

Feasibility of using near-infrared measurements to detect changes in water quality

BTO 2020.025

Date

20 april 2020

Client

BTO Themagroep Bronnen en Omgeving

More information

Frederic Been, PhD

T +3130611365219

E Frederic.Been@kwrwater.nl

Authors

Dr. F. (Frederic) Béen (KWR),

ir. S. (Stijn) Beernink (KWR),

Dr. ir. Y.J.A. (Yannick) Weesepeel

(Wageningen Food Safety Research)

Project number

402045-018

Sent to

This report is distributed to BTO-participants and is public.

Quality Assurance

Dr. N. (Niels) Hartog

Project manager

ir. M.L. (Martin) van de Schans

Page

1/10

Summary

This study investigates the feasibility of using near infrared (NIR) measurements in early warning systems for sources of drinking water. Recent studies show that NIR could be used to detect changes in water quality due to the presence of chemicals. This study aims to test if this technique is capable of detecting relevant concentrations (milligram to microgram per litre range) of different chemicals, comparable to concentrations found in drinking water sources. NIR spectroscopy is interesting because of its low-costs, rapid analysis time (i.e., potential for online applications) and the broad range of substances that it can potentially detect. Water samples were taken from the surface water intake 'Brakel' of the drinking water company Dunea and spiked at different concentrations with 5 chemicals representative of substances that can be potentially found in surface water. The measurements and analysis were done in collaboration with Wageningen Food Safety Research (WFSR, formerly RIKILT). Results showed that 2 of the 5 tested substances could be detected using the NIR at relevant concentrations. The results therefore suggest that, at least for certain types of compounds, there is a potential to detect these using NIR spectroscopy. Although the implementation of NIR to measure aqueous matrices remains challenging due to the substantial absorption of water, promising results have been obtained. Further research is thus highly recommended to better understand the potential of this technique, but implementation of NIR technology as an early warning system for detecting organics directly in surface water in µg/l level will not be possible in the nearest future. In particular the lack of commercially available instruments which can be used online and fulfil the needed specification (i.e., sample filtration prior to analysis) currently hinders the applicability of this technique for early warning (i.e., online monitoring). Yet, very similar online tools are being used in other industries. Depending on the urgency to develop this tool further and the available financing, implementation for the water sector could be possible between 1 and 5 years from now, provided that the remaining knowledge gaps raised in this report are successfully addressed.

Contents

Summary	1
1 Introduction	3
2 Materials and methods	3
3 Results and discussion	5
4 Conclusion	8
5 Further research	9
6 References	10

1 Introduction

The BTO project “Early Warning Systems for the quality monitoring of water resources for drinking water production” focuses on evaluating new techniques that can potentially improve current early warning systems (EWS) used to monitor the quality of ground- and surface-water used for drinking water production.

In this context, recent studies have shown that near-infrared (NIR) could be used to detect changes in water quality due to the presence of chemicals (Kovacs et al. 2016). Possible advantages of NIR measurements compared to other water quality measuring techniques (e.g., HPLC-UV) are short response times (rapid analysis), low costs and the ability to measure a different range of substances (e.g. detect substances which do not absorb UV light). Based on a concept referred to as “Aquaphotomics”, the approach monitors the spectrum of water itself which contains information about covalent OH- and hydrogen bonds which can be influenced by the presence of chemicals such as solutes (Tsenkova 2009). Kovacs et al. (2016) tested the approach on a series of ultrapure water samples which had been spiked at various concentrations, ranging from 100 to 0.01mM, of three chemicals, namely acetic acid, lactose monohydrate and sodium chloride. In their study, the authors were capable of detecting changes in the water spectrum down to 0.8-1 mM. Although promising, the concentrations tested in this context are not relevant for the water sector as they correspond to mass concentrations in the gram to milligram per litre. Concentrations of chemicals encountered in surface water are generally in the in the microgram per litre range, or even lower. Furthermore, the compounds tested in the study by Kovacs et al. (2016) are not of particular concern from the perspective of drinking water production.

The objective of this pilot study was to assess if NIR measurements are capable of detecting changes in the water spectrum caused by lower concentrations of relevant chemicals for the drinking water sector. To achieve this, surface water samples were spiked with decreasing concentrations of 5 chemicals belonging to different classes (i.e., surfactants, pharmaceuticals, artificial sweeteners, corrosion inhibitors and insecticides) and which are currently monitored in surface waters in the Netherlands. Analyses were carried out using a benchtop instrument in collaboration with the Wageningen Food Safety Research (WFSR)¹.

2 Materials and methods

Samples collection

A surface water sample was provided by *Het Water Laboratorium* (HWL) and was collected from the abstraction location Brakel. A 2 litres sample was collected and stored in two 1L HDPE bottles which were immediately transported to KWR Water Research Institute and stored at 4°C.

¹ Formerly known as RIKILT: <https://www.wur.nl/en/Research-Results/Research-Institutes/food-safety-research.htm>

Chemicals

For the spiking experiments, five chemicals were selected, namely dichlorvos, 1h-benzotriazole, sucralose, propranolol and perfluorooctanoic acid (PFOA). All chemicals were readily available at KWR in solid form (purities > 98%) and used to make stock solutions from which the surface water samples were spiked.

Chemicals and spiked concentrations

An aliquot of the sample (approximately 300mL) was then filtered (0.45 μ m nitrocellulose filter) to remove suspended solids (Kovacs et al. 2016) and was then used for the spiking experiments. 10 mL aliquots of the filtered samples were then spiked with individual chemicals at concentrations of 1000000 μ g/L, 10000 μ g/L, 100 μ g/L, 10 μ g/L and 1 μ g/L. To avoid any presence of solvents, the highest concentration sample (i.e., 1000000 μ g/L) was prepared by dissolving 10 mg of the pure substance (solid form) in 10 mL of the filtered surface water. The sample was then used to prepare the lower concentration samples by sequential dilution with the filtered surface water. Non-spiked surface water samples were also included and used as blanks/reference samples.

Near-infrared measurements

NIR measurements were carried out using a NIRFlex N-500 (Büchi AG, Flawil, Switzerland) benchtop instrument. Spectra were recorded in transmission mode in the range 1000-2500nm using 1mm open-top liquid cuvettes. The temperature was set to 30°C \pm 0.1. For each measurement, 32 scans were acquired with a resolution of 0.5 nm. The measurement time was approximately 1 minute. All samples were measured randomly and for each chemical, the measurement of a blank surface water sample was also included. A total of 30 spectra was acquired. The open-top liquid cuvettes were thoroughly cleaned with methanol followed by ultra-pure water and subsequently dried with a nitrogen stream between each measurement.

Data processing

Acquired spectra were processed according to the protocol established by Kovacs et al. (2016), namely the spectra were first smoothed using the Savitzky-Golay filter (2nd order polynomial, 25 points window and no derivative calculation). Subsequently, multiplicative scatter correction (MSC) was applied to the spectra using the mean spectra of the blank water samples (5 spectra) as reference. MSC is commonly used to pre-process spectral data, in particular it allows to compensate for additive and/or multiplicative effects in spectral data (Maleki et al. 2007). Subsequently, only the region of the spectrum from 1300 to 1600 nm was used. Principal component analysis (PCA) was used to explore differences in spectra between blank and spiked samples. Furthermore, the PCA quality control charts (PCA-QCC) developed by Kovacs et al. (2016) were calculated and plotted to visualize changes in the water spectrum. Data analysis and processing were carried out using R (Rstudio).

3 Results and discussion

An example of the measured spectra is illustrated in Figure 1. As can be seen, except for the regions where the signal is saturated and should thus not be considered (i.e., 1800-2000nm and around 2500nm), no differences can be observed between the spectra of blank samples and samples spiked with varying concentrations of dichlorvos.

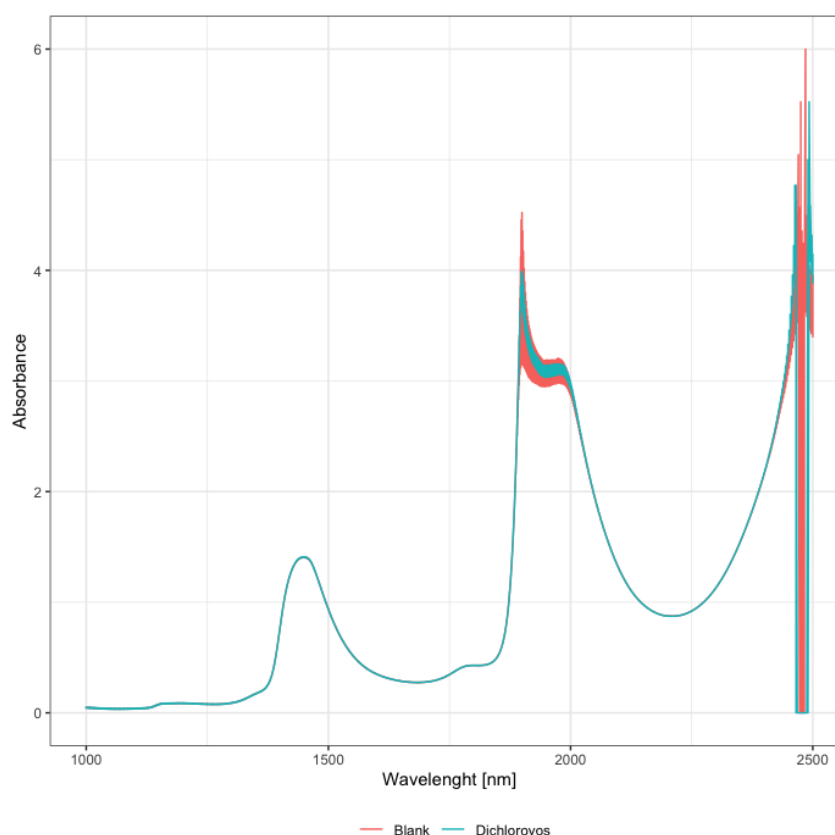


Figure 1: Raw spectra of blanks and samples spiked with dichlorvos. Areas between 1800-2000nm and around 2500 correspond to a saturated signal and are not relevant as they cannot be interpreted.

The PCA plot obtained after processing the spectra as described above is illustrated in Figure 2, whilst the variance explained by the obtained principal components is illustrated in Figure 3. As can be seen, a clear distinction could be made between water samples spiked with dichlorvos and benzotriazole and blank surface water. On the other hand, propranolol, sucralose and PFOA could not be separated from the non-spiked water samples as their distribution across the PCA plot overlapped. In fact, the latter chemicals as well as non-spiked water samples showed were characterised by a large variability. Interestingly, the separation of dichlorvos and benzotriazole could be linked to the presence, or absence, of hydroxyl groups (OH-) in the tested chemicals. In fact, these two chemicals do not possess OH groups with which they can form hydrogen bonds with water, whilst this is the case for the other chemicals tested. Another difference is also linked to the solubility of the tested chemicals. Dichlorvos and benzotriazole have logKow of 1.43 and 1.44, respectively, while propranolol and PFOA have logKow of 3.48 and

4.81. However, sucralose, which could also not be separated from the blank samples has a lower logKow, estimated at -1 (all logKow values were retrieved from ("PubChem" 2019)). In terms of the concentrations considered here, for dichlorvos, all samples could be distinguished from blank surface water, whilst for benzotriazole only samples above 100 µg/L were distant enough from the ellipse derived from blank water samples.

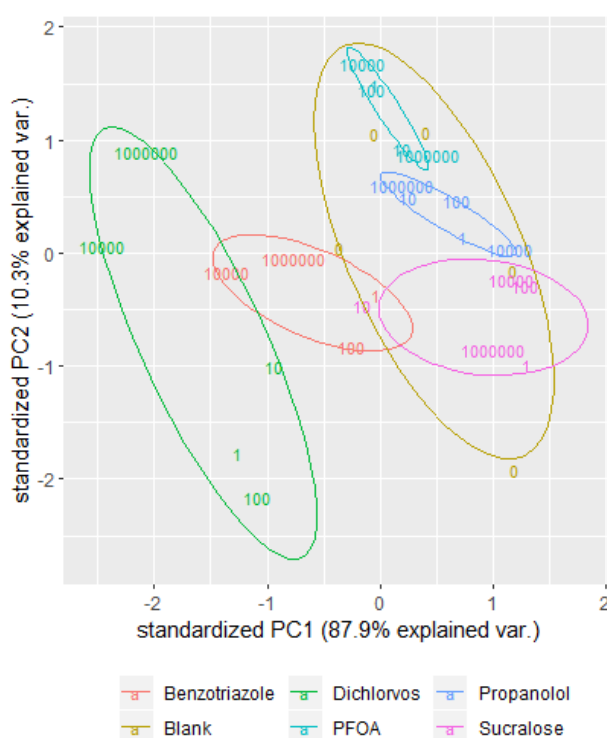


Figure:2 Principal component analysis of water spectra. Only the region from 1300 to 1600 nm was used here. Numbers represent the concentration in µg/L. The ellipses represent a normal distribution.

When observing separation using higher components (i.e., PC3 and above), no further discrimination could be obtained between spiked and non-spiked samples. As can be seen from Figure 3, beyond PC3, the amount of variance explained by the higher components is very low. Interestingly, in their work, Kovacs et al. (2016) were able to separate spiked versus non-spiked samples using higher components (i.e., PC2 and 3), whilst in this particular case, separation mainly occurred on PC1.

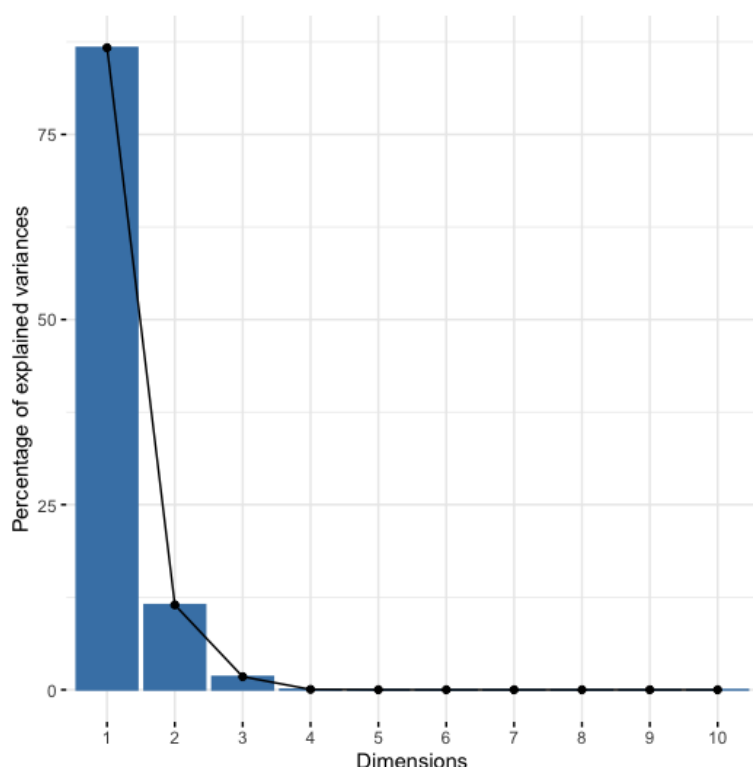


Figure 3 Variance explained by the computed principal components

In Figure 4, the PCA-QCC plot for dichlorvos is illustrated. This was calculated following the approach suggested by Kovacs et al. (2016), namely by taking the scores of PC1 for blank water samples and calculating the standard deviations. If new samples fall outside the 2xSD or 3xSD band, a significant deviation from the a “normal” pattern is assumed. In the particular case of dichlorvos, which could be easily separated based on the PCA plot, only 1 out 5 samples is outside both bands. This might indicate that the metric (i.e., 2 and 3 times the standard deviation) might not be adequate in this particular case. On the right-hand side of Figure 4, a similar plot is shown, however in this case the data was transformed to z-scores (i.e., $z_i = x_i - \overline{x_{blank}}/sd$) and the margins represent the ± 2 and ± 3 z-score values. It should be noted that in this case, the z-scores of the sample points were calculated using the mean PC score of the blanks (according to ISO 13528:2015). Using this approach to compute the quality control chart, all dichlorvos samples were outside the -2 and -3 z-score boundary. For benzotriazole, only the samples with concentration $> 100 \mu\text{g/L}$ (i.e., 2 out of 5) fell outside the boundaries. Interestingly, also for PFOA three samples were outside the boundaries. Yet in this case there seems to be no link to concentration since samples at 1, 100 and $10'000 \mu\text{g/L}$ fell outside the margins while $1'000'000$ and $1\mu\text{g/L}$ did not.

The obtained results show that NIR measurement have a potential to detect the presence of chemicals at relevant concentrations (i.e., low $\mu\text{g/L}$ range) in water samples. However, additional and more thorough measurements need to be carried out. In particular, additional non-spiked water samples need to be measured to obtain a more exhaustive collection of water spectra from the location which is being investigated. In fact, the goal is to capture the natural variability of the background (i.e., non-contaminated samples) in order to detect actual calamities (i.e., sudden presence of a chemical which would cause the water spectrum to deviate from its normal variability) and minimize both false positives and false negatives. Similarly, a large number of samples and chemicals should be measured to obtain a broad collection of spectra of different chemicals at different concentrations. For routine

monitoring, cleaning protocols should be defined to avoid cross-contaminations. In the case of this study, these were avoided by thoroughly cleaning cuvettes with an organic solvent and ultra-pure water, as well as by measuring samples randomly. Finally, a broader range of chemicals should be tested to determine which type of compounds NIR is capable of detecting at relevant concentrations and which not. A selection of potentially relevant chemicals could be made from the current lists of chemicals being monitored (e.g., RIWA database) based on their capacity (or not) to form hydrogen bonds. Measuring a larger set of blanks and spiked samples could also allow to determine if additional separation can be obtained from higher principal components as, for the moment, most of the variability remains explained only by the first component.

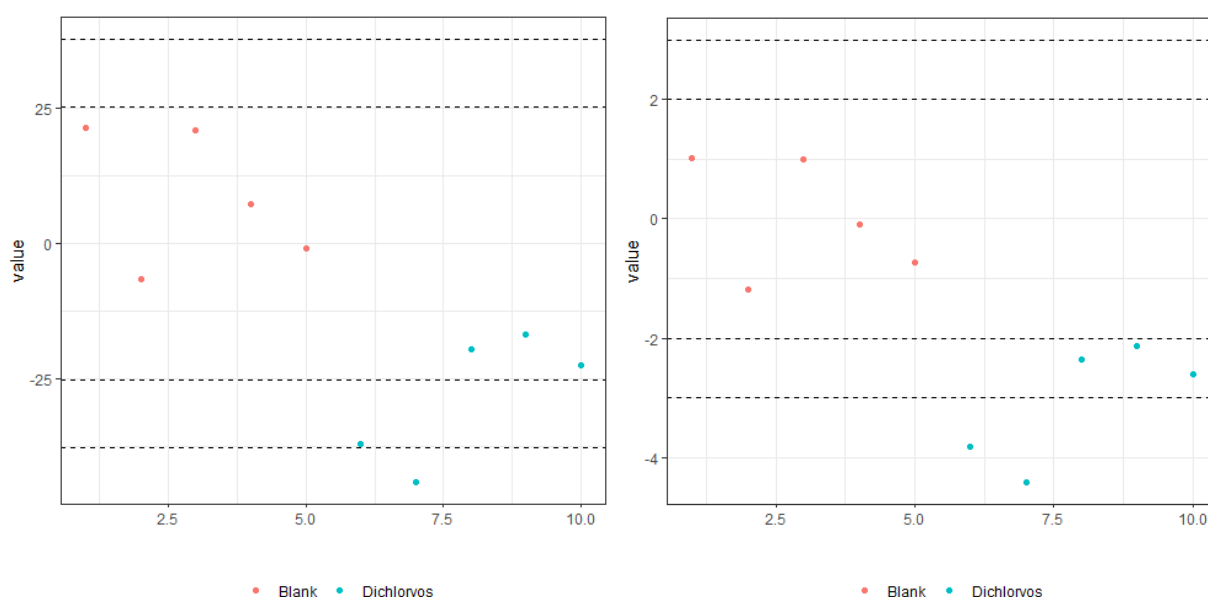


Figure 4 **Left**: PCA-QCC plot for dichlorvos. The upper and lower dashed lines indicate ± 2 and ± 3 standard deviations in the PC1 scores of the blank samples. **Right**: z-score plot calculated from PC1 of blank samples. Lower and upper border represent the ± 2 and ± 3 z-score.

4 Conclusion

The application of near-infrared spectroscopy to detect chemicals in highly diluted aqueous solution remains a challenging task due to the dominant absorption of water molecules in the infrared region. Nevertheless, the results obtained here with NIR seem to suggest that there is a potential, at least for certain types of compounds, to detect changes in specific regions of the water spectrum. In particular, results from principal component analysis seem to suggest that the presence of compounds which cannot form hydrogen bonds through hydroxyl groups can be more readily detected. The two types of quality control charts computed also showed that there is a potential to detect the presence of certain types of compounds, even at relevant concentrations (i.e., low $\mu\text{g/L}$ range).

Nevertheless, additional and more thorough testing is necessary. A large set of different non-spiked water samples needs to be measured at different days to account for both variability in matrix as well as in instrumental measurements. The direct measurement of MilliQ water could also be included. This possibility was contemplated and discussed at the beginning of this study but expert spectroscopists from the WFSR did not deem it relevant given its substantial difference with real surface water. On the other hand, the measurement of a larger set of water samples, collected from different locations and at different times is more relevant. A sample clean-up to remove suspended solids is necessary for the moment and, in the case of developing online tools, should be taken into account. Finally, a broader range of chemicals and concentrations should be included to further understand which types of chemicals can be detected and at which concentrations, thus allowing to determine the complementarity of this method to other monitoring tools (e.g., HPLC-UV).

Currently, this technique is not ready to be implemented in EWS strategies for drinking water companies in the Netherlands. However, further research could determine the full potential of NIR in the near future (i.e., 1 to 5 years, depending on the available financing and urgency to develop this tool further). This study gives a clear perspective on further research that is necessary to a) determine the capability of NIR to detect relevant substances at low concentrations and b) develop an online measuring device that is usable in an EWS strategy.

5 Further research

Based on the current study we suggest further research to be done in two phases.

1 Range of chemicals at different concentrations and natural variability of surface water at intake point

A broader range of chemicals at different concentrations should be tested. The first hypothesis is that some substances can be measured if no hydroxyl group is present. To corroborate this, more substances should be sampled varying in the degree with which they can form hydrogen bonds. For instance, PFOA did not give a significant signal in this first test, yet it might also be possible to use another fluorinated substance without a hydroxyl group and to compare this to the previously measured PFOA.

Similarly, non-spiked samples collected at different times and different locations should be measured to account for the natural variability of surface waters (i.e., capture variability in background concentrations). This research can possibly be done in cooperation with WFRS.

2 Online NIR instruments

Current benchtop NIR instruments like the one that has been used here are not applicable for an early warning (online monitoring) approach due to the lack of automatization. However, NIR-online analysers² are available and are commonly used in other sectors (e.g. dairy processing). If step 1 shows that NIR measurements can be used as a valuable addition to currently used techniques, the use of online-NIR tools has to be tested in an EWS setting. This will probably include collaboration with manufacturers (e.g. Büchi).

² Example: <https://www.buchi.com/en/products/nirsolutions/nir-online-process-analyzer>

6 References

ISO. 2015. Statistical methods for use in proficiency testing by interlaboratory comparison. ISO 13528:2015, issued 2015. <http://www.iso.org/cms/render/live/en/sites/isoorg/contents/data/standard/05/61/56125.html>.

Kovacs, Zoltan, György Bázár, Mitsue Oshima, Shogo Shigeoka, Mariko Tanaka, Akane Furukawa, Airi Nagai, Manami Osawa, Yukari Itakura, and Roumiana Tsenkova. 2016. "Water Spectral Pattern as Holistic Marker for Water Quality Monitoring." *Talanta* 147 (January): 598–608. <https://doi.org/10.1016/j.talanta.2015.10.024>.

Maleki, M.R., A.M. Mouazen, H. Ramon, and J. De Baerdemaeker. 2007. "Multiplicative Scatter Correction during On-Line Measurement with Near Infrared Spectroscopy." *Biosystems Engineering* 96 (3): 427–33. <https://doi.org/10.1016/j.biosystemseng.2006.11.014>.

"PubChem." 2019. 2019. <https://pubchem.ncbi.nlm.nih.gov/>.

Tsenkova, Roumiana. 2009. "Aquaphotomics: Dynamic Spectroscopy of Aqueous and Biological Systems Describes Peculiarities of Water." *Journal of Near Infrared Spectroscopy* 17 (6): 303–13. <https://doi.org/10.1255/jnirs.869>.

Year of publishing
2020

More information

Stijn Beernink MSc

T +31306069607

E Stijn.Beernink@kwrwater.nl

Keywords

Early Warning Systems, EWS, Near Infrared,
NIR, water quality monitoring

Groningenhaven 7

Postbus 1072

3430 BB Nieuwegein

The Netherlands

T +31 (0)30 60 69 511

F +31 (0)30 60 61 165

E info@kwrwater.nl

I www.kwrwater.nl

BTO 2020.025 | 20 april 2020 ©KWR

All rights reserved. No part of this publication may be reproduced, stored in an automatic database, or transmitted, in any form or by any means, be it electronic, mechanical, by photocopying, recording, or in any other manner, without the prior written permission of the publisher.