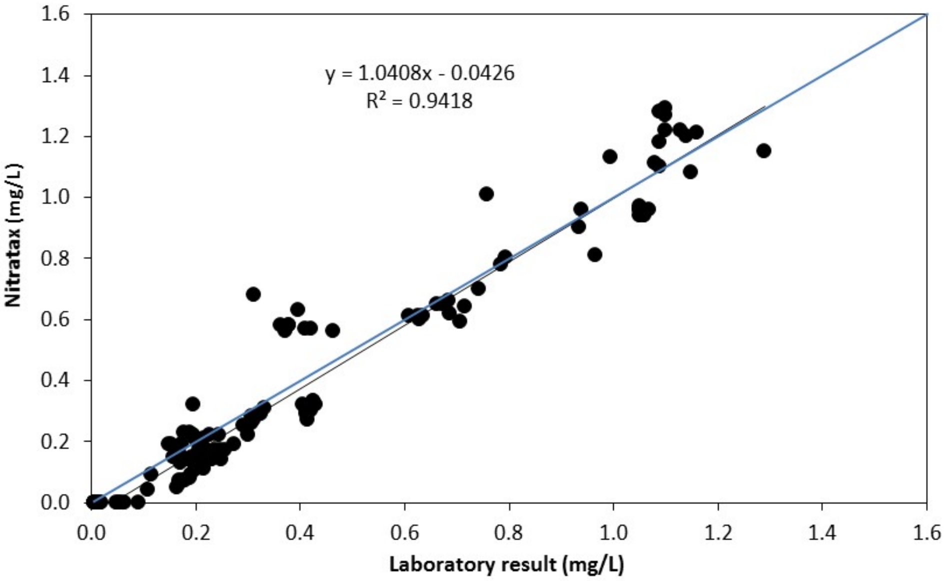

Figure 1. Calibration between laboratory measured and NITRATAX nitrate-N concentrations [adjusted NITRATAX value = (NITRATAX + 0.0426)/1.0408]. The blue line is the 1:1 line.

Assessing precision

The precision of the NITRATAX sensor was assessed by repeatedly testing sensor nitrate-N concentrations against standard solution concentrations of 0, 1, 5 and 12.5 mg nitrate-N/L. The actual concentration of the standard solutions was adjusted based on IC analysis and graphed in Fig. 2a. The standard errors (SE) around the mean NITRATAX nitrate-N concentrations measured for each standard solution, were very low, particularly the two lowest standard concentrations (0 mg/L, SE=0 and 1 mg/L, SE=0.006), however the SE increased with increasing standard solution concentration (Fig. 2b). This result confirms that the NITRATAX had a high level of *precision*, particularly when nitrate-N concentrations were < 1 mg/L.

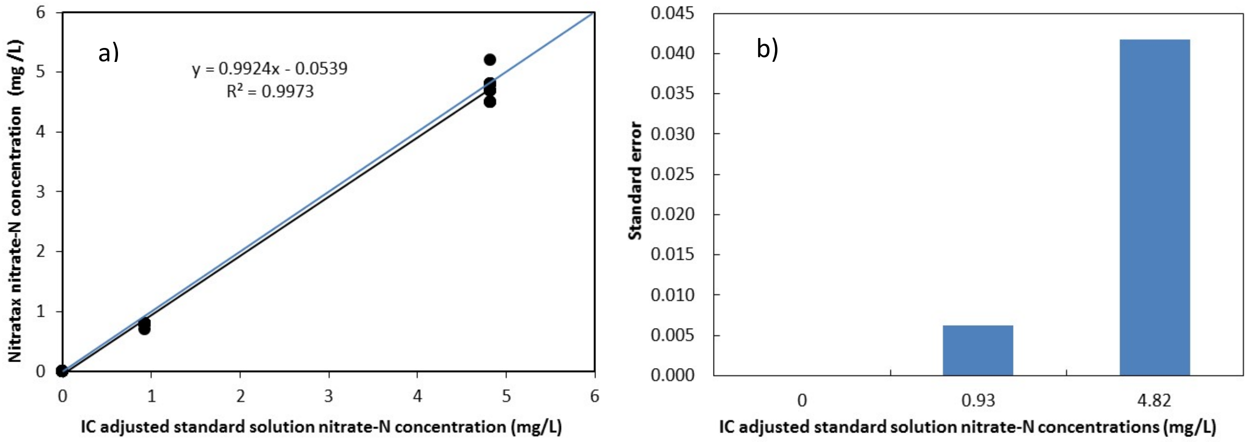

Figure 2. a) Calibration between ion chromatography measured standard solutions and NITRATAX nitrate-N concentrations [adjusted NITRATAX value = (NITRATAX + 0.0539)/0.9924] and b) standard error around the mean for NITRATAX nitrate-N concentrations when calibrated against ion chromatography measured standard solutions. The blue line is the 1:1 line.

A comparison with intensive 24 hr laboratory grab sampling analysis showed that the unadjusted NITRATAX sensor results were further *precisely* monitoring small changes in nitrate-N concentrations over time (Fig. 3). This suggests that even at low nitrate-N concentrations (<0. 25 mg/L), the NITRATAX sensor was precise enough to define small changes in nitrate-N concentrations in the river.

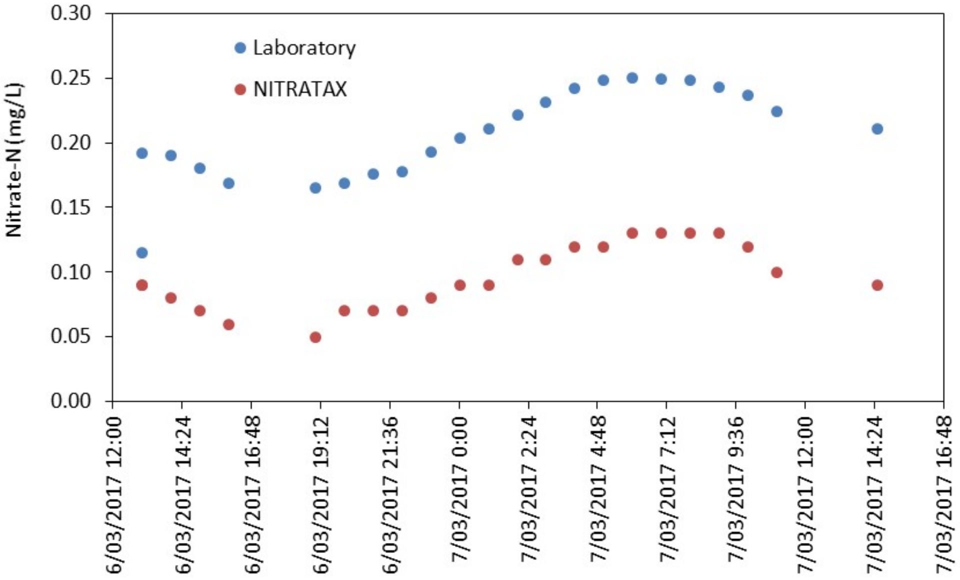

Figure 3. Comparison between the unadjusted NITRATAX nitrate-N concentration and nitrate-N concentrations measured using the laboratory grab sampling method over a ~24 hr period on March 6-7 2017, in the Manawatu River at the Teachers College monitoring site.

Although technically, the standard solution calibrations should be the most accurate calibration to use, as errors are associated with each step of the standard laboratory method, there are two compelling reasons why the authors suggest the laboratory grab sample calibration be used in this case (Fig. 1). The first is that 165 manual water samples were analysed by the laboratory method to assess and calibrate the NITRATAX nitrate-N concentrations, whereas only 16 standard solution calibrations were undertaken. The second is that, although inherent errors with the laboratory method are well recognized, the standard laboratory method has been used for analysing nitrate-N in surface waters nationally and internationally for many decades and all water quality guidelines and historic data are based on these methods. On this basis, NITRATAX nitrate-N concentrations were adjusted (see Fig. 5) based on the laboratory method calibration, using the equation presented in Fig. 1. It is recommended that any new sensors be calibrated using both the standard solutions and laboratory method to assess the accuracy and precision of measurement and to adjust concentrations, if required.

Diurnal fluctuations in nitrate-N concentrations

Figure 4 presents an example of the diurnal fluctuations in unadjusted NITRATAX nitrate-N concentration measured during periods of low flow and elevated air temperatures in Feb 2016 and Mar 2017 (summer/early autumn). Figure 4a presents an example of the typical unadjusted NITRATAX nitrate-N concentrations observed during summer/early autumn 2016, where nitrate-N concentrations increased during the day and peaked at around 5pm. In contrast, Fig. 4b presents an example of the nitrate-N concentrations measured in autumn 2017 and shows the nitrate-N concentrations decreasing during the day, with the lowest concentrations measured at around 6pm and then increasing overnight, peaking at around 6am. The diurnal change in nitrate-N concentrations measured in autumn 2017 is considered characteristic of periphyton processing of nitrate-N in streams and rivers (R. Death, pers. comm., freshwater ecologist at Massey University). Periphyton is likely to utilise nitrate-N during sunlight hours (Toetz 1971), although this phenomenon is not well understood or reported in New Zealand rivers and is an area requiring further study.

It is unclear however, why a different pattern of diurnal change in nitrate-N concentrations was measured in summer/early autumn 2016 (Fig. 4a). Potential causes for these diurnal changes in nitrate-N concentrations have been considered carefully and possible explanations include point source disposal of treated sewage upstream of the monitoring site and stream bank modifications occurring at the ANZAC cliffs during Jan-Feb 2016. However, enquiries about these activities has shown no clear relationship with the diurnal changes measured, i.e. the point source disposal occurring upstream is released continually over a 24 hr period and diurnal changes were also measured on days that stream bank modifications were not occurring, such as weekends and public holidays (M. Patterson pers. comm.). Although we cannot discount these explanations entirely, as sediment activity from stream bank modification may influence the river for many days following activity for example, it appears an unlikely explanation at this stage. These findings highlight however, the need for more research in this area.

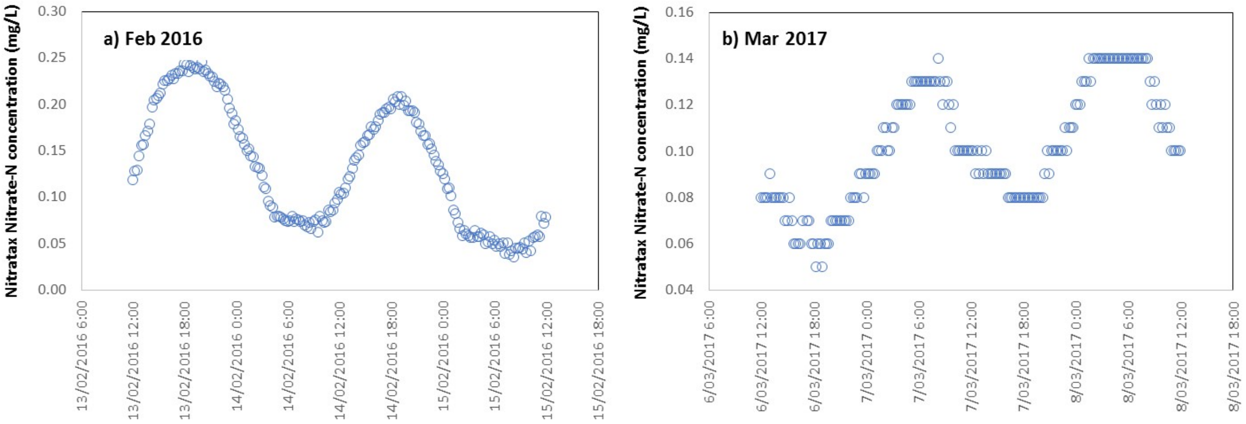

Figure 4. Comparison of diurnal variations in unadjusted NITRATAX nitrate-N concentrations measured in (a) Feb 2016 and (b) Mar 2017, in the Manawatu River at the Teachers College monitoring site.

Annual fluctuations in Nitrate-N concentrations

The high-resolution NITRATAX sensor data indicated higher nitrate-N concentrations at the start of the drainage/runoff season (May, Jun, Jul 2016), when the river flow rate increased (Fig. 5). However, nitrate-N concentrations decreased later in the season (Oct 2016) and remained low (<0.6 mg/L) for the remainder of the year, as nitrate-N may have drained through the soils in the catchment, despite high flow events over summer. These results correspond with the findings previously documented from plot scale leaching studies (Christensen 2013), but these processes have rarely been studied at a catchment scale in New Zealand. It is also possible that the decrease in nitrate-N concentrations measured later in the season is due to surface runoff being the dominant loss process at this time of year compared to drainage, as surface runoff is known to generate less nitrate-N loss (Burkitt 2014). Figure 5 also shows that nitrate-N concentrations in the Manawatu River peak generally within 24 hrs of peak flow rates, giving some indication of the time lag between soil drainage/baseflow reaching the river. This rapid nitrate-N response to high flow events, highlights the limitations of a monthly grab sample method to accurately capture the fluctuations in nitrate-N concentrations in the river.

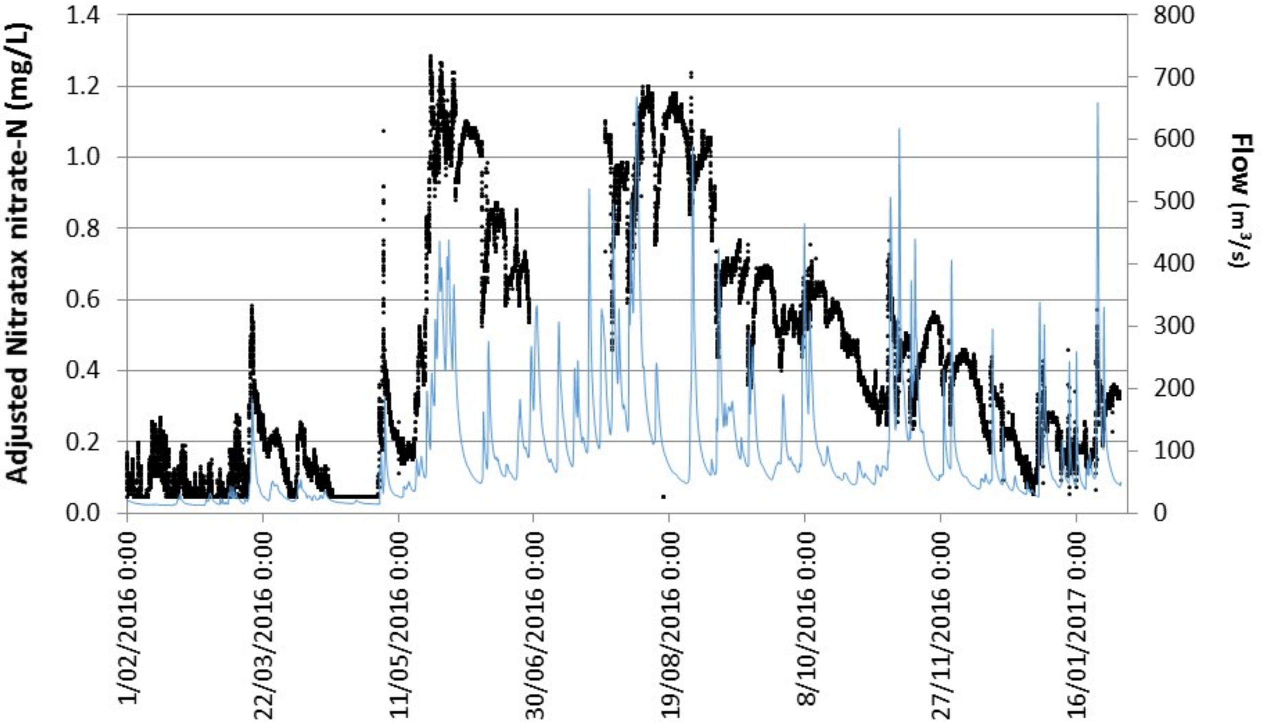

Figure 5. Changes in adjusted NITRATAX nitrate-N concentrations (black circles) in relation to river flow rate (blue line), from Feb 2016 to Jan 2017, in the Manawatu River at the Teachers College monitoring site.

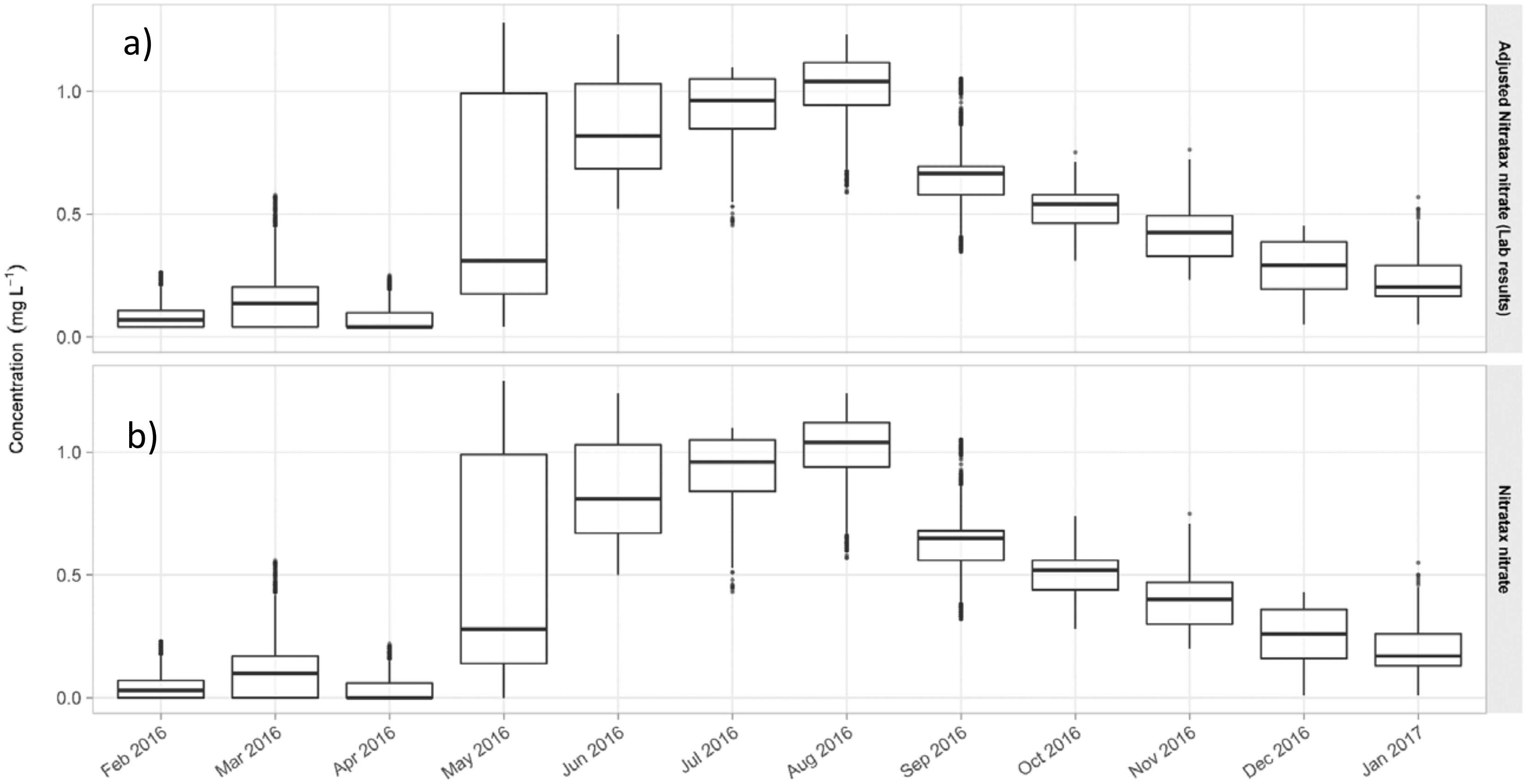

Fig. 5. Box and whisker plot presenting a) adjusted (lab) NITRATAX nitrate-N concentrations and b) unadjusted NITRATAX nitrate-N concentrations on a monthly basis, from Feb 2016 to Feb 2017, in the Manawatu River at the Teachers College monitoring site. The box indicates the inter-quartile range, the horizontal bar within the box indicates the median and 95% of the data lies within the whiskers. Outliers are indicated by closed circles.

Annual Nitrate-N loads

The flow-weighted and flow-stratified methods were used to calculate annual nitrate-N loads, using both the high-resolution NITRATAX sensor and the standard monthly grab sampling data, from Feb 2016 to Jan 2017 (Fig. 7). These methods were selected based on their evaluation and superior performance in calculating average annual river loads in the Manawatu River (Elwan *et al.* 2014).

Using the monthly grab samples (routinely sampled by HRC), the flow-stratified method resulted in lower annual nitrate-N load compared to the flow-weighted method (Fig. 7). However, both methods resulted in consistent estimation of annual nitrate-N loads using the high-resolution NITRATAX sensor data. The flow-stratified method is generally preferred when there are many water quality concentrations coving the full range of flow rates. In the case of the grab sampling method, there were only 12 samples collected between Feb 2016 and Jan 2017. This required the monthly grab sampling data to be grouped into only five flow-deciles bins, rather than the standard ten, for the flow-stratified method (Elwan *et al.* 2014). This could have resulted in an underestimation of the annual nitrate-N load using the flow-stratified method. Therefore, the flow-weighed method was considered a more accurate measure of annual nitrate-N loads in this study, to allow a comparison between the high-resolution NITRATAX sensor and the standard monthly grab sampling data (Fig. 7).

Figure 7 shows that the estimates of annual nitrate-N loads were higher when the NITRATAX concentrations were adjusted using the IC adjusted standard solution calibration from Fig. 2a. Given the reasons discussed in the calibration section described above, adjustment of the NITRATAX concentrations based on the laboratory calibration (Fig. 1), was considered the preferred approach in this study.

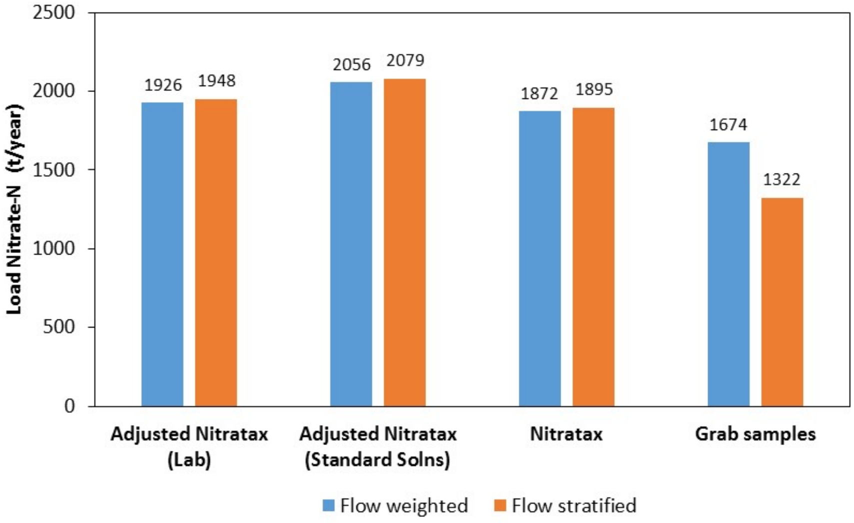

Fig. 7. Comparison of the annual nitrate-N loads calculated using the adjusted and non-adjusted high-resolution NITRATAX sensor and the monthly grab sample method in the Manawatu River at the Teachers College monitoring site, from Feb 2016 to Jan 2017. The nitrate-N loads (t/year) were calculated using the flow-weighted and flow-stratified river load calculation methods, with actual loads denoted above the bars.

Comparing the annual nitrate-N loads calculated using the flow weighed method, there was a 14 % difference in nitrate-N loads between the adjusted (lab) NITRATAX data and the monthly grab samples (Fig. 7). The grab sample method was unable to represent all of the elevated nitrate-N concentrations in relation to the flow rates, particularly in the highest flows (Fig. 8). This emphasises the value of using high-resolution sensor data to monitor nitrate-N concentrations, to accurately quantify nitrate-N loads in streams and rivers.

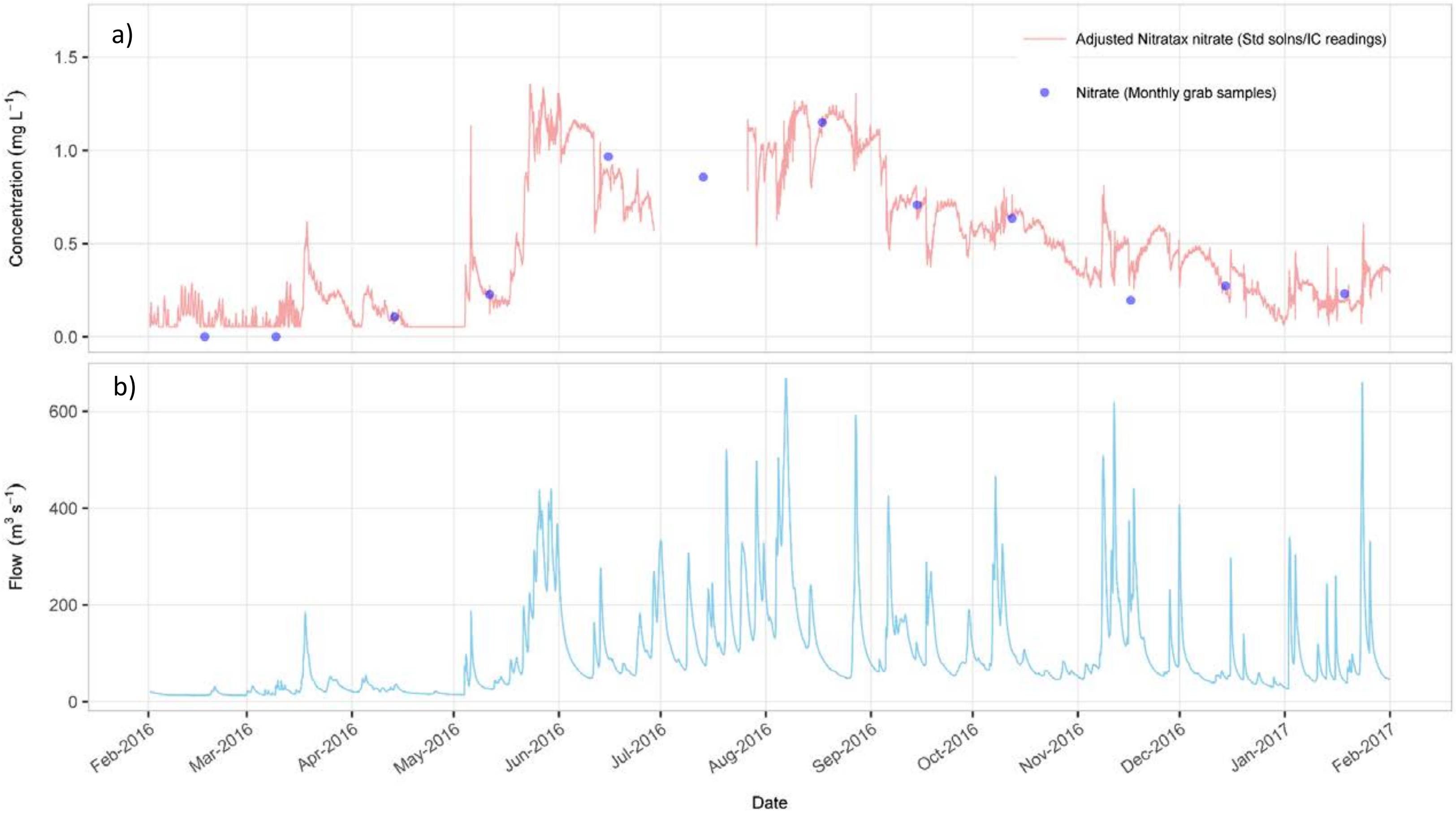

Figure 8. Comparison of nitrate-N concentrations measured by a) monthly grab samples (blue circles) and adjusted NITRATAX concentrations (red line) and b) flow rate (m^3/s) (blue line), from Feb 2016 to Jan 2017, in the Manawatu River at the Teachers College monitoring site.

Nitrate-N concentrations measured by the OPUS sensor

The short-term deployment of the OPUS sensor under low flow and low nitrate-N conditions during summer (Dec 2016 – Jan 2017) provided an opportunity for a primary assessment of the accuracy of this sensor to monitor nitrate-N concentrations in the Manawatu River. Unfortunately, the OPUS sensor data collection was inhibited by the absence of a lens cleaner, as fouling of the lens by high sediment concentrations resulted in negative or unusually low nitrate-N concentrations. This resulted in only two discreet sets of data being used in this comparison (Fig. 9). This issue highlights the critical importance of having a cleaning mechanism fitted to these devices. Cleaning is usually via compressed air or in remote locations, where access to electricity is difficult, via an ultrasonic cleaner. The sensor also intermittently reported single close to zero negative values, despite no apparent issue with fouling. This requires further investigation, but doesn't pose a significant issue, as careful checking and quality control of the collected data prior to further analysis, should be standard practice.

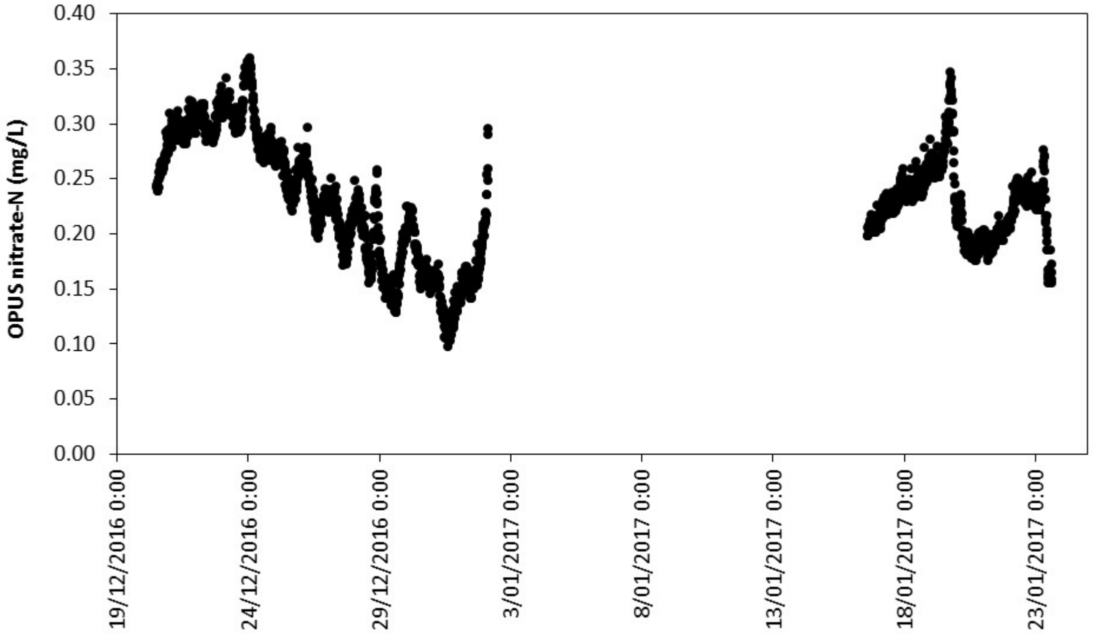

Figure 9. Nitrate-N concentrations measured by the OPUS sensor for two periods of measurement (20 Dec 2016 to 2 Jan 2017 and 16 Jan to 23 Jan 2017) in the Manawatu River at the Teachers College monitoring site.

Comparison between OPUS and NITRATAX measurements

The OPUS nitrate-N sensor manufacturers state that with a 10mm path length, the detection limit is 0.03 mg/L. This is lower than the detection limit for the NITRATAX at the same path length (0.1 mg/L), which is a distinct advantage in New Zealand's comparatively low nitrate-N surface waters. However, the calibration checks undertaken in the current study show that the NITRATAX was capable of accurately and *precisely* measuring changes in nitrate-N concentrations below 0.1 mg/L

(Figs. 1-3). When the nitrate-N concentrations measured by both sensors were compared, the nitrate-N concentrations measured by the OPUS were slightly higher, compared to the NITRATAX data (Fig. 10). A comparison of the nitrate-N concentrations measured using the laboratory method over this sampling period, shows that although the OPUS concentrations were slightly higher than the laboratory method, the OPUS concentrations were closer to the laboratory values (mean difference of 0.021 mg/L) compared to the NITRATAX (mean difference of -0.063 mg/L) (Appendix 2, Table 1,). The manual laboratory checks and the standard solution calibrations have previously shown that the NITRATAX sensor concentrations were slightly negatively *biased,* particularly at the low concentration range (Fig. 1 and 2b). The small positive *bias* measured with the OPUS sensor is not of concern, but confirms that detailed calibration checks and data adjustment are required if these sensors are to be used for routine water quality monitoring in streams and rivers in the region.

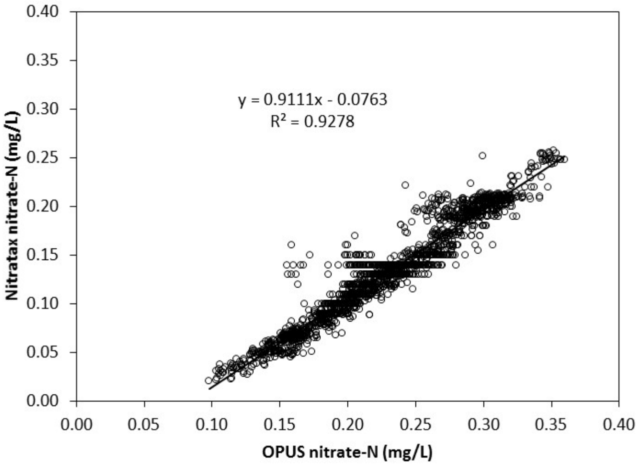

Figure 10. Comparison of the unadjusted nitrate-N concentrations measured by the OPUS and NITRATAX sensors from 20 Dec 2016 to 2 Jan 2017 and 16 Jan to 23 Jan 2017 in the Manawatu River at the Teachers College monitoring site.

Summary

The NITRATAX provided robust nitrate-N measurements, which coupled with calibration and correction, could reliably be used in New Zealand's low nitrate-N rivers. The high-resolution data provided detailed information on the seasonal and diurnal fluctuations of nitrate-N in the Manawatu river, that were previously not possible or observed. These data also allowed the calculation of more accurate annual nitrate-N load, which is critical to resource accounting for water quality management in agricultural catchments.

A preliminary study of the performance of the OPUS sensor indicated that this sensor also provides reliable nitrate-N measurements, provided a lens cleaner is in operation.

Overall, both the NITRATAX and OPUS sensors appeared promising instruments to provide detailed measurement of nitrate-N concentrations and loads in the Manawatu River. These sensors are recommended for further testing and evaluation, as new tools, to improve our understanding of nitrate-N loss processes from New Zealand catchments.

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Appendix 1

Table 1. NITRATAX nitrate-N concentrations (mg/L) measured from standard nitrate solutions of a known concentration.

Calibration date	Standard nitrate solution concentrations (mg/L)			
	0	**1**	**5**	**12.5**
16/03/2016	0	0.8	5.2	11.8
19/04/2016	0	0.8	4.8	11.8
12/05/2016	0	0.8	4.8	11.9
1/06/2016	0	0.8	4.7	11.9
23/06/2016	0	0.8	4.8	11.9
28/07/2016	0	0.8	4.7	12.0
25/08/2016	0	0.8	4.8	12.2
15/09/2016*	0	0.8	4.7	12.0
10/10/2016	0	0.8	4.5	11.3
3/11/2016*	0	0.8	4.5	11.3
22/11/2017	0	0.7	4.5	11.2
9/12/2016	0	0.8	4.8	12.0
22/12/2016	0	0.8	4.8	12.1
16/01/2017	0	0.8	4.8	11.4
16/02/2017*	0	0.8	4.8	11.9
6/03/2017	0	0.8	4.7	11.8

*Green rows represent the standard solution samples that were analysed using the Ion Chromatography method (see Table 2 below).

Table 2. Concentration of standard solutions measured using ion chromatography.

Analysis date	Standard concentration (mg/L)	Measured concentration using Ion Chromatography (mg/L)
20/09/2016	1.0	0.9
20/09/2016	5.0	4.9
20/09/2016	12.5	12.9
8/11/2016	1.0	0.9
8/11/2016	5.0	4.9
8/11/2016	12.5	12.6
16/02/2017	1.0	0.9
16/02/2017	5.0	4.7
16/02/2017	12.5	12.3

Appendix 2

Table 1. Comparison between nitrate-N concentrations determined by the laboratory method, OPUS sensor and NITRATAX sensor.

Date/time	Laboratory nitrate-N (mg/L)	OPUS nitrate-N (mg/L)	Difference	NITRATAX nitrate-N (mg/L)	Difference
20/12/2016 13:30	0.248	0.242	-0.006	0.170	-0.078
16/01/2017 15:00	0.157	0.199	0.042	0.150	-0.007
16/01/2017 16:00	0.160	0.208	0.048	0.150	-0.010
16/01/2017 19:00	0.174	0.217	0.043	0.150	-0.024
17/01/2017 7:00	0.205	0.228	0.023	0.140	-0.065
17/01/2017 7:00	0.184	0.228	0.044	0.140	-0.044
17/01/2017 8:00	0.200	0.226	0.026	0.130	-0.070
17/01/2017 9:00	0.203	0.227	0.024	0.140	-0.063
17/01/2017 10:00	0.207	0.223	0.016	0.130	-0.077
17/01/2017 11:00	0.207	0.219	0.012	0.130	-0.077
17/01/2017 12:00	0.210	0.222	0.012	0.130	-0.080
17/01/2017 13:00	0.212	0.227	0.015	0.130	-0.082
17/01/2017 14:00	0.218	0.218	0.000	0.130	-0.088
17/01/2017 14:00	0.211	0.218	0.007	0.130	-0.081
18/01/2017 14:30	0.232	0.244	0.012	0.140	-0.092
Mean difference			**0.021**		**-0.063**

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