Enhancing UV-Vis Spectrophotometry Technology with Data Analytics for Real-time Water Quality Monitoring and Treatment Process Operation

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“Believe you can and you’re halfway there.” – Theodore Roosevelt

Abstract

Water quality monitoring is an essential element of the water quality management system and water treatment process. Conventional water quality monitoring relies on grab sampling and laboratory analysis, which is unable to provide quick responses to water quality events as it often takes hours and even days to transport and analyse water samples. Online water quality monitoring measures water quality continuously and allows quick responses to water quality events by providing real-time water quality data. In recent years, the online UV-Vis spectrophotometer has been reported as a promising technology for continuous water quality monitoring and process control. It reveals the real-time water quality changes and enables the development of surrogate parameters for online water quality monitoring and process control. However, there are some technic and data processing issues with using the online instruments for water quality monitoring. Besides, limited knowledge and research were reported on the utilisation of the online UV-Vis spectrophotometers for water quality management.

This thesis project uses advanced data analytics to enhance the UV-Vis spectrophotometer for real-time water quality monitoring and treatment process control. Laboratory investigations were conducted to explore the impact of water matrix and suspended particles on the online water quality measurements using a submersible UV-Vis spectrophotometer, and to assess the water quality monitoring performance for different water sources. Both particle types and particle concentrations were found to have significant impacts on the UV_{254} measurements, showing that water quality data measured by the submersible UV-Vis spectrophotometer varied when the water matrix changes. These findings provide evidence that the particle influence on the UV-Vis measurements is source-water dependent.

Surrogate models were developed as software techniques to eliminate particle impact from the measurements. Various software particle compensation techniques (surrogate models) including single wavelength compensation, linear regression compensation and multiplicative scatter correction methods were developed for online UV-Vis measurements of water quality. Moreover, cost-effective simple UV-Vis instruments could be employed in the field to monitor water quality instead of using sophisticated full-spectrum UV-Vis instruments.

The real-time water quality measurement technology, UV-Vis spectrophotometer, was used for water treatment process control. Surrogate modelling approaches were used for the first to build coagulant dose determination models using only online UV-Vis spectra of raw water quality combined with chemometrics to determine coagulant doses and control the coagulation process for a drinking water treatment plant. The results revealed that an online UV-Vis spectrophotometer combined with a software surrogate model is a promising technology that determinates coagulant doses for real-time process control.

Publications and Presentations

First-authored papers

Shi, Z., Chow, C.W., Fabris, R., Zheng, T., Liu, J. and Jin, B., 2021. Evaluation of the impact of suspended particles on the UV absorbance at 254 nm (UV254) measurements using a submersible UV-Vis spectrophotometer. *Environmental Science and Pollution Research*, *28*(10), pp.12576-12586.

Shi, Z., Chow, C.W., Fabris, R., Liu, J. and Jin, B., 2020. Alternative particle compensation techniques for online water quality monitoring using UV–Vis spectrophotometer. *Chemometrics and Intelligent Laboratory Systems*, *204*, p.104074.

Shi, Z., Chow, C.W., Fabris, R., Liu, J., Sawade, E. and Jin, B., 2022. Determination of coagulant dosages for process control using online UV-Vis spectra of raw water. *Journal of Water Process Engineering*, 45, p.102526.

Shi, Z., Chow, C.W., Fabris, R., Liu, J., and Jin, B., 2022. Applications of Online UV-Vis Spectrophotometer for Drinking Water Quality Monitoring and Process Control: A Review. *Sensors*, 2022, 22, 2987.

Shi, Z, Online Water Quality Monitoring and Process Control Using UV-Vis Sensors. Water e-Journal, *Online Journal of the Australian Water Association*, 7, 2022 (Accepted on 27th Jan 2022).

Co-authored paper

Huang, J., Chow, C.W., Shi, Z., Fabris, R., Mussared, A., Hallas, G., Monis, P., Jin, B. and Saint, C.P., 2021. Stormwater monitoring using on-line UV-Vis spectroscopy. Environmental Science and Pollution Research, pp.1-10.

Conferences

Presented, ‘Online analyser without sample filtration for water quality monitoring’ at OzWater’21 conference, Adelaide 2021.

Presented, ‘The use of real-time data analytic tools to enhance water treatment plant operations’ at SA regional conference on CWMS, Port Pirie 2019.

Declaration

I certify that this work contains no material which has been accepted for the award of any other degree or diploma in my name, in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text. In addition, I certify that no part of this work will, in the future, be used in a submission in my name, for any other degree or diploma in any university or other tertiary institution without the prior approval of the University of Adelaide and where applicable, any partner institution responsible for the joint-award of this degree.

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Signature: _____________LS____________

Date: __________26/03/2022________

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Table of Contents

Chapter 1 Introduction

Research Questions:

- Why and how particles in the water affect the measurements of water quality using online UV-Vis instruments?

- How to obtain accurate measurements using online UV-Vis instruments?

- Can we use only UV-Vis spectra for water treatment process control?

1. 1 Background and Significance

Water quality management is an important task carried out by the water industry to ensure the delivery of a safe drinking water supply service. Climate change has affected source water quality in many ways. One of the most relevant to the water industry is through increased frequencies of extreme hydrological events [1, 2]. These result in more frequent and larger variations of water quality of water sources caused by unstable weather conditions such as floods and droughts [3]. Source water quality change with increased turbidity and organic content is a challenging issue for the operation of water treatment plants. This adds stress to many water treatment facilities as they may reach their design capacity and cannot handle the situations [4]. It is expected to become a more challenging task to manage water quality from catchment to tap due to climate change for the supply of safe and clean drinking water [5]. Therefore, it is essential to have robust and advanced process control systems to improve the treatment performance which can handle the large changes in source water quality. Water quality management systems are developed specifically by water utilities to manage their own drinking water supply according to their local situations and must comply with drinking water quality guidelines established by the World Health Organization. Water quality monitoring and treatment process control are two vital aspects of the water quality management systems to detect events and manage risks that can compromise the supplied water quality [6]. Both aspects provide operational control and preventive measures for assuring safe and reliable drinking water to consumers.

There are several commercial or in-house water quality monitoring and treatment process control options, and solution packages available for treatment operators, including feedback control, employing empirical models, and more recently applying advanced control algorithms based on machine learning [7, 8]. Modelling is one of the most commonly used methods that can be applied in process control to improve water treatment plant performance [9, 10]. Studies have shown that the operation of water treatment facilities can be improved through modelling methods [7, 11, 12]. Models can be developed and applied to simulate the drinking water treatment processes for predictions of process behaviours under changing conditions and the determination of water quality [13, 14]. Water treatment process control knowledge would be accumulated via years of experience which can be considered as the human version of data analytics. The most recent development of control strategies is based on advanced data analyses of online water quality measurements using advanced computing to extract useful control information [9, 15]. Data analytics is a process of extracting valuable information from raw data using the computational power of computer systems, which can be used to improve the operational efficiencies of water utilities. Data analytics has been proved to improve water treatment plants performance by data visualisation (graphically showing water quality trends) and data analytics (identifying potential instrument problems, and discovering relationships between process parameters, process train anomalies and unusual patterns) [16-18].

Online water quality monitoring can provide two parallel functions for water treatment process control, which can assist in treatment process improvement with the simultaneous assessment of water quality by identification of contaminant sources and determination of the corrective actions to control the treatment processes. Monitoring of water quality can occur at many locations of the supply system and mostly at the inlets and outlets of the water treatment plants, as well as locations within the treatment train to monitor the treatment processes, which is considered fundamental to water treatment. Conventional water quality monitoring relies on the laboratory analysis of grab samples which has great limitations in terms of process control purpose. Laboratory analytic data may not represent the true variances of water quality conditions as the data may have a low temporal resolution. Furthermore, the laboratory data are unable to provide quick responses to water quality changes, as it generally takes hours or even days to transport and analyse water samples in the laboratory [19, 20]. There is a high possibility that the conventional monitoring method may miss major water events which leads to negative impacts on process management and thus water quality [21, 22] In contrast, online water quality monitoring measures water quality continuously which allows real-time measurements and process control to be carried out simultaneously [9, 23]. Online water quality monitoring has been proved useful in improving treatment process performance via real-time, source water contaminant detection and control of the treatment process [8, 24]. In other words, online water quality monitoring allows quicker responses to water quality events and treatment process optimisation, as well as provides real-time data for the development and refinement of online surrogate water quality parameters [22, 25]. Further process optimisation development trend within water treatment plants is predicated on the transformation of online water quality data for the real-time evaluation of water treatment systems to enable process optimisation [22, 26].

Under this development trend, smart analytics will play a major role in advanced approaches for water treatment control. Smart analytics utilises advanced computer techniques to analyse a large volume of data for the improvement of process control. A surrogate parameter is an example of how an indictor can be developed from smart analytics. The use of surrogate parameters is a well-established practice for monitoring water quality and controlling the water treatment processes. Surrogate measurement represents a practical alternative to the detection and quantification of specific contaminants that require sophisticated and expensive laboratory-based analytical techniques [27]. Surrogate parameters can also function as a valuable screening tool for the evaluation of raw water quality [28] and can be used to rapidly determine changes in water quality caused by individual processes and overall treatment processes [17, 29]. The surrogate parameters can be generated from empirical modelling and/or advanced computing techniques. Simple surrogate parameters such as turbidity, colour, and UV_{254} have been commonly used for water quality indicators by estimating concentrations of organic matter to monitor and control treatment plant operations for the removal of particulate matter [30, 31]. Other more complex surrogate parameter examples using UV-Vis absorbance measurements for real-time monitoring of chlorine demand [32, 33], DBPs [34], and alum dose [35]. It is believed that these online surrogate parameters can provide valuable information to assist the water treatment operators and inform decisions. However, as in other technology development cases, it requires long term investigation and validations of these surrogates at full scales. The water industry worldwide continually searches for better ways for water quality monitoring and process control. Using surrogate water quality parameters may be the most promising option. A few existing online surrogate parameters can be applied to substitute for the traditional water quality parameters.

There are many cases of successful use of water quality sensors with great practical benefits. Water quality sensors have been widely used for source water protection, automated operation of drinking water treatment and many other examples. The online UV-Vis spectrophotometer is a useful instrument for developing a simple and effective measuring device for real-time water quality monitoring that can fulfil the industry requirements as a real-time monitoring tool. Currently, UV-Vis spectrophotometers are commonly used in the laboratory for water quality analysis, which is operated by multiple technic steps, including sample pre-treatment filtration and chemical reagents. In recent years, online UV-Vis spectrophotometers have been used for continuous water quality monitoring and process control by several water utilities [36, 37]. However, there are many technical issues involved in water sample treatment and data analysis, such as the high frequency of changing filters for instruments that required physical filtrations and measurement difficulties [32, 38, 39]. It is not practical to use a spectrophotometer with physical filtration in the field for continuous online water quality monitoring [40]. Yet, submersible UV-Vis spectrophotometers with smart analytics to determine water quality parameters have gained attention and are suitable for continuous online water quality monitoring as they do not require water sample pre-treatments and are adaptable with a selectable range of pathlengths for various applications. These UV-Vis spectrophotometers usually have built-in particle compensation algorithms that can mathematically analyse and automatically minimise the particle effects from measurements by the onboard computer, which are able to determine commonly used water quality parameters as so-called calculated equivalents (surrogate) including UV_{254}, colour, nitrate and dissolved organic carbon (DOC).

Submersible UV-Vis spectrophotometers have been used widely for surface water quality monitoring, drinking water quality monitoring and process control [38, 41, 42]. It allows to measure real-time changes in water quality [43] and enables the development of alarm parameters to detect unusual changes in water compositions. Some studies have been conducted using submersible UV-Vis spectrophotometers to carry out in-situ measurements using surrogate parameters for water treatment process control [44, 45]. However, there is still limited knowledge and research on the utilisation of the submersible UV-Vis spectrophotometers for online water quality monitoring and process control, particularly for drinking water supply. Therefore, it is necessary to obtain in-depth knowledge of the utilisation of the online water quality data and the development of surrogate parameters for water quality monitoring and process control based on online UV-Vis spectral data and advanced computing techniques. This is an important development of water measurement technology towards the online water quality monitoring for process control in real-time for the proactive management of drinking water supply.

In this thesis study, time series spectral water quality data measured by UV-Vis instruments from industrial water treatment plants were analysed using advanced data analytics. Case studies for this project were selected based on ten years' water quality data from a local water utility in South Australia (SA). Water sources in these treatment plants include stormwater, drinking water, wastewater and recycled water. The selected online UV-Vis instrument for this study has been used by the water industry for about 15 years. Moreover, rigid data selection process was conducted to ensure the good quality of data used in this study. This will allow better utilisation of online water quality and operational data for decision-making that will improve the efficiency of water treatment processes and result in better water quality management.

1. 2 Research Objectives

This project aimed to develop the next generation process optimisation and decision support tools to improve the efficiency of the water treatment plant operations. The research approach was to develop and use surrogates with advanced computing techniques utilising operations data from industrial water treatment plants combined with water quality measurements using online UV-Vis instruments.

The research objectives of this thesis study were:

1. To explore the potential of applications of UV-Vis sensors for online water quality monitoring.
2. To provide in-depth knowledge of the impact of suspended particles on the measurements of water quality using online UV-Vis spectrophotometers.
3. To identify and provide solutions to overcome the challenges of using submissible UV-Vis instruments for online water quality measurements.
4. To develop and evaluate software particle compensation techniques for accurate measurements of water quality parameters (surrogates) using online UV-Vis spectral data.
5. To extend the application of time series UV-Vis spectral data for water treatment process control.
6. To develop surrogate models using UV-Vis spectra of raw water to predict chemical dosing for water treatment process control.

1. 3 Thesis Outline

This thesis reports the research outcomes of my PhD study, which is presented in the form of journal publications. Each chapter states specific research objectives that are related to the aim of this study. The chapters in this thesis are presented in the following sequence:

- **Chapter 1** introduces the background to the research, the significance of the project and, outlines the research objectives and key contributions in the field of online water quality monitoring and process control using UV-Vis spectrophotometers.
- **Chapter 2** reviews the progress of applying online UV-Vis spectrophotometers for drinking water quality management in the last two decades. This chapter also discusses the issues and potential solutions related to the application of online instruments. At the end of Chapter 2, it identifies research gaps and provides a background for the following chapters. One aspect of the research gap is that there is a lack of studies on the utilisation of the water quality data from the online UV-Vis spectrophotometers and the development of surrogate parameters for water

quality monitoring and process control. In Chapters 3 to 5, further specific literature reviews are presented that are related to the research objective in each chapter.

- To develop in-depth knowledge of the online water quality monitoring with the employment of UV-Vis sensors, **Chapter 3** investigates the impact of suspended particles in the water on the measurements of a submersible UV-Vis spectrophotometer and the performance of the factory built-in algorithms under laboratory-controlled conditions. This Chapter provides essential knowledge of the particle impacts on the water quality measurements which is fundamental to the surrogate development from online UV-Vis spectrophotometers.
- To overcome the measurement issue of online UV-Vis sensors and obtain reliable and accurate measurements, the study in **Chapter 4** develops various alternative particle compensation techniques (Surrogate models) for online water quality monitoring using water quality data collected from three selected water sources in two drinking water treatment plants. UV_{254} as a surrogate is used as an illustration of the development of water quality surrogate parameters using UV-Vis spectra.
- To assist the water treatment process control, the study in **Chapter 5** develops surrogate models to determine coagulant dosages for process control using online UV-Vis spectra of raw water from a water treatment plant. This study might be the first to build coagulation dose perdition models (surrogate model) with the utilisation of only online raw water quality data.
- **Chapter 6** presents the conclusions of this research project and perspectives for further work on the application of online UV-Vis spectrophotometers for drinking water supply.

1. 4 References

1. Delpla, I., Jung, A.V., Baures, E., Clement, M. and Thomas, O., *Impacts of climate change on surface water quality in relation to drinking water production.* Environment International, 2009. **35**(8): p. 1225-1233.
2. CSIRO, *State of the climate change.* Australian Government, 2016.
3. Whitehead, P.G., Wilby, R.L., Battarbee, R.W., Kernan, M. and Wade, A.J., *A review of the potential impacts of climate change on surface water quality.* Hydrological Sciences Journal, 2009. **54**(1): p. 101-123.
4. Misra, A.K., *Climate change and challenges of water and food security.* International Journal of Sustainable Built Environment, 2014. **3**(1): p. 153-165.
5. Bates, B., Kundzewicz, Z.W., Wu, S. and Palutikof, J., *Climate change and Water.* IPCC Technical Paper VI, Intergovernmental Panel on Climate Change (IPCC)Intergovernmental Panel on Climate Change (IPCC), 2008.
6. *Australian Drinking Water Guidelines* in *National Water Quality Management Strategy*. 2011, Australian Government.
7. Bello, O., Hamam, Y. and Djouani, K., *A Survey of Modelling Techniques and Control Strategies Employed for Coagulation Process in Drinking Water Treatment Plants.* International Journal of Engineering Research & Technology, 2016. **5**(2): p. 229-236.
8. Ratnaweera, H. and J. Fettig, *State of the art of online monitoring and control of the coagulation process.* Water, 2015. **7**(11): p. 6574-6597.
9. Li, L., Rong, S., Wang, R. and Yu, S., *Recent advances in artificial intelligence and machine learning for nonlinear relationship analysis and process control in drinking water treatment: A review.* Chemical Engineering Journal, 2021(405): p. 126673.
10. Aliashrafi, A., Zhang, Y., Groenewegen, H. and Peleato, N.M., *A review of data-driven modelling in drinking water treatment.* Reviews in Environmental Science and Bio/Technology, 2021. **20**(4): p. 985-1009.
11. Baxter, C.W., Zhang, Q., Stanley, S.J., Shariff, R., Tupas, R.R. and Stark, H.L., *Drinking water quality and treatment: the use of artificial neural networks.* Canadian Journal of civil engineering, 2001. **28**(S1): p. 26-35.

12. Rietveld, L.C., *Improving operation of drinking water treatment through modelling*, in *TU Delft*. 2005, Delft University of Technology.

13. Page, R.M., Waldmann, D. and Gahr, A., *Online water-quality monitoring based on pattern analysis*, in *Computing and Control for Water Industry*. 2017: Sheffield.

14. Saravanan, K., Anusuya, E., Kumar, R. and Son, L.H., *Real-time water quality monitoring using Internet of Things in SCADA.* Environmental Monitoring and Assessment, 2018. **190**(9): p. 1-16.

15. Ramadhan, A.J., Ali, A.M., Kareem, H.K., Hawas, M.N., Mohammed, A.A. and Fahem, A.H., *Smart water-quality monitoring system based on enabled real-time internet of things.* Journal of Environmental Science and Technology, 2020. **15**: p. 3514-3527.

16. George, J.P., Chen, Z. and Shaw, P., *Fault detection of drinking water treatment process using PCA and Hotelling's T2 chart.* World Academy of Science, Engineering and Technology, 2009. **3**(2): p. 803-808.

17. Zhang, J., Hou, D., Wang, K., Huang, P., Zhang, G. and Loáiciga, H., *Real-time detection of organic contamination events in water distribution systems by principal components analysis of ultraviolet spectral data.* Environmental science and pollution research, 2017. **24**(14): p. 12882.

18. Asheri-Arnon, T., Ezra, S. and Fishbain, B., *Contamination detection of water with varying routine backgrounds by UV-spectrophotometry.* Journal of Water Resources Planning and Management, 2018. **144**(9): p. 04018056.

19. Banna, M.H., et al., *Online drinking water quality monitoring: review on available and emerging technologies.* Critical Reviews in Environmental Science and Technology, 2014. **44**(12): p. 1370-1421.

20. Mussared, A., Chow, C., Holmes, M., Van Leeuwen, J. and Kaeding, U., *Implementation of predictive alum dose control systems*, in *77th Annual WIOA Victorian Water Industry Operations Conference and Exhibition*. 2014: Bendigo Exhibition Centre.

21. Van den Broeke, J., Carpentier, C., Moore, C., Carswell, L., Jonsson, J., Sivil, D., Rosen, J.S., Cade, L., Mofidi, A., Swartz, C. and Coomans, N.,

Compendium of sensors and monitors and their use in the global water industry. 2014.

22. Chow, C., et al., *Online water quality monitoring: The voice of experience.* Water: Journal of the Australian Water Association, 2014. **41**(2): p. 60.
23. Capodaglio, A.G., Callegari, A., *Water supply systems security: novel technologies for the online monitoring of unforeseeable events.* WIT Transactions on The Built Environment, Safety and Security Engineering, 2015. **51**: p. 251-263.
24. Cascone, C., *Optical sensors in drinking water production: Towards automated process control in relation to natural organic matter*, in *Faculty of Natural Resources and Agricultural Sciences*. 2021, Faculty of Natural Resources and Agricultural Sciences.
25. Fabris, R., Chow, C., Dexter, R., Colton, J., Knoblauch, J. and Drikas, M., *Feed-forward coagulant control using online UV/Vis monitoring.* Water Science and Technology: Water Supply, 2013. **13**(2): p. 420-426.
26. Byrne, A.J., Brisset, T., Chow, C.W.K., Lucas, J. and Korshin, G.V., *Development of online surrogate parameters using uv-vis spectroscopy for water treatment plant optimisation.* Australia Water Association Water Journal, 2014. **41**: p. 94-100.
27. AWWA, *The search for a surrogate.* AWWA Research Foundation, 1988.
28. Shi, B., Wang, P., Jiang, J. and Liu, R., *Applying high-frequency surrogate measurements and a wavelet-ANN model to provide early warnings of rapid surface water quality anomalies.* Science of the Total Environment, 2018. **610**: p. 1390-1399.
29. Fei, C., Cao, X., Zang, D., Hu, C., Wu, C., Morris, E., Tao, J., Liu, T. and Lampropoulos, G., *Machine learning techniques for real-time UV-Vis spectral analysis to monitor dissolved nutrients in surface water*, in *In AI and Optical Data Sciences II*. 2021, International Society for Optics and Photonics. p. 117031.
30. Matilainen, A., Gjessing, E.T., Lahtinen, T., Hed, L., Bhatnagar, A. and Sillanpää, M., *An overview of the methods used in the characterisation of*

natural organic matter (NOM) in relation to drinking water treatment. Chemosphere, 2011. **83**(11): p. 1431-1442.

31. Yan, M., et al., *Enhanced coagulation for high alkalinity and micro-polluted water: the third way through coagulant optimization.* Water Res, 2008. **42**(8-9): p. 2278-86.
32. Chow, C., Dexter, R., Sutherland-Stacey, L., Fitzgerald, F., Fabris, R., Drikas, M., Holmes, M., Kaeding, U., *UVspectrometry in drinking water quality management*, in *WATER-MELBOURNE THEN ARTARMON*. 2007. p. 40-43.
33. Fitzgerald, F., Chow, C.W. and Holmes, M., *Disinfectant demand prediction using surrogate parameters–a tool to improve disinfection control.* Journal of Water Supply: Research and Technology—Aqua, 2006. **55**(6): p. 391-400.
34. Korshin, G.V., Sgroi, M. and Ratnaweera, H., *Spectroscopic surrogates for real time monitoring of water quality in wastewater treatment and water reuse.* Current Opinion in Environmental Science & Health, 2018. **2**: p. 12-19.
35. Shi, Z., Chow, C.W., Fabris, R., Zheng, T., Liu, J. and Jin, B., *Determination of coagulant dosages for process control using online UV-Vis spectra of raw water.* Journal of Water Process Engineering, 2022. **45**: p. 102526.
36. Guo, Y.L., C; Ye, R. and Duan, Q., *Advances on Water Quality Detection by UV-Vis Spectroscopy.* Applied Sciences, 2020. **10**(19): p. 6874.
37. Li, P. and J. Hur, *Utilization of UV-Vis spectroscopy and related data analyses for dissolved organic matter (DOM) studies: A review.* Critical Reviews in Environmental Science and Technology, 2017. **47**(3): p. 131-154.
38. Hu, Y. and X. Wang, *Application of surrogate parameters in characteristic UV–vis absorption bands for rapid analysis of water contaminants.* Sensors and Actuators B: Chemical, 2017. **239**: p. 718-726.
39. Lepot, M., Torres, A., Hofer, T., Caradot, N., Gruber,G., Aubin, J., Bertrand-Krajewski, J., *Calibration of UV/Vis spectrophotometers: A review and comparison of different methods to estimate TSS and total and dissolved COD concentrations in sewers, WWTPs and rivers.* Water Research, 2016. **101**: p. 519-534.

40. Langergraber, G., Fleischmann, N., Hofstaedter, F., *A multivariate calibration procedure for UV/VIS spectrometric quantification of organic matter and nitrate in wastewater.* Water Science and Technology, 2003. **47**(2): p. 63-71.

41. van den Broeke, J., G. Langergraberb, and A. Weingartnera, *On-line and in-situ UV/vis spectroscopy for multi-parameter measurements: a brief review.* Spectroscopyeurope, 2006. **18**(4).

42. Hou, D.B., J. Zhang, and L. Chen, Huang, P.J. and Zhang, G.X., *Water quality analysis by UV-Vis spectroscopy: A review of methodology and application.* Spectroscopy and Spectral Analysis, 2013. **33**(7): p. 1839-1844.

43. Lee, S.J., Lee, G., Suh, J.C. and Lee, J.M., *Online burst detection and location of water distribution systems and its practical applications.* Journal of Water Resources Planning and Management, 2016. **142**(1): p. 04015033.

44. Miguntanna, N.S., Egodawatta, P., Kokot, S. and Goonetilleke, A., *Determination of a set of surrogate parameters to assess urban stormwater quality.* Science of the Total Environment, 2010. **408**(24): p. 6251-6259.

45. Altmann, J., Massa, L., Sperlich, A., Gnirss, R. and Jekel, M., *UV254 absorbance as real-time monitoring and control parameter for micropollutant removal in advanced wastewater treatment with powdered activated carbon.* Water Research, 2016. **94**: p. 240-245.

1. 5 Supporting Information

I co-authored a technical article, entitled ‘Stormwater monitoring using on-line UV-Vis spectroscopy’, which was published in the journal of Environmental Science and Pollution Research, as shown in the Appendix A. Stormwater is a type of water source for the drinking water supply, thus this article is relevant to this PhD research project. My contributions to the article were data analysis, writing and editing of the manuscript. However, the data analysis for the article was standard methods, not advanced, which is beyond the scope of this research project.

Chapter 2 Literature Review

- Overview of online UV-Vis spectrophotometers
- Recent outcomes of advanced spectral data processing and applications
- Challenges and solutions associated with the development and application of the instruments

Water quality management is essential to water utilities for the drinking water supply from catchment to tap. Water quality monitoring is a vital component of the water quality management system. Online UV-Vis spectrophotometers are simple but effective tools to provide continuous measurements of water quality parameters to allow quicker responses to water quality changes compared to conventional water quality monitoring [1, 2]. Studies of online water quality monitoring have shown that online UV-Vis spectrophotometers have the potential for real-time water quality monitoring and process control [3, 4]. Due to a limited number of published research that was related to online monitoring of using UV-Vis spectrophotometers, there is a need to expand the literature search to cover not only journal articles and books, but also existing guidance documents and industry reports in applications of online UV-Vis instruments, which are necessary to identify the knowledge gaps [3, 4]. Besides, there were only several published reviews on the industry applications of UV-Vis spectrophotometers [5-7]. These reviews either presented a broad view, concluded the principles of the instruments, or focused on a particular water quality parameter. Therefore, this chapter covers the practical aspects by reviewing the research progress of online UV-Vis spectrophotometers for water quality monitoring and process control in terms of drinking water supply, particularly, techniques for industrial applications that could make the UV-Vis instruments more acceptable. Various methods of anomaly detection and early warning were also discussed for drinking water quality monitoring at the source or in the distribution system. As most studies of online UV-Vis instruments in the drinking water field were conducted in the lab- and pilot- scale, future work is needed for industrial-scale applications. Issues and potential solutions associated with online instruments for water quality monitoring have been provided. Based on the industry feedbacks of the current technique development, future research and development work are needed for the integration of early warning and real-time water treatment process control systems for water quality management.

Chapter 2 provides updated research achievements and outcomes which are beneficial for identifying the research gaps to determine research objectives for Chapters 3-5. One large aspect of the knowledge gaps is limited studies on the research of online UV-Vis spectrophotometers for water quality monitoring and process control. The project structures and arrangements of Chapters 3 to 5 are shown in Figure 2-1. Firstly, research is needed to expand the knowledge of implementation of the online instruments for water quality monitoring in the field. The study in Chapter 3 presents systematic investigations to discover the influence of suspended particles in the water on the online measurements of a submersible UV-Vis spectrophotometer, which is fundamental to the surrogate development from online UV-Vis spectrophotometers. To overcome the challenges of using online UV-Vis sensors for accurate water quality measurements, research in Chapter 4 is conducted to develop surrogate parameters as alternative particle compensation techniques for online water quality monitoring based on UV-Vis spectra. The study in Chapter 5 reports the research approach and outcomes for the development of surrogate models of coagulation dose determinations and predictions for process control using UV-Vis spectra.

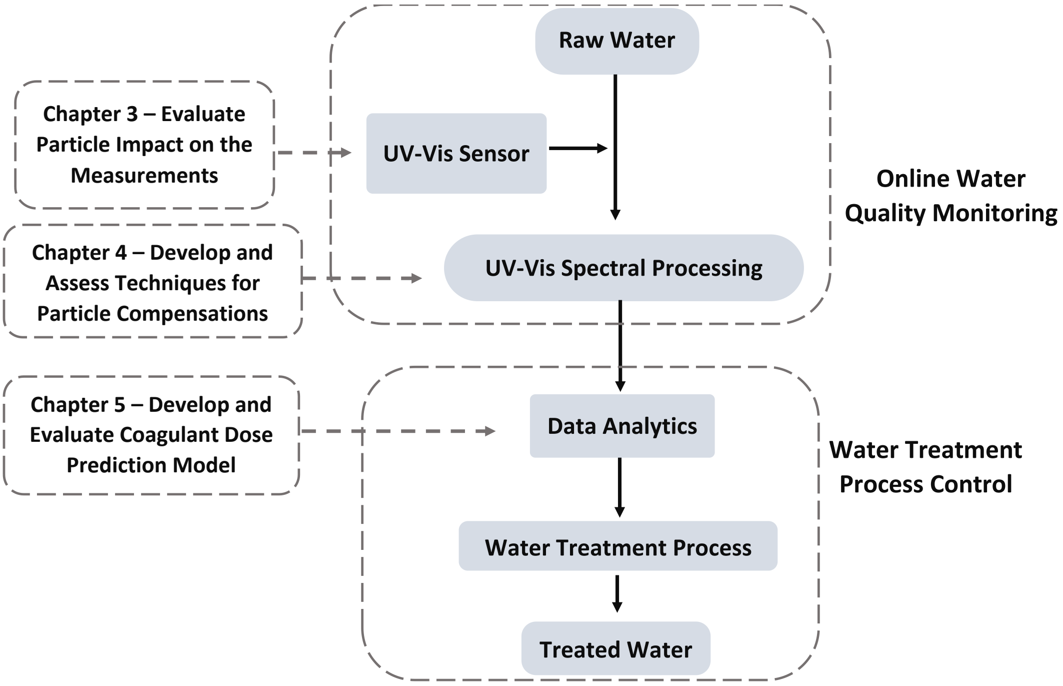

Figure 2-1 Flow chart of arrangements of Chapters 3 to 5.

The following content of this chapter is presented as a review paper that has been published by the journal of Sensors, as shown in appendix B.

Statement of Authorship

Title of Paper	Applications of Online UV-Vis Spectrophotometer for Drinking Water Quality Monitoring and Process Control: A Review
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Overall percentage (%)	78		
Certification:	This paper reports on original research I conducted during the period of my Higher Degree by Research candidature and is not subject to any obligations or contractual agreements with a third party that would constrain its inclusion in this thesis. I am the primary author of this paper.		
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By signing the Statement of Authorship, each author certifies that:

i. the candidate's stated contribution to the publication is accurate (as detailed above);
ii. permission is granted for the candidate in include the publication in the thesis; and
iii. the sum of all co-author contributions is equal to 100% less the candidate's stated contribution.

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2.1 Introduction

Drinking water quality is a key performance indicator for water utilities and is important to public health. Water utilities are committed to drinking water quality management to ensure that the supplied water meets the drinking water standards. Water quality management systems have been developed by water utilities to manage the water supply from catchment to tap, covering source water transportation, water treatment and distribution systems, for the safe supply of drinking water. Most drinking water quality management systems followed the World Health Organization drinking water quality guidelines. Water quality monitoring and treatment are two main water quality management systems to detect hazards and events that can compromise water quality and provide operational control for assuring safe and reliable drinking water as preventive measures.

Water quality monitoring is needed to ensure that the supplied water to the consumers meets the standards. Conventionally, water quality monitoring for drinking water treatment plants relies on a regular sampling program (collection, transportation, followed by laboratory analysis) which only captures small snapshots over a period of time and may not represent the true variances of water quality. It also frequently suffers from feedback delay and is unable to provide rapid responses to water incidents [8]. Water analysis using standard laboratory methods requires long sample preparation and analysis processing time such as sample pre-treatment or adding reagents. There is also a higher risk that the conventional monitoring method may miss water events that could lead to negative impacts on water quality and treatment process management. In contrast, online monitoring measures water quality continuously which allows real-time water quality measurements and process control [9]. In summary, online water quality monitoring can improve the treatment process with real-time assessment of both source and treated water quality, identification of contaminants and control of the treatment process [10]. It is also useful during the period of rapid water quality changes when quick responses are needed to optimise the process [11].

There are many well-established online water quality sensors, including chlorine, total organic carbon (TOC), turbidity, conductivity, temperature and pH sensors, which are able to only measure one water quality parameter. Biosensors and optical sensors have received a lot of attention in recent years for online water quality monitoring [8, 12]. Biosensors are mainly based on fluorescence and are used for the detection of microorganisms such as bacteria and viruses. Optical sensors measure light absorption, light scattering, or fluorescence. A classic example of an optical sensor is a turbidity meter. More advanced optical sensors are infrared, fluorescence, and UV-Vis spectrophotometers. Infrared optical sensors can continuously measure organic compounds at wavelengths greater than 760 nm and can analyse water samples at liquid or gas phases [13]. The infrared sensors are not commonly used for online water quality for water treatment processes. Fluorescence sensors can continuously determine dissolved organic matter. Microorganisms could be determined as microbial indicators of water quality by analysing fluorescence from a molecule according to its fluorescent properties. UV-Vis sensors can continuously measure water quality parameters by determining the amount of light absorbed by compounds, such as TOC and dissolved organic carbon (DOC), colour, nitrate and specialist parameters. Both fluorescence and UV-Vis sensors do not require sample pre-treatment, reagent free, and allow fast measurements [12]. UV-Vis sensors can measure multiple parameters for water quality monitoring and treatment process control.

Water quality analysis using UV-Vis spectrophotometers is a simple but effective method to measure water quality. In conventional laboratory water quality analysis using spectrophotometers, sample pre-treatment is needed, physical filtration using 0.45 μm filters is to eliminate particle interference for measuring UV_{254} and reagents are used for nitrate determinations. Some commercial online UV-Vis spectrophotometers have built-in particle compensation and other algorithms to eliminate sample pre-treatment and can provide calculated equivalents of water quality parameters such as UV_{254}, colour, nitrate, DOC, and TOC [14].

In recent years, additional parameters have been included in water quality monitoring using online UV-Vis spectrophotometers [15] such as measurements of dissolved organic matter [2], chemical oxygen demand (COD) in water [16], and disinfectant in drinking water [17]. It has gradually been applied for process control of water treatment, particularly for the coagulation process [18]. However, it could be challenging to obtain accurate water quality measurements for those online UV-Vis instruments with built-in algorithms. Main technique issues include under-compensation, over-compensation, and failure to generate reasonable measurements for real-time monitoring and process control [3, 6, 7, 19]. In contrast, reliable measurements were also reported using the online UV-Vis instruments for water quality detection and water treatment process control [20-22]. Various studies have been conducted to develop algorithms based on certain wavelengths (regions) of UV-Vis spectra to determine water quality such as the use of absorbance ratios to monitor the variation of DOC in the water and multiple linear regression to estimate the total carbon contents in water [23, 24].

Applications of UV-Vis spectrophotometers for water quality analysis have been reported in several review articles. A brief product review on a submersible UV-Vis spectrophotometer (probe) was conducted in 2006 which summarised the typical applications for wastewater treatment, environmental monitoring, and drinking water applications [25]. The use of UV-Vis spectrophotometers for dissolved organic matter studies was reviewed, which summaries the use of derivatives and differential absorption spectra methods for DOC determinations in 2017 [2]. A recent publication reviews the advances of water quality detection by UV-Vis spectrophotometers in 2020 [15]. In this work, the principle of the instruments and modelling methods for predicting water quality were outlined. These reviews validate the principles of UV-Vis spectrophotometers and the general use of UV-Vis spectrophotometers.

There were only several published reviews on the industry application of the UV-Vis spectrophotometers. These reviews either presented a broad view, concluded the principles of the instruments, or focused on particular water quality parameters. There is a lack of published research covering the practical aspect of using online UV-Vis spectrophotometers in drinking water supply applications. Therefore, it is necessary to expand the literature search to cover not only journal articles and books, but also existing guidance documents and industry reports in applications of online UV-Vis instruments [3, 4]. This updated information on research and technology development is beneficial for identifying the knowledge gaps and research needs in this field. Therefore, this paper presents an overview of the status and research progress of the UV-Vis instruments for online water quality monitoring and process control. These updates are particularly important to provide practical knowledge that makes UV-Vis instruments more acceptable to the drinking water utilities. Firstly, an overview of online UV-Vis instrumentation is presented. Recent outcomes for the development of online water quality monitoring using UV-Vis spectrophotometers for anomaly detection and early warning are discussed in detail. Finally, field applications of online UV-Vis spectrophotometers and integration into the water quality management system are briefed and discussed. Challenges and solutions associated with the development and application of the online UV-Vis spectrophotometers for water quality monitoring are addressed. This paper also highlights perspectives for future research needs in the development and applications of online UV-Vis spectrophotometers.

2.2 Online UV-Vis Spectrophotometers

Online UV-Vis spectrophotometers can be effective and practically useful for continuously measuring water quality parameters. Particle influence on water quality measurement using UV-Vis spectrophotometers can be minimised using software particle compensation techniques. The water industry has deployed more online instruments to monitor water quality from catchment to tap for online and in-situ measurements as well as the treatment process control. However, the reputation of lacking reliability of the measurements is the general restriction to the use of these instruments for a wider range of water quality management applications. This section discusses those issues and limitations.

2.2.1 Online UV-Vis Spectroscopic Instrumentation

With the advancement of photodetector development, there is an increasing variety of online UV-Vis spectrophotometers. Various UV-Vis sensors developed from different detection technologies and instrument designs are available for water quality monitoring and process control. The principle of UV-Vis spectrophotometry is based on the substance molecules in the water that can absorb UV-Vis light of a specific wavelength. Water quality can be determined by the correlation between the absorption spectrum and the concentration of the substance [15]. These sensing devices generally do not require sample filtrations (software particle compensation), are reagent free, and allow fast measurements of water quality. They also have low maintenance requirements for parameters such as UV_{254} and spectral absorption coefficient (SAC254). These instruments are equipped with automatic ultrasonic cleaning systems. However, regular / on-demand manual cleanings of the measurement ports are still required to ensure reliable measurements for turbid source waters. Commonly used commercially available online UV-Vis instruments are summarised in Table 2-1. There are mainly two categories of these online instruments: single wavelength (SW) and spectrum (full or partial).

Online SW UV-Vis instruments determine concentrations of a particular parameter in water based on the absorbance of a selected single wavelength [5]. The SW UV-Vis instruments also called UV sensors are manufactured with a specific wavelength to measure UV_{254} or nitrogen as nitrate and nitrite. The most common SW instrument is UV_{254} sensors which measure the absorbance at 254 nm with the absorbance at 550 nm for particle compensation. UV_{254} sensors can generate surrogate parameter - SAC254 to determine dissolved organics and provides measurements of correlated parameters such as DOC and COD [5]. These surrogate parameters determined by the sensors are generated based on the correlations (often linear) of UV_{254} absorbance and parameters which indicate organic matter in the water. This concept is used by some commercial instruments including the HACH UV probe [26], Burkert SAC254 sensor [27], and YSI UV-Vis sensor, which employ a single wavelength (absorbance at 550 nm) to compensate for particle effect. These instruments are SW instruments, in many cases, that utilise absorbance at 254 nm to determine the concentrations of a particular parameter such as DOC.

In comparison to the SW UV sensors, UV-Vis spectral or full-spectrum sensors record the absorbance of a certain band of wavelengths or full spectra. These sensors produce fingerprints of spectra which are then employed to determine and calculate concentrations of water quality parameters based on built-in algorithms of the instruments. The spectral sensors can provide measurements for various parameters such as UV_{254}, colour, DOC, and turbidity using the algorithms. These instruments are generally factory calibrated for the particular water quality parameters using their proprietary algorithms with site-specific re-calibration options. The instruments built-in proprietary algorithms are first used to remove the particle effect on the measurements of the water to replace the physical filtration step [1]. Some instruments such as IQ Sensor NET provide surrogate parameters for DOC and COD. However, the results gained from these instruments are not comparable to standard laboratory methods without specific calibration. This is because the correlations between the surrogate and standard analytical methods depend on the compositions of the water [21]. Re-calibration is often needed if significant changes happen in the compositions of water [21, 28] which is different to the specific water type applied in the original algorithm development [1].

Comparing the performance of full-spectrum and SW sensors, SW sensors can provide measurements and trends of the parameters varied during certain periods. SW sensors may not be able to compensate for particle effect accurately, particularly when comparing the results with the standard laboratory procedures and measurements. The SW sensors may only provide a rough surrogate measurement of organic content, and total nitrogen content of nitrate and nitrite, but do not have accurate particle compensation for most surface waters. In comparison, the spectral sensors provide better particle compensation and can be calibrated to specific locations with higher accuracy. Spectral sensors are better for precise applications, such as real-time water monitoring and treatment process. In addition, calibrations of online sensors are based on the grab sample collected at the same time of the measurement compared to laboratory measurement of the same water sample. These calibration procedures are more susceptible to the errors of grab samples.

Table 2-1 Summary of common online UV-Vis instruments for water quality monitoring and process control.

Sensor	Manufacturer	Optical system	Measured wavelength	Measured parameter	Advantages	Accuracy	Operating range	Source
AMI SAC254	SWAN, Switzerland	Two-wavelength photometer with one optical channel, light-emitting diode (LED) light	254 nm	Surrogate parameter to determine dissolved organics	Measuring interval: 30 sec to 3 min	± 1% m^{-1}	UV absorption: 0-6 mg/L DOC, TOC: 0-6 mg/L SAC254: 0 to 300 m^{-1} Temperature: 5-30 °C	[29]
ProPS-UV Photometer	Trios GmbH, Germany	Dectector type: UV spectrometer, light source: deuterium lamp	200 – 385 nm	nitrate, CODeq and TOCeq	Customize path lengths, Spectral analysing software, Additional calibration functions	± 0.01% mg/L	Temperature 0-30 °C, 32-86 °C; Measuremnts: 0.62 – 600 mg/L	[30]
IQ Sensor NET	WTW GmbH, Germany	256 channel silicon photodiode array detector, deuterium lamp	200 - 720 nm	A range of parameters, eg. SAC, UVT	Data logger	± 3% mg/L	SAC: 0.0-3000m^{-1} Temperature: 0-45 °C	[31]
spectro::lyser	s::can Messtechnik GmbH, Austria	256-pixel photodiode array detector, xenon flash lamp	200 - 720 nm; 220 - 390 nm	Various parameters	Various parameters Differ path lengths	± 2% mg/L	Temperature: 0-45 °C; TOC: 0 -180 mg/L; NO$_2$-N: 0-40 mg/L; NO$_3$-N: 0-100 mg/L; UV$_{254}$: 0-500 abs/m	[32]
Real UV254 probe	RealTech, Germany	Mercury UV lamp and LED lamp	253.7 nm	SAC254	Various parameters Various path length Field calibration	± 5% m^{-1}	Temperature: 0 to 45°C UV254: 0-20 abs/cm	[33]
UV absorption sensor	Endress+Hauser, Switzerland	Hotovoltatic cells detector, low-pressure mercury lamp	254 nm	SAC254	Data logger	± 3% m^{-1}	0 - 2.5 abs/cm 0 to 90 °C	[34]
IQ SensorNet system	YSI, Germany	Detector: LED and phtotdiode	254 nm	UVT-254 and SAC254	Has a controller	± 2% m^{-1}	Temperature 0 to 45 °C; UVT-254: 0-100; SAC254 0- 3000 m^{-1}	[35]

2.2.1 Water Quality Measurements with Proprietary Algorithms

Some advanced full-spectrum online UV-Vis spectrophotometers can determine a range of water quality parameters including UV$_{254}$, colour, DOC, turbidity and nitrate. The parameters can be computed through the instrument built-in proprietary algorithms. These algorithms were developed based on chemometrics techniques, such as partial least squares (PLS) and multiple linear regression, to establish the relationship between UV-Vis spectra and laboratory measurements of water samples [14]. The algorithms were created by hundreds of global datasets containing both UV-Vis spectra and reference laboratory data obtained from a wide range of water quality [14]. Instruments have default configurations to apply the generic calibration for particle compensation to the raw spectral data using the built-in algorithms.

UV_{254} measures the amount of light absorbed by conjugated organic compounds. UV_{254} systems have been widely used as a rapid water quality measurement technique to control water treatment processes [36]. UV_{254} from the online UV-Vis instruments based on built-in algorithms generally performs well for the treated water as less interference exists [1]. However, site-specific calibrations may be needed if it is used for source water with a complex matrix. It is more difficult to judge the accuracy of the colour measurement using the online UV-Vis instruments, as the standard laboratory colour measurement method relies on SW measurement. Besides, the wavelength selected to measure colour may be different based on regions and water sources. For instance, 456nm is used in Australia and USA while 410 nm is applied in Russia to measure colour in natural water [37]. To measure the colour of water, the online instrument needs to be set up according to the required wavelength. DOC is used to monitor water quality from catchment to tap water. The measurement is usually carried out using the laboratory-based standard method. Online UV-Vis instruments with built-in algorithms can be applied as alternative measurements. However, they are frequently reported as water-specific and lacking accuracy. Thus, additional calibrations against different water matrices are needed [38]. Turbidity determined by the online UV-Vis spectrophotometers with the generic built-in algorithms is comparable to the turbidity results analysed in the laboratory [39, 40]. Nitrates generated from the online instruments with the generic built-in algorithms are generally not satisfactory [39]. It was reported that the results are comparable with laboratory analysis [40]. This could be related to the specific algorithm employed and the monitoring application.

The measurements of water quality parameters using the online UV-Vis spectrophotometers are often source-water dependent. Thus, additional site-specific calibrations are needed to improve the accuracy of measurements [14, 21, 41-43]. The site-specific calibration function provided to enter the laboratory determined values of the collected grab samples measured at the same time by the online instrument. The site-specific calibration process involves modifying the slope and intercept of the built-in regression function using laboratory data from the reference grab samples [21, 41]. To achieve the best calibration results, grab samples are needed to be representative and cover the whole measurement range of the water. Measurement accuracies can be enhanced with the use of an increased number of grab samples for the calibrations of the online UV-Vis spectrophotometers.

Applications of online UV-Vis instruments can reveal that the significant fluctuations in water quality could affect the accuracy of the measurements and long-term monitoring required regular calibration to compensate for the variation of particle character issue [1, 3, 41]. A site-specific calibration was conducted for a submersible UV-Vis instrument to monitor water quality in a forested catchment and comparable results were achieved [42]. In contrast, a site-specific calibration was performed for a UV-Vis submersible instrument to measure the water quality of stream water, but concentrations were overestimated because of inaccurate particle compensation [43]. Therefore, accurate site-specific calibration of the UV-Vis instrument is crucial to obtain measurements for water quality monitoring.

Calibrations of online UV-Vis instruments should be performed as needed for situations such as new instruments, location changes, and poor accuracy. Routine calibration may not be necessary for monitoring less variable source water or stable water quality such as treated water. However, routine verification of the measurements using lab references is recommended to ensure the accuracy of the instruments [38]. Site-specific calibrations have been approved to achieve the desirable measurement outcomes and can adequately account for the differences in large water quality changes or between different types of water [6, 19, 44-46].

2.2.2 User Developed Algorithms for Spectral Absorbance Measurements

A water engineer may have difficulties obtaining accurate continuous measurements using online UV-Vis spectrophotometers with or without the instrument built-in algorithms, alternative particle compensation (calibration) techniques can be developed by end-users. To better utilise the online monitoring instruments with low maintenance costs, and more importantly gain in-house experience and knowledge of the instruments, researchers and water utilities want to seek alternative techniques for particle compensation to the built-in particle compensation methods. The particle compensation techniques based on the UV-Vis spectra can be categorised into direct subtraction compensation and chemometric modelling. Table 2-2 summarises particle compensation techniques from the literature for online water quality monitoring using the UV-Vis instruments.

Direct subtraction compensation is based on the absorbance of wavelength characterised by the particles in the water [14, 59]. Wavelengths: 275 nm, 350 nm, 545 nm, 546 nm and 550 nm have been utilised to characterise the particles in the water and to remove the particle effect from the UV-Vis measurements [47-49]. The absorbance at 546 nm was used to remove the particle effect on the COD in river water [48]. The wavelength at 545 nm was employed to reduce the particle influence on the UV for surface water [49]. The wavelength at 550 nm is commonly selected for SW particle compensation for individual water quality parameters and has been commonly applied for UV_{254} measurements [1]. UV at 350 nm has been utilised to compensate for the online measurements of COD using UV spectrophotometry to detect groundwater quality to remove the influence from particles [47]. Absorbance at 275 nm was used in some case studies to compensate for nitrate at 220 nm. Figure 2-2 shows an example of using a SW particle compensation method to remove the particle influence on a raw spectrum for surface water [1].

Table 2-2 Summary of indirect particle compensation methods for online water quality monitoring.

Methods	**Wavelengths (nm)**	**Parameter**	**Data type**	**Sources**	**Source**
SW	350 nm	COD	Lab	Ground water	[47]
SW	546 nm	COD	Lab	Simulated water samples	[48]
SW	545 nm	UV_{254}	Lab, field	Surface water	[49]
SW, MSC	550 nm	UV_{254}	Field	Surface water, treated water	[1]
Two wavelengths	254, 340 nm	DOC	Field data	Surface water	[50]
MSC	Full spectra	COD	Lab	Stream water, Simulated water	[51]
PLS	200-400 nm	COD	Lab	Lake water	[22]
PLS	Full spectra	DOC		River water	[52]
PLS	full	Nitrate	Lab	Simulated water	[53]
PLS	380-750 nm	Nitrate, TOC, COD	Lab	Seawater	[54]
PLS	Full spectra	assimilable organic carbon	Pilot	Simulated lake water	[55]
MSC, PLS, PCR	250 -740 nm	DOC	Field	Surface water	[21]
PLS, lasso regression, and MSR	Full spectra	Nitrate, DOC	Field	Brackish water	[56]
MSR	250, 290, 307.5, 437.5, 447.5, 630, 645 nm	DOC, Fe	Lab, Field	Stream water	[20]
PLS, MSR, local and global	250 – 740 nm	DOC	Field	Surface water	[57]
Multiple linear regression	260, 265, 280, and 285 nm	TOC	Lab	Drinking water, seawater, river water	[24]
SVM	Full spectra	Nitrate	Lab	River water	[58]

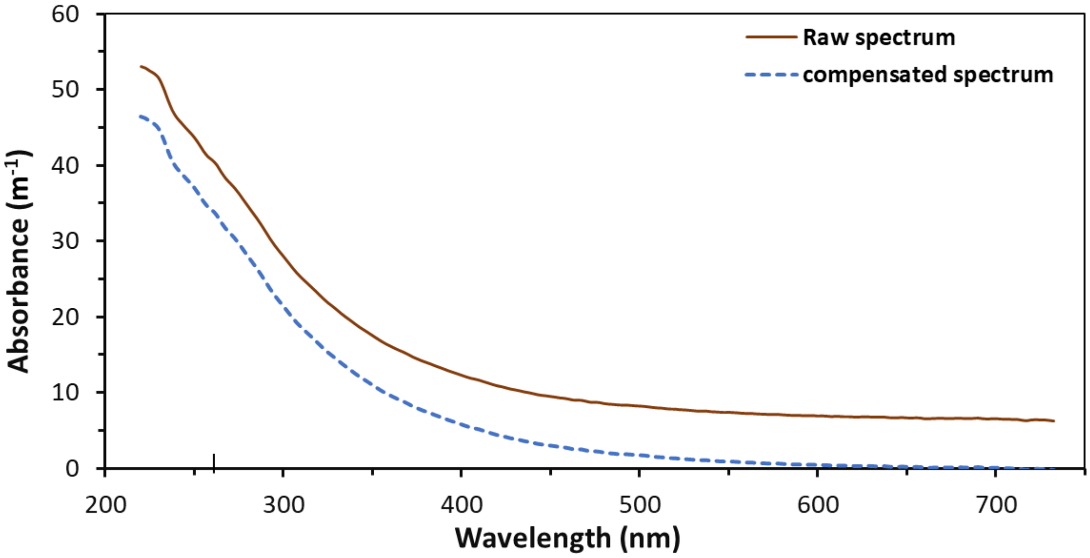

Figure 2-2 Illustration of particle compensation of a raw spectrum for surface water using a single-wavelength method.

Multi-wavelength particle compensation techniques, also called chemometric modelling, include a selection of chemometrics such as multiple linear regression (MLR), multiple stepwise regression (MSR), support vector machine (SVM), support vector regression (SVR), multiplicative scatter correction (MSC), principal-component analysis and PLS. The multi-wavelength particle compensation technique is based on relationships between the raw spectra and laboratory reference values of the water quality parameters. The MLR determines the linear relationship between a dependent variable (the laboratory values) and independent variables (wavelengths of the raw spectra) which can directly define the coefficient of each variable. MLR was employed to remove the particle effect on the UV-Vis spectra of brackish water for rapid measurement of water quality parameters [56]. Multiple linear regression was also used to quantify DOC content in the stream water [20] and TOC in the drinking water, seawater and river water [24]. Multiple stepwise regression was utilised to compensate for the particle effect on the DOC measurements for surface water [57]. SVM is a machine learning algorithm that can be used for classification, regression, and outlier detection. SVM was employed to determine the concentration of dissolved nutrients in surface water using the full spectral wavelengths and laboratory values and demonstrated the effectiveness of the approach [58]. SVR is a similar machine learning method as SVM but works with continuous values instead of classification as SVM. SVR was applied to predict the combined nitrate and nitrite concentration for treated water samples using spectral features and the predicted values were matched with the standard laboratory values [60]. MSC is a normalization technique to correct particle effect on spectra by changing the scale and the offset based on the reference spectrum which is the mean of the spectra. The MSC method was applied to compensate for the particle effect on the COD in lake water [22], UV_{254} in reservoir water [1], simulated surface water [51], and DOC in drinking water production [52].

PLS constructs components by projecting the predictor variables to a new space. Then the linear regression models were built between new predictors and responses. PLS can be utilised to extract important information from a large data matrix [61]. PLS regression is a commonly utilised method to remove the particle effect on the measurements of water quality parameters based on the multiple wavelength spectra. It has been used to remove the particle effect on the water quality multi-parameter such as COD in artificial seawater [62], suspended solid in brackish water [56], COD in lake water [63], COD and TOC in seawater [54], stream water [20], nitrate in water [53], nitrate and nitrite in seawater [64], DOC in surface water [57] and drinking water [52], ozone in drinking water [55].

The use of a subtraction method for particle compensation generally works well for low and medium turbid source water and treated water, but may lead to less accurate measurements in some cases such as highly turbid water [50, 57]. The accuracies of the measurements such as DOC in the surface waters can be improved by using the multi-wavelength particle compensation methods. Water matrix specific particle compensation is frequently recommended for water quality monitoring. There are some benefits of using alternative particle compensation methods to the built-in algorithms. Firstly, it creates simplicity and flexibility of custom-made particle compensation methods for water quality measurements of particulate water matrix as the details of the built-in algorithms for the commercial online instruments are often not accessible to the users. Secondly, the employment of alternative particle compensation methods can lower the calibration costs of the instruments. Moreover, cost-effective UV-Vis instruments with a single wavelength or short wavelength band could be employed in the field to monitor water quality instead of using full-spectrum UV-Vis instruments.

2.3 Advanced Spectral Data Processing and Applications

UV-Vis spectrophotometers can be used for real-time water quality monitoring and integrated with early warning systems to detect rapidly changing water quality. Water quality parameters including turbidity, SAC254, nitrate, TOC and DOC can be monitored and provide early warning. The warning occurs when the current measurements exceed limits that are specific to each parameter or anomalous patterns are detected [65], then the appropriate actions can be taken. One example is to monitor spring water. The spring water of concern would not be utilised for drinking water production when the measurements go beyond the limits of the measuring parameters [66]. The anomaly detection methods using the UV-Vis instruments can be easily configured for real-time monitoring of water pollution and early warning [24, 65, 67].

UV-Vis spectra contain valuable information on the composition and quality of water and can be used as a fingerprint of the water matrix. The fingerprint can be utilised to derive specific parameters such as turbidity and DOC. Online UV-Vis instruments have fingerprint which can also be employed to monitor changes in the water composition and offers the possibility to set alarm levels based on the magnitude of the variations in the spectra and early warning systems by water utilities [25, 68]. It is an advanced spectral data processing and can be applied for early warning of anomaly detection and identification of contaminants. Online UV-Vis instruments have been used by some water utilities to develop early warning systems to monitor drinking water quality at the source or in the distribution system for water quality control as a component of the drinking water quality management system. It can detect not only natural contamination but also accidentally or intentional contamination.

2.3.1 Anomaly Detection of Water Quality

Water utilities could face minor and major water quality incidents. Concerning major events can occur due to extreme concentrations of water quality contents or pollutants or accidents of pollutant events. Rapid fluctuations in source water quality could happen. For instance, turbidity and organic matter could be suddenly raised by storm events. Quick detection of the water quality in response to the contaminant events is essential to reduce risks when water quality events occur. The use of online UV-Vis instruments allows near- or real-time detection of anomalies and contaminations of drinking water systems. Early detections are vital for effective responses that reduce or prevent contamination events that compromise water quality and avoid possible failures of WTP operation [68]. The utilisation of water quality anomalies detection from UV-Vis spectra contributes to the safety of water quality. Detection using UV-Vis spectra for water quality monitoring is mostly applied for organic contaminant monitoring as UV-Vis monitoring has the advantage reported earlier, without the need for sample preparation, regent-free, and low operational cost compared to standard laboratory analysis of organics [24, 69, 70].

An anomaly detection method may have three components: data analysis, event detection and performance assessment, which are able to provide a reliable indication of contamination by analysing the real-time water quality data [69]. The first step is to establish a baseline of the stable water quality in the normal condition. Data analysis is to remove the particle effect, instrument noise, and drifting from the water quality measurements. Event detection is to analyse the real-time water quality data by comparing the pattern of new data with the pattern of normal data based on machine learning and chemometrics. Performance assessment is to evaluate the detection method to meet the required accuracy [69].

A proximate entropy approach was applied to measure UV-Vis spectra and differentiate normal and abnormal spectra of water in distribution systems. This method had a good detention outcome [57]. In addition, the fitness measure combined both Pearson correlation and Euclidean distance was assessed as a technique to identify contaminated water from drinking water using a submersible UV-Vis instrument in a controlled study [71]. The method was flexible to identify the source of water and distinguish the contaminated water. This method was further tested to cope with various backgrounds with changing proportions of water from different sources using a combination of UV-Vis spectral data from both laboratory experiments and an operational water supply system [67]. The detections were based on combinational changes in water sources, operational, and maintenance actions. Contaminants at low concentrations were detected.

2.3.2 Early Warning Systems for Water Supply

An early warning system integrated with a UV-Vis spectrophotometer has been extensively tested in a lab-scale and achieved robust results. The early warning system is able to detect and quantify specific compounds, but also detects unknown compounds that do not fit in the normal fluctuation of the water matrix [72]. Alarm parameters can be developed from the spectral data. Abrupt spectral signals can be extracted by using anomaly detection techniques. The process of alarm development of water quality monitoring includes a learning period, abnormality definition, alarm level definition and sensitivity definition [73]. Various methods have been employed to identify anomaly events, such as probabilistic principal component analysis (PPCA), Bayesian algorithm, principal component analysis, and Euclidean distance method [65, 74, 75]. A PPCA based method was used to identify anomaly events with the employment of online UV-Vis instruments. PPCA algorithm was utilised to simplify the large number of spectra data and retain the essential spectral information. It was tested for online water quality monitoring in a small-scale water distribution system [75]. The PPCA method was combined with a multivariate monitoring chart to provide a reliable and flexible alarm system. Bayesian algorithm combined with a UV-Vis spectrometry probe along with a message-passing schedule was applied to analyse patterns for event classification. It was conducted for long-term online monitoring of the water distribution system in a pilot-scale [76]. Water quality anomalies were detected using the integration of principal component analysis and chi-square distribution combined with UV-Vis sensors for a distribution system. It was conducted in a pilot-scale and proved to be a promising method [74]. In addition, an early warning system was employed for remote river water quality monitoring for COD content and early detection, which had real-time display and storage and warning functions [35].

Early warning systems need to be able to identify whether variation in sensor measurements is caused by equipment noise, and presence of contamination or high levels of concentrations. Pearson correlation Euclidean distance-based method, multivariate Euclidean distance method and linear prediction filters method have been applied to detect changes in water quality and differentiate between fluctuations caused by equipment noise and those due to contamination [77]. This method was able to detect 95% of contamination events correctly with a 2% false alarm rate from a contaminant injection experiment [77]. The Pearson correlation Euclidean distance method was applied to a real contamination accident study, the results showed that this method has better potential to be used in the field [76].

Various water quality detection methods based on UV-Vis spectral data have been developed and assessed. However, the evaluation of detection performance is mainly based on simulation or laboratory study. Reported evaluation of detection performance was rarely based on real contamination events. There are arguments that lab- and pilot-scaled studies may not cover the variation of water quality that occurs in the actual water systems as real water quality data may contain more background noise and fluctuations [76]. Therefore, it is important to test the detection method in a real water event situation.

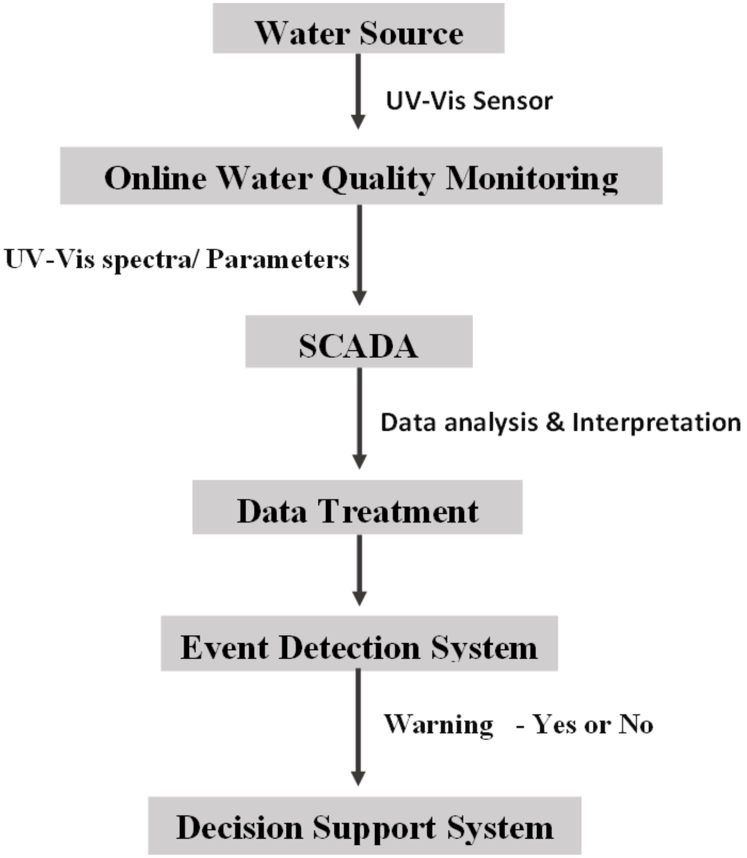

Figure 2-3 Structure of an early warning system.

2.3.3 Integrated Early Warning and Real-time Control System

An integrated early warning and real-time control system for drinking water combines the functions of water quality monitoring, early warning system and decision making. It is an integrated approach to detect and respond to water quality events that use advanced monitoring technologies to provide warnings of potential contamination incidents and quick responses [75]. An integrated early warning system should contain an online monitoring system, supervisory control, and data acquisition (SCADA), event detection system, and decision support system as shown in Figure 2-3. Event detection provides indications of abnormal water conditions. Early warning systems should be able to quickly detect water quality and contamination events with high levels of accuracy, reliability, cost-effectiveness, user-friendly, and low maintenance [78]. An integrated system with event-driven functions for detecting, reporting, and handling water quality contamination events automatically in real-time.

An integrated system can provide water quality monitoring and warning performances to monitor hazard and forecast hazard evaluation, and issue timely and accurate warnings of water quality anomalies. It fits well with the drinking water management system. Online UV-Vis instruments have been employed as part of the integrated system to continuously provide water quality data. Studies have been conducted by deploying UV-Vis instruments for real-time online analysis of water quality and anomaly detection, particularly in Europe and the United States [78]. A semi-supervised learning model combined with UV-Vis spectra was used to detect organic contamination events successfully in water distribution systems. This adaptive method modified the baseline using dynamic orthogonal projection correction and adjusts the support vector regression model in real-time [79]. Discrete wavelets transform and principal component analysis can also be applied for detecting organic contamination events from UV-Vis spectral data. This approach was tested online using a pilot-scale setup and experimental data [65]. Abrupt changes in the spectra were captured, and an alarm of contamination event was able to be identified.

Another event detection approach is based on UV-Vis signal processing and data-driven techniques. Early warning systems combine automatic measurements with automatic data evaluation and data transfer for water quality monitoring such as surface water [80]. A web interface of the system works as a control centre constantly checking for anomalies in water quality based on automatic data evaluation. Maintenance can be reduced as remote checking of water quality is available [81].

2.4 UV-Vis Spectrophotometer Application and Integration of the Water Quality Management System

The online UV-Vis spectrophotometers can continuously measure water quality online in real-time. UV-Vis spectrophotometers have a broad application in drinking water networks from monitoring source water quality, treatment processes and treated water as part of the drinking water quality management system. Many reported studies of the online instruments have been conducted in the lab-scale as shown in Table 2-2. It has been widely recognised in the water industry that current applications of UV-Vis instruments in real-time for water quality monitoring remain limited. There is an increasing trend of using online UV-Vis instruments, especially in water quality monitoring and process control and as early warning systems [82]. The use of online UV-Vis instruments for water quality monitoring allows for better water quality management compared to conventional water quality monitoring, as it supports continuous updating of water quality and can detect any potential water quality events and provides timely decision support. The ability of online UV-Vis instruments to detect issues in real-time to allow rapid response to any water quality event is valuable to the water quality management system [83]. It also allows for real-time understanding of operational causes which in turn contributes to the optimisation of the water treatment processes.

2.4.1 Requirements and Supports of Using Online UV-Vis Spectrophotometers in Real Operations

Online water quality monitoring using spectrophotometers allows fast and effective responses to water quality events. Online UV-Vis instruments have been employed for determinations of process upset or deterioration in water quality, as well as operation and control of the drinking WTPs. Applications of the online UV-Vis instruments in water treatment and distribution networks can identify water quality parameters such as nitrate and organic pollutants rapidly, and measure and analyse the parameters simultaneously. An illustration of applications of online UV-Vis sensors for real-time water quality monitoring and process control is shown in Figure 2-4. Field applications of online UV-Vis spectrophotometers were summarised in Table 2-3. Most field applications of the online UV-Vis instruments were on water quality monitoring. Some case applications were conducted on anomaly detection and early warning system. Very few cases were employed for process control of drinking WTP.

The most important applications of UV-Vis instruments are monitoring of the source water and treatment process control [25]. Field applications of UV-Vis instruments showed that the instruments are suitable for the estimation of DOC concentration. A study assessed the performance of a portable UV-Vis spectrometer in measuring DOC concentrations of surface water under the field condition [57]. It demonstrates the possibility of facilitating rapid, robust and continuous measurements. A contaminant warning system was developed in Texas, USA to monitor the drinking water quality in the distribution system [84]. This warning system consisted of online UV-Vis instruments which provide continuous analysis at 16 checkpoints in the distribution system. Anomalies are constantly checked for water quality parameters such as nitrate, total chlorine turbidity, TOC, conductivity, UV_{254}, DOC, pH, and free ammonia. All the information is web-accessible to the operators for the detection of water quality changes at treatment plants.

The operation of drinking water treatment plants is mainly based on laboratory analysis data of grab samples and the experiences of operators. In recent years, there is an increasing need of using model-based monitoring for the optimisation and control of water treatment plants. However, most studies were conducted in lab- or pilot- scale. The use of model-based monitoring has shifted the operation of drinking WTPs from experience-driven to knowledge-based [28]. Modelling in combination with online monitoring and real-time control can improve the treatment operation, leading to better control of more stable water quality [85]. An online UV-Vis instrument was used for feed-forward coagulant dose prediction to avoid the increase in turbidity of settled water and support the operation of a WTP. The predicted coagulant doses were used as inputs of the plant control system to automatically control the coagulant dose in response to the online measurements of raw water quality [86].

The online UV-Vis instruments combined with advanced data analysis techniques such as machine learning allow real-time water quality monitoring and provide valuable tools for effective water quality management. The combination of real-time water quality data and advanced data analysis techniques can be efficient for the management of water quality. The recent advances in technologies enable the application of web-based data platforms for analysing real-time data for water quality management. Efficient and real-time monitoring of water quality as a key component of water quality management can predict future trends of water quality and enable rapid response to water quality events [83].

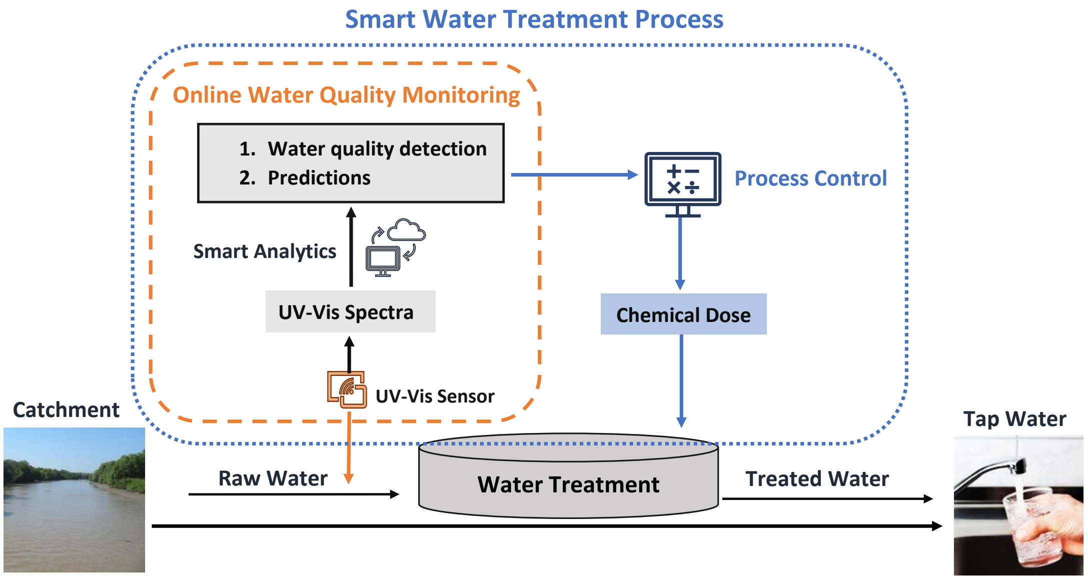

Figure 2-4 Applications of online UV-Vis sensors for real-time water quality monitoring and process control.

Table 2-3 Summary of field applications of online UV-Vis spectrophotometers.

Water type	**Application**	**Measurement**	**Location**	**Reference**
Surface water	Rea-time Monitor testfilters	DOC, TOC	Danuba Island, Austria	[87]
River water	Real-time Monitor water quality	Nitrate, DOC, TSS	Kervidy-Naizi, West France	[88]
Stream water	In-situ Monitor stream DOC	DOC	South Korea	[89]
Drinking water	Online monitoring and process control	Surrogate A_{254}, A_{202}, A_{290}, A_{310}, A_{350},	SA Water, South Australia	[90]
Drinking water	Early warning system in the drinking water supply	Nitrate, TOC, SAC254	Bratislava Water Company Austria	[91]
Drinking water	Coagulant control	Turbidity, alum dose	Morgan WTP, South Australia	[86]
Drinking water	Measure dissolved ozone and AOC concentrations	Assailable organic carbon	Vienna Waterworks, Austria	[55]
Filtered water	Real-time Monitor water quality	UV254	SA Water, South Australia	[19]
Lake water	Monitor variation of carbon content	DOC using Absorbance at 285 nm	Lake Ipê, MS, Brazil	[23]
Surface water	Measure DOC content in situ	DOC	Europe	[21]
River water	Monitor water quality in situ	DOC, Fe	Krycklan river, Sweden	[20]
Surface water	Monitor dissolved nutrients in real-time	Nitrate	Windsor, Canada	[58]
Groundwater	High-resolution monitoring	Nitrate	Southwest Ireland	[41]
Stream water	Monitor storm events	DOC	Haean Basin, South Korea	[43]
River water	Real-time Monitor of water quality	NO3-N, DOC	Saarland	[46]
Spring water	Online monitoring	SAC254, Nitrate, TOC, DOC	Vienna Waterworks, Austria	[66]
Treated water	In situ anomaly detection	Spectra	Hangzhou, China	[92]
Drinking water	Online monitoring anomaly in water distribution systems	Spectra	Hangzhou, China	[75]
River water	Real-time monitoring	COD	Jialing River, China	[35]
Groundwater	Early warning	Nitrate, nitrite	Vienna, Austria	[80]
Drinking water	Contamination warning system	Spectra	Dallas, US	[84]
Fresh water	Simultaneous determination of nitrate and nitrite	nitrate and nitrite	UK	[30]
Spring water	Online Water-Quality Monitoring	SAC254	NW Switzerland	[34]

2.4.2 Challenges and Solutions of Using Online UV-Vis Spectrophotometers

Many studies have shown that online UV-Vis spectroscopy can detect water quality changes, such as rapid detection of changes in the raw water quality, and allow for real-time adjustment of process. There are still challenges remaining for the practical applications. There is a lack of harmonisation of standards and regulatory practices in using online instruments for water quality monitoring [3]. Some regulatory guidelines of drinking water only mention online instruments in general terms. It is important to highlight the need for accurate measurements and recommend online continuous monitoring of water where possible. One of the main issues is the detection limit as the field environment is complex. Another issue is the difficulty to detect the UV-Vis spectra of some pollutants in the water, such as suspended solids, dissolved inorganic substances, and pathogenic microorganisms. Most of the difficulties in using the online instrument are caused by the highly challenging nature of the source water. Solutions were developed to allow realisable monitoring of the source water, including determining appropriate manual cleaning intervals.

UV-Vis instruments generally work well for real-time monitoring of treated drinking water as fewer interferences exist [58]. However, it has experienced measurement issues in field applications for source water quality monitoring, particularly surface water that has complex chemical compositions. Field experience shows that the path lengths of the UV-Vis instruments had a significant influence on the sensitivity and the range of water quality parameters [41]. The selection of path length is related to the water matrix. The sensitivity increases with the path length. A longer path length leads to a higher sensitivity but a reduced maximum concentration level at which the instrument can operate [82]. The typical path length is within 0.5 - 100 mm. Normally, a path length of 100 mm is suitable for drinking water, 35 mm and 10 mm for surface water and 5 mm for wastewater applications. The natural variation occurrence can be determined, which requires measurements of the fingerprint spectrum across several months for training and local calibration of the instruments.

In the absence of site-specific calibration, the determination of DOC concentration can be inaccurate due to varying absorbance strengths of the interference of other elements in the water [57]. For instance, absorbance measurements can be influenced by changes in the source water [1]. The accuracy of the water quality measurements can be affected if the content such as turbidity or organic matter varies after the instrument has been calibrated to a particular water matrix [41]. Corresponding laboratory data should cover the seasonal variations of the site-specific water source for calibrating the instruments. Regular validations of the online measurements are needed to eliminate temporal drifts and maintain accuracy. The re-calibration of particle compensation could be complicated if the water matrix varies significantly and lacks support from experts.

Water operators may face various challenges in the use of the online UV-Vis instrument, including instrument maintenance, installation, data processing, and variability in parameter performance. Typical issues and solutions associated with the online UV-Vis spectrophotometers are summarised in Table 2-4. An example of installation issues of the online instrument is the accelerated probe corrosion issue caused by the jetty cathodic protection system in monitoring river water [82]. The solution to this problem was to use an ‘on-demand’ pump sampling system to protect the instrument from corrosion, reduce fouling by silt and biofilm, and reduce the maintenance requirements.

Potential data storage and processing could be problematic in the online monitoring using the UV-Vis instruments. Online instruments can collect and store some acquired data but are not able to collate the data for easy access and interpretation. Pre-processing of the UV-Vis spectra data is required to assure the data quality, including the removal of faulty spectra and outliers, as well as the performance of particle compensation. The issue of data processing is that standard data storage and analysis programs such as Microsoft Excel cannot handle the large volume and high dimensional complexity of the UV-Vis spectra data. Development has been made in data processing with specialised tools to tackle the challenges [78]. An example of the specialised software, Visual Basic 6.0, has functions such as selective display of water quality parameters, automatic detection of invalid data, automatic deletion of invalid data, the exportation of data from selective periods, and also data resolution options that allows easier plotting of long-term data [38]. Advanced systems need to be suitable for instrument operation in the long term. Expertise is needed to design and troubleshoot the program, and the data analytic system is needed to link with the control system, such as SCADA. An open-source Python toolbox called 'AbspectroscoPY' was developed for pre-processing and analysis of the large volume of raw UV-Vis absorbance time-series data [10]. The toolbox has the functions of automated outlier detection and removal based on the interquartile range. Some online UV-Vis Spectrophotometers only provide water quality parameter data, in which case a simple data logger can be built to manage data collections. For example, a web data extraction was built with a Python library and data store to automatically monitor the water quality of reservoirs [31].

Table 2-4 Challenges and solutions of using the online UV-Vis spectrophotometers.

Challenges	**Causes**	**Solutions**	**Source**
Installation issues	Probe corrosion issue	Use 'on-demand' pump sampling system	[38]
Measurement accuracy	Missing calibrations Low water level	Proper calibration in-situ and maintenance, Pump water to the instrument	[93]
Detection difficulty	Challenging nature of the source water	Site-specific compensation, Regular maintenance, Select the correct pathlength, Develop surrogate parameters	[41, 82, 90]
Data processing	Large volume of data, Data type, Faulty data	Use or develop specialised tools, Expertise	[10, 38, 78, 90]
Maintenance cost	Calibration issue	Use alternative particle compensation method, Provide training for maintenance skills	[38]

To achieve the best outcomes of water quality monitoring and process control using online UV-Vis sensors, the following operation steps are needed: (1) the instruments should be calibrated for new sites or source water change over, (2) pre-treatment of the UV-Vis spectra should be performed to eliminate the errors and particle effect, and

(3) forecast methods should be developed to employ the online monitoring in real-time for water quality monitoring and water treatment process control. There are two approaches to applying the online UV-Vis instruments for water quality measurements: direct water quality parameter measurements from the built-in algorithms and indirect measurements through the combinations of chemometrics and UV-Vis absorbance time series from the instruments.

2.4.3 Future Research of Online UV-Vis Spectrophotometers

The future trend of the application of online UV-Vis instruments is that the instrument will be a key component for water quality monitoring as a part of drinking water quality management. As most of the reported studies on the use of online UV-Vis instruments were conducted in lab- or pilot-scale, future work is needed particularly for large-scale applications such as field applications. To have correct measurements, it is necessary to have trials when the instruments are used for new sites. A site-specific particle compensation (calibration) may be needed. The difference in the methods of determination of various water quality parameters is also a challenge for practical applications. Further studies are necessary to find out the best solutions for the specific applications. A possible solution is the detection of water quality parameters based on multiple data fusion technology. It evaluates the analysis of different water quality parameters data and extracts more completed information than a single data source [15].

Future research needs to include the progress in the field application of UV-Vis instruments. Real-time monitoring using UV-Vis instrument combined with advanced data processing can provide real-time measurements for rapid data analysis, which in turn, contributes to the real-time water quality management system. Integration of the instrument and data analytics for data pre-treatment and processing is a key factor for measuring UV-Vis spectra in real-time [15], allowing anomaly detection and building early warning systems. Data analytics of water quality data using the UV-Vis instruments combined with data platforms have capabilities to automatically analyse and correct data in real-time, then predict to improve water quality monitoring and process control. Since each water quality detection method based on the UV-Vis spectra has its strengths and drawbacks, multiple methods should be conducted to assess their performance and analyse which methods can be used to construct decision support tools for the optimisation of a particular WTP [81]. The future application of the UV-Vis instrument also includes exploring the use of raw spectra as inputs to determine the measurements of other water quality parameters. With the assistance of chemometrics such as PLS and artificial neural networks [61], more accurate measurements can be obtained [2].

2.4 Conclusions

This review covers the practical aspects of the employment of online UV-Vis spectrophotometers for water quality monitoring and process control, particularly, techniques for industrial applications. The recent studies on online UV-Vis spectrophotometers for drinking water quality management have been discussed. Commonly employed online UV-Vis instruments for drinking water were briefly introduced. Water quality parameters, including UV_{254}, colour, DOC, turbidity and nitrate, can be directly generated from the built-in algorithms of the online UV-Vis instruments. Site-specific calibrations can be conducted to improve the accuracies of the measurements if the generic built-in algorithms are under-performing for a water source. Alternative particle compensation methods to the built-in particle compensation method were detailed. These methods are based on the UV-Vis spectra of water and chemometrics which offer simplicity and flexibility in removing particle effects from the measurements. Various techniques of anomaly detection and early warning were also discussed to monitor water quality at the source or in the distribution system for water quality control as a part of the drinking water quality management system. As most studies of online UV-Vis instruments in the drinking water area were in the lab- and pilot- scale, future work is needed particularly for industrial-scale applications. Issues and potential solutions to using the online instruments were provided. Future research also needs to work towards the integration of early warning and real-time water process control systems for water quality management.

2.5 References

1. Shi, Z., Chow, C.W., Fabris, R., Liu, J., Jin, B., *Alternative particle compensation techniques for online water quality monitoring using UV–Vis spectrophotometer*. Chemometrics and Intelligent Laboratory Systems, 2020. **204**(104074).
2. Li, P. and J. Hur, *Utilization of UV-Vis spectroscopy and related data analyses for dissolved organic matter (DOM) studies: A review*. Critical Reviews in Environmental Science and Technology, 2017. **47**(3): p. 131-154.
3. Waterra, *Optimisation of existing instrumentation to achieve better process performance*. 2017, Water research Australia.
4. Van den Broeke, J., Carpentier, C., Moore, C., Carswell, L., Jonsson, J., Sivil, D., Rosen, J.S., Cade, L., Mofidi, A., Swartz, C. and Coomans, N., *Compendium of sensors and monitors and their use in the global water industry*. 2014, Water Environment Research Foundation: IWA Publishing.
5. van den Broeke, J., G. Langergraberb, and A. Weingartnera, *On-line and in-situ UV/vis spectroscopy for multi-parameter measurements: a brief review.* Spectroscopyeurope, 2006. **18**(4).
6. Lepot, M., Torres, A., Hofer, T., Caradot, N., Gruber,G., Aubin, J., Bertrand-Krajewski, J., *Calibration of UV/Vis spectrophotometers: A review and comparison of different methods to estimate TSS and total and dissolved COD concentrations in sewers, WWTPs and rivers.* Water Research, 2016. **101**: p. 519-534.
7. Hu, Y. and X. Wang, *Application of surrogate parameters in characteristic UV–vis absorption bands for rapid analysis of water contaminants.* Sensors and Actuators B: Chemical, 2017. **239**: p. 718-726.
8. Banna, M.H., et al., *Online drinking water quality monitoring: review on available and emerging technologies.* Critical Reviews in Environmental Science and Technology, 2014. **44**(12): p. 1370-1421.
9. Capodaglio, A.G., Callegari, A., *Water supply systems security: novel technologies for the online monitoring of unforeseeable events.* WIT

Transactions on The Built Environment, Safety and Security Engineering, 2015. **51**: p. 251-263.

10. Cascone, C., *Optical sensors in drinking water production: Towards automated process control in relation to natural organic matter*, in *Faculty of Natural Resources and Agricultural Sciences*. 2021, Faculty of Natural Resources and Agricultural Sciences.
11. Chow, C., et al., *Online water quality monitoring: The voice of experience.* Water: Journal of the Australian Water Association, 2014. **41**(2): p. 60.
12. BlueTech, *Online water and wastewater sensors and analyzers: 2019 update*. 2019, BlueTech Researvh.
13. Mizaikoff, B., *Infrared optical sensors for water quality monitoring.* Water Science and Technology, 2003. **47**(2): p. 35-42.
14. Langergraber, G., Fleischmann, N., Hofstaedter, F., *A multivariate calibration procedure for UV/VIS spectrometric quantification of organic matter and nitrate in wastewater.* Water Science and Technology, 2003. **47**(2): p. 63-71.
15. Guo, Y.L., C; Ye, R and Duan, Q, *Advances on Water Quality Detection by UV-Vis Spectroscopy.* Applied Sciences, 2020. **10**(19): p. 6874.
16. Liu, F., Zheng, P., Huang, B., Zhao, X., Jiao, L. and Dong, D., *A review on optical measurement method of chemical oxygen demand in water bodies.* In International Conference on Computer and Computing Technologies in Agriculture, 2015: p. 619-636.
17. Hossain, S., Chow, C.W., Hewa, G.A., Cook, D. and Harris, M., 2020, *Spectrophotometric online detection of drinking water disinfectant: A machine learning approach.* Sensors, 2020. **20**(22): p. 6671.
18. Ratnaweera, H. and J. Fettig, *State of the art of online monitoring and control of the coagulation process.* Water, 2015. **7**(11): p. 6574-6597.
19. Chow, C., et al., *UV Spectrometry in Drinking Water Quality Management.* Journal of the Australian Water Association, 2007. **34**(4): p. 63.
20. Zhu, X., Chen, L., Pumpanen, J., Keinänen, M., Laudon, H., Ojala, A., Palviainen, M., Kiirikki, M., Neitola, K. and Berninger, F. , *Assessment of a portable UV–Vis spectrophotometer's performance for stream water DOC and Fe content monitoring in remote areas.* Talanta, 2021. **224**: p. 121919.

21. Avagyan, A., Runkle, B.R and Kutzbach, L., *Application of high-resolution spectral absorbance measurements to determine dissolved organic carbon concentration in remote areas.* Journal of Hydrology, 2014. **517**: p. 435-446.
22. Li, J., Tong, Y., Guan, L., Wu, S. and Li, D., *A turbidity compensation method for COD measurements by UV–vis spectroscopy.* Optik, 2019. **186**: p. 129-136.
23. Giancoli Barreto, S.R., Nozaki, J. and Barreto, W.J., *Origin of Dissolved Organic Carbon Studied by UV-vis Spectroscopy.* Acta hydrochimica et hydrobiologica, 2003. **31**(6): p. 513-518.
24. Kim, C., Eom, J.B., Jung, S. and Ji, T., *Detection of organic compounds in water by an optical absorbance method.* Sensors, 2016. **16**(1): p. 61.
25. van den Broeke, J., Brandt, A., Weingartner, A. and Hofstädter, F., *Monitoring of organic micro contaminants in drinking water using a submersible UV/vis spectrophotometer*, in *In Security of Water Supply Systems: From Source to Tap*. 2006, Springer: Dordrecht. p. 19-29.
26. HACH, *UVAS sc.* HACH user manual, HACH Company, 2014.
27. Burkert, *Miniaturised SAC measurement for continuous monitoring of water quality.* Burkert fluid control systems, 2015.
28. Van Schagen, K.M., *Model-based control of drinking-water treatment plants*. 2009: Delft Center for Systems and Control.
29. SIGRIST, *Water Book Measurement Technology for "Water Treatment", SIGRIST Process-photometer*. 2017.
30. Sandford, R.C., A. Exenberger, and P.J. Worsfold, *Nitrogen cycling in natural waters using in situ, reagentless UV spectrophotometry with simultaneous determination of nitrate and nitrite.* Environmental Science & Technology, 2007. **41**(24): p. 8420-8425.
31. Budiarti, R.P.N., Widyatmoko, N., Hariadi, M. and Purnomo, M.H., *Web scraping for automated water quality monitoring system: A case study of PDAM Surabaya.* International Seminar on Intelligent Technology and Its Applications, 2016: p. 641-648.
32. Raich, J., *Review of sensors to monitor water quality.* European reference network for critical infrastructure protection (ERNCIP) project, 2013.

33. De Das, A., Pramanik, A., Adak, A., *Evolution in Water Monitoring Technology*. In Proceedings of the 21st International Conference on Distributed Computing and Networking, 2020: p. 1-5.

34. Page, R.M., Waldmann, D., Gahr, A., *Online water-quality monitoring based on pattern analysis*, in *CCWI 2017 – Computing and Control for the Water Industry*. 2017. p. 11.

35. Yuan, T., Biao, W., De-chao, W., Juan, L., Shuang-fei, X., Zhen, Z., Ge, T. and Peng, F., *A Water Monitoring and Early Warning System of COD Using UV-Vis Spectroscopy.* International Journal of Environmental Monitoring and Analysis, 2015. **3**: p. 298-303.

36. Chow, C.W., Fabris, R., Leeuwen, J.V., Wang, D., Drikas, M., *Assessing natural organic matter treatability using high performance size exclusion chromatography.* Environmental science & technology, 2008. **42**(17): p. 6683-6689.

37. Kubínová, T., and Kyncl, M. *Comparison of standard methods for determining the color of water in several countries*. in *IOP Conference Series: Earth and Environmental Science*. 2021. IOP Publishing.

38. Byrne, A.J., Botimi, D.., Cruaux, L., Fabris, R., Chow C. Adams K., Dexter R., *Five-year experience in using online UV-vis spectrolyser for river water quality monitoring*, in *OzWater conference*. 2012: Sydney.

39. Lopez-Roldan, R., Gonzalez, S., Pelayo, S., Piña, B., Platikanov, S., Tauler, R., De La Cal, A., Boleda, M.R. and Cortina, J.L., *Integration of on-line and off-line methodologies for the assessment of river water quality*, in *Water Science and Technology: Water Supply*. 2013. p. 1340-1347.

40. C. Chow, R.F., M. Dixon, *Case Studies Using S::CAN On-line Monitoring System*, in *Research Report 75*. 2009, CRC Water Quality and Treatment / Water Quality Research Australia Ltd.

41. Huebsch, M., Grimmeisen, F., Zemann, M., Fenton, O., Richards, K.G., Jordan, P., Sawarieh, A., Blum, P. and Goldscheider, N., *Field experiences using UV/VIS sensors for high-resolution monitoring of nitrate in groundwater.* Hydrology and Earth System Sciences, 2015. **19**: p. 1589-1598.

42. Strohmeier, S., Knorr, K.H., Reichert, M., Frei, S., Fleckenstein, J.H., Peiffer, S. and Matzner, E., *Concentrations and fluxes of dissolved organic carbon in runoff from a forested catchment: insights from high frequency measurements.* Biogeosciences, 2013. **10**(2): p. 905.
43. Jeong, J.J., Bartsch, S., Fleckenstein, J.H., Matzner, E., Tenhunen, J.D., Lee, S.D., Park, S.K. and Park, J.H., *Differential storm responses of dissolved and particulate organic carbon in a mountainous headwater stream, investigated by high-frequency, in situ optical measurements.* Journal of Geophysical Research: Biogeosciences, 2012. **117**(G3).
44. Leigh, C., Alsibai, O., Hyndman, R.J., Kandanaarachchi, S., King, O.C., McGree, J.M., Neelamraju, C., Strauss, J., Talagala, P.D., Turner, R.D. and Mengersen, K., *A framework for automated anomaly detection in high frequency water-quality data from in situ sensors.* Science of The Total Environment, 2019. **664**: p. 885-898.
45. Caradot, N., Sonnenberg, H., Rouault, P., Gruber, G., Hofer, T., Torres, A., Pesci, M. and Bertrand-Krajewski, J.L., *Influence of local calibration on the quality of on-line wet weather discharge monitoring: feedback from five international case studies.* 13th International Conference on Urban Drainage, Sarawak, Malaysia, 7–12 September 2014, 2014.
46. Meyer, A., et al., *Real-time monitoring of water quality to identify pollution pathways in small and middle scale rivers.* Science of the Total Environment, 2019. **651**: p. 2323-2333.
47. Wu, X., Tong, R., Wang, Y., Mei, C. and Li, Q., *Study on an online detection method for ground water quality and instrument design.* Sensors, 2019. **19**(9): p. 2153.
48. Zhao, Y., Li, Y., Zhen, Y., Fang, Y., *A novel monitoring system for COD using optical ultraviolet absorption method.* Procedia Environmental Sciences, 2011. **10**: p. 2348-2353.
49. Mrkva, M., *Automatic UV-control system for relative evaluation of organic water pollution.* Water Research, 1975. **9**(5-6): p. 587-589.
50. Tipping, E., Corbishley, H.T., Koprivnjak, J.F., Lapworth, D.J., Miller, M.P., Vincent, C.D. and Hamilton-Taylor, J., *Quantification of natural DOM from*

UV absorption at two wavelengths. Environmental Chemistry, 2009. **6**: p. 472-476.

51. Tang, B.W., Biao; Wu, De-cao; Mi, De-ling; Zhao, Jing-xiao; Feng, Peng; Jiang, Shang-hai; Mao, Ben-jiang, *Experimental research of turbidity influence on water quality monitoring of COD in UV-visible spectroscopy*. Spectroscopy and Spectral Analysis, 2014. **34**(11): p. 3020–3024.
52. Hoffmeister, S., Murphy, K.R., Cascone, C., Ledesma, J.L. and Köhler, S.J., *Evaluating the accuracy of two in situ optical sensors to estimate DOC concentrations for drinking water production.* Environmental Science: Water Research & Technology, 2020. **6**(10): p. 2891-2901.
53. Chen, Y., He, L., Cui, N., *Study on Nitrate Nitrogen Turbidity Compensation Based on Ultraviolet Spectrum.* Spectrosc. Spect. Anal., 2020. **40**: p. 472–477.
54. Hu, Y., Y. Wen, and X. Wang. *Detection of water quality multi-parameters in seawater based on UV-Vis spectrometry*. in *OCEANS 2016-Shanghai*. 2016. IEEE.
55. Van den Broeke, J., Ross, P.S., Van der Helm, A.W.C., Baars, E.T. and Rietveld, L.C., *Use of on-line UV/Vis-spectrometry in the measurement of dissolved ozone and AOC concentrations in drinking water treatment.* Water Science and Technology, 2008. **57**(8): p. 1169-1175.
56. Etheridge, J.R., Birgand, F., Osborne, J.A., Osburn, C.L., Burchell, M.R. and Irving, J., *Using in situ ultraviolet-visual spectroscopy to measure nitrogen, carbon, phosphorus, and suspended solids concentrations at a high frequency in a brackish tidal marsh.* Limnology and Oceanography: Methods, 2014. **12**(1): p. 10-22.
57. Avagyan, A., *Spatial variability and seasonal dynamics of dissolved organic matter in surface and soil pore waters in mire-forest landscapes in the Komi Republic, Northwest-Russia*. 2013, Universität Hamburg: Geowissenschaften.
58. Fei, C., Cao, X., Zang, D., Hu, C., Wu, C., Morris, E., Tao, J., Liu, T. and Lampropoulos, G., *Machine learning techniques for real-time UV-Vis spectral analysis to monitor dissolved nutrients in surface water,* in *In AI and Optical Data Sciences II*. 2021, International Society for Optics and Photonics. p. 117031.

59. X. Wang, Z.L., X. Jin, , J., *Ultraviolet scanning technique for water COD measurement and its instrument development.* Zhejiang Univ. Eng. Sci., 2006. **40**: p. 1951.

60. Hossain, S., Cook, D., Chow, C.W. and Hewa, G.A., *Development of an Optical Method to Monitor Nitrification in Drinking Water.* Sensors, 2021. **21**(22): p. 7525.

61. Shi, Z., Chow, C.W., Fabris, R., Zheng, T., Liu, J. and Jin, B., *Determination of coagulant dosages for process control using online UV-Vis spectra of raw water.* Journal of Water Process Engineering, 2022. **45**: p. 102526.

62. Hu, Y., C. Liu, and X. Wang, *Novel local calibration method for chemical oxygen demand measurements by using UV–Vis spectrometry.* IOP Conference Series: Earth and Environmental Science, 2017. **63**: p. 012016.

63. Li, J., Tong, Y., Guan, L., Wu, S. and Li, D., *Optimization of COD determination by UV–vis spectroscopy using PLS chemometrics algorithm.* Optik, 2018. **174**: p. 591-599.

64. Wang, H., Ju, A. and Wang, L, *Ultraviolet Spectroscopic Detection of Nitrate and Nitrite in Seawater Simultaneously Based on Partial Least Squares.* Molecules, 2021. **26**(12): p. 3685.

65. Zhang, J., Hou, D., Wang, K., Huang, P., Zhang, G. and Loáiciga, H., *Real-time detection of organic contamination events in water distribution systems by principal components analysis of ultraviolet spectral data.* Environmental science and pollution research, 2017. **24**(14): p. 12882.

66. Weingartner, D.A., and Hofstädter, D.F., *On-line monitoring networks for drinking water security of Karst water.* All About Karst and Water, 2006.

67. Arnon, T.A., S. Ezra, and B. Fishbain, *Water characterization and early contamination detection in highly varying stochastic background water, based on Machine Learning methodology for processing real-time UV-Spectrophotometry.* Water Research, 2019. **155**: p. 333-342.

68. Langergraber, G., Broeke, J.V.D., Lettl, W. and Weingartner, A., *Real-time detection of possible harmful events using UV/vis spectrometry.* Spectroscopy Europe, 2006. **18**(4): p. 19-22.

69. Zhao, H., Hou, D., Huang, P., Zhang, G., *Water quality event detection in drinking water network.* Water, Air, & Soil Pollution, 2014. **25**(11): p. 1-15.

70. Hou, D.B., J. Zhang, and L. Chen, Huang, P.J. and Zhang, G.X., *Water quality analysis by UV-Vis spectroscopy: A review of methodology and application.* Spectroscopy and Spectral Analysis, 2013. **33**(7): p. 1839-1844.

71. Asheri-Arnon, T., Ezra, S. and Fishbain, B., *Contamination detection of water with varying routine backgrounds by UV-spectrophotometry.* Journal of Water Resources Planning and Management, 2018. **144**(9): p. 04018056.

72. Guercio, R. and E. Di Ruzza, *An early warning monitoring system for quality control in a water distribution network.* WIT Transactions on Ecology and the Environment, 2007. **103**: p. 143-152.

73. Perfler, R., Langergraber, G., Lettl, W. and Fleischmann, N., *Use of UV-vis spectrometry for drinking water supply*, in *In Security of Water Supply Systems: from Source to Tap*. 2006, Springer: Dordrecht. p. 85-98.

74. Hou, D., Zhang, J., Yang, Z., Liu, S., Huang, P. and Zhang, G., *Distribution water quality anomaly detection from UV optical sensor monitoring data by integrating principal component analysis with chi-square distribution.* Optics express, 2015. **23**(13): p. 17487-17510.

75. Hou, D., Liu, S., Zhang, J., Chen, F., Huang, P. and Zhang, G., *Online monitoring of water-quality anomaly in water distribution systems based on probabilistic principal component analysis by UV-Vis absorption spectroscopy.* Journal of Spectroscopy, 2014.

76. Wang, K., Yu, J., Hou, D., Yin, H., Yu, Q., Huang, P. and Zhang, G., *Optical detection of contamination event in water distribution system using online Bayesian method with UV–Vis spectrometry.* Chemometrics and Intelligent Laboratory Systems, 2019. **191**: p. 168-174.

77. Liu, S., Smith, K. and Che, H., *A multivariate based event detection method and performance comparison with two baseline methods.* Water Research, 2015. **80**: p. 109-118.

78. Storey, M.V., B. Van der Gaag, and B.P. Burns, *Advances in on-line drinking water quality monitoring and early warning systems.* Water Research, 2011. **45**(2): p. 741-747.

79. Yu, Q., Yin, H., Wang, K., Dong, H. and Hou, D., *Adaptive detection method for organic contamination events in water distribution systems using the UV-vis spectrum based on semi-supervised learning.* Water, 2018. **10**(11): p. 1566.

80. Fleischmann, N., Staubmann, K., Langergraber, G., *Management of sensible water uses with real-time measurements.* Water science and technology, 2002. **46**(3): p. 33-40.

81. Plazas-Nossa, L., Hofer, T., Gruber, G. and Torres, A., *Forecasting of UV-Vis absorbance time series using artificial neural networks combined with principal component analysis.* Water Science and Technology, 2017. **75**(4): p. 765-774.

82. Scozzari, A., Mounce, S., Han, D., Soldovieri, F. and Solomatine, D.P., *ICT for Smart Water Systems: Measurements and Data Science*. 2021: Springer.

83. Park, J., K.T. Kim, and W.H. Lee, *Recent advances in information and communications technology (ICT) and sensor technology for monitoring water quality.* Water, 2020. **12**: p. 510.

84. Sanchez, C. and K. Brashear, *City of Dallas Water Utilities Contamination Warning System*. 2011, Dallas Country.

85. Rietveld, L., *Improving operation of drinking water treatment through modelling*, in *Water Research Centre - Almanac 2006*. 2006, Delft University of Technology.

86. Fabris, R., Chow, C., Dexter, R., Colton, J., Knoblauch, J. and Drikas, M., *Feed-forward coagulant control using online UV/Vis monitoring.* Water Science and Technology: Water Supply, 2013. **13**(2): p. 420-426.

87. Staubmann, K., Fleischmann, N. and Langergraber, G., *UV/VIS spectroscopy for the monitoring of testfilters.* In Proceedings of the IWA 2nd World Water Congress, 2001.

88. Faucheux, M., Fovet, O., Gruau, G., Jaffrézic, A., Petitjean, P., Gascuel-Odoux, C. and Ruiz, L. *Real time high frequency monitoring of water quality in river streams using a UV-visible spectrometer: interest, limits and consequences for monitoring strategies*. in *EGU General Assembly Conference*. 2013.

89. Lee, E.J., Yoo, G.Y., Jeong, Y., Kim, K.U., Park, J.H. and Oh, N.H., *Comparison of UV–VIS and FDOM sensors for in situ monitoring of stream DOC concentrations.* Biogeosciences, 2015. **12**(10): p. 3109-3118.
90. Byrne, A.J., Brisset, T., Chow, C.W.K., Lucas, J. and Korshin, G.V., *Development of online surrogate parameters using UV-Vis spectroscopy for water treatment plant optimisation*, in *Water: Journal of the Australian Water Association*. 2014. p. 94-100.
91. Libovic, M., Trancikova, A., Langergraber, G., Hofstädter, F. and van den Broeke, J. *Evaluation of online UV/Vis spectrometry based event detection systems at Bratislava waterworks*. in *10th IWA Conference on Instrumentation*. 2006.
92. Huang, P., Wang, K., Hou, D., Zhang, J., Yu, J. and Zhang, G., *In situ detection of water quality contamination events based on signal complexity analysis using online ultraviolet-visible spectral sensor.* Applied Optics, 2017. **56**(22): p. 6317-6323.
93. Pressl, A., Winkler, S., Gruber, G., *In-line river monitoring–new challenges and opportunities.* Water Science and Technology, 2004. **50**(11): p. 67-72.

Chapter 3

Evaluation of the Impact of Suspended Particles on Water Quality Measurements Using A Submersible UV-Vis Spectrophotometer

- Software particle compensation is an alternative to physical filtration
- Particle concentrations and character can affect software compensation accuracy
- Correlations were determined between measurements of lab and field instruments

Online water quality monitoring systems are progressively used by water utilities to manage water treatment operations. Online water quality monitoring using a UV-Vis spectrophotometer is one of the popular options as it does not require sample pre-treatment or reagents [1]. Some submersible UV-Vis spectrophotometers have built-in generic particle compensation algorithms to remove the physical filtration step [2]. However, industrial applications of using online instruments have experienced underperformance of the built-in algorithms and difficulty to obtain accurate measurements of water quality [3-7]. The study of this chapter explores the influence of suspended particles on the measurements of a submersible UV-Vis spectrophotometer as well as the performance of the built-in particle compensation technique under laboratory-controlled conditions.

This chapter provides in-depth knowledge to understand the impact of suspended particles on the measurements of water quality with a submersible UV-Vis spectrophotometer. Particle contributions to the UV_{254} measurements of water samples varied differently when particle types or concentrations changed. The results indicated that the performance of built-in generic compensation algorithms of the submersible UV-Vis spectrophotometer depends on the water matrix. Particle contributions to the UV-Vis measurements vary when particle type or particle concentration changes. These findings from this research provide evidence that the particle influence on the UV-Vis measurements is source-water dependent. It helps users to understand the behaviour of submersible UV-Vis spectrophotometers and why the built-in generic calibration does not generate comparable measurements in most cases.

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Overall percentage (%)	75		
Certification:	This paper reports on original research I conducted during the period of my Higher Degree by Research candidature and is not subject to any obligations or contractual agreements with a third party that would constrain its inclusion in this thesis. I am the primary author of this paper.		
Signature		Date	26th March 2022

Co-Author Contributions

By signing the Statement of Authorship, each author certifies that:

2 the candidate's stated contribution to the publication is accurate (as detailed above);

3 permission is granted for the candidate in include the publication in the thesis; and

4 the sum of all co-author contributions is equal to 100% less the candidate's stated contribution.

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3.1 Introduction

Water utilities are progressively using online water quality monitoring systems to manage the operations of water treatment plants (WTPs) because of the increasingly strict regulations and advances in technologies. Online water quality monitoring eliminates chemical contaminants due to minimising sample handling and allows continuous monitoring in real-time. Online water quality monitoring may provide decision-making information for early warning responses [8, 9]. The online UV-Vis spectrophotometer is a popular choice for water utilities to monitor water quality as it does not require sample pre-treatment or chemical reagents [10]. There are several commercially available systems, such as submersible UV-Vis spectrophotometers. Some submersible instruments provide generic calibrations with built-in particle compensation algorithms [11]. These algorithms were developed using advanced computing techniques, such as partial least squares, to establish the relationship between UV-Vis spectra and laboratory measurements of water samples. They extracted information from the spectra to determine measurements of certain water quality parameters such as UV_{254}, colour and dissolved organic carbon (DOC). The algorithms were developed based on hundreds of datasets containing both UV-Vis spectra and reference laboratory data [11]. However, the details of the algorithms are proprietary and are not provided by the manufacturers.

Peer-reviewed studies have documented various methods of compensating particle effect on the UV-Vis measurements of water quality using the submersible UV-Vis spectrophotometer. Algorithms were built in the spectrophotometer based on the chemical compositions and the morphology features of UV-Vis spectra obtained from wastewater samples, which were used to eliminate measurement derivation [7]. The fourth derivative spectrum was used to eliminate the interference of particles in the measurements of total organic carbon for seawater [12]. Additionally, partial least squares regression was employed to eliminate the particle effect on measuring water quality in urban drainage systems [13]. Moreover, a multiple linear regression method was adapted to remove the particle effect on the UV-Vis spectra of brackish water for rapid measurements of multiple material concentrations [14].

Some research findings showed that particle compensation of submersible UV-Vis spectrophotometers is source water dependent and site-specific calibrations are required to obtain accurate measurements [11, 15-19]. A study on the determination of water quality for wastewater samples concluded that the calibration of the submersible instrument needs to be matched with the specific wastewater type in some situations [16]. Comparable water quality results were gained from a study on monitoring water quality of surface waters in the field using a submersible instrument with a multilinear calibration method. It was found that the calibration was water matrix dependent and recommended to use site-specific calibration to improve the accuracy of the quantification. Another field study using submersible UV-Vis spectrophotometers to monitor groundwater revealed that the significant fluctuations of water quality could affect the accuracy of the water quality measurements and long-term monitoring could be limited by particle compensation [17]. A customised calibration was conducted for a submersible spectrophotometer to measure water quality in a forested catchment and comparable results were achieved [19]. A site-specific calibration was performed for a submersible instrument using the built-in compensation algorithms to measure the water quality of stream water but concentrations were overestimated because of inaccurate turbidity compensation [18]. Thus, accurate site-specific calibration is important for water quality monitoring.

To obtain accurate water quality measurements using submersible UV-Vis spectrophotometers can be challenging and it depends on their application, particularly for real-time monitoring and process control. Submersible UV-Vis spectrophotometers have been implemented at some water utilities to monitor water quality online for the assistance of water treatment process control [20-22]. However, measurement issues tend to occur to the submersible instruments when water quality changes dramatically or water source changes [4]. Industrial applications of the submersible instruments have encountered particle compensation issues such as under-compensation or over-compensation or even failure to generate reasonable measurements [4-7, 22]. Industrial experience and peer-reviewed studies show that the impact of particles is source water specific and generic calibrations could not adequately account for the differences in large water quality changes or between different types of water [5, 6, 23-25].

Even though there are studies on improving the accuracies of submersible UV-Vis spectrophotometers with site-specific calibrations, the studies of characterised particle impact on the measurements are limited. There is only one reported study of particle effect on the measurements of a UV spectrophotometric nitrate sensor [26, 27]. This chapter provides a systematic study utilising six types of stimulated water samples with both artificial and natural water particles for each type of water. The research aim was to study the particle effect on the measurements of a submersible UV-Vis spectrophotometer. This work also determines whether the built-in compensation method can generate comparable measurements as the physical filtration method or not under lab-controlled conditions

3.2 Materials and Methods

3.2.1 Materials

Three types of particles were chosen including, kaolin clay (P_1), Myponga silt (P_2), and Hope Valley silt (P_3). P_1 particles are clay minerals (Chem-Supply Pty Ltd, Australia) that were chosen because they are standardised particles. P_2 particles are silica-based and were collected from the catchment of the Myponga Reservoir in South Australia (SA). P_2 particles were selected as they represented the typical particles from an enclosed water catchment of reservoirs in SA. P_3 particles are clay-based, which were sediment from Hope Valley WTP in SA. P_3 particles were selected as they represented particles of a surface water catchment of a chain of reservoirs in SA. P_2 and P_3 were dried in an oven at 40 ^{o}C overnight before use.

Two types of water, Mill-Q water (W_1) and Myponga treated water (W_2), were selected as water-bases for making up the simulated water samples. W_1 was collected from a Milli-Q Gradient system (Millipore, France) with a conductivity of 0.10 µS/cm at 25°C. Myponga WTP utilises dissolved air flotation and filtration process (DAFF) with free chlorine disinfection, to treat source water into drinking water. W_2 was collected from Myponga WTP after the filtration process and before the chlorination process. W_1 was pure water that was used to eliminate interference from other solutes.

W_2 contains residual UV-absorbing material. It was used to assess any additional matrix effects that may confound accurate particle compensation.

3.2.2 Preparation of Water Samples

Six types of concentrated stock solutions were prepared: 5 g of P_1, P_2 and P_3 particles were suspended in 1 L of W_1 water-base, respectively; 5 g of P_1, P_2 and P_3 particles were also suspended in 1 L of W_2 water-base, respectively. Each type of the stock solution was diluted with W_1 or W_2 water-base to generate five different levels of turbidity to make up 1 L of each sample, which was defined as A, B, C, D and E. The turbidity of the water samples was within 2 - 110 NTU, which was based on the turbidity range of water sources in South Australia [28]. Six types of water samples, which were made up with three kinds of particles (P_1, P_2, and P_3) and two types of waters (W_1 and W_2), are defined as P_1W_1, P_2W_1, P_3W_1, P_1W_2, P_2W_2 and P_3W_2 based on their combinations. The water samples were organised into unfiltered and filtered water samples. Water samples with P_1 were considered the control as P_1 particles were composed of pure inorganics. Water samples with P_2 and P_3 were simulated natural surface waters, containing both organic and inorganic solids.

The selected six types of simulated water samples, in the combinations of different particles and water-bases, represent different types of water quality. All measurements of water samples were made in triplicate and averaged. Water samples containing P_1 were used as reference samples as they were highly reproducible. The simulated water samples with P_2 or P_3 type particles were used to represent local surface source waters.

3.2.3 Sample Analysis

Water quality parameters, particle size distribution, and inorganic chemical analysis were conducted in laboratories accredited by the National Association of Testing Authorities (NATA), Australia. All the water samples were analysed at room temperature.

Water quality

Turbidity was measured in NTU without physical filtration using a turbidimeter (2100AN, Hach, USA). Prior to UV_{254}, colour at wavelength 456 nm (true $colour_{456}$) and dissolved organic carbon (DOC) measurements, water samples were filtered through 0.45 µm polyethersulfone (PES) membrane filters (ANPEL Laboratory Technologies, China) to remove all the non-dissolved particles under a constant vacuum. 100 ml of water samples were filtered each time to minimise the effects of membrane fouling [29]. UV_{254} and $colour_{456}$ were analysed with a bench-top UV-Vis spectrophotometer (Evolution 60, Thermo Scientific, USA) using a standard method [30]. DOC was determined using a total organic carbon analyser (900, Sievers Instruments Inc., USA) with a standard method [30].

Particle size distribution

Particle size distributions of the three types of particles in the Milli-Q water were analysed using a LISST-Portable particle counter (Sequoia, USA). Particle size distribution data were collected by following the operational instruction of the manufacturer. The particle distributions were analysed as particle volume concentration based on the particle size increment.

Inorganic chemicals

Chemical compositions of three types of particles in Milli-Q water (2g/L) including metals and silica were analysed using Inductively Coupled Plasma - Mass Spectrometer (Agilent ICP-MS, 7500cx) instruments following the standard method [30]. Nitrogen as nitrate and nitrite were analysed using a discrete analyser according to the standard method [30].

Submersible UV-Vis spectrophotometer analysis

A submersible UV-Vis spectrophotometer (spectro::lyser; s::canGmbH, Austria) with a 35 mm pathlength was used to analyse the unfiltered and filtered water samples. The water samples were measured within a range of 200 - 750 nm with 2.5 nm intervals. The submersible UV-Vis spectrophotometer was connected to a controller (con::stat) which had an installed data processing software (ana::pro). The submersible UV-Vis spectrophotometer could measure the unfiltered water samples directly as the software has built-in generic particle compensation algorithms. The software can also convert the UV-Vis spectrum into water quality parameters such as compensated UV$_{254}$. Zero or baseline check was performed using Milli-Q water before use. The water samples were measured by filling the sample waters in the measurement port of the submersible instrument. The port and lens were cleaned before each measurement to make sure that progressive fouling and sample carryover did not impact the measurements. The outputs of the submersible instrument were stored in the controller and contained uncompensated UV-Vis spectra and derived water quality parameters.

3.2.4 Data Processing

Particle contribution is the amount of particle impact on the measurements, using a submersible UV-Vis spectrophotometer, which needs to be compensated to get accurate measurements. The particle contribution to UV$_{254}$ measurement of the submersible instrument was calculated as a subtraction between the absorbance of unfiltered and filtered same water samples. Particle contribution to the UV-Vis spectrum of the submersible instrument was also calculated as a subtraction between the absorbance of a spectrum for unfiltered and filtered water samples. An illustration of the calculation of the particle contribution is shown in Figure 3-1.

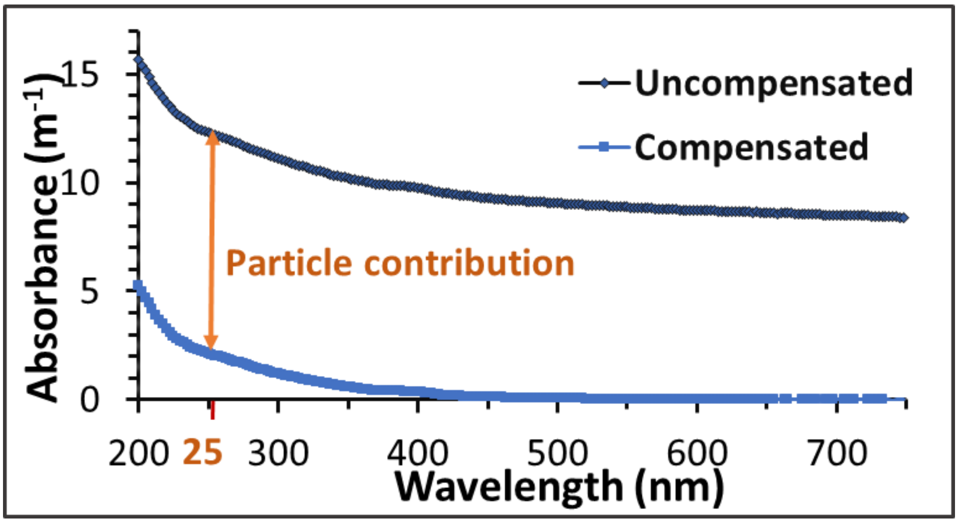

Figure 3-1 An illustration of particle contribution to the spectrum of a water sample.

The UV_{254} measurements of the filtered water samples using a bench-top spectrophotometer were defined as lab UV_{254}. The UV_{254} of unfiltered water samples measured by the submersible instrument with the built-in generic calibration were referred to as compensated UV_{254}. The compensated UV_{254} was compared with the lab UV_{254} to evaluate the performance of built-in generic algorithms of the submersible instrument.

3.3 Results and Discussion

3.3.1 Characteristics of Particles and Water Samples

Particle size distribution and chemical compositions of P_1, P_2, and P_3 in Milli-Q water were analysed. The results are shown in Table 3-1 and Figure 3-2. Each type of particle had distinguishable particle size distribution. P_1 particles had the smallest mean particle size of 2.20 µm among the three types of particles. 90% of the P_1 particle size was 0.85 - 8.65 µm. P_2 particles had the largest mean size of 14.6 µm, while the majority (90%) of P_2 particle size varied from 2.27 to 103.72 µm. P_3 particles had a mean size of 7.6 µm and 90% of P_3 particles had a size range between 2.30 and 32.55 µm. Thus, natural particles (P_2, P_3) generally had larger particle sizes than the standard particle (P_1).

Table 3-1 Particle size of Kaolin (P_1), Myponga (P_2) and Hope Valley (P_3) particles in the water.

Particle Type	Mean Size (µm)	Std of particle size (µm)	Size range (µm)	90% size (µm)
P_1	2.2	21.8	0.37- 14.22	0.85 – 8.65
P_2	14.6	54.2	1.19 - 237.35	2.27 - 103.72
P_3	7.6	16.2	1.01-63.11	2.3 - 32.55

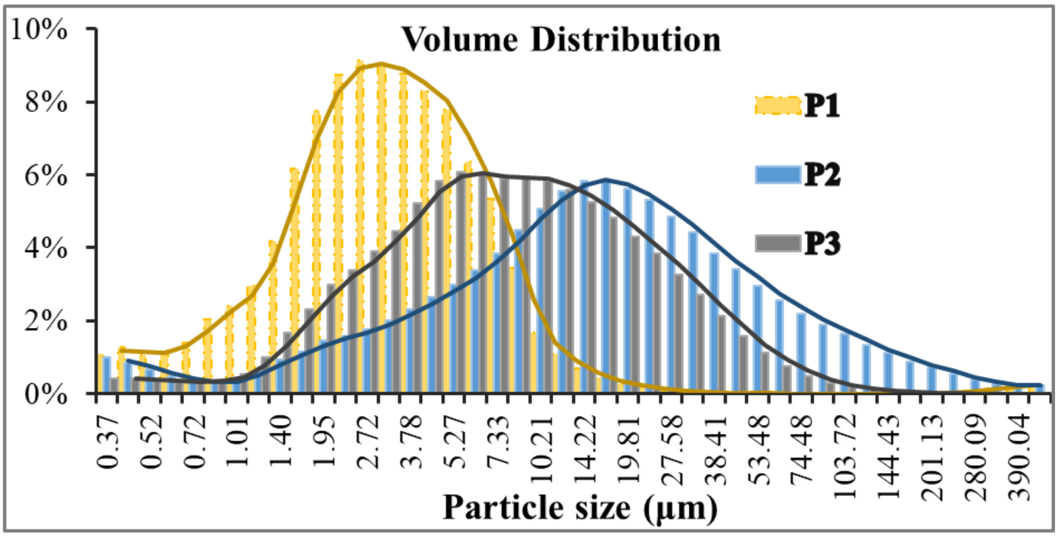

Figure 3-2 Particle size distributions of Kaolin, Myponga and Hope Valley particles.

Chemical contents of the particles in water are shown in Table 4-2. Each type of particle sample was prepared in Milli-Q water with the same particle concentration of 2.0 g/L. For metal content, P_1 particles contain only 0.03 mg/mg of Al. P_2 particles did not have any reportable amount of metals. P_3 particles contain low levels of Al, Ca and Fe which were less than 0.10 mg/mg. The nitrogen content of total nitrogen of nitrate and nitrite for all three particles was below the detection limit. The low level of nitrogen content is common in SA water sources [28]. Metal and nitrogen contents were analysed because high concentrations of inorganic species such as iron and nitrate could interfere with the UV absorbance of water [31]. However, there was no evidence that metal and nitrogen at very low concentrations in the water samples can affect the UV measurements in this work. Both water samples with P_1 particles and water samples with P_2 particles had low alkalinity as $CaCO_3$ (<50mg/L), while water samples with P_3 particles had the highest alkalinity (200mg/L). A previous study used the UV-Vis spectrophotometric method to determine water quality and achieved comparable results. The instrument was robust in the high alkalinity condition with water alkalinity up to 459 mg/L [32]. Therefore, the alkalinity of the water samples containing P_1, P_2 or P_3 could not affect the measurements of UV-Vis spectrophotometers.

Table 3-2 Inorganic chemistry of particles in Milli-Q water: Kaolin (P1), Myponga (P2) and Hope Valley (P3).

Particle Type	Metal (mg/mg)		N as (NO_2^- + NO_3^-) (mg/mg)	Alkalinity as $CaCO_3$ (mg/L)
P_1	Al	0.03	0.00	20
	Ca	0.00		
	Fe	0.00		
	P	0.00		
	Na	0.00		
	Mg	0.00		
P_2	Al	0.00	0.00	40
	Ca	0.00		
	Fe	0.00		
	P	0.00		
	Na	0.00		
	Mg	0.00		
P_3	Al	0.07	0.00	200
	Ca	0.01		
	Fe	0.03		
	P	0.00		
	Na	0.00		
	Mg	0.00		

The water quality parameters include turbidity, lab UV_{254}, true $colour_{456}$, DOC and pH, of all simulated water samples were analysed using the laboratory standard methods, and the results are shown in Table 3-3. In general, all six types of simulated water samples had different lab UV_{254} responses. The lab UV_{254}, true $colour_{456}$, and DOC of P_1W_1 water samples were close to zero as P_1 is purely clay mineral. All the P_1W_2 samples had constant values of lab UV_{254}, true $colour_{456}$, and DOC as W_2 water-base contain natural organics.

Table 3-3 Water quality characteristics of six types of simulated water samples that were made up of three types of particles (P_1, P_2, and P_3) and two base-waters (W_1 and W_2).

Water samples	Sample level	Particle Conc.	Turbidity (NTU)		Lab UV_{254} (m^{-1})		True $Colour_{456}$ (m^{-1})		DOC (mg/L)		pH	
		mg/L	Unfiltered		Filtered		Filtered		Filtered		Unfiltered	
			mean	SD	mean	SD	mean	SD	mean	SD	mean	SD
W_1	-	0	<0.1	0	<0.1	0	<0.1	0	<0.1	0	7.0	0
P_1W_1	A	2.5	2.3	0.2	0.1	0	<1	0	0.1	0	5.6	0
	B	25	21	0.1	0.1	0	<1	0	0.1	0	5.6	0.1
	C	50	43	0.9	0.1	0	<1	0	0.1	0	5.5	0.1
	D	100	85	0.6	0.1	0	<1	0	0.1	0	5.6	0.1
	E	125	105	1.0	0.1	0	<1	0	0.1	0	5.6	0.1
P_2W_1	A	25	2.3	0.1	0.1	0	<1	0	0.2	0	6.5	0.1
	B	250	21	0.5	1.1	0	3	0.1	0.4	0	6.3	0.1
	C	500	44	0.4	2.2	0	4	0.1	0.7	0	6.2	0.1
	D	1000	86	1.1	4.3	0	7	0.1	1.2	0	6.1	0.1
	E	1300	107	1.0	5.3	0	11	0.2	1.5	0	6.0	0.1
P_3W_1	A	5	2.4	0.1	0.0	0	<1	0	0.2	0	8.0	0
	B	50	21	0.6	0.1	0	<1	0	0.3	0	8.2	0.1
	C	100	43	0.7	0.3	0	2	0.1	0.5	0	8.3	0.1
	D	200	85	1.1	0.8	0	3	0.1	0.7	0	8.2	0.1
	E	250	106	1.0	1.0	0	5	0.2	0.8	0	8.3	0.2
W_2	-	0	0.2	0.0	10.7	0	6	0	5.1	0	7.1	0
P_1W_2	A	5	2.3	0.0	11.3	0	6	0	5.2	0	7.1	0
	B	50	21	0.3	11.3	0	6	0	5.2	0	7.1	0.1
	C	100	44	0.5	11.3	0	6	0	5.2	0	7.2	0.1
	D	175	86	0.4	11.3	0	6	0	5.3	0	7.1	0.1
	E	225	107	1.0	11.3	0	6	0	5.2	0	7.1	0
P_2W_2	A	25	2.4	0.1	11.2	0	7	0.1	5.2	0	6.7	0.1
	B	250	21	0.2	11.6	0	8	0	5.3	0	6.6	0.1
	C	500	43	0.7	12.1	0	9	0.2	5.4	0	6.8	0.1
	D	875	85	0.5	13.1	0	10	0.1	5.7	0	6.7	0.1
	E	1125	106	0.8	13.6	0	11	0.	5.8	0	7.0	0.1
P_3W_2	A	5	2.3	0.1	11.4	0	7	0.1	5.2	0	7.1	0.1
	B	50	21	0.3	11.6	0	7	0.1	5.3	0	7.2	0.1
	C	100	44	0.7	11.8	0	8	0.1	5.5	0	7.3	0.1
	D	175	86	0.9	12.3	0	8	0.1	5.8	0	7.3	0.1
	E	225	107	0.8	12.5	0	9	0.2	5.9	0	7.2	0.1

Note: measurement error was shown as standard deviation (SD).

All the simulated natural water samples with P_2 and P_3 particles contain organics. Lab UV_{254} measurements of P_2W_1, P_3W_1, P_2W_2, and P_3W_2 samples were from 0.1 to 5.3 m^{-1}, 0.0 to 1.0 m^{-1}, 11.2 to 13.6 m^{-1}, and 11.4 to 12.5 m^{-1}, respectively. Water samples with the W_2 water-base had higher values of lab UV_{254}, true $colour_{456}$ and DOC than the water samples with the W_1 water-base. Myponga treated water was employed as the W_2 water-base, which had a high DOC content that was in line with the historical data [33].

Water quality results in Table 3-3 indicate that the pH of all the water samples was within a range of 5.5 to 8.3, which is similar to the reported pH range (6 to 8.5) of most surface water in SA [28]. There was no significant influence of water sample pH on the lab UV_{254}. Thus, the pH of the water samples was not adjusted. Weishaar et al. [31] reported that the minor pH effect on UV absorbance measurements was observed for river water samples. A study also concluded that only relatively high or low pH had impacted on the UV absorbances of the lake water samples [34].

3.3.2 Relationships between Water Quality Parameters and UV Measurements

Particle compensation is also called turbidity compensation for the measurements of water quality using UV-Vis spectrophotometers. Turbidity measures light scattering which is interactions between light and suspended particles. Suspended particles can cause light scattering and affect the light absorption of the water samples. Accordingly, turbidity has a major and direct connection to the measurements of UV-Vis spectrophotometers. UV_{254} is commonly used as a surrogate to determine the concentration of organic matter in water. Therefore, to understand the UV response of water samples, we investigated relationships between water quality parameters, such as turbidity and DOC, and UV_{254} measurements using a bench-top UV-Vis spectrophotometer.

Lab UV_{254} is plotted as a function of turbidity for all six types of simulated natural water samples which is shown in Figures 3-3a and 3-3b. As the increase in turbidity of P_1W_1 and P_1W_2 water samples, lab UV_{254} measurements were constant (Table 3-3). P_1 particles were purely inorganics and insoluble in water which can be removed by physical filtration. There were statistically robust linear relationships between turbidity and lab UV_{254} for P_2W_1, P_2W_2, P_3W_1, and P_3W_2 water samples with $R^2 \geq 0.99$. As the turbidity level increased, the lab UV_{254} of the water samples increased linearly. The slopes and intercepts of the water samples with P_2 type particles were different from that of water samples with P_3 type particles. For water samples with P_2 and P_3 particles, water samples with W_1 water-base had intercepts of almost 0 m^{-1}, whereas the intercepts of water samples with the W_2 water-base were around 11 m^{-1}. It was because the W_2 water-base contains high levels of dissolved organics.

UV_{254} is also plotted against DOC for all the water samples, shown in Figures 3-3c and 3-3d. The relationship between DOC and UV_{254} of P_1W_1 and P_1W_2 water samples was not taken into consideration, as P_1 type particles do not contain any organics. For all P_2W_1 and P_2W_2 water samples, an increase in DOC leads to an increase in UV_{254}. DOC had linear correlations with the UV_{254} for P_2W_1, P_2W_2, P_3W_1 and P_3W_2 water samples with R^2 of 1.00 and 0.99, respectively, with different slope and intercept for each water type. The slopes of water samples containing particle type P_3 were lower than the water samples containing particle type P_2, which could be explained by the UV of supracolloidal particles having lower slopes than fine colloidal particles [35]. Thus, different types of simulated natural waters had different linear relationships between DOC and UV_{254}.

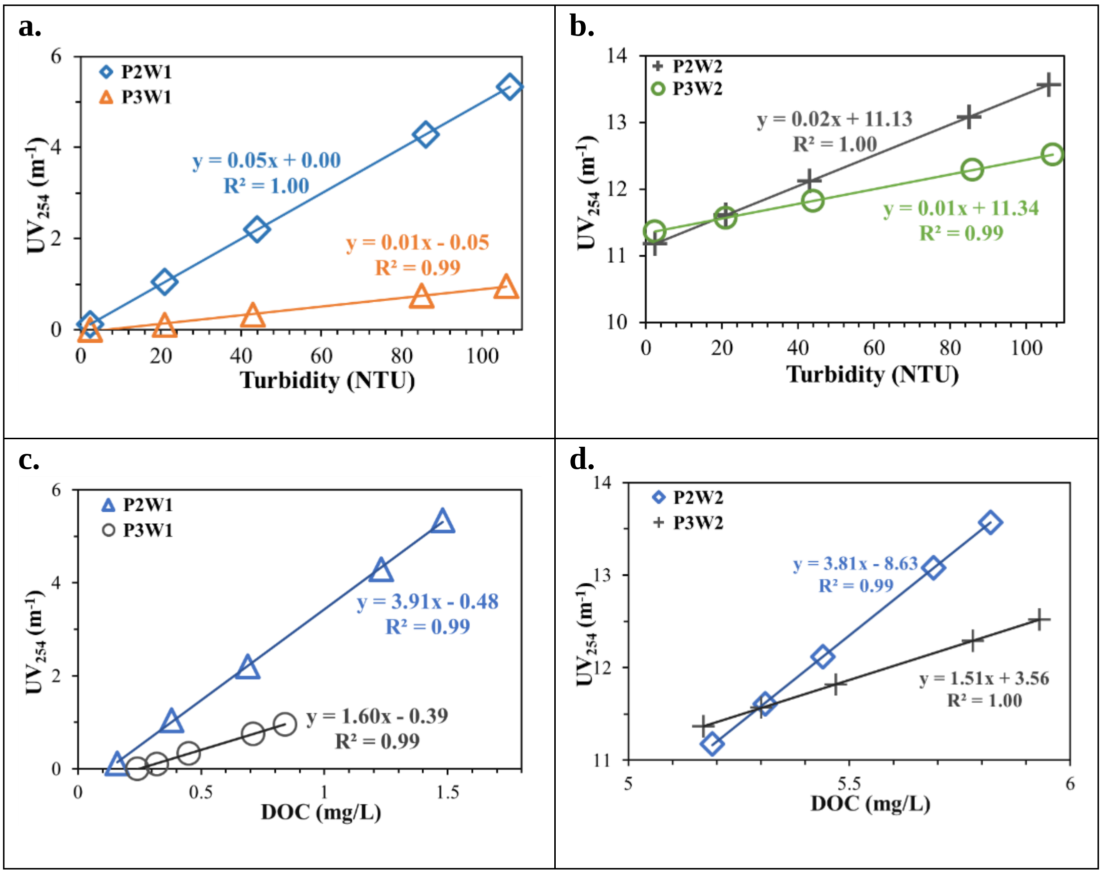

Figure 3-3 Correlations between turbidity and lab UV_{254} of simulated natural water samples are shown in a) and b); relationships between DOC and lab UV_{254} of simulated natural water samples are shown in c) and d). P_2W_1, P_2W_2, P_3W_1, and P_3W_2 were simulated water samples that were made up of two types of particles (P_2 and P_3), and two types of water-bases (W_1 and W_2), respectively.

Overall, different natural water samples had different lab UV_{254} responses using a bench-top UV-Vis spectrophotometer combined with a physical filtration method. The UV response of the turbidity for the filtered water samples was caused by DOC. In general, particle characters that affect measurements of bench-top UV-Vis spectrophotometers are mainly DOC. There were linear relationships between turbidity and UV_{254} as well as DOC and UV_{254} of surface catchments water in SA, such as river water and reservoir water. The findings were supported by two reported studies. Mamane et al. [36] reported that with the increase of particle concentration in the water, the associated UV absorbance increase linearly. UV_{254} measured by the bench-top UV-Vis instrument was changed directly with the change of DOC in the river waters [37].

3.3.3 Particle Contribution to Measurements of A Submersible UV-Vis Spectrophotometer

Particle contribution was calculated based on the measurements of a submersible UV-Vis spectrophotometer as mentioned in section 2.4. According to the results present in Figure S3-1 in Supporting Information (SI), the turbidity of all six types of water samples increased when the particle concentrations increased. The particle contribution to UV-Vis spectra and UV_{254} for the six types of water samples with five different turbidity levels (A, B, C, D, E) are shown in Figures 3-4a, S3-2 and S3-3 in SI. As water turbidity increased, the particle contributions in P_1W_1 also increased. Similarly, an increase in turbidity was associated with the increase in the particle contributions to P_2W_1, P_3W_1, P_1W_2, P_2W_2, and P_3W_2 water samples. Thus, an increase in the turbidity of water samples can lead to an increase in particle contribution. P_3 particle had the highest contribution to the UV-Vis spectra and P_2 had the least particle contribution, among the three types of particles, for each turbidity level of water samples: turbidity level A to turbidity level E.

For UV_{254} measurement, the particle contribution of each water sample was distinguished according to their absorbance values in Figures 3-4b and S3-3 (in SI). At the same turbidity level in the water samples with W_1 water-base, P_3 type particles had the largest particle contribution to UV_{254} measurements, while P_2 particles had the lowest particle contribution to the UV_{254} measurements. Interestingly, in the water samples prepared with W_2 water-base, P_1 particles were found to demonstrate a slightly higher particle contribution to the UV_{254} measurements than P_3 particles. The difference between P_2 had the lowest particle contribution to the UV_{254} measurements. Thus, the influence of the particle contributions on the UV_{254} measurements could be dependent on the water matrix.

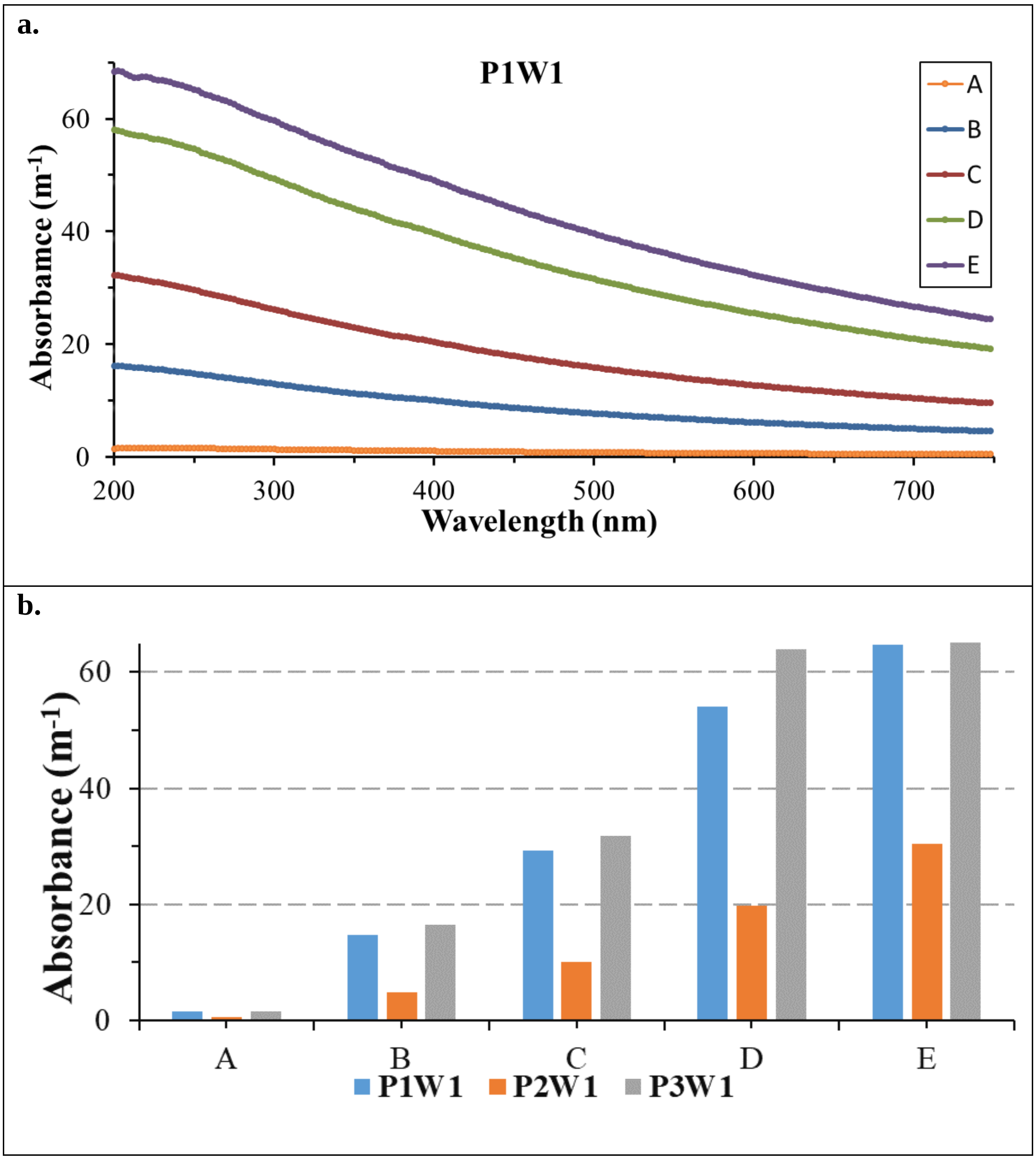

Figure 3-4 a) Particle contributions of P_1W_1 water samples to spectra at five different concentration levels; (b) Particle contribution of different types of waters to UV_{254} measurements. Particle concentration levels were from low to high (water sample A to water sample E).

Overall, the particle contribution to the UV-Vis measurements is dependent on the particle type and particle concentration. As particle concentration increases, suspended particles in the water cause light scattering. Particle contributions caused by the light scattering of the suspended particles are common in natural waters. Light scattering could significantly affect the UV-Vis measurements, which can be influenced by the particle concentration, particle type and particle size [36-38]. For small particles, light scattering has a linear relationship with particle concentration. Thus, an increase in the particle concentration leads to an increase in particle contribution to the UV-Vis measurement. Particle type influences the light scattering which can, in turn, affect the particle contribution. Particle size could largely affect the intensity of the scattering light. Increase of the small particle size, the intensity of the scattered light is likely to increase. P_1 particle type was pure clay, P_2 particle type was silica-based and P_3 particle type was clay-based. Both P_2 and P_3 particles were collected from the natural surface source water. Clay particle has 50% of light scatter away and particles from natural waters have 20%-30% light scatter away [37]. The differences in particle sizes and particle types contribute to the different light scattering effects, in turn, lead to the difference in their particle contribution. It can be explained that P_1 and P_3 had much higher particle contributions to the UV-Vis measurements than P_2.

Understanding the particle contribution caused by the particle types and concentrations, which assists to discover the built-in compensation behaviour of submersible UV-Vis spectrophotometers. The particle contribution to the measurements of water samples could be determined by particle compensation, which can be conducted to remove the particle interference in the measurements of water quality [12]. The particle contributions can be varied with the water sources type and concentration, thus leading to corresponding changes in measurements of a submersible UV-Vis spectrophotometer. Thus, a universal particle compensation is not always effective.

3.3.4 Evaluation of the Performance of A Submersible UV-Vis Spectrophotometer

The performance of the built-in generic particle compensation algorithms of the submersible instrument was evaluated in an offline mode, by comparing it with the bench-top instrument. The UV_{254} of water samples measured by the submersible instrument were compensated for the particle effect using the built-in generic calibration (compensated UV_{254}). The lab UV_{254} of the same water samples measured by the bench-top spectrophotometer were used as references. Compensated UV_{254} and lab UV_{254} of all the water samples were plotted as a bar chart and are shown in Figure 3-5 and Figure S3-4 (in SI). UV_{254} was used as it is an essential absorbance-based water quality parameter for the concentrations of organic matter and disinfection by-product precursors in the water.

According to Figure S3-4 in SI, the compensated UV_{254} was much lower than the lab UV_{254} for P_1W_1 and P_1W_2 water samples. The compensated UV_{254} of P_1W_1 and P_1W_2 water samples were highly over-compensated by the built-in generic compensation algorithms, which was probably because the P_1 contained purely inorganics. The built-in compensation algorithms were based on hundreds of natural water samples, which may not be suitable for compensating water contains purely inorganics. For P_2W_1 water samples, the compensated UV_{254} was slightly lower than the lab UV_{254} as shown in Figure 3-5, which indicates the submersible instrument slightly over-compensated the UV_{254} measurements. For P_2W_2 water samples, the compensated UV_{254} seemed close to the values of lab UV_{254}. This finding was agreed with the conclusion that the submersible instrument was effective in compensating for the particle effect on the measurements [26]. It was found that the compensated UV_{254} had strong linear correlations with lab UV_{254} with a slope of 1.34 and 1.71 and R^2 of 0.99 for P_2W_1 and P_2W_2 (Figure S3-5 in SI). It is interesting to note that the compensated UV_{254} was higher than lab UV_{254} for some types of water samples whereas was lower than lab UV_{254} for other types of water samples. There are also linear relationships between compensated UV_{254} and lab UV_{254} for water samples with P_3. An increasing linear relationship was found for P_3W_1 water samples whereas a decreasing linear relationship was found for P_3W_2 water samples.

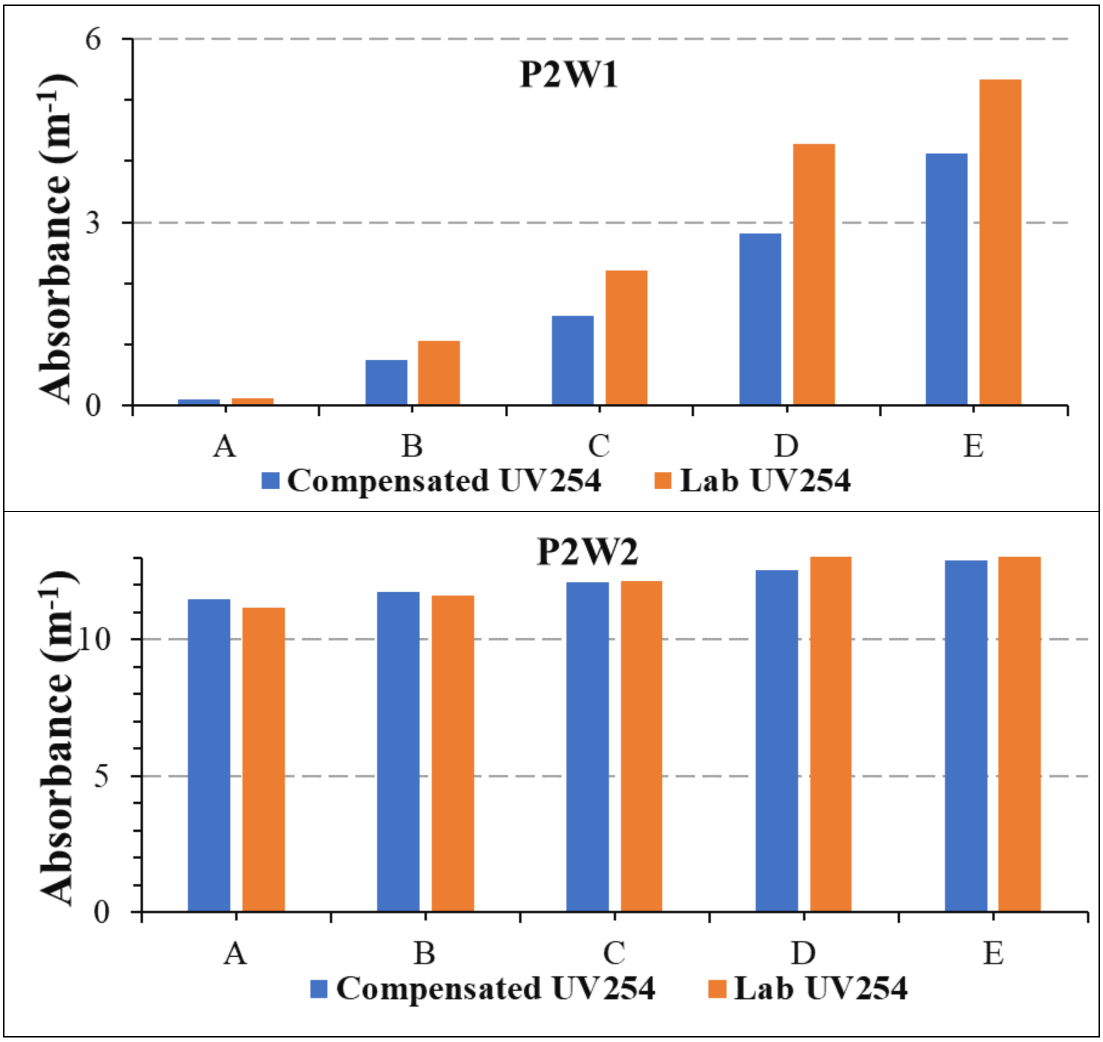

Figure 3-5 Comparisons between UV_{254} measurements of submersible and bench-top UV-Vis instruments. Compensated UV_{254} is obtained from the outputs of a submersible UV-Vis spectrophotometer. Lab UV_{254} is measured using a bench-top UV-Vis spectrophotometer. P_2W_1 and P_2W_2 were water samples made up of P_2 type particles and W_1 or W_2 water-bases.

Overall, there were linear relationships between compensated UV_{254} and lab UV_{254} for all the simulated natural water samples with P_2 or P_3 particles. The built-in compensation algorithms of a submersible UV-Vis spectrophotometer do not always generate comparable compensated UV_{254} for natural water samples as the bench-top UV-Vis instrument. For natural waters, the built-in generic particle compensation methods may generate either under or over-compensated measurements. A previous study also reported the incomparable measurements of UV measurements of the built-in generic algorithms for waters [16]. This work shows that particle compensation is source water specific and the site-specific particle compensation should be performed when using the submersible instrument to measure water quality. Some scientists also believed that particle compensation based on the water matrix needs to be considered to achieve comparable measurements using the submersible instrument [7, 11, 13, 15, 18, 39]. Industrial applications of using the submersible instrument to monitor water quality had experienced those the generic compensation algorithms were unable to generate accurate measurements for some water sources [4-7, 21, 22]. Particle compensation is one of the barriers to online instrument implementation in industrial applications. It is essential to perform site-specific particle compensation and establish the frequency of the compensation to achieve accurate measurements [40-43]. Therefore, it is recommended that the evaluation of the accurate measurements of the submersible instrument is conducted before using it to monitor water quality.

3.4 Conclusion

Laboratory-scale investigations were conducted to understand relationships between turbidity and UV_{254}, DOC and UV_{254}, and particle compensation behaviour of a submersible UV-Vis spectrophotometer. Six kinds of simulated waters, in the combinations of artificial standard particles, natural water particles, ultrapure water and treated water from a drinking WTP. Both turbidity and DOC were linearly correlated with UV_{254} measurements with $R^2 \geq 0.99$. Different types of simulated water samples had different UV absorbance responses. Particle contributions to the UV-Vis measurements not only vary when particle types changes but also particle concentrations change. The compensated UV_{254}, measured by a submersible instrument with the build-in generic particle compensation algorithms, were compared with the lab UV_{254}, tested by the bench-top instrument with the physical filtration method. The results showed that the built-in generic calibration compensation algorithms of the submersible instrument tend to generate under-compensated or over-compensated UV_{254} for surface waters. These findings provide evidence that the particle influence on the measurements of the submersible instrument is source water dependent. It helps users to understand the behaviour of submersible UV-Vis spectrophotometers and why the built-in generic calibration does not generate comparable results in many cases.

3.5 References

1. Shi, Z., Chow, C.W., Fabris, R., Liu, J., Jin, B., *Alternative particle compensation techniques for online water quality monitoring using UV–Vis spectrophotometer.* Chemometrics and Intelligent Laboratory Systems, 2020. **204**(104074).
2. Langergraber, G., Fleischmann, N., Hofstaedter, F., *A multivariate calibration procedure for UV/VIS spectrometric quantification of organic matter and nitrate in wastewater.* Water Science and Technology, 2003. **47**(2): p. 63-71.
3. Chow, C., Dexter, R., Sutherland-Stacey, L., Fitzgerald, F., Fabris, R., Drikas, M., Holmes, M., Kaeding, U., *UVspectrometry in drinking water quality management*, in *WATER-MELBOURNE THEN ARTARMON*. 2007. p. 40-43.
4. Waterra, *Optimisation of existing instrumentation to achieve better process performance*. 2017, Water research Australia.
5. Lepot, M., Torres, A., Hofer, T., Caradot, N., Gruber,G., Aubin, J., Bertrand-Krajewski, J., *Calibration of UV/Vis spectrophotometers: A review and comparison of different methods to estimate TSS and total and dissolved COD concentrations in sewers, WWTPs and rivers.* Water Research, 2016. **101**: p. 519-534.
6. Chow, C., et al., *UV spectrometry in drinking water quality management*, in *OZwater'17, Australian Water Association*. 2017. p. 63.
7. Hu, Y. and X. Wang, *Application of surrogate parameters in characteristic UV–vis absorption bands for rapid analysis of water contaminants.* Sensors and Actuators B: Chemical, 2017. **239**: p. 718-726.
8. Dong, J., et al., *A survey of smart water quality monitoring system.* Environmental Science and Pollution Research, 2015. **22**(7): p. 4893-4906.
9. Hou, D., et al., *An early warning and control system for urban, drinking water quality protection: China's experience.* Environmental Science and Pollution Research, 2013. **20**(7): p. 4496-4508.
10. Zhang, J., et al., *Real-time detection of organic contamination events in water distribution systems by principal components analysis of ultraviolet spectral*

data. Environmental Science and Pollution Research, 2017. **24**(14): p. 12882-12898.

11. Langergraber, G., N. Fleischmann, and F. Hofstaedter, *A multivariate calibration procedure for UV/VIS spectrometric quantification of organic matter and nitrate in wastewater.* Water Science and Technology, 2003. **47**(2): p. 63-71.
12. Hu, Y., Y. Wen, and X. Wang. *Detection of water quality multi-parameters in seawater based on UV-Vis spectrometry*. in *OCEANS 2016-Shanghai*. 2016. IEEE.
13. Torres, A. and J.L. Bertrand-Krajewski, *Partial least squares local calibration of a UV-visible spectrometer used for in situ measurements of COD and TSS concentrations in urban drainage systems.* Water Science and Technology, 2008. **57**(4): p. 581-588.
14. Etheridge, J.R., Birgand, F., Osborne, J.A., Osburn, C.L., Burchell, M.R. and Irving, J., *Using in situ ultraviolet-visual spectroscopy to measure nitrogen, carbon, phosphorus, and suspended solids concentrations at a high frequency in a brackish tidal marsh.* Limnology and Oceanography: Methods, 2014. **12**(1): p. 10-22.
15. Avagyan, A., Runkle, B.R and Kutzbach, L., *Application of high-resolution spectral absorbance measurements to determine dissolved organic carbon concentration in remote areas.* Journal of Hydrology, 2014. **517**: p. 435-446.
16. Drolc, A. and J. Vrtovšek, *Nitrate and nitrite nitrogen determination in waste water using on-line UV spectrometric method.* Bioresource Technology, 2010. **101**: p. 4228-4233.
17. Huebsch, M., Grimmeisen, F., Zemann, M., Fenton, O., Richards, K.G., Jordan, P., Sawarieh, A., Blum, P. and Goldscheider, N., *Field experiences using UV/VIS sensors for high-resolution monitoring of nitrate in groundwater.* Hydrology and Earth System Sciences, 2015. **19**: p. 1589-1598.
18. Jeong, J.J., Bartsch, S., Fleckenstein, J.H., Matzner, E., Tenhunen, J.D., Lee, S.D., Park, S.K. and Park, J.H., *Differential storm responses of dissolved and particulate organic carbon in a mountainous headwater stream, investigated*

by high-frequency, in situ optical measurements. Journal of Geophysical Research: Biogeosciences, 2012. **117**(G3).

19. Strohmeier, S., Knorr, K.H., Reichert, M., Frei, S., Fleckenstein, J.H., Peiffer, S. and Matzner, E., *Concentrations and fluxes of dissolved organic carbon in runoff from a forested catchment: insights from high frequency measurements.* Biogeosciences, 2013. **10**(2): p. 905.
20. Banna, M.H., et al., *Online drinking water quality monitoring: review on available and emerging technologies.* Critical Reviews in Environmental Science and Technology, 2014. **44**(12): p. 1370-1421.
21. Byrne, A.J., Brisset, T., Chow, C.W.K., Lucas, J. and Korshin, G.V., *Development of online surrogate parameters using uv-vis spectroscopy for water treatment plant optimisation.* Australia Water Association Water Journal, 2014. **41**: p. 94-100.
22. Chow, C., Dexter, R., Sutherland-Stacey, L., Fitzgerald, F., Fabris, R., Drikas, M., Holmes, M. and Kaeding, U., *UV spectrometry in drinking water quality management*, in *WATER-MELBOURNE THEN ARTARMON*. 2007. p. 63.
23. Caradot, N., Sonnenberg, H., Rouault, P., Gruber, G., Hofer, T., Torres, A., Pesci, M. and Bertrand-Krajewski, J.L., *Influence of local calibration on the quality of on-line wet weather discharge monitoring: feedback from five international case studies.* 13th International Conference on Urban Drainage, Sarawak, Malaysia, 7–12 September 2014, 2014.
24. Leigh, C., Alsibai, O., Hyndman, R.J., Kandanaarachchi, S., King, O.C., McGree, J.M., Neelamraju, C., Strauss, J., Talagala, P.D., Turner, R.D. and Mengersen, K., *A framework for automated anomaly detection in high frequency water-quality data from in situ sensors.* Science of The Total Environment, 2019. **664**: p. 885-898.
25. Meyer, A., et al., *Real-time monitoring of water quality to identify pollution pathways in small and middle scale rivers.* Science of the Total Environment, 2019. **651**: p. 2323-2333.
26. Snazelle, T.T., *The effect of suspended sediment and color on ultraviolet spectrophotometric nitrate sensors*. 2016, US Geological Survey.

27. Van Eerdenbrugh, B., D.E. Alonzo, and L.S. Taylor, *Influence of particle size on the ultraviolet spectrum of particulate-containing solutions:implications for in-situ concentration monitoring using UV/Vis fiber-optic probes.* Pharmaceutical Research, 2011. **28**(7): p. 1643-1652.
28. SA Water, *Drinking Water Quality Report*. 2016, Government of South Australia.
29. Drikas, M., et al., *Getting the right result.* Australian Water Association Water E-journal, 2017.
30. Rice, E.W., et al., *Standard methods for the examination of water and waste water*. 2007, Federation, Water Environment, American Public Health Association,Washington, DC, USA: American public health association (APHA).
31. Weishaar, J., et al., *Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon.* Environmental Science & Technology, 2003. **37**: p. 4720-4708.
32. Bowker, J.D., *The Robustness of a Simple UV-vis Spectrophotometric*, in *Method to Determine the Concentration of Eugenol in Water*, A.A.D.A. Partnership, Editor. 2011, U.S. Fish & Wildlife Service.
33. Fabris, R., C.W. Chow, and M. Drikas, *Comparison of coagulant type on natural organic matter removal using equimolar concentrations.* Journal of Water Supply: Research and Technology-Aqua, 2012. **61**: p. 210-219.
34. Pace, M.L., et al., *pH change induces shifts in the size and light absorption of dissolved organic matter.* Biogeochemistry, 2012. **08**(1-3): p. 109-118.
35. Vaillant, S.P., M.F, and Thomas, O, *Basic handling of UV spectra for urban water quality monitoring.* Urban Water, 2002. **4**(3): p. 273-281.
36. Mamane, H., J.J. Ducoste, and K.G. and Linden, *Effect of particles on ultraviolet light penetration in natural and engineered systems.* Applied Optics, 2006. **45**: p. 1844-1856
37. Volk, C., et al., *Fluctuations of dissolved organic matter in river used for drinking water and impacts on conventional treatment plant performance.* Environmental Science & Technology, 2005. **39**: p. 4258-4264.

38. Bohren, C. and D.R. Huffman, *Absorption and scattering of light by small particles*. 2008: John Wiley & Sons.
39. Shi, Z., et al., *Alternative particle compensation techniques for online water quality monitoring using UV–Vis spectrophotometer.* Chemometrics and Intelligent Laboratory Systems, 2020: p. 104074.
40. Chow, C., et al., *Online water quality monitoring: The voice of experience.* Water: Journal of the Australian Water Association, 2014. **41**(2): p. 60.
41. Mussared, A., et al., *Implementation of predictive alum dose control systems.* 77th Annual WIOA Victorian Water Industry Operations Conference and Exhibition, Bendigo Exhibition Centre, 2014.
42. Langergraber, G., Fleischmann, N., Hofstaedter, F., Weingartner, A., *Monitoring of a paper mill wastewater treatment plant using UV/VIS spectroscopy.* Water science and technology, 2004. **49**(1): p. 9-14.
43. Liu, X., et al., *Absorption and fluorescence properties of chromophoric dissolved organic matter: implications for the monitoring of water quality in a large subtropical reservoir.* Environmental Science and Pollution Research, 2014. **21**(24): p. 14078-14090.

3.5 Supporting Information

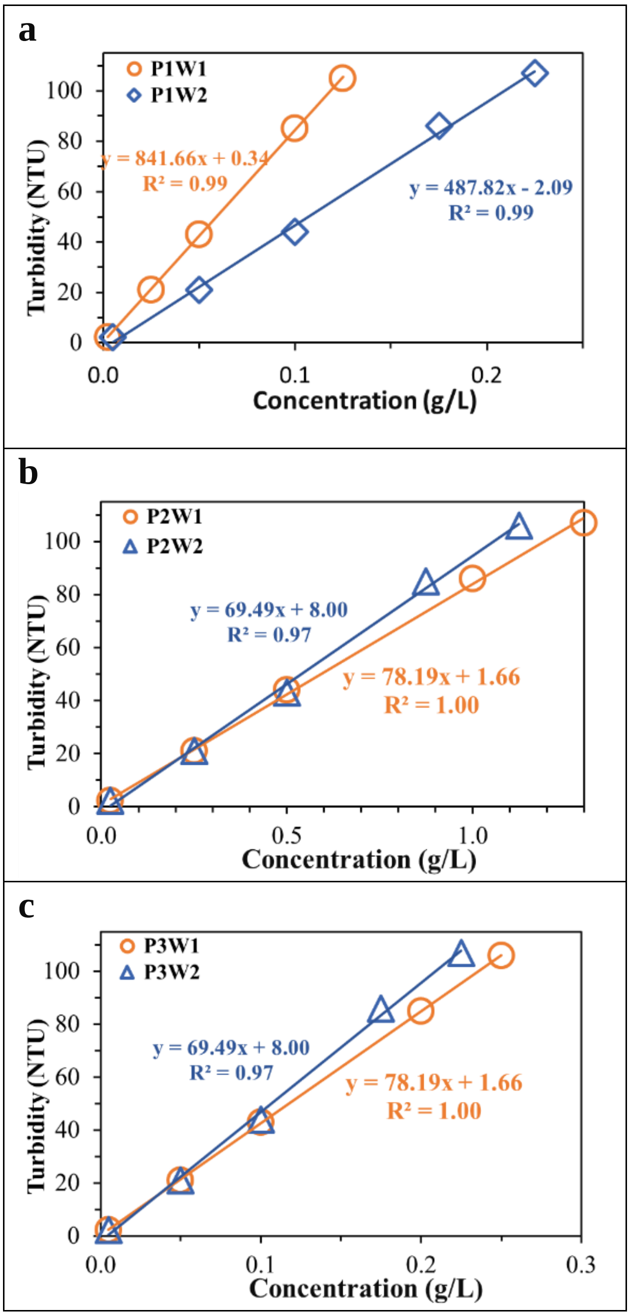

Figure S3-1 The linear relationships between particle concentrations and turbidity of water samples for six types of water samples: P_1W_1, P_2W_1, P_3W_1, P_1W_2, P_2W_2, P_3W_2. The water samples were made up of three kinds of particles (P_1, P_2, and P_3) and two types of waters (W_1 and W_2).

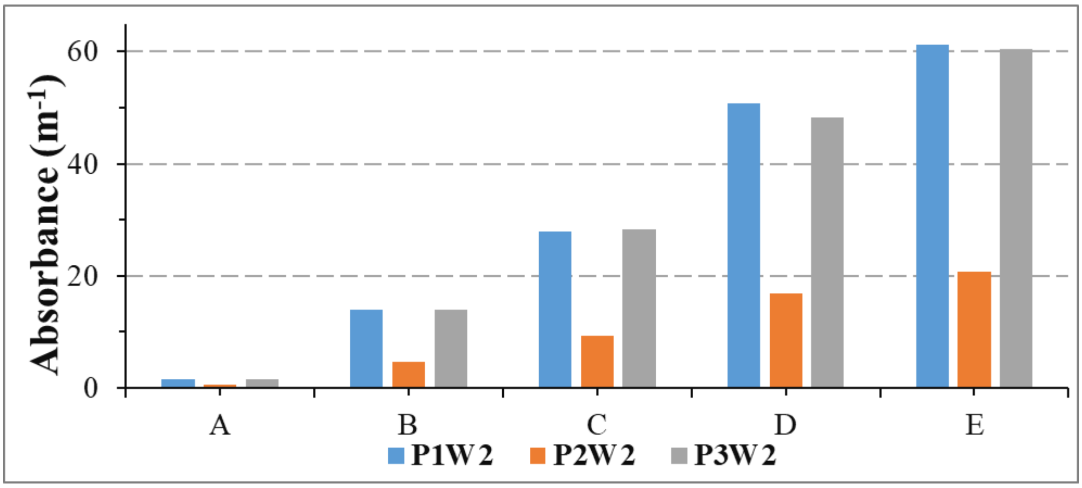

Figure S3-2 Particle contributions to the measurements of UV_{254} for six types of water samples with five levels of concentrations for each type of water from low to high (water samples A to E).

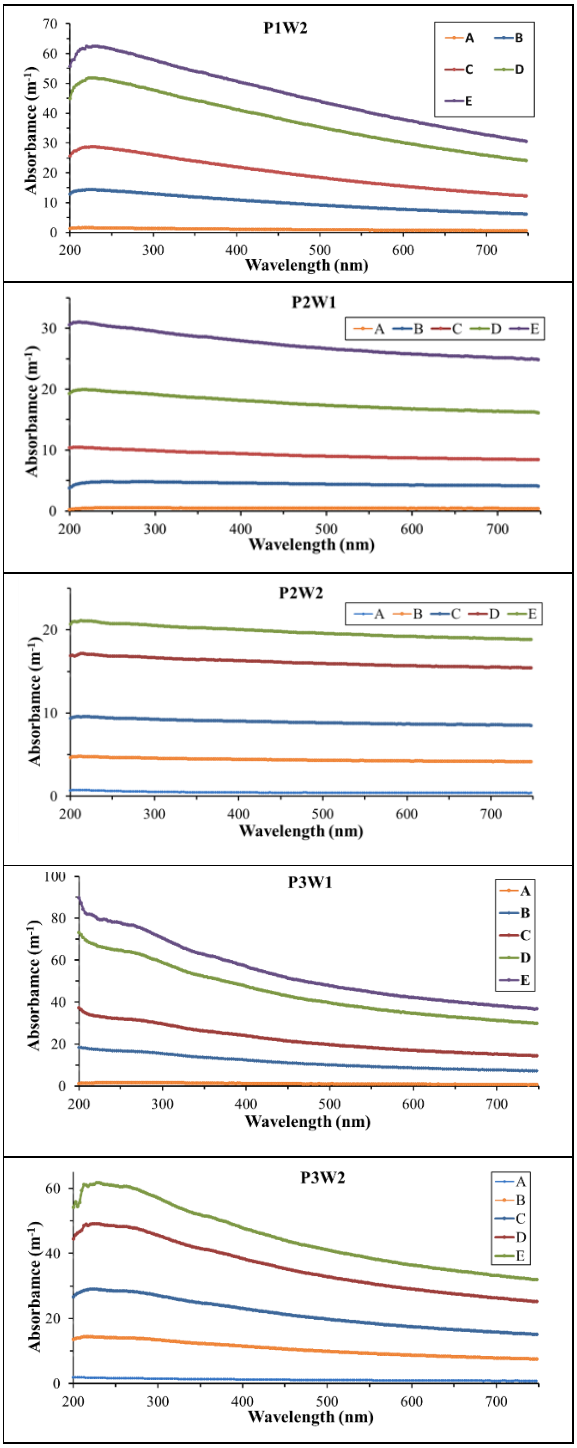

Figure S3-3 Particle contributions of P_1W_2, P_2W_1, P_2W_2, P_3W_1, P_3W_2 water samples at five different turbidity concentration levels from low to high (water samples A-E).

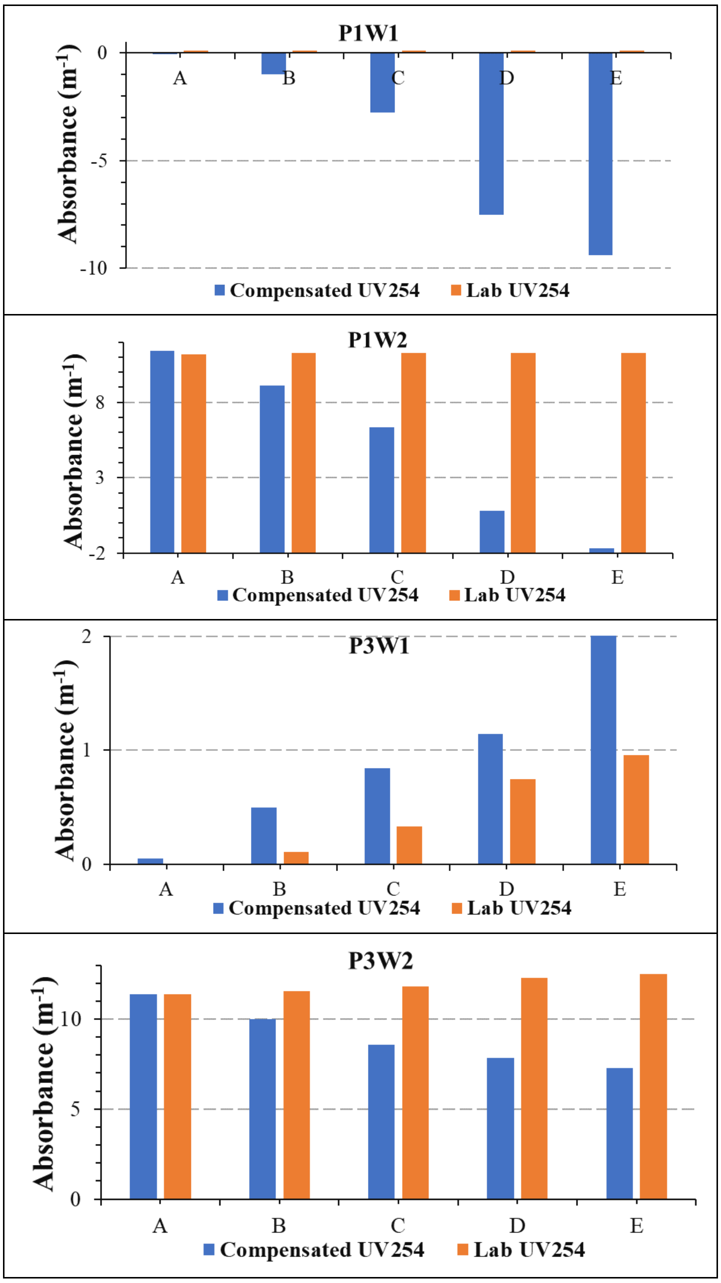

Figure S3-4 Comparisons between the measurements of compensated UV_{254} and lab UV_{254}, measured by a submersible and the bench-top UV-Vis instrument, for P_1W_1, P_1W_2, P_3W_1 and P_3W_2 water samples.

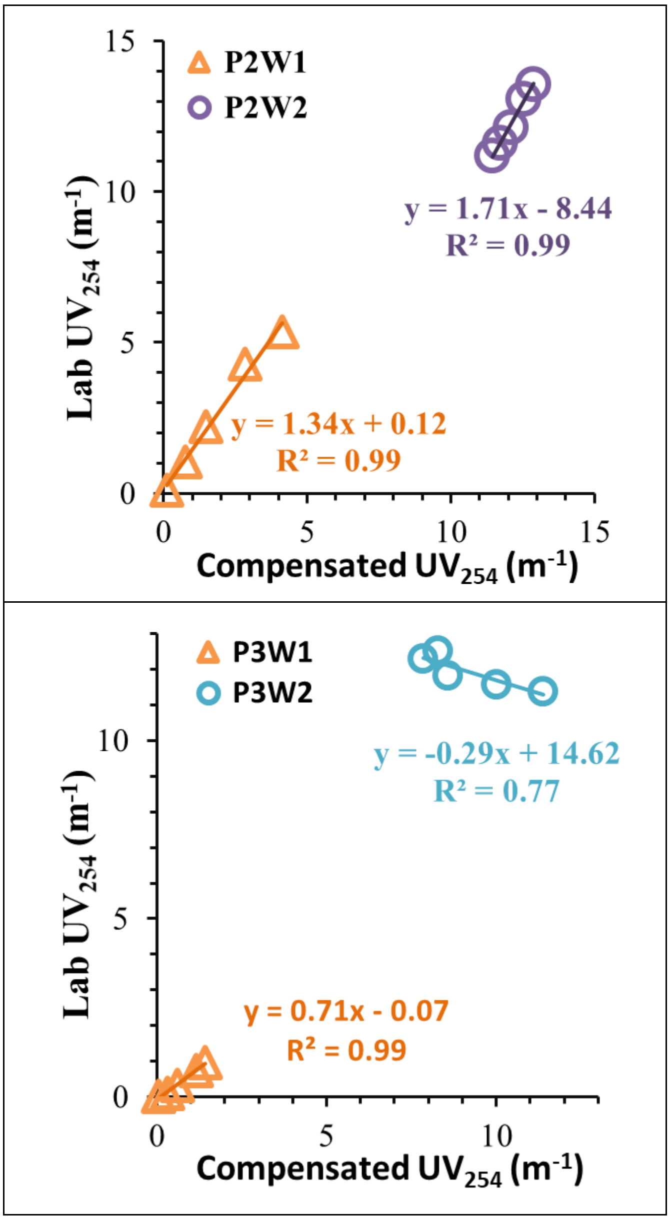

Figure S3-5 Comparisons between the measurements of a submersible and a bench-top UV-Vis spectrophotometer: compensated UV_{254} and lab UV_{254}. P_2W_1, P_2W_2, P_3W_1, and P_3W_2 were simulated water samples that were made up of two types of particles (P_2 and P_3), and two types of water-bases (W_1 and W_2), respectively.

Chapter 4

Develop and Assess Particle Compensation Techniques for Online Water Quality Monitoring Using UV-Vis Spectrophotometer

- Linear calibration methods can be used to correct different compensation techniques
- The utilised three compensation techniques are comparable to the built-in compensation
- The three compensation techniques are comparable to physical filtration method

This chapter presents research approach and progresses for the development of software techniques (surrogate parameters) to eliminate particle impact on the measurements. This is needed by the water industry as water utilities are suffering from measurement issues of using UV-Vis spectrophotometers for online water quality monitoring [1-5]. Particle compensation is a key component for online water quality monitoring and process control [6]. Thus, software techniques that were investigated and used for particle compensations, including single wavelength compensation, linear regression compensation and multiplicative scatter correction method for online UV-Vis measurements using time series spectra data from water treatment plants.

The results presented in this chapter reveal that these particle compensation techniques can provide reliable UV_{254} measurements for online water quality monitoring for water treatment. This chapter also shows the benefits of using the software compensation technique for site-specific compensation instead of relying on the instrument built-in algorithms for online water quality monitoring. The research explores the potential benefits of using online UV-Vis instruments for water quality management by improving online measurements using software compensations, which are able to replace physical filtrations (needed in laboratory-based measurements) to minimize maintenance requirements for both time and consumables. Moreover, it identifies that cost-effective simple UV-Vis sensors could be employed in the field to monitor water quality instead of using sophisticated full-spectrum UV-Vis instruments.

The following content of this chapter was published as a technical paper in the Journal of Chemometrics and Intelligent Laboratory Systems, 204, p.104074, as shown in Appendix D.

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Principal Author

Name of Principal Author (Candidate)	Zhining Shi		
Contribution to the Paper	Conceptualization, Methodology, Writing - Original draft preparation		
Overall percentage (%)	75		
Certification:	This paper reports on original research I conducted during the period of my Higher Degree by Research candidature and is not subject to any obligations or contractual agreements with a third party that would constrain its inclusion in this thesis. I am the primary author of this paper.		
Signature		Date	26th Mar 2022

Co-Author Contributions

By signing the Statement of Authorship, each author certifies that:

5 the candidate's stated contribution to the publication is accurate (as detailed above);

6 permission is granted for the candidate in include the publication in the thesis; and

7 the sum of all co-author contributions is equal to 100% less the candidate's stated contribution.

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Signature		Date	8th April 2020

4.1 Introduction

Absorbance using UV-Vis spectroscopy at a wavelength of 254 nm (UV_{254}) is an important water quality parameter. UV_{254} measures the concentration of organic matter and disinfection by-product precursors, which has been widely used by water treatment plant operators as a quick water quality measurement to control water treatment processes. Traditionally UV_{254} measurement relies on the laboratory analysis of water samples collected from ecosystem sites. This laboratory process frequently suffers from feedback delay and an inability to respond rapidly to water events through the water sample collection, transportation, storage and preparation [7]. Whereas, online water quality monitoring can provide quick responses to sudden water quality changes, which has been employed by some water utilities in recent years to manage water quality and assist water treatment process control [8].

Conventional laboratory UV_{254} analysis requires a filtration step using membrane filters to remove particles in the sample and eliminate the particle interference on the ultra-violet and visible (UV-Vis) measurements. Mathematical algorithms are used to eliminate particle interference for UV_{254} measurements, adjusting the results equivalent to conventional laboratory measurement using filtration. The use of mathematical algorithms to eliminate the sample filtration step would be particularly useful for online UV-Vis spectrophotometer. The mathematical algorithms are even implemented into some commercial online spectrophotometers and these online UV-Vis spectrometers can report UV_{254} as laboratory equivalent. However, the accuracy of particle compensation is still a major concern in terms of how the results could be comparable to analytical data using the conventional laboratory method for the variable water samples under different conditions.

Particle compensation is called either solid compensation by some instrument manufacturers or turbidity compensation, as turbidity measures light scattering which is the interaction of light and suspended solids in the water. Suspended particles affect the light absorption and consequently influence the whole UV-Vis spectrum which leads to attenuation of the transmitted light intensity [9]. Studies show that there are two types of particle compensation algorithms which can be used to remove the particle effect on the UV–Vis: compensation/subtraction technique and empirical modelling technique. The compensation technique is defined as the direct subtraction of absorbance of the single wavelength characterised by the particles in the water [10, 11]. Tang *et al.* concluded that individual single wavelengths including 275 nm, 350 nm, and 550 nm could be utilised to characterise the particles and successfully applied the compensation technique to remove the particle effect [12]. The compensation technique of correcting the turbidity by correlating with the blue shift was also reported as an option to eliminate the deviation and improve the accuracy of UV–Vis measurement in wastewaters [9].

Empirical modelling approaches can also be used as an alternative to the compensation technique to obtain the laboratory equivalent results using the measured parameters and the corresponding spectra. Hu and Wang developed surrogate parameters based on the integration of spectra for different functional groups of compounds and then eliminated the turbidity impact by deducting the turbidity component from surrogate parameters [13]. A dynamic partitioning algorithm was used based on the fourth-order derivative spectrum to analyse and predict the groups of contaminants. Hu *et al.* analysed the impact of chemical compositions in wastewater samples and extracted the morphology features of their absorptive spectra to eliminate the measurement derivation [14]. Partial least square (PLS) calibration models have been computed with the fourth derivative UV-Vis spectrum to remove the particle effect on the detection of water quality multi-parameter in artificial seawater [15]. Torres and Bertrand-Krajewski employed the partial least square to eliminate the particle effect on measuring chemical oxygen demand and total particles in urban drainage systems using Matlab software [16]. They commented that further tests for the application of the PLS method are needed to evaluate the robustness and variation of the regression. Empirical modelling using a multiple linear regression from the ‘lars’ package in the R software was adapted to remove the particle effect on the UV-Vis spectra of brackish water for rapid measurement of multiple material concentrations [17]. This study indicated that site-specific compensation should be developed individually for future applications. Besides, the instrument built-in compensation algorithm of some commercial UV-Vis spectroscopy software is developed based on PLS to link the spectra and laboratory data [10]. However, the details of the built-in algorithm method and technique for these commercial online spectrophotometers are not accessible to the users. Most of the reported compensation methods are relatively complex and may need a long processing time to conduct the analysis, making these techniques unsuitable for online water quality monitoring [13]. Due to the complexity and poor adaptability of the aforementioned methods, a simple and easy technique for particle compensation is needed for online water quality monitoring using UV-Vis spectrometry.

In this study, software compensation techniques including single wavelength (single point) and linear regression (multiple points) models were developed to remove the particle effect on the UV_{254} measurements. In addition, a well-established software compensation technique was also used to reduce the particle effect as a comparison. Online UV-Vis measurement systems were set up in two industrial water treatment plants with three water sources. The accuracies of the three compensation techniques were assessed through comparison with the instrument built-in compensation method. Bland-Altman analysis, a statistical analysis technique, was used to determine the agreement limits of the three compensation techniques as a comparison against the built-in algorithms.

4.2 Material and Methods

4.2.1 Water Sources

Water quality data were provided by two Water Treatment Plants (WTPs), Anstey Hill WTP and Happy Valley WTP in South Australia for this study. Both WTPs employ conventional water treatment practices comprising coagulation, flocculation, sedimentation and filtration to produce drinking water for South Australia. Anstey Hill WTP plant has a switchable water source system, taking water from Millbrook Reservoir or River Murray water (via the Mannum-Adelaide pipeline). Happy Valley WTP has a single water source from the Happy Valley Reservoir with water originating from both the River Murray and local catchment areas. These two WTPs were selected because of the differences in the water quality of the water sources. Three natural water matrices including Anstey Hill raw water (RW1), Happy Valley raw water (RW2) and Happy Valley treated water (TW), were selected as they represent different water qualities in terms of particle concentrations as determined by turbidity (NTU) and dissolved organic content (DOC). RW1 contained high turbidity (10 to 93 NTU) and moderate DOC (3.8 to 8.4 mg/L); RW2 had moderate turbidity (2 to 10 NTU) and high DOC (6.4 to 10.1 mg/L), and TW had low concentrations of both turbidity (0.1 to 0.8 NTU) and DOC content (0.3 to 4.5 mg/L). Turbidity and DOC ranges represent seasonal and water source variations between April and December 2013.

4.2.2 Instrument and Monitoring Locations

Three s::can spectro::lysers (s::can Messtechnik GmbH, Austria) were installed at three locations in the two selected WTPs to monitor the real-time water quality of RW1, RW2 and TW. The s::can spectro::lyser comprises a double beam photodiode array 256 pixel UV-Vis spectrometer and uses a Xenon lamp as a light source. It measures a UV-Vis spectrum at a wavelength range of 200-720 nm with a selectable optical path length range between 5 and 100 mm for different applications based on the required sensitivities. The installation locations were at the inlet of Anstey Hill WTP and both inlet and outlet of Happy Valley WTP. The path length of the spectro::lyser used was 5 mm, 5 mm and 100 mm for the inlet of Anstey Hill WTP (RW1), the inlet of Happy Valley WTP (RW2) and the outlet of Happy Valley WTP (TW), respectively. The instruments were first zero checked / baseline adjusted with ultrapure water to ensure a zero baseline. The spectro::lysers were equipped with automatic cleaning using compressed air before each measurement. Scheduled maintenance (manual cleaning) of the instruments was conducted fortnightly to ensure the cleanliness of the lens to eliminate drifting caused by fouling and that the sample lines were unobstructed. The three water quality monitoring locations were also used as sampling points for routine water quality monitoring (grab sampling), including inlet at Anstey Hill WTP, inlet and outlet of Happy Valley WTP.

4.2.3 Water Quality Monitoring Period

The three water sources were monitored between April and December 2013. Online spectro::lyser data and standard laboratory UV absorbance at 254 nm (UV_{254}) data were utilised in this study. The spectro::lyser was set to monitor water quality at a two-minute interval. Grab samples of raw water were collected for laboratory analyses weekly and fortnightly for the treated water. Water quality parameters of grab samples for routine monitoring including UV_{254}, colour at 456 nm, turbidity, and DOC were utilised to characterise the water quality. Prior to measuring UV_{254}, colour and DOC, the water samples were filtered using 0.45 µm PES membrane filters (ANPEL Laboratory Technologies, China). UV_{254} and colour were determined with a UV-Vis spectrophotometer (Evolution 60, Thermo Scientific, USA) using the method described in published study [18]. Turbidity was measured using a turbidity meter (2100AN, Hach, USA) and DOC using a total organic carbon analyser (900, Sievers Instruments Inc., USA) and determined using the methods described in Standard Methods [19].

4.2.3 Data Acquisition and Processing

The UV-Vis spectra were acquired by the s::can spectro::lyser, with the full UV-Vis spectral data saved as fingerprint (FP) files stored in the instrument hard-drive. FP files contain time-series data of spectral absorbance values which has a timestamp column (first column) to record the time of each measurement for wavelengths ranging from 200 to 720 with a 2.5 nm interval. FP files contain raw non-compensated data. Initial data pre-treatment was guided by the instrument integrated data diagnostic status (a column in the data stream to flag instrument issues). Those UV-Vis spectral data caused by known instrument issues or failure were manually eliminated. Further data pre-treatment was conducted by a time resolution optimisation algorithm using R and R-Studio [20, 21]. From the initial studies, the hourly average of the FP data did not reduce the resolution. Thus, the hourly average was used in this study to reduce the data volume for easier comparisons and without losing resolution. R scripts (codes) were developed to handle the large volume of UV-Vis spectral data generated by the spectro::lyser and perform the required compensation calculations and statistical analysis.

4.2.4 Particle Compensation Techniques

Four particle compensation techniques were used to remove the particle effect on the UV_{254} for online water quality monitoring of three water sources: RW1, RW2 and TW.

1. Ana::pro is the acquisition software supplied for the s::can spectro::lyser by the manufacturer (s::can Messtechnik, Austria). The compensation can be conducted by the instrument integrated ana::pro software in the real-time or offline standalone PC version. It contains algorithms using PLS based on the results of hundreds of water sources [22]. In this study, ana::pro was used in offline mode to process the raw spectral data (FP files) according to the procedures from the manual [23]. FP files of the three selected water sources were imported separately into the ana::pro software (offline mode) to generate compensated UV_{254} as an output parameter.

2. The single wavelength compensation (SWC) is a direct subtraction method. However, as s::can spectro::lyser has a 2.5 nm resolution and absorbance of UV_{254} was not given in the raw FP, an interpolate algorithm (R-script) was first applied to generate the spectral data in 1 nm resolution. Then the compensated UV_{254} was determined by subtracting the absorbance between 254 nm and 550 nm.

3. The linear regression compensation (LC) technique is based on the visible region of 380-750 nm which is the most impacted by particles given responses occur [15]. As explained previously, 1 nm resolution spectra (FPs) were generated first then an R algorithm was used to perform the calculations. For each spectrum, a linear regression (linear fit) was performed using a wavelength range of 550 to 580 nm as the x-axis and their corresponding absorbance as the y-axis. The obtained linear equation was then used to determine the particle absorbance at 254 nm. Compensated UV_{254} was a subtraction between UV_{254} and particle contribution of UV_{254}.

4. The multiplicative scatter correction (MSC) method is a normalization technique to correct particle effect (light scattering) on spectra. MSC method can correct the spectra by changing the scale and the offset based on the reference spectrum which is the mean of the spectra [24]. The hourly averaged UV-Vis spectra were processed for MSC using the unscrambler X software (version 10.4, CAMO). Then compensated UV_{254} were extracted from the spectra for analysis purposes.

A brief illustration of removing particle effect on the UV_{254} using different compensation methods is shown in Figure 4-1. Detailed explanations of these compensation techniques are shown in the results and discussion.

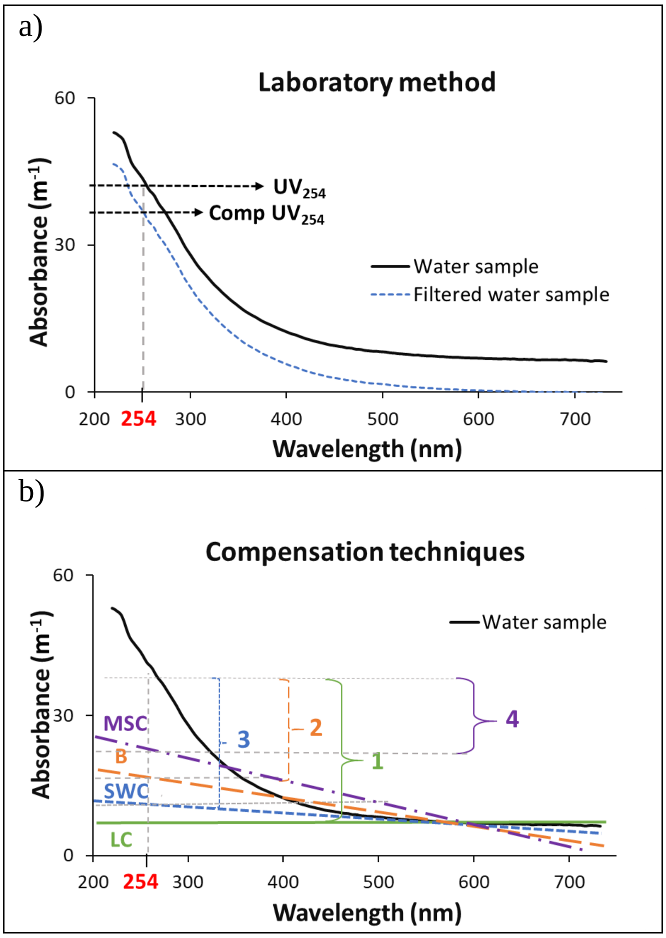

Figure 4-1 Illustration of particle compensation of UV_{254} using a) laboratory method and b) compensation techniques, i. single wavelength compensation (SWC), ii. instrument built-in compensation algorithm (B), iii. linear regression compensation (LC), and iv. multiplicative

scatter correction (MSC) method. 1, 2, 3 and 4 in Figure 4-1b represent the compensated (Comp) UV_{254} of SWC, B, LC and MSC, respectively.

4.2.5 Local Calibrations

The instrument built-in compensation algorithm (B) was developed using PLS based on hundreds of water samples. This technique is also considered as a generic method (average compensation) which may require a local calibration using grab samples [25]. The compensated UV_{254} of the built-in compensation method for the three water sources were calibrated using a simulated local calibration method which conducted the offline calibration using the laboratory grab sample measurements based on the linear model. Similarly, the compensated UV_{254} of three particle compensation techniques were also conducted local calibrations based on the linear modes.

4.2.6 Statistical Analysis

Data sets in this study were assumed to be generated from a large number of water samples from which the water quality data tend to follow normal distribution regardless of the shape of the data [26]. The bland-Altman analysis was used to assess the comparability of single wavelength and linear regression compensation techniques against the instrument built-in algorithm for UV_{254} of RW1, RW2 and TW. Bland-Altman analysis studies the difference of the compensation techniques by constructing the limits of agreement, which is determined by the bias (mean of the differences) of UV_{254} plus and minus 1.96 times its standard deviation of the differences between the two compensation methods [27]. It defines that 95% of data points lie within the limits of agreements. In this work, the differences between the two techniques were plotted as percentages. Percentage differences were calculated using the difference between the two methods divided by the means of the two methods and then multiplied by 100%. The Bland-Altman method only defines the intervals of agreements and does not indicate whether the limits are acceptable or not. Therefore, the acceptable limits need to be defined and compared with the limits of agreement generated by the Bland-Altman analysis. The limit of the acceptable percentage difference of UV_{254} (compensated) was defined as plus/minus 10% of the instrument built-in compensation method. A flowchart of the data analysis procedure of particle compensation techniques is shown in Figure 4-2.

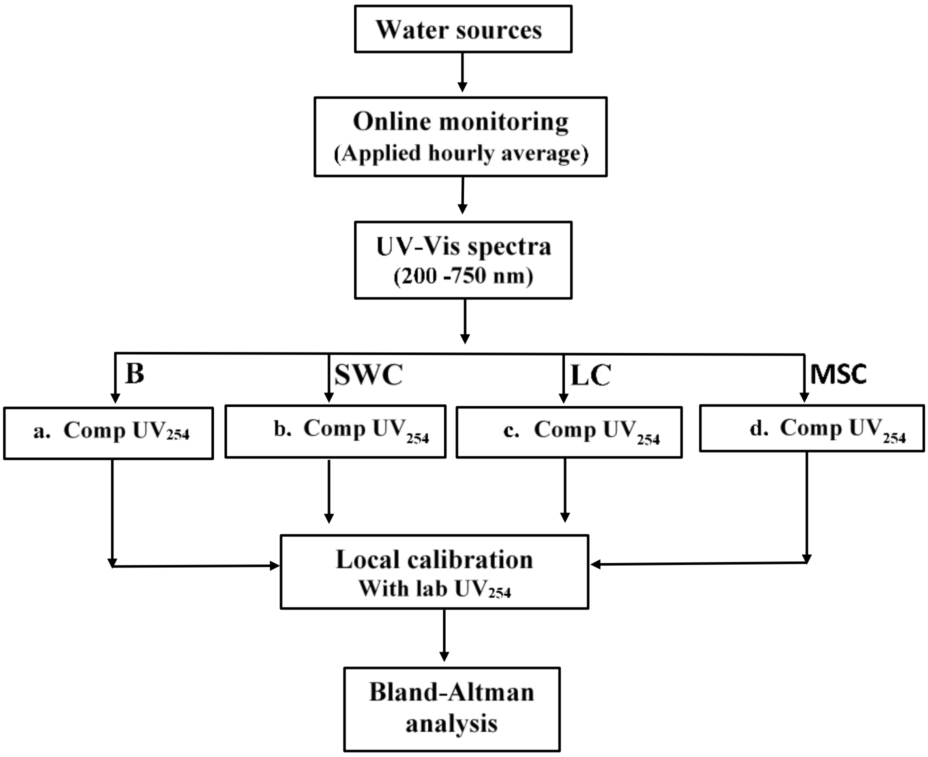

Figure 4-2 Flow chart to show the comparison procedures of single wavelength compensation (SWC), linear regression compensation (LC) and multiplicative scatter correction (MSC) techniques against the instrument algorithm (B) for UV_{254}.

4.3 Results and Discussion

4.3.1 Instrument Built-in Compensation and Calibration

UV-Vis spectral data of RW1, RW2 and TW monitored from April to December 2013 were processed using the ana::pro software. It should be noted that the water source for Anstey Hill WTP was switched from Millbrook Reservoir water to River Murray water in May and June 2013 as indicated in Figure 4-3. The three sets of data were compensated using the built-in compensation algorithms in offline mode. The compensated UV_{254} and calibrated UV_{254} (after calibrations using laboratory UV_{254} measurements) were plotted against time for the three water sources as shown in

Figure 4-3 and Figure 4S-1 in Supporting Information (SI). The plots of the built-in compensation for RW1 and RW2 water are shown in Figure 4-3.

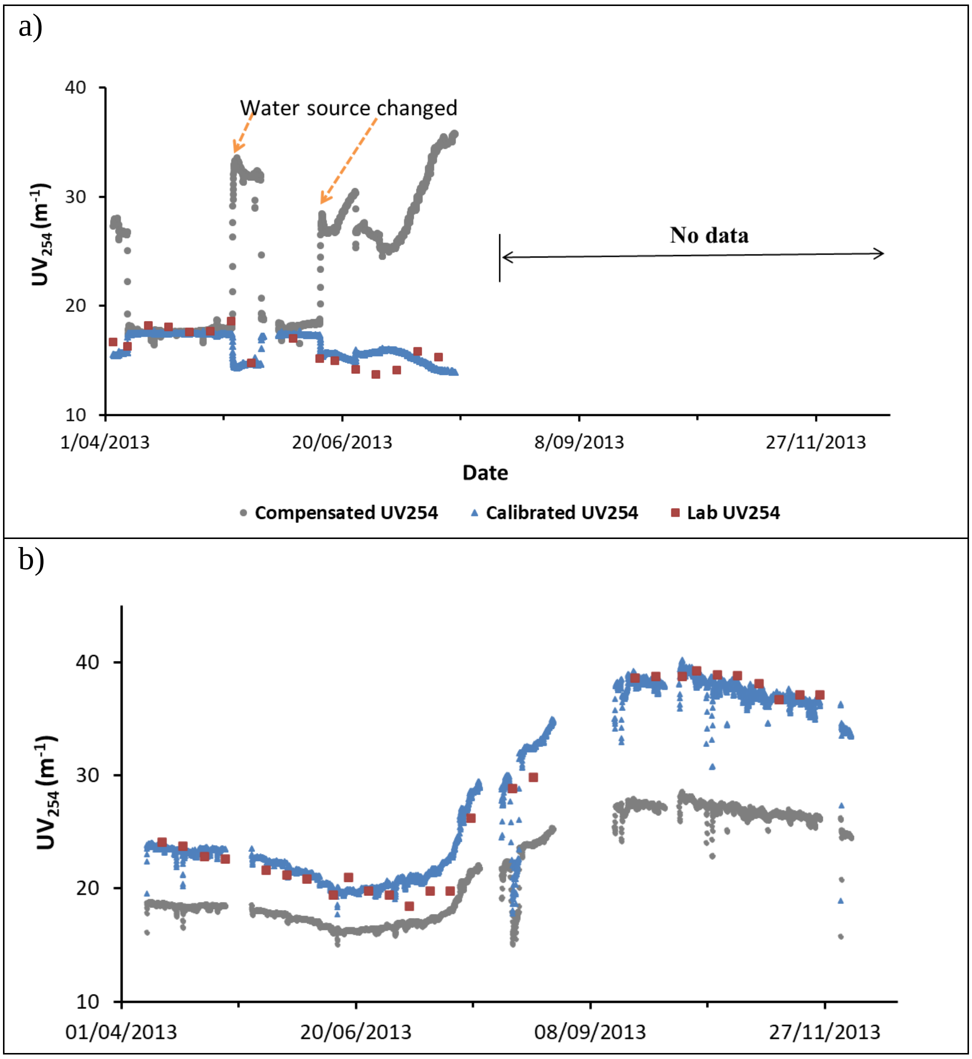

Figure 4-3 Comparisons between compensated UV_{254} and calibrated UV_{254} measurements against laboratory UV_{254} for a) Anstey Hill raw water (RW1) and b) Happy Valley raw water (RW2). Note: no data was recorded after August 2013 (Figure 4-3a), the instrument software could not perform the calculation for compensated UV_{254} due to the high turbidity of the water.

The water quality profiles as measured by UV_{254}, turbidity and DOC are shown in Figure 4-4a indicates that the turbidity of RW1 was dramatically increased when the source water was switched from Millbrook Reservoir water to River Murray water. The built-in compensation method was unable to generate the compensated UV_{254} measurements when the turbidity is higher than 60 NTU for Anstey Hill raw water, which may be beyond the compensation limit. Therefore, this result indicates that it is important and necessary to seek alternative particle compensation methods for online water quality measurements using UV-Vis spectroscopy, especially in highly variable water sources.

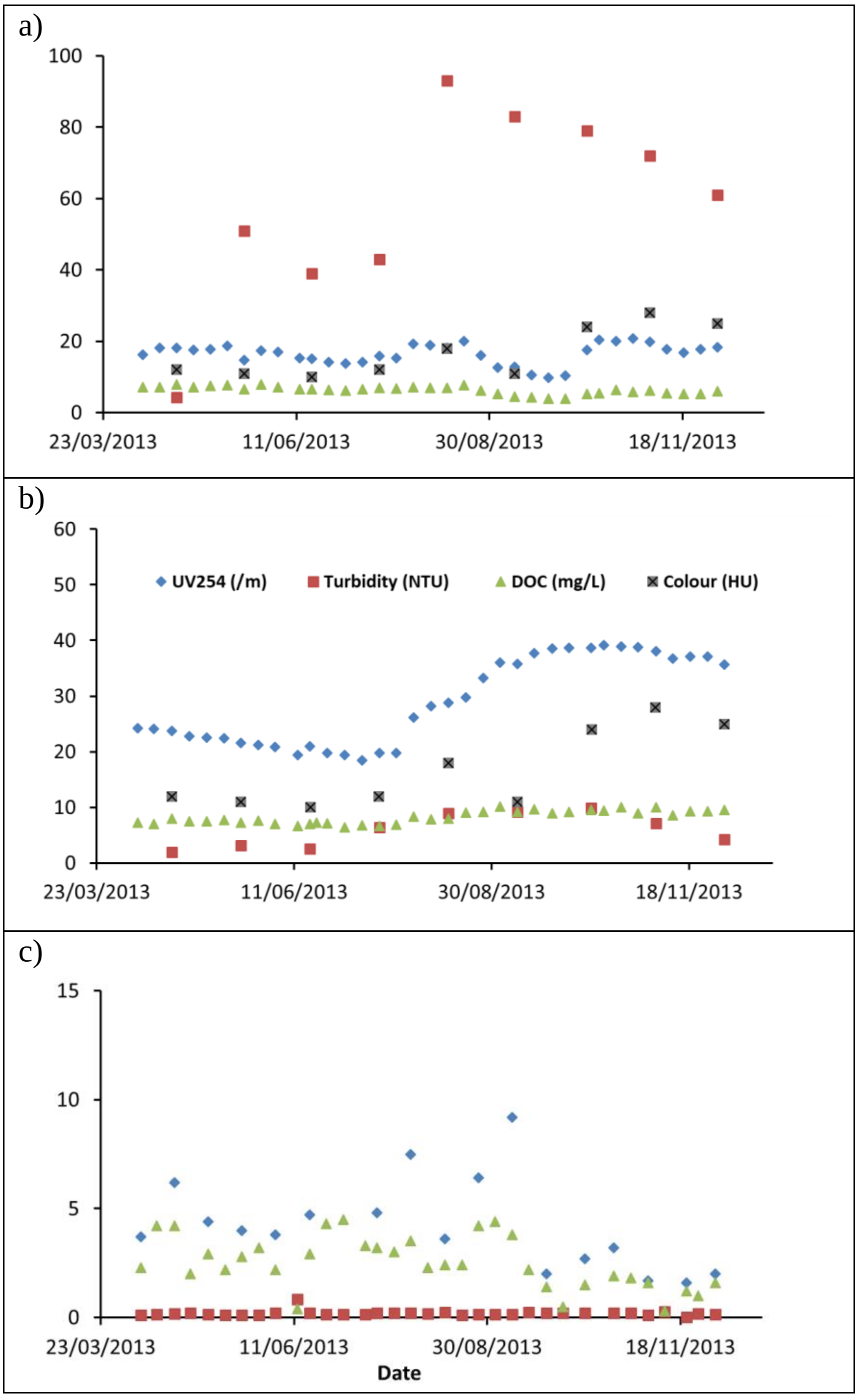

Figure 4-4 Laboratory results of water quality parameters of a) Anstey Hill raw water (RW1) and b) Happy Valley raw water (RW2) and c) Happy Valley treated water (TW) from April 2013 to December 2013.

Large differences were observed between the compensated UV_{254} and the UV_{254} of the grab samples for RW1 when the water source was switched from Millbrook Reservoir water with a turbidity level of less than 40 NTU to River Murray water with a turbidity level over 40 NTU. After the local calibration was applied (in simulated mode), the compensated and laboratory analytical UV_{254} data were well matched with each other. It indicates the results of the built-in compensation method are not comparable with the laboratory filtration method for water such as RW1 with large turbidity changes. However, with the adjustment of the local calibration, the built-in compensation is comparable with the laboratory filtration method even when large turbidity changes occur. Similar observations were obtained from the RW2 according to Figure 4-3. There was a gradual increase in turbidity of the RW2 from July to October 2013, during which much larger deviations between the UV_{254} of the built-in compensation method and that of the laboratory method at medium turbidity level over 5 NTU could be observed. Yet, after having performed the calibration, a good match between the compensated and laboratory analytical UV_{254} data was found for RW2. A similar observation can also be seen for the TW with a low turbidity level and low DOC content (Figure 4S-1 in SI). The DOC remained quite stable for all three water sources in which the turbidity changed significantly for raw waters. Therefore, the built-in compensation method with local calibration is comparable with the laboratory filtration method. Local calibrations have been established by other researchers to improve the accuracy of the online measurements of UV-Vis spectrometers [28, 29]. Therefore, our results reveal that with proper calibration, the built-in compensation method can perform the same particle compensation as the laboratory filtration. Our results reveal that the particle compensation techniques can assist the online UV measurements to provide acceptable water quality results for raw water with high turbidity and medium DOC content, raw water with medium turbidity and high DOC content and treated water with low turbidity and low DOC content. The built-in compensation method was used as a reference method to assess the two developed compensation methods in this study.

4.3.2 Software Compensation Techniques and Correction Methods

Nephelometric turbidity units (NTU) have been widely used as a surrogate measure of suspended particles. The turbidity signal was determined by selecting the wavelength range from 380-750 nm to eliminate the particle effects on the UV-Vis absorbance measurements of water samples. Studies have shown that the wavelength at 550 nm is the best for turbidity compensation in drinking water samples and has frequently been used in conjunction with UV_{254} measurements [30]. Absorbance at 546 nm was reported to eliminate the particle effect on the DOC for river water [31]. Mrkva used wavelength 545 nm in an automatic UV analyser to deduct the absorbance of particles for surface and wastewaters [32]. Some commercial instruments including the HACH UV probe [33] and Burkert spectral absorption coefficient sensors compensate for particle effect using a reference measurement at 550 nm [34]. Shimadzu UV instruments include UV-probe Type LXG 139 and type LXG 144, which also compensate for particle effect through a reference measurement at 550 nm. Thus, the single wavelength compensation (SWC) technique in this study was developed by direct subtraction between the absorbance of wavelength at 254 nm and 550 nm. The second compensation method developed in this study was linear regression compensation (LC) technique. It is based on the characteristic of particles between 550 - 580 nm to remove the particle effect on the UV-Vis spectra. A wavelength range of 550 - 580 nm was used in the LC technique as it represents the visible region most impacted by particles given responses that occurs within the wavelength range of 380 - 750 nm [15]. The third particle compensation method, multiplicative scatter correction (MSC), is a well-documented technique. The MSC is a transformation method to compensate for the particle effect in spectral data. MSC method can be used to reduce the particle effect by separating the chemical light absorption from the physical light scatter [35]. MSC technique is a commonly used method for processing NIR spectral data, however, it has not been widely used for processing UV-Vis spectra data. Studies have shown the MSC method can reduce the particle effect on the spectra [36-38].

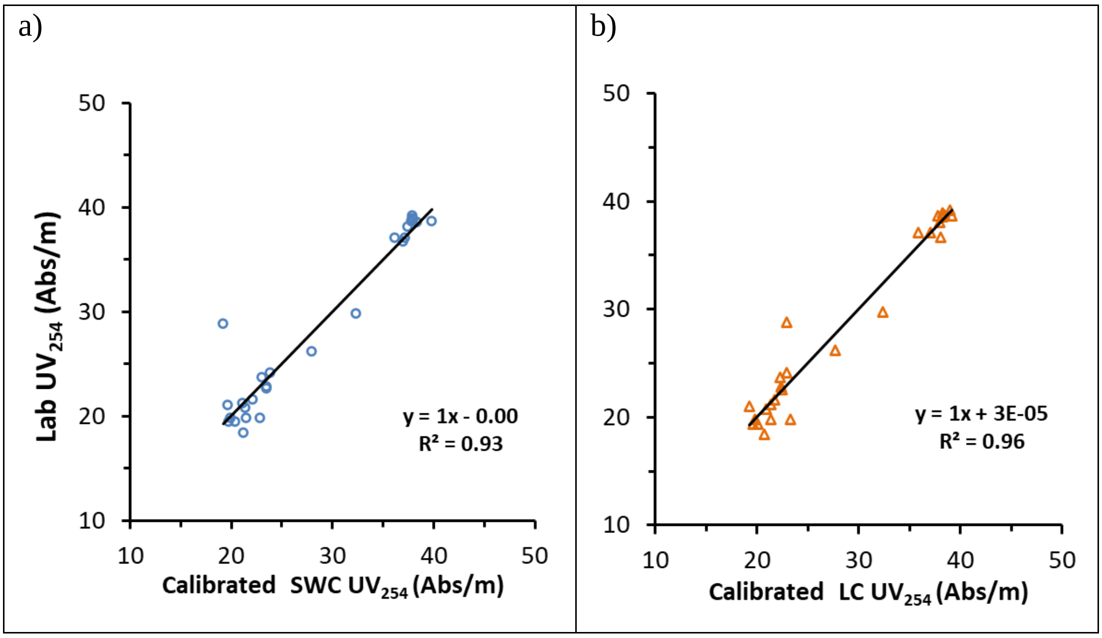

Figure 4-5 Comparison of calibrated UV_{254} of a) single wavelength compensation (SWC) and b) linear regression compensation (LC) with laboratory UV_{254} for Happy Valley raw water (RW2).

SWC, LC, and MSC techniques were applied to determine UV_{254} by removing the particle effect for RW1, RW2 and TW. It was observed that in a similar way as the built-in compensation behaviour, SWC, LC and MSC have different compensated results for different waters (Table S4-2 in SI) because of the different particle contents. Since the compensation is water source dependent, local calibration to compensate the background water matrix is required. Well-fitted linear relationships are found between the compensated UV_{254} obtained from the compensation techniques and laboratory UV_{254} measurements for all three water sources using the three compensation techniques, except for TW using the MSC. There was no linear correlation between the compensated UV_{254} and lab UV_{254} after conducting MSC could because all the compensated UV_{254} were very close to each other for different data. MSC may not be suitable for compensating UV spectral data of clean water such as treated water. This is because it was designed to remove large particle effects on spectra. Linear regression has been commonly used as a calibration method to improve the measurement accuracy for analytical methods and has been used for spectroscopy [39]. The spectro::lyser also uses a linear calibration mode. Thus, the compensated UV_{254} readings were corrected based on the linear relationships between the compensated UV_{254} of the developed techniques and laboratory UV_{254}. After adjustment, the corrected UV_{254} were plotted with their closest corresponding laboratory UV_{254} measurements, the slopes, y-intercepts and the coefficient of determination (R^2) from the linear regression line were determined for comparisons. A linear plot of the corrected UV_{254} of SWC compared to laboratory UV_{254} for RW2 is shown in Figure 4-5. According to the trend, the slope between the corrected UV_{254} and laboratory UV_{254} is 1.00 and the y-intercept is 0.00 with R^2 of 0.93, which means that SWC can generate the same compensated UV_{254} as the reference laboratory method. The linear regression line of the calibrated UV_{254} of LC and laboratory UV_{254} has a slope of 0.96, intercept of 1.21 and R^2 of 0.96 for RW2. It indicates that SWC can also generate the same compensated UV_{254} as the laboratory method. After adjustment, all the compensation methods including SWC, LC and MSC are comparable to the laboratory filtration method for RW2. Similar interpretations can also be stated for RW1 and TW according to Figure 4S-2 in SI. The results reveal that linear regression models can be used to correct the compensation methods. The stable level of DOC in each of the three water sources may contribute to the success of using linear calibration to adjust the compensation techniques. Linear regression methods have been employed by Torres and Bertrand-Krajewski to calibrate the particle compensation method of an online UV-Vis spectrophotometer for different water matrices [16]. Another study showed the linear curve fit was able to optimise the performance of UV-Vis spectrophotometers [40]. Linear regression is proven as a robust and sustainable adjustment method of UV-Vis spectrophotometers to estimate concentrations of water quality parameters [3].

4.3.3 Evaluation of Particle Compensation Methods

In this study, SWC, LC and MSC techniques were investigated in comparison with the instrument built-in compensation method using the Bland-Altman analysis, which was used to assess the accuracies of the three techniques for raw (natural water quality) and treated waters (drinking water quality).

4.3.3.1 Assessment of Single Wavelength Compensation Technique

The SWC technique was assessed for the performance of compensating the particle effects on the UV_{254}, for RW1, RW2 and TW, against the instrument built-in algorithm using Bland-Altman analysis. After adjustments of compensated UV_{254} measurements (calibrated UV_{254}) from the SWC technique and the built-in algorithm, the percentage differences between corrected UV_{254} of these two methods were plotted against the mean of the two methods, as Bland-Altman plots, for the three water sources, respectively. Bias (mean of percentage difference) is represented by the space between the x-axis and the zero percentage differences in the Bland-Altman plots. The analytical results of the Bland-Altman analysis are shown in Table 4-1.

Table 4-1 Bland-Altman analysis of assessing single wavelength (SWC), linear regression compensation (LC) and multiplicative scatter correction (MSC) techniques against the built-in algorithm (B) for Anstey Hill (RW1) and Happy Valley raw waters (RW2), and Happy Valley treated water (TW).

Water sources	**Methods after adjustment**	**Bland-Altman Analysis**			
		Mean of difference (%)	Limit of agreement (%)	Acceptable limit of agreement (%)	Agreement between two methods
RW1	SWC vs. B	1.71	[-6.21, 9.62]	[-10, 10]	Yes
	LC vs. B	1.45	[-5.37, 8.28]	[-10, 10]	Yes
	MSC vs. Lab	-0.94	[-8.33, 6.45]	[-10, 10]	Yes
RW2	SWC vs. B	-1.14	[-7.32, 5.04]	[-10, 10]	Yes
	LC vs. B	-0.77	[-5.18, 3.65]	[-10, 10]	Yes
	MSC vs. Lab	-1.52	[-9.81, 6.77]	[-10, 10]	Yes
TW	SWC vs. B	0.25	[-6.10, 6.67]	[-10, 10]	Yes
	LC vs. B	0.30	[-5.82, 6.68]	[-10, 10]	Yes
	MSC vs. Lab	-	-	-	-

The bias between the corrected UV_{254} of SWC technique and built-in compensation was determined as 1.71% for RW1. Agreement limits of the corrected UV_{254} between the two methods varied in a range of -6.21% and 9.62%. Compared to the pre-defined acceptable agreement limits of the interval from -10% to 10% of the differences, the SWC technique is comparable to the built-in compensation algorithm for compensating the particle effect on UV_{254} for RW1. For RW2 as shown in Figure 4-6, the bia between corrected UV_{254} of SWC technique and that of built-in compensation was -1.14%. Agreement limits between corrected UV_{254} of the two methods were found in the range of -7.32% and 5.04% for RW2. The percentage differences between corrected UV_{254} using two methods varied from -7.32% to 5.04% when the average of the corrected UV_{254} of these two methods increased. Compared to the pre-defined acceptable agreement limits, the SWC technique can generate good results as those using the built-in compensation algorithm for RW2. Similarly, for TW the agreement limits between these two methods were relatively small and varied within the range of the interval of -10% to 10% of the UV_{254} (Figure S4-3 SI). The SWC technique generated similar compensated UV_{254} measurements compared to that of the built-in compensation algorithm for RW2. Statistically, it can be 95% confident that the SWC technique is comparable to the built-in compensation method for removing the particle effect on the UV_{254} of raw and treated waters if the percentage differences between the two methods are acceptable within the plus/minus 10%.

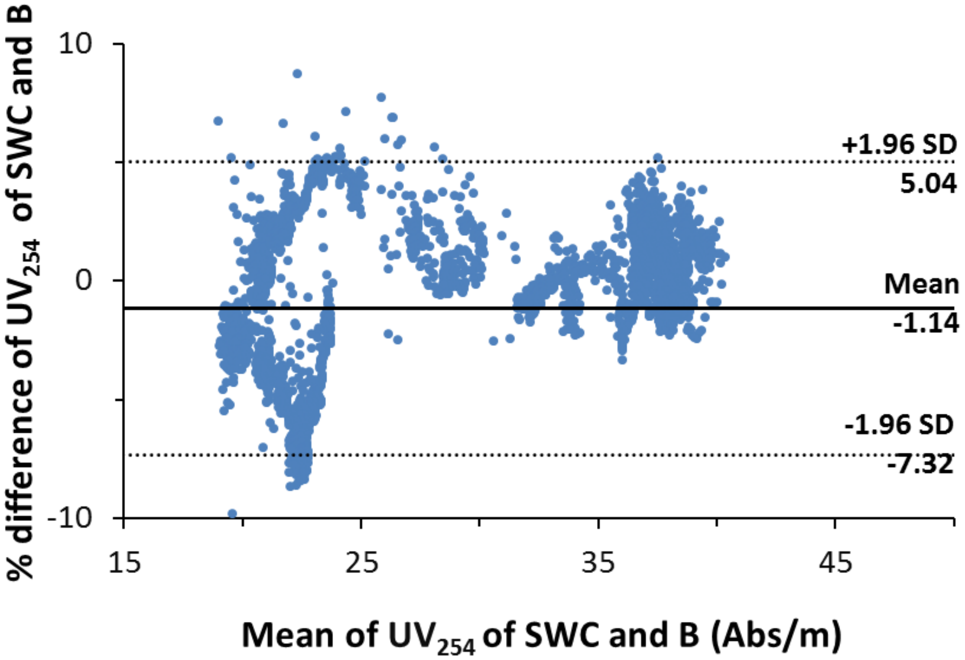

Figure 4-6 Bland-Altman plot of UV_{254} after application of single wavelength compensation technique (SWC) and the built-in algorithm (B) for Happy Valley raw water (RW2). The solid line represents the mean of percentage differences in UV_{254} of the two methods. Horizontal

dotted lines indicate upper (+1.96SD) and lower (-1.96SD) limits of agreement of the two methods.

4.3.3.2 Assessment of Linear Regression Compensation Technique

After adjustments, the LC technique was evaluated in comparison with the built-in algorithm in terms of the performance of compensating the particle effects on the UV_{254}, using Bland-Altman analysis for RW1, RW2 and TW. The differences between corrected UV_{254} measurements using the LC technique and that of the built-in algorithm were plotted against the mean of corrected UV_{254} of the two methods, as Bland-Altman plots, for three water sources, respectively (Table 4-1).

Bias between the corrected UV_{254} of LC technique and the built-in compensation was 1.45% for RW1. Agreement limits between the two methods varied from -5.37% to 8.28%, which is within the acceptable limit of intervals. Hence the LC technique is comparable to the built-in compensation method for RW1. For both RW2 and TW, the bias between the corrected UV_{254} of the LC technique and that of built-in compensation was less than 1% in Figure 4-7 and Figure 4S-4 (SI). Agreement limits between corrected UV_{254} of the two methods were within the acceptable limit agreement. Therefore, the LC technique generated similar compensated UV_{254} compared to that of the built-in compensation algorithm for RW1, RW2 and TW. Statistically, there is 95% certainty that the LC technique is comparable to the built-in compensation method of raw and treated waters within a plus/minus 10% difference between the two methods.

Along with adjustments, LC has similar particle compensation behaviour as the built-in compensation method on the UV_{254} for different water sources. The LC technique considers particle contribution on the UV_{254} within a wavelength range of 500-580 nm. Similar to the SWC technique, the LC technique is also water source dependent and linear adjustment methods can improve the accuracies of compensating the particle effect on UV_{254} of raw and treated waters.

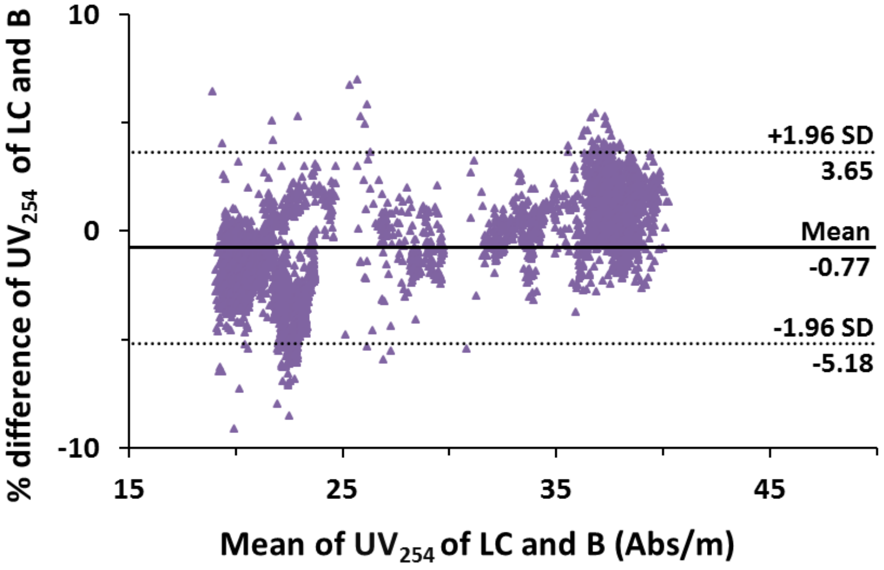

Figure 4-7 Bland-Altman plot of UV_{254} after application of linear regression compensation technique (LC) and the built-in algorithm (B) for Happy Valley raw water (RW2). The solid line represents the mean of percentage differences in UV_{254} of the two methods. Horizontal dotted lines indicate upper (+1.96SD) and lower (-1.96SD) limits of agreement of the two methods.

4.3.3.3 Assessment of Multiplicative Scatter Correction Technique

After performing local calibration of the multiplicative scatter correction (MSC) method, the performance of the MSC method was evaluated by comparing with the instrument built-in algorithm for RW1 and RW2, using Bland-Altman analysis. The percentage difference between the calibrated UV_{254} of MSC was plotted against the mean of the two methods as shown in the Bland-Altman plots for RW1 and RW2 (Figure 4S-5 in SI). The mean difference between the calibrated UV_{254} of MSC and the built-in compensation methods was -0.94% and -1.52% for RW1 and RW2, respectively. The limit of agreement between the two methods was within the intervals of acceptance limit. Hence, the MSC technique is comparable to the built-in compensation method for RW1 and RW2. However, MSC is not comparable to the built-in compensation method for TW. This could be because the nature of MSC is to correct the light scattering of the particle in the water. TW contained a very low particle content. It should be pointed out that MSC is commonly used for turbid solutions such as wine and solid materials such as meat [24, 35].

In the case of comparison of SWC, LC and MSC with the built-in compensation method, all three particle compensation methods had different particle compensation behaviour when compared to the built-in compensation method on UV_{254} for different water types. SWC, LC and MSC techniques need to be adjusted for individual waters to remove the particle effect. It shows that particle compensation is water source dependent. This finding is in agreement with the previous studies [3]. This is probably because compensation techniques generally cannot directly handle the large change in water quality, particularly turbidity character changes [11] [13]. Water quality characteristics are different for individual water sources. Variation of the water quality, particularly turbidity can affect the compensation ability of the compensation method on the UV_{254}. Reported studies showed that it is difficult to compensate for the particle effect when there is a large variation of turbidity [11] [13]. The industrial experience of monitoring water quality also shows that compensating particle effect on the UV-Vis absorbance measurement is difficult when water turbidity is fluctuating or the water source changes [41].

Provided linear correction (local calibration) method with acceptable error, the developed single wavelength compensation and linear regression compensation techniques could be used as alternative methods to eliminate the particle effect on the UV_{254} measurements for raw and treated waters. Also, the multiplicative scatter correction technique could be used as an alternative particle compensation method to remove the particle effect for raw waters.

Overall, our results reveal that SWC, LC and MSC techniques with the linear adjustment can be applied in practice for online water quality monitoring. SWC is a relatively simple method to remove the particle effect on the UV_{254} in the water. Simple UV-Vis instruments with a single wavelength in the visible region (500nm) could be employed in the field to monitor water quality instead of using sophisticated full-spectrum UV-Vis instruments. These findings can assist water treatment plant operators to monitor water quality more effectively because the utilization of software compensation methods and local calibrations allow more accurate and reliable UV-Vis readings. Further research is necessary to investigate how these compensation methods can be applied to the situation of real-time water quality monitoring.

4.4 Conclusion

Our results reveal that after applying a local calibration method, instrument built-in compensation methods can be comparable to the reference laboratory methods for the UV_{254} measurements for raw and treated waters from two drinking water WTPs. In the same way as the built-in compensation method, the developed SWC and LC techniques as well as the multiplicative scatter correction method are also water source dependent. Linear correction methods as local calibrations are based on the linear relationships of compensated UV_{254} of the developed techniques and the laboratory UV_{254} measurements of the grab samples. It could be applied for the development of techniques to improve the accuracies of online measurements of water quality monitoring. The bland-Altman analysis was employed to assess the calibrated UV_{254} using developed SWC and LC as well as MSC techniques. The compensated UV_{254} generated from these two methods were found to be comparable with that of the built-in compensation method using online UV-Vis spectral data from drinking water treatment plants. According to the Bland-Altman analysis, with the assistance of the linear correction (local calibration) method, both SWC and LC had very similar compensation behaviours on the UV_{254} as the built-in compensation algorithm for varied raw and treated waters. MSC was comparable to the built-in compensation method for raw waters. Potentially, along with the linear correction method, both the single wavelength and the linear regression compensation, as well as the multiplicative scatter correction methods could be used as alternatives to remove the particle effect on the UV_{254} for online water quality monitoring. The use of the alternative compensation techniques may allow less maintenance of the instrument and possibly improve the reliability and usability in online mode by WTP operators. Moreover, simple UV-Vis instruments with a single wavelength in the visible region (500 nm) could be employed in the field to monitor water quality instead of using sophisticated full-spectrum UV-Vis instruments.

4.5 References

1. Chow, C., Dexter, R., Sutherland-Stacey, L., Fitzgerald, F., Fabris, R., Drikas, M., Holmes, M., Kaeding, U., *UVspectrometry in drinking water quality management*, in *WATER-MELBOURNE THEN ARTARMON*. 2007. p. 40-43.
2. Waterra, *Optimisation of existing instrumentation to achieve better process performance*. 2017, Water research Australia.
3. Lepot, M., Torres, A., Hofer, T., Caradot, N., Gruber,G., Aubin, J., Bertrand-Krajewski, J., *Calibration of UV/Vis spectrophotometers: A review and comparison of different methods to estimate TSS and total and dissolved COD concentrations in sewers, WWTPs and rivers.* Water Research, 2016. **101**: p. 519-534.
4. Chow, C., et al., *UV spectrometry in drinking water quality management*, in *OZwater'17, Australian Water Association*. 2017. p. 63.
5. Hu, Y. and X. Wang, *Application of surrogate parameters in characteristic UV–vis absorption bands for rapid analysis of water contaminants.* Sensors and Actuators B: Chemical, 2017. **239**: p. 718-726.
6. Matilainen, A., M. Vepsäläinen, and M. Sillanpää, *Natural organic matter removal by coagulation during drinking water treatment: a review.* Advances in Colloid and Interface Science, 2010. **159**(2): p. 189-197.
7. Banna, M.H., Imran, S., Francisque, A., Najjaran, H., Sadiq, R., Rodriguez, M., and Hoorfar, M., *Online drinking water quality monitoring: review on available and emerging technologies.* Critical Reviews in Environmental Science and Technology, 2014. **44**(12): p. 1370-1421.
8. Matilainen, A., Vepsäläinen, Mikko., Sillanpää, Mika., *Natural organic matter removal by coagulation during drinking water treatment: a review.* Advances in Colloid and Interface Science, 2010. **159**(2): p. 189-197.
9. Hu, Y., Wen, Y, Wang, X., *Novel method of turbidity compensation for chemical oxygen demand measurements by using UV–vis spectrometry.* Sensors and Actuators B: Chemical, 2016. **227**: p. 393-398.
10. Langergraber, G., Fleischmann, N., and Hofstaedter, F., *A multivariate calibration procedure for UV/VIS spectrometric quantification of organic*

matter and nitrate in wastewater. Water Science and Technology, 2003. **47**(2): p. 63-71.

11. Wang, X., Lin, Z., Jin, X., *Ultraviolet scanning technique for water COD measurement and its instrument development.* Journal-ZheJiang University Engineering Science, 2006. **40**(11): p. 1951.
12. Tang, B., et al., *Experimental research of turbidity influence on water quality monitoring of COD in UV-visible spectroscopy.* Spectroscopy and Spectral Analysis, 2014. **34**(11): p. 3020-3024.
13. Hu, Y., and Wang, X., *Application of surrogate parameters in characteristic UV–vis absorption bands for rapid analysis of water contaminants.* Sensors and Actuators B: Chemical, 2017. **239**: p. 718-726.
14. Hu, Y., Liu, C., and Wang, X., *Novel local calibration method for chemical oxygen demand measurements by using UV–Vis spectrometry*, in *IOP Conference Series: Earth and Environmental Science*. 2017, IOP Publishing. p. 012016.
15. Hu, Y., Wen, Y., and Wang, X., *Detection of water quality multi-parameters in seawater based on UV-Vis spectrometry*, in *OCEANS 2016-Shanghai*. 2016, IEEE. p. 1-4.
16. Torres, A., and Ertrand-Krajewski, J. L., *Partial Least Squares local calibration of a UV–visible spectrometer used for in situ measurements of COD and TSS concentrations in urban drainage systems.* Water Science and Technology, 2008. **57**(4): p. 581-588.
17. Etheridge, J.R., Birgand, F., Osborne, J.A., Osburn, C.L., Burchell, M.R., and Irving, J., *Using in situ ultraviolet-visual spectroscopy to measure nitrogen, carbon, phosphorus, and suspended solids concentrations at a high frequency in a brackish tidal marsh.* Limnology and Oceanography: Methods, 2014. **12**(1): p. 10-22.
18. Bennett, L.E., Drikas, M., Kapralos, C., Kozlik, E., and Fabris, R., *The evaluation of colour and natural waters.* Water Research, 1993. **27**(7): p. 1209-1218.
19. APHA, A., WEF, *Standard Methods for the Examination of Water and Waste Water*. 21st ed. 2005, Washington, DC.

20. R Core Team, *A language and environment for statistical computing.* R Foundation for Statistical Computing, 2013.
21. RStudio Team, *RStudio: Integrated development for R.* RStudio (Version 1.0.143), Inc., Boston, MA 2015.
22. Van den Broeke, J., Langergraberb, G., Weingartnera, Andreas., *On-line and in-situ UV/vis spectroscopy for multi-parameter measurements: a brief review.* Spectroscopyeurope, 2006. **18**(4).
23. GmbH., s.c.M., *Spectrometer Probe V2.* Manual 2011.
24. Preys, S., Roger, J.M. and Boulet, J.C., *Robust calibration using orthogonal projection and experimental design. Application to the correction of the light scattering effect on turbid NIR spectra.* Chemometrics and Intelligent Laboratory Systems, 2008. **91**(1): p. 28-33.
25. Fabris, R., Chow, C., Dexter, R., Colton, J., Knoblauch, J., Drikas, M., *Feed-forward coagulant control using online UV/Vis monitoring.* Water Science & Technology: Water Supply 2013. **13**(2): p. 420-426.
26. Elliott, A.W., WA., *Statistical analysis quick reference guidebook with SPSS examples.* Sage Publications, 1st ed. London, 2007.
27. Giavarina, D., *Understanding Bland Altman analysis.* Biochemia Medica, 2015. **25**(2): p. 141-51.
28. Byrne, A.J., Brisset, T., Chow, C.W.K., Lucas, J., and Korshin, G.V., *Development of online surrogate parameters using UV-VIS spectroscopy for water treatment plant optimisation.* Australia Water Association Water Journal 2014. **41**: p. 94-100.
29. Mussared, A., Chow, C, Holmes, M, Van Leeuwen, J, Kaeding, U., *Implementation of predictive alum dose control systems.* 77th Annual WIOA Victorian Water Industry Operations Conference and Exhibition, Bendigo Exhibition Centre, 2014.
30. Saunier, B.M., Selleck, Robert E., Trussell, R Rhodes., *Preozonation as a coagulant aid in drinking water treatment.* American Water Works Association, 1983: p. 239-246.

31. Zhao, Y., Li, Y., Zhen, Y., and Fang, Y., *A novel monitoring system for COD using optical ultraviolet absorption method.* Procedia Environmental Sciences, 2011. **10**: p. 2348-2353.

32. Mrkva, M., *Automatic UV-control system for relative evaluation of organic water pollution.* Water Research, 1975. **9**(5-6): p. 587-589.

33. HACH, *UVAS sc.* HACH user manual, HACH Company, 2014.

34. Burkert., *Miniaturised SAC measurement for continuous monitoring of water quality.* Burkert fluid control systems, 2015.

35. Geladi, P., MacDougall, D. and Martens, H., *Linearization and scatter-correction for near-infrared reflectance spectra of meat.* Applied spectroscopy, 1985. **39**(3): p. 491-500.

36. Wu, Y., Peng, S., Xie, Q., Han, Q., Zhang, G. and Sun, H., *An improved weighted multiplicative scatter correction algorithm with the use of variable selection: Application to near-infrared spectra.* Chemometrics and Intelligent Laboratory Systems, 2019(185): p. 114-121.

37. Huang, Z., Tao, W., Fang, J., Wei, X. and Du, Y., *Multivariate calibration of on-line enrichment near-infrared (NIR) spectra and determination of trace lead in water.* Chemometrics and intelligent laboratory systems, 2009. **98**(2): p. 195-200.

38. Kovacs, Z., Bázár, G., Oshima, M., Shigeoka, S., Tanaka, M., Furukawa, A., Nagai, A., Osawa, M., Itakura, Y. and Tsenkova, R., *Water spectral pattern as holistic marker for water quality monitoring.* Talanta, 2016. **147**: p. 598-608.

39. Boulet , J., Brown,S. D., and Roger, J., *A simple, projection-based geometric model for several linear pretreatment and calibration methods.* Chemometrics and Intelligent Laboratory Systems, 2014. **138**: p. 48–56.

40. Adeeyinwo, C.E., Okorie, N. N., Idowu, G. O., *Basic calibration of UV/ Visible Spectrophotometer.* International Journal of Science and Technology, 2013. **2**(3).

41. Chow, C., Dexter, R., Sutherland-Stacey, L., Fitzgerald, F., Fabris, R., Drikas, M., Holmes, M. and Kaeding, U., *UV spectrometry in drinking water quality management*, in *Ozwater'17*. 2007. p. 63.

4.6 Supporting Information

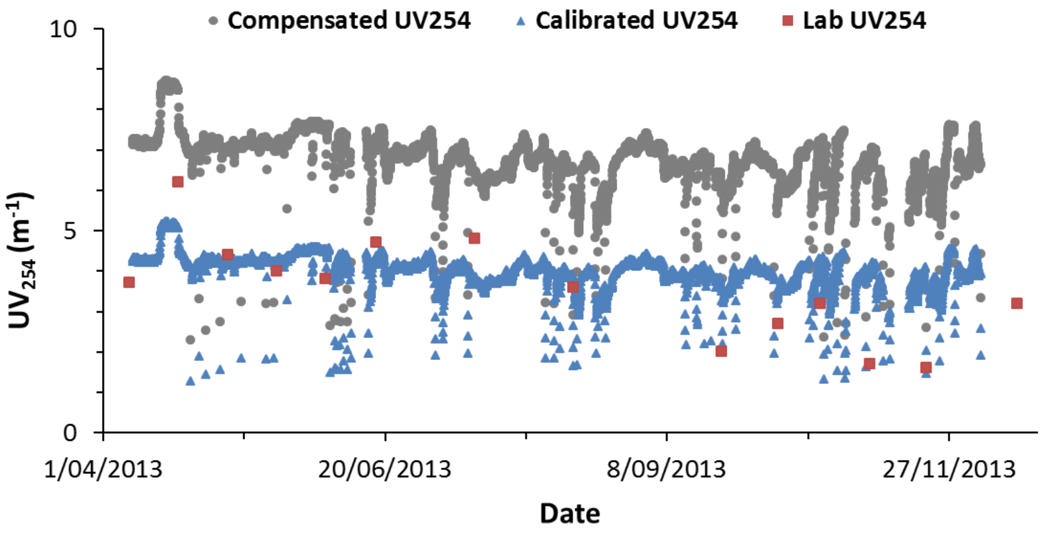

Figure S4-1 Laboratory equivalent UV$_{254}$ after built-in compensation and local calibration, as well as laboratory UV254 of Happy Valley, treated water (TW).

Table S4-1: Water quality characteristics of Anstey Hill raw water (RW1), Happy Valley raw water (RW2) and Happy Valley treated water (TW) from April 2013 to December 2013.

Water quality	**RW1**			**RW2**			**TW**		
Parameters	Min	Max	Ave	Min	Max	Ave	Min	Max	Ave
UV$_{254}$ (Abs/m)	9.8	20.1	16.4	18.4	39.2	30.0	1.6	9.2	4.1
Colour (HU)	10.0	28.0	17.0	18.0	65.0	44	–	–	–
Turbidity (NTU)	4.2	93.0	60.5	1.9	9.9	5.7	0.1	0.8	0.2
DOC (mg/L)	3.8	8.4	6.1	6.4	10.1	8.3	0.3	4.5	2.3
pH	7.4	7.8	7.6	7.6	8.4	8.0	7.1	7.8	7.5
Temperature (°C)	7	22	15.3	10	22	16.0	11.0	22	16.3
Conductivity (µS/cm)	198	547	385	520	592	559	207	670	41
Algae –total (cells/mL)	84	4920	1256	2400	1200000	207275	-	-	-

Legend: DOC refers to dissolved organic carbon.

Table S4-2: Calibration of single wavelength compensation (SWC), linear regression compensation method (LC) and multiplicative scatter correction (MSC) based on their linear regression with laboratory measurements for Anstey Hill raw water (RW1), Happy Valley raw water (RW2) and Happy Valley treated water (TW).

Water sources	**Methods**	**Calibration based on linear regressions**		
		Slope	*Intercept*	*coefficient of determination (R^2)*
RW1	B & Lab	-0.19	20.90	0.58
	SWC & Lab	-0.09	19.68	0.65
	LC & Lab	-0.19	20.90	0.58
	MSC & Lab	1.83	-59.76	0.88
RW2	B & Lab	0.67	-7.28	0.93
	SWC & Lab	1.06	-0.75	0.96
	LC & Lab	1.22	-0.98	0.96
	MSC & Lab	-156.13	4663.6	0.97
TW	B & Lab	0.61	-0.13	0.24
	SWC & Lab	0.42	0.93	0.21
	LC & Lab	0.43	1.06	0.21
	MSC & Lab	-	-	-

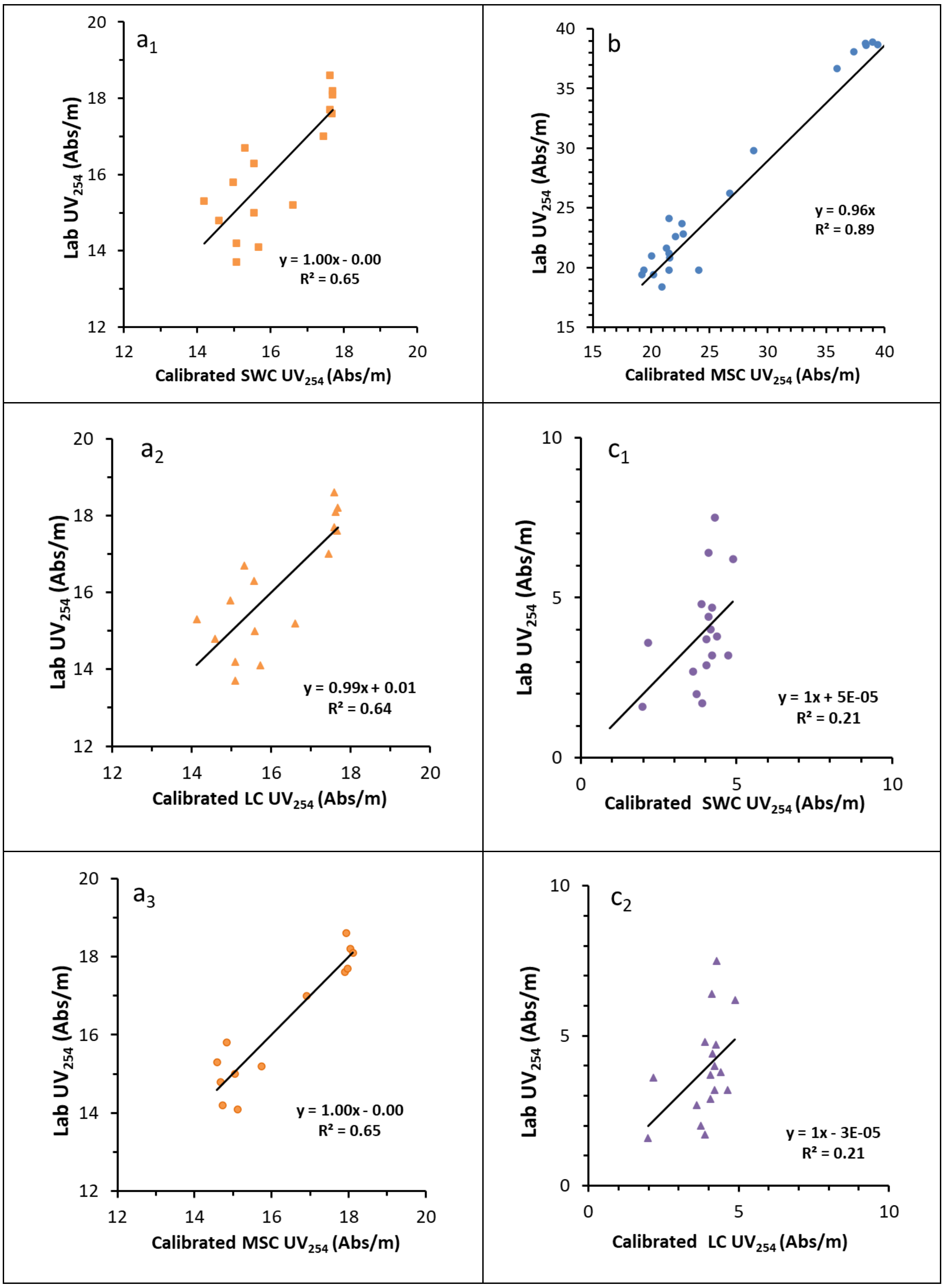

Figure S4-2 Comparisons between calibrated UV_{254} of single wavelength compensation (SWC) method, linear wavelength compensation (LC) and multiplicative scatter correction (MSC) method against lab UV_{254} of laboratory filtration method for Anstey Hill raw water (a_1, a_2, a_3), Happy Valley raw water (b) and Happy Valley treated water (c_1, c_2).

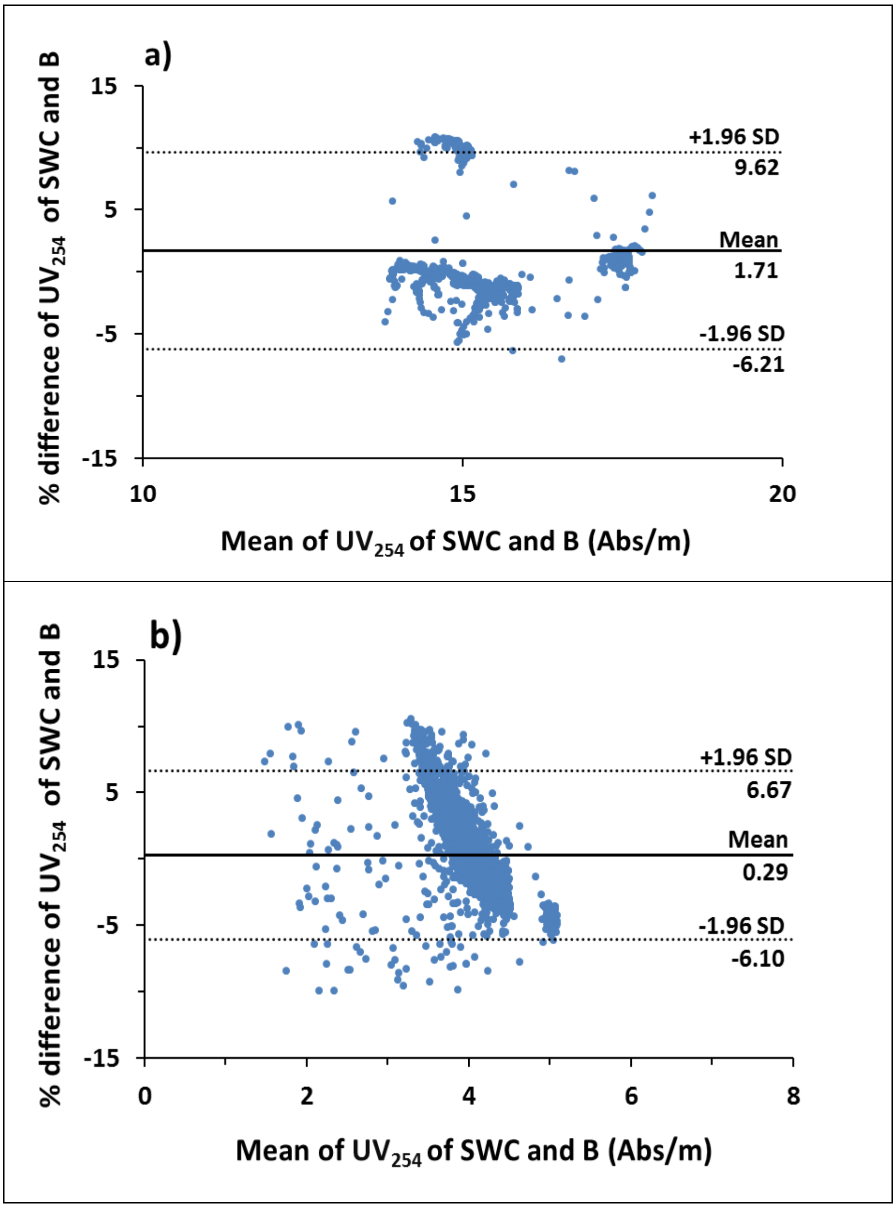

Figure S4-3: Bland-Altman plot of calibrated UV_{254} of single wavelength compensation technique (SWC) and the built-in algorithm (B) for a) Anstey Hill raw water and b) Happy Valley treated water. The solid line represents the mean of percentage differences in UV_{254} of the two methods. Horizontal dotted lines indicate higher (+1.96SD) and lower (-1.96SD) limits of agreement between the two methods.

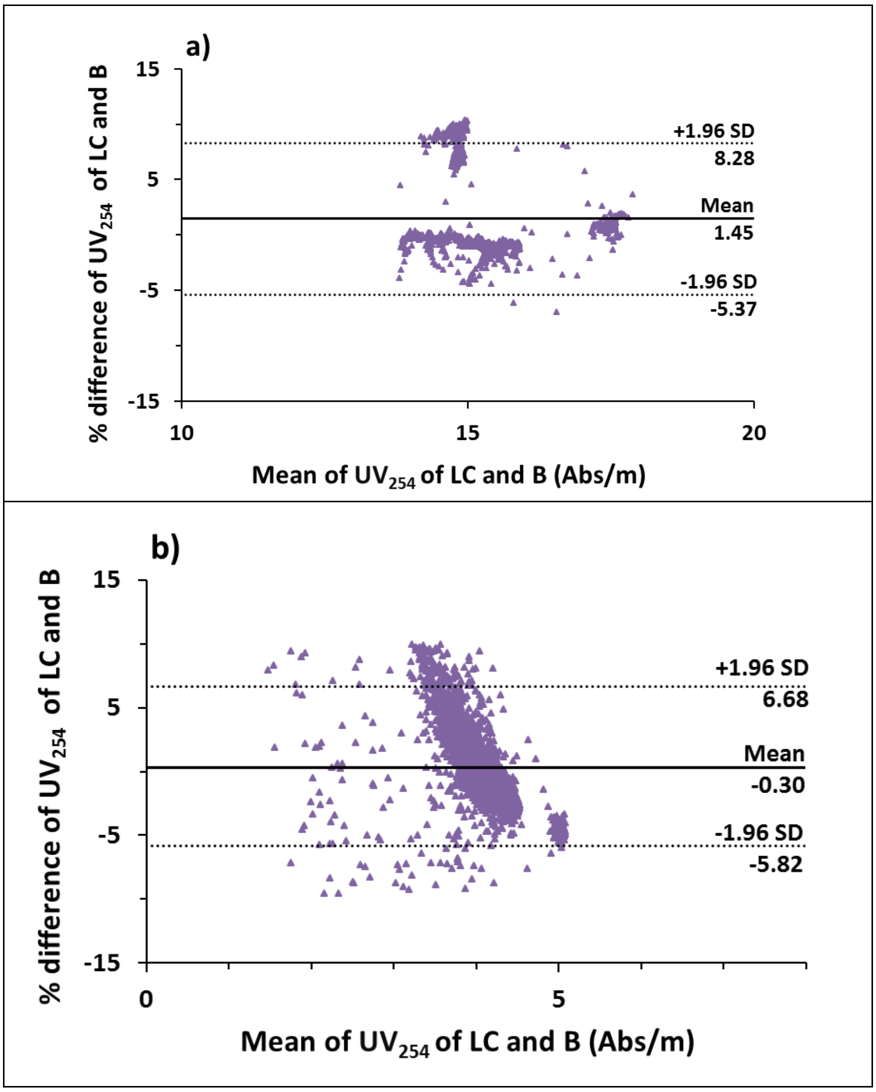

Figure S4-4 Bland-Altman plot of calibrated UV_{254} of linear regression compensation technique (LC) and the built-in algorithm (B) for a) Anstey Hill raw water and b) Happy Valley treated water. The solid line represents the mean of percentage differences in UV_{254} of the two methods. Horizontal dotted lines indicate higher (+1.96SD) and lower (-1.96SD) limits of agreement between the two methods.

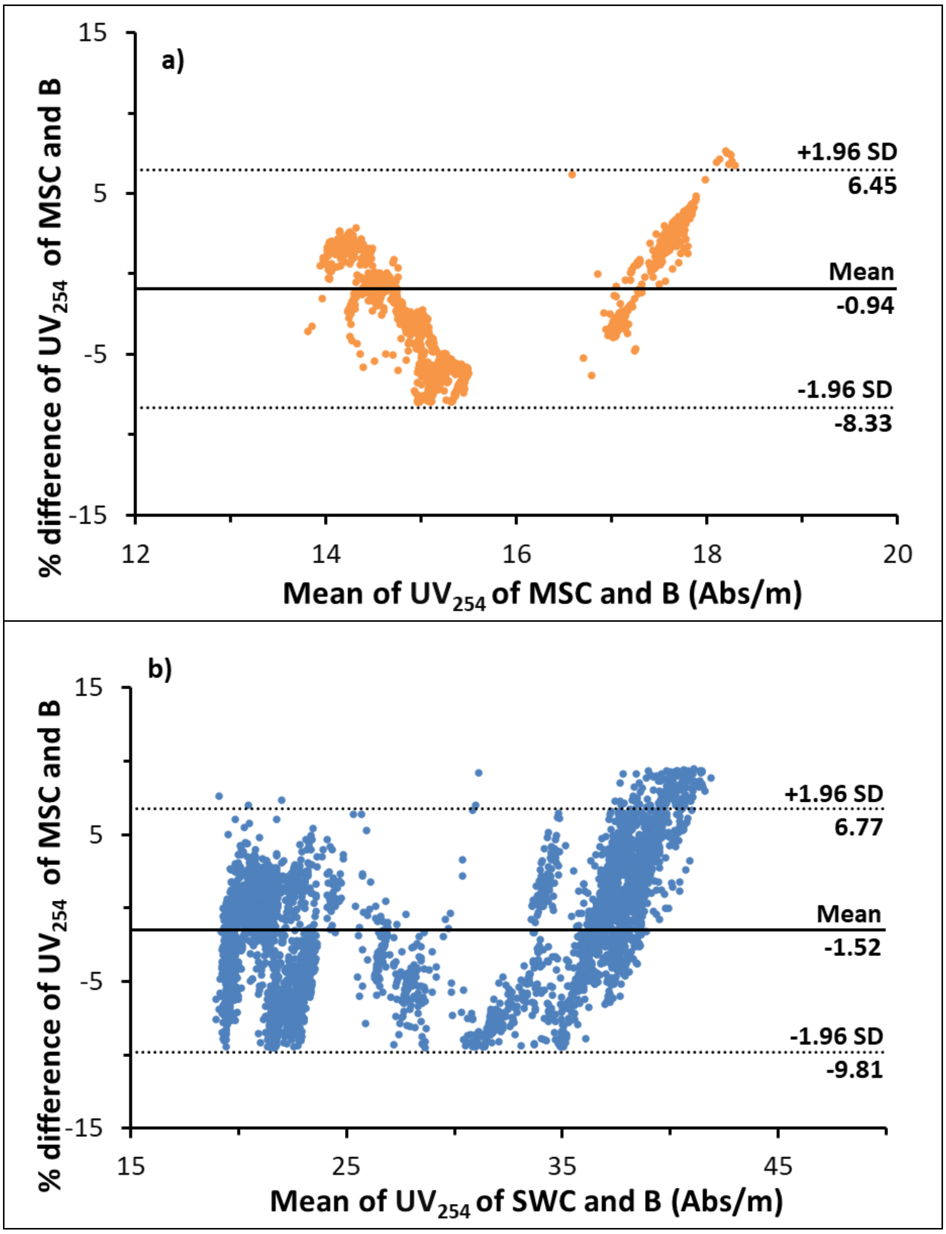

Figure S4-5 Bland-Altman plot of calibrated UV_{254} of multiplicative scatter correction (MSC) technique and the instrument built-in algorithm (B) for a) Anstey Hill raw water and b) Happy Valley treated water. The solid line represents the mean of percentage differences in UV_{254} of the two methods. Horizontal dotted lines indicate higher (+1.96SD) and lower (-1.96SD) limits of agreement between the two methods.

Chapter 5 Development of Coagulant Dose Prediction Models for Process Control using Online UV-Vis Spectra

- Raw water UV-Vis spectra can mimic operator decision to determine coagulant dose
- Multiple linear regression and partial least squares regression can extract chemical signatures from spectra for coagulation control
- Coagulant doses can be predicted using only raw water quality data

Results presented in previous chapters indicate that UV-Vis spectrophotometers can be used for online water quality monitoring, particularly for continuous monitoring and early warning of water quality events. High accuracy of water quality measurements using the UV-Vis instruments can be achieved using the developed software compensation techniques. This online water quality measurement technique can be a promising tool to control water treatment process. Conventional water treatment is the most widely applied water treatment process which contains the following steps: coagulation, flocculation, sedimentation and filtration [1]. The majority of drinking water treatment plants employ the conventional water treatment method. The coagulation process largely affects the processing efficiency of the water treatment plants [2, 3]. It is essential to determine the optimal coagulant dosage as under-dosing leads to poor drinking water quality, but over-dosing can result in operational issues and increase the treatment cost [4, 5]. The conventional method for controlling the coagulation process in drinking water treatment plants relies on water quality data and operators’ experiences [6, 7]. Jar tests using raw water could be only conducted once every two months or when sudden water change occurs in some cases [8]. The coagulant dosage levels cannot be adjusted until a process upset occurs, leading to under- or over- dosing. It can be challenging to determine appropriate coagulant doses proactively for tight control of coagulation with the traditional method as the increasingly stringent regulations for drinking water. However, modelling approaches for determinations of coagulant dosages can demonstrate fast responses to the raw water quality changes and allow more precise dosing control to achieve stable treated water quality [7, 9].

This study presented in this chapter was to establish alternative approaches for coagulation control. This may be the first investigation to build coagulant dose determination models using online raw water quality data (UV-Vis spectra) combined with chemometrics to determine coagulant doses for a drinking water treatment plant. Online UV–Vis spectra of raw water were directly used to mimic operators' decisions in the determination of coagulant dose for process control combined with advanced computing. The results revealed spectral information that could be used as input for the decision support tools. It demonstrates that an online UV–Vis spectrophotometer combined with a software model has the potential to be a decision-support tool for real-time determination of coagulant doses for process control, under the fluctuation of the raw water quality.

The following content of this chapter was published as a technical paper in the Journal of Water Process Engineering, 45, p.102526, as shown in Appendix E.

Statement of Authorship

Title of Paper	Determination of coagulant dosages for process control using online UV-Vis spectra of raw water
Publication Status	☑ Published ☐ Accepted for Publication ☐ Submitted for Publication ☐ Unpublished and Unsubmitted work written in manuscript style
Publication Details	Shi, Z., Chow, C.W., Fabris, R., Liu, J., Sawade, E. and Jin, B., 2022. *Journal of Water Process Engineering*, 45, p.102526.

Principal Author

Name of Principal Author (Candidate)	Zhining Shi		
Contribution to the Paper	Conceptualization, Methodology, Writing - Original draft preparation		
Overall percentage (%)	75		
Certification:	This paper reports on original research I conducted during the period of my Higher Degree by Research candidature and is not subject to any obligations or contractual agreements with a third party that would constrain its inclusion in this thesis. I am the primary author of this paper.		
Signature		Date	26th Mar 2022

Co-Author Contributions

Name of Co-Author	Christopher Chow		
Contribution to the Paper	Conceptualization, Methodology, Supervision, Writing - Reviewing and Editing.		
Signature		Date	28th Mar 2022

Name of Co-Author	Bo Jin		
Contribution to the Paper	Methodology, Supervision, Writing - Reviewing and Editing		
Signature		Date	5th April 2022

Name of Co-Author	Rolando Fabris
Contribution to the Paper	Supervision, Methodology, Writing - Reviewing and Editing

Signature		Date	30th March 2022

Name of Co-Author	Jixue Liu		
Contribution to the Paper	Supervision, Writing - Reviewing and Editing		
Signature		Date	8th April 2022

Name of Co-Author	Emma Sawade		
Contribution to the Paper	Writing - Reviewing and Editing		
Signature		Date	8th April 2022

5.1 Introduction

Coagulation is an essential chemical process of the conventional water treatment operation for water clarification and is particularly effective for removing natural organic matter (NOM). NOM is a precursor for the formation of disinfection by-products, which can have significant environmental and health risks in the water distribution system. The traditional method for controlling the coagulation system in water treatment plants (WTPs) relies on jar tests which require over six hours to carry out depending on sample collection and analysis arrangement [7, 9, 10]. It may lead to under- or over- dosing, particularly when a wide fluctuation of water quality occurs as jar tests may not offer quick turnover time. Overdosing of coagulants for the coagulation process may lead to higher operational costs and excessive sludge production while underdosing may fail to meet the water quality targets [4, 5]. Determination of coagulant doses using modelling approaches can demonstrate fast responses to the changes of raw water quality and allow more precise dosing control to achieve stable treated water quality. Coagulant dosing predictions based on mathematic modelling have been developed in recent years. A few models were even employed to predict the coagulant doses and assist the water treatment processes [7, 11].

A variety of techniques have been used to develop the coagulation model and predict coagulant doses for drinking water treatment based on raw water quality parameters, including multiple linear regression (MLR), adaptive neuro-fuzzy inference system (ANFIS), fuzzy weighting, partial least squares regression (PLS), and artificial neural networks (ANNs) [12-17]. Coagulant dose determination models were built using ANNs and regression equations for surface water treatment with raw water quality parameters, including dissolved organic carbon (DOC), UV absorbance at 254 nm (UV_{254}), turbidity, alkalinity, dissolved oxygen and pH [9, 15, 18, 19].

Some studies have utilised PLS combined with UV-Vis spectral data to predict water quality parameters in water [20, 21] and wastewater [22, 23]. Most of the reported prediction models for coagulant doses are operated based on the water quality results provided from laboratory analysis. There were very few reported studies using PLS to predict coagulant doses. PLS can extract information from a large volume of data matrix which is suitable to apply when the matrix has more independent variables than dependent variables and there is multicollinearity among the independent variables. In comparison with PLS, ANNs is a popular prediction model for coagulant dose prediction. ANNs can also handle large datasets, detect complex relationships, learn patterns and make decisions based on similar situations. Most of the prediction models rely on the raw water quality data of grab samples as inputs to predict the coagulant doses. It is unlikely to capture the rapid variations of the water quality to get correct predictions based on the data of grab samples when water quality changes as there are significant delays in obtaining the laboratory data. However, predictions based on the online UV-Vis spectral data could be a promising approach, which can use continuous water quality data to predict doses, with the ability to capture the rapid variations of water quality to get the correct predictions. Colton [24] reported a unique method using the online UV-Vis spectra to predict coagulant doses for WTPs. However, this was an indirect method that first needs to quantify the water quality (turbidity, UV_{254} and DOC) of the raw water using the spectra and then utilised the quantified water quality data as inputs for an exponential model to determine the coagulant doses. Zhou and Meng [25] conducted a lab-based study to use spectral data from a bench-top UV-Vis instrument to determine optimal coagulant doses for the removal of dissolved organic matter from a combined coagulation and ultrafiltration system. The optimal doses were determined in their study based on the correlations between spectral data and fouling behaviour.

This study was to establish an in-situ coagulation dosing prediction and control method integrated with the online UV-Vis spectra monitoring technique. We employed online UV-Vis spectral data of raw water from a municipal drinking WTP to build coagulant dose determination models and to determine coagulant doses for coagulation process control. This study also aimed at directly using raw water UV-Vis spectra to mimic operators' decisions in the determination of coagulant dose for process control. Three different models with different levels of complexity were evaluated, including multiple linear regression (MLR), partial least squares (PLS) and artificial neural networks (ANNs).

5.2 Materials and Methods

5.2.1 Water Treatment Plant

Happy Valley (HV) WTP in South Australia was selected for this study. The HV WTP employs conventional water treatment practices comprising coagulation, flocculation, sedimentation, and filtration units. This WTP provides drinking water across the metropolitan area in the capital city of South Australia (SA). The raw water for the WTP is provided by the Happy Valley Reservoir with water originating from both the River Murray and local catchment areas. The raw water is characterised by moderate turbidity (0.1 to 10 NTU) and high DOC ranging from 6 to 10 mg/L. Turbidity and DOC ranges represented seasonal variations between April and December 2013. The HV WTP was selected as the source water is the representation of enclosed surface water catchment of a reservoir in SA.

5.2.2 Monitoring Location and Instrument

The inlet of HV WTP was the sample point for real-time water quality monitoring with a submersible UV-Vis spectrophotometer. The instrument, s::can spectro::lyser (s::can Messtechnik GmbH, Austria), is a double beam photodiode array 256 pixel UV–Vis spectrometer with an optical path of 5mm and spectral resolution of 2.5 nm. The online instrument measures the absorbance of wavelengths within 220-720nm. The details of the instrument and the maintenance can be found in the previous study [26].

5.2.3 Data Source

The water source was monitored between April and December 2013. Raw UV-Vis spectra in the range of 220 -720 nm were acquired from the submersible instrument at two-minute intervals. The plant alum dose record in the same period was also obtained for this study. Alum, aluminium sulphate [$Al_2(SO_4)_3.18H_2O$)], was used as the primary coagulant. WTP alum doses were determined by the operators, to achieve treated water with DOC less than 5mg/L, under pH conditions of 6 (plant record). The WTP alum doses were determined by WTP operators mainly based on jar tests of raw water and operators' experience, in some water quality event situations such as heavy rainfalls, the operators may refer to the WTC-Coag software and the treated water quality [27]. Jar tests of raw water were conducted once every two months or when there were sudden changes in the water quality. WTC-Coag is a mathematical model for real-time prediction of optimal alum dose, which has been used in metropolitan WTPs in SA for over 10 years including the HV WTP [11]. This software requires UV_{254}, colour, and turbidity of raw water as inputs to generate predicted alum doses. The operators can select certain % removal of the total coagulable DOC and choose to refer to the coagulant doses determined based on the 80-90% DOC removal using the WTC-Coag software when they were deciding the dose levels.

Overall, UV-Vis spectral data of raw water quality and plant dose data of the HV WTP were utilised in this study. The UV-Vis spectral data were collected from the online instrument. The data of plant doses were extracted from an internal operational database of SA Water Corporation (SA Water) with hourly extrapolation.

5.2.4 Data Pre-treatment

Initial data pre-treatment was based on the instrument operation status. The online UV-Vis spectra related to the instrument issues and non-operational period of WTP were excluded. Further data pre-treatment was conducted using a time resolution optimisation algorithm and hourly average [26]. Particles in the water can affect the online UV-Vis measurements [28]. Thus, the averaged UV-Vis spectra were processed using a particle compensation method to remove particles. The baseline correction method was based on the absorbance of particles is at a wavelength of 550 nm. Particle compensation of source water using UV_{550} has been proved to be an effective method to remove the particle effect on the online UV-Vis measurements [26].

5.2.5 Data Processing

The data pre-treatment and processing were conducted in the workspace of R and R-Studio [29]. Figure 5-1 shows a flow chart of modelling development and validation of coagulant dose determinations. The online UV-Vis spectra of raw water quality data of the HV WTP were utilised to determine the coagulant dose. Important wavelengths of the online UV-Vis spectra were selected using variable selection methods. The absorbances of the selected wavelengths were used as model inputs to predict plant alum doses. The plant doses determined by operators were utilised as the model output. The DOC level of treated water during the same period was under 5mg/L (Figure 5S-1 in SI) which met the drinking water quality target. It indicates that the plant doses were accurate for the coagulation control.

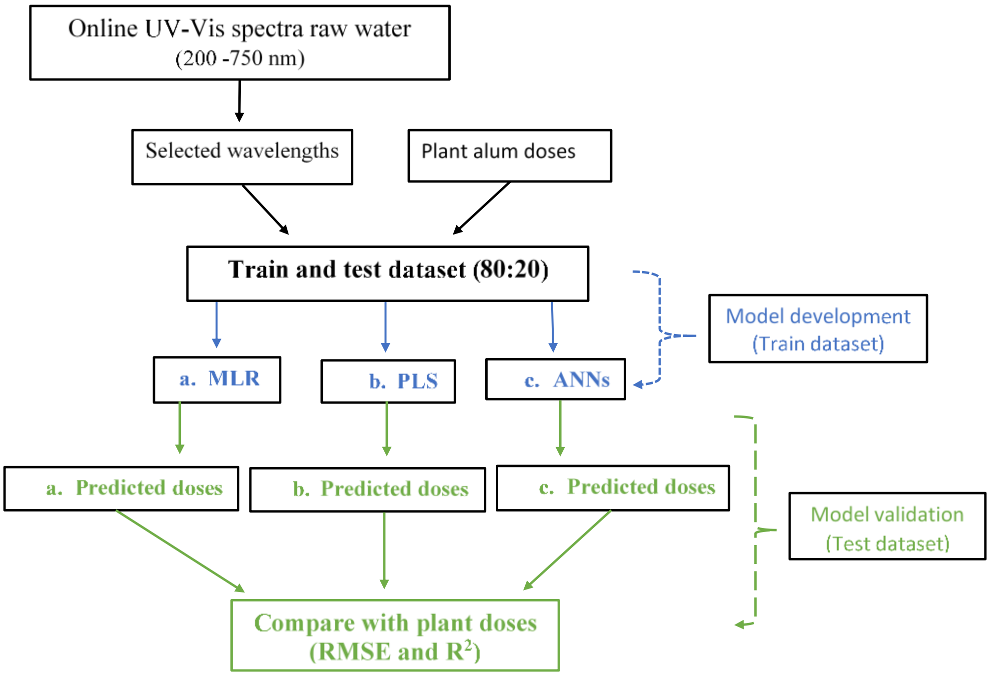

Figure 5-1 Flow chart of modelling development and validation of coagulant dose determinations.

5.2.5.1 Input Variable Optimisation Methods

Three variable optimisation methods: Variable Importance in Projections (VIP), Selectivity Ratio (SR) and correlation coefficient (R) were used to select the most important wavelengths that influence the coagulant dose prediction models. These methods are frequently used for variable selections in chemometrics [30]. These methods for X variable (input) importance related to the explanation of Y variance (output) are useful for prediction. The optimisation of spectral wavelengths (variables) can enhance the predictive ability of the full spectrum [31-33]. First, the full spectra of 220 - 720 nm were screened down to 250 - 600 nm as the absorbance at these wavelengths show characteristics that indicate the matrix of water quality [34]. Organic and turbidity in the water are represented by the wavelengths between 250 - 370 nm and 370 - 600 nm.

VIP scores were obtained from the construction of the initial PLS model. A higher VIP score indicates that the wavelength is more important to predict the alum doses, while the wavelength having a lower VIP score has less impact on the prediction [30]. VIP scores select the variables that contribute the most to the Y variance explanation. Generally, the threshold score of a VIP is defined as 1.0. The threshold score can be higher if the number of variables is large [30]. SR associates the statistical significance based on target projections for variable selection. SRs are based on the calculations of the ratio of explained to the residual variance of X obtained variance. An F-test (95%) has been chosen to define the threshold value of SR with a F-value to determine the significance. The pair-wise correlation coefficients (R) were the correlation between absorbances of wavelengths for the raw water and alum doses of HV WTP.

5.2.5.2 Development Methods of Coagulant Dose Prediction

Three model development methods: multiple linear regression (MLR), partial least squares (PLS) and artificial neural networks (ANNs) were used to determine alum doses. MLR is used to model the linear relationship between a dependent variable and independent variables which can directly define the coefficient of each parameter, while PLS can indirectly reveal the functional relationships and define the coefficient of each parameter. ANNs learn to recognise patterns in data between inputs and outputs. These modelling methods were applied to capture and incorporate the operators' decisions in selecting the alum doses using the spectral data of the raw water quality.

PLS constructs components (latent variables) by projecting the predictor variables to a new space. The observation variables are also projected. Then the linear regression models were built between new predictors and responses. PLS regression is particularly suitable to use when the matrix of predictors has more variables than observed variables and there is multicollinearity among the predictors. PLS can easily extract relevant information from a large data matrix and generate reliable models. Therefore, PLS was used to develop the coagulant prediction model in this study. Package 'pls' was used in the R and R-Studio for the calculations of PLS models [35]. PLS was analysed with leave-one-out cross-validation to avoid under- or over- fitting of the model. The optimal number of components (minimum number of latent variables) is 6 for PLS.

ANNs are computational techniques based on biological neurons which can learn complex patterns among the variables through training. ANNs employ a learning process that is similar to the human brain process to solve problems [36]. One of the commonly used ANNs is Multi-Layer Perceptron (MLP). MLP consists of three layers: the input layer, hidden layer and output layer. The input layer contains the input parameters. The hidden layer processes the data. And the output layer extracts the results. Package 'neuralnet' is used for modelling alum dose predictions with MLP ANNs [37]. The best ANNs architecture for this study is with one input layer, one hidden layer and 3 nodes, and one output layer. The number of hidden layers and the nodes are determined by the trial-and-error method.

The whole set of data, containing online UV-Vis spectral data of the raw water and their corresponding plant alum dose data, was divided into train and test datasets using a randomization method with a ratio of 80:20 to develop and validate the developed models for coagulant dose determination. The datasets were scaled to '0 to 1' using the formula: x_i - minimum/ (maximum - minimum) before they were used to develop PLS and ANNs models.

5.2.6 Evaluation of Coagulation Determination Model Performance

Coefficient of determination (R^2) and root mean square error (RMSE) are commonly used to evaluate the performance of models. R^2 is commonly used to assess the 'goodness of fit' for regression models. R^2 close or equal to 1 is an indicator of a good model. RMSE is commonly used to measure the differences between the predicted values and the actual values. RMSE value is considered the most important criterion for prediction model fit. The smaller the RMSE, the better the model. Another common way of using RMSE to assess the developed model is to compare the RMSE values of models for both train and test data; the model is good if the values are similar. RMSE and R^2 were used to evaluate the performance of the models.

5.3 Results and Discussion

5.3.1 Optimisation of Input Variables

The best representative wavelengths of the pre-processed UV-Vis spectral data of HV raw water that impact on the alum determination models were evaluated by three variable optimisation methods, VIP, SR and R. The high-dimensional data of original spectra contain a proportion of redundant and irrelevant information for building coagulant models. This is because parts of the spectra collect unnecessary water quality information and the absorbance measured at some wavelengths may represent noise rather than the real water quality. Optimisation of input variables reduces the complexity and calculation time for modelling while enhancing the extraction of essential information [38]. Wavelength optimisation methods have been used by other researchers to determine the water quality parameters using UV-Vis spectra [21, 32, 39]. Application of these variable selection methods before modelling could lead to better and less complex prediction models [34].

VIP and SR were performed with partial least squares regressions. Online UV-Vis spectral data of wavelength range from 250 to 600 nm were X variables (model input) and the corresponding alum doses were Y variables (model output). Both variables were normalised from 0 to 1 to make sure they had an equal influence on the model. An initial PLS regression model was built with leave-one-out cross-validation. VIP scores and SR values were obtained from the results of the PLS regression model. Pair-wise correlation coefficients (R) between the absorbances of the UV-Vis spectra for the raw water quality and alum doses for the WTP with their level of significance (*p*-value) were calculated. The results of wavelength optimisation from the online UV-Vis spectra using VIP, SR and R approaches are presented in Table 5-1.

Table 5-1 Selection of important variables for models using three methods, including VIP, SR and R.

Model Input	**Model Output**	**Variables**	**VIP** scores	**SR**			**Correlation coefficient**	
				scores	F-value	Significant	R	*p*-value
Online UV-Vis Spectra	Plant dose	250	2.42	1.51	1.06	Yes	0.77	<0.001
		252.5	2.34	1.50			0.77	
		255	2.13	1.51			0.77	
		257.5	2.05	1.52			0.77	
		260	2.01	1.51			0.77	
		262.5	1.93	1.50			0.77	
		265	1.86	1.49			0.76	
		267.5	1.84	1.49			0.76	
		270	1.82	1.48			0.76	
		272.5	1.77	1.47			0.76	
		275	1.71	1.46			0.76	
		277.5	1.67	1.45			0.76	
		280	1.65	1.44			0.76	

First, important wavelengths were selected based on VIP and SR, and R for modelling alum dose determination associated with the spectral data as X variables (inputs) and plant alum doses as Y variables (outputs). Due to a large number of filtered variables and the strength of influence of the variables, a trial-and-error method was also applied. The most important wavelengths were determined based on the overlapping variables of the three selection methods and the trial-and-error method. The trial-and-error results showed that wavelengths within 250-270 nm are the most important variables that influence the modelling of the plant coagulant dose determination and lead to the improved prediction performance of the models. More detailed results are given in Table 5S-1 in Supplementary Information (SI). The selected wavelengths are determined in a range of 250-270 nm with a 2.5 nm interval, including nine wavelengths: 250, 252.5, 255, 257.5, 260, 262.5, 265, 267.5 and 270 nm. The corresponding thresholds of the selected wavelengths were 1.82 and 1.48 for VIP scores and SR (F-test, 95%). When the correlation coefficient of X variables and Y variables were considered, variables with R of 0.76-0.77 were the same as the variable selected by the VIP and SR methods.

The nine selected wavelengths were considered to have significant contributions to the model development for alum dose determinations for the HV WTP. All the important wavelengths are in the UV spectral region. It is shown that the determination of coagulant doses of HV WTP is mainly characterised in the UV region. A major purpose of coagulation is to remove the natural organic matter from the raw water. The natural organic matter of the raw water is characterised within a wavelength range of 250 - 300 nm [32, 40], In addition, UV_{254} is a preferred indicator for selecting alum dosing for WTPs [11, 41]. The selected wavelengths in this study also contained UV_{254} for modelling coagulant dose determination. These studies supported that the selected wavelengths are the important variables that influence the modelling of the alum dose determinations and result in improved model interpretation and performance [30, 33, 42]. Literature has shown that the variable selections can extract the most important variables and led to enhanced performance of models [21, 34, 38].

5.3.2 Coagulant Determination Using UV-Vis Spectra with MLR

The absorbances of selected nine wavelengths were also used as inputs to build MLR determination models of plant doses for the HV WTP. MLR has been used to predict water quality [43, 44] and coagulant dose using water quality parameters [14, 15]. A train dataset was used to build the calibration MLR. Then a test dataset was used to validate the developed model.

The results of MLR were shown in Figure 5-2. The coefficients of the MLR model were obtained and the MLR model can expressed as below:

Y (alum dose) = 200.69 * X250 - 335.33 * X252.5 -58.91 * X255 + 185.27 * X257.5 + 12.68 * X260 + 140.26 * X262.5 -154.85 * X265 + 312.20* X267.5 - 305.24* X270 -34.41

In the MLR model equation, X refers to the absorbance at a certain wavelength. For instance, X250 indicates the absorbance at wavelength 250 nm. According to R^2 and RMSE of MLR presented in Figure 5-2, the predicted alum doses of MLR and actual plant doses were strongly correlated. For the calibration model, RMSE and R^2 for plant alum doses were 4.19 mg/L and 0.90, respectively. For the validation model, RMSE and R^2 for plant alum doses were 4.31 mg/L and 0.90, respectively. RMSE values of the MLR were small compared to that the plant alum doses were between 40 and 90 mg/L. It is confirmed that the MLR model with online UV-Vis spectral data as inputs can be used to determine the alum doses for WTPs.

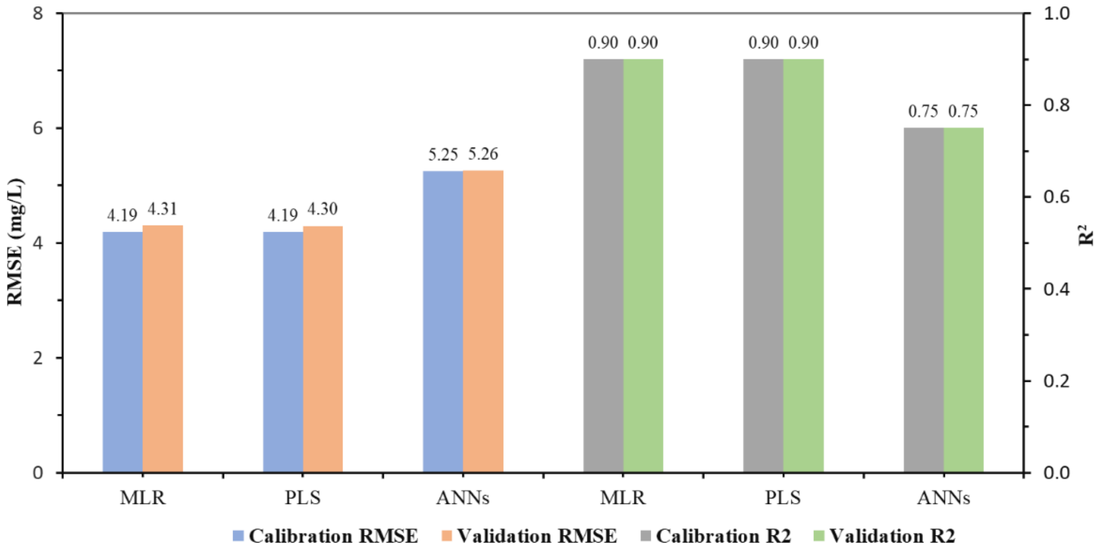

Figure 5-2 Summary of the best models developed for alum dose determination using UV-Vis spectra of raw water.

Modelling results shown in Table 5-2 and Figure 5-2 reveal a minor difference between the predicted alum doses using the MLR method and their corresponding observed (plant) alum doses. MLR can be used to model the alum dose determination using online UV-Vis spectral data because the correlations are high between the variables and the alum doses. This indicates that the determination of alum doses using online UV-Vis spectral data combined with MLR is comparable to the plant dose determination method (jar tests and operator experience). MLR results could mimic the operators' decisions in selecting the appropriate alum doses. This seems contradictory to an argument that MLR is unable to provide a high-level relation between water quality variables and coagulant doses because of the high nonlinearity and the multiple factors affecting the coagulation process [45]. However, MLR has been used to predict coagulant doses with physico-chemical water quality parameters and was recognised as an appropriate approach to predict coagulant doses to assist water [14, 15, 46] and wastewater treatment operations [47]. In this work, the online UV-Vis spectra instead of water quality parameters of raw water were used to build a coagulant dose prediction model with MLR under the optimal coagulation pH of 6 to achieve a target DOC level of less than 5 mg/L for treated water quality.

5.3.3 Coagulant Determination Using UV-Vis Spectra with PLS

PLS was also used to build the coagulant determination models for the HV WTP using the selected wavelengths in the UV range of 250-270 nm of raw water. PLS is a popular modelling method for spectral analysis which also has been used to generate water quality parameters [21, 22, 48] and coagulant dose prediction [49]. The absorbances of the 9 wavelengths were used as model inputs and plant alum doses of HV WTP were used as model outputs. The optimal number of components (minimum number of latent variables) of the PLS model was established by the cross-validation, leaving one sample at a time, to avoid under- or over- fitting of the model.

The RMSE of the PLS model was plotted against the rank of the number of the components, as shown in Figure 5-3. The optimal number of components for the model is that the lowest number of components gives the lowest RMSE. The results indicate that 6 was the optimal number component for the PLS calibration model. The established PLS model was assessed with the test dataset. The PLS results for plant alum determination using train and test datasets are shown in Figure 5-2. RMSE of the PLS based on the train dataset was 4.19 mg/L and the corresponding R^2 was 0.90. The RMSE of the validation was 4.30 mg/L and the corresponding R^2 was 0.90. Both RMSE values of the PLS models are small compared to the alum doses which ranged from 40 to 90 mg/L. Therefore, a good PLS model of determination of plant alum doses was obtained based on the online spectral data of a submersible UV-Vis instrument. Our results reveal that UV-Vis spectral data can be used to determine the alum doses and model the operators' decisions in the selection of the suitable doses using PLS.

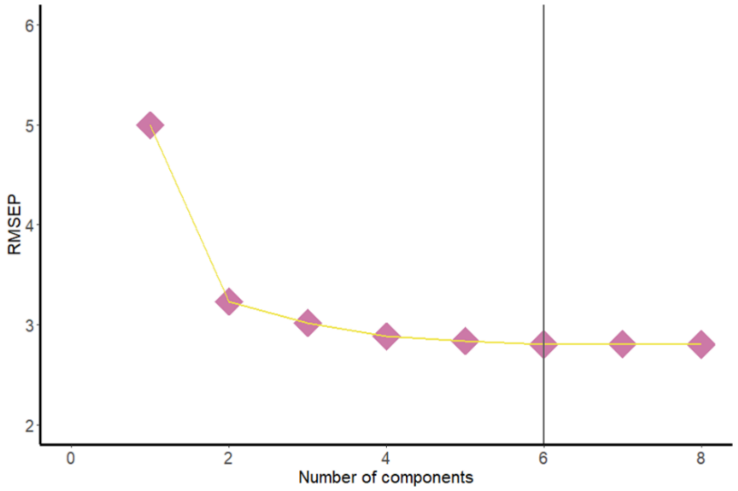

Figure 5-3 Optimal number of components for PLS model with UV-Vis spectra to predict alum doses.

Our results reveal that PLS is effective in modelling alum doses using the UV-Vis spectra and is capable of capturing the operator experience in the determination of alum dose. This statement is supported by the following two reasons. Firstly, PLS was used to develop coagulant dosage predictions with water quality parameters as inputs. PLS regression analysis was used for the development of coagulant dosage prediction models using water quality parameters to remove phosphate from wastewater. PLS was proven to be an efficient tool for coagulant dose prediction [23]. PLS was also used to develop a decision support system for control of the coagulant dosage at a drinking WTP, using water quality parameters including UV, colour, chemical oxygen demand, TOC and conductivity. Thus, PLS could be recognised as a promising and useful estimation tool for coagulant dosing prediction [49]. Furthermore, PLS combined with UV-Vis spectra has also been employed to determine water quality parameters such as TOC in Karst water [20], TOC in wastewater [22] and COD in water [21]. Therefore, UV-Vis spectra of the raw water combined with PLS is able to determine the coagulant dose in the WTPs under the optimal pH of 6 to achieve a target DOC level of less than 5 mg/L for the treated water quality.

5.3.4 Coagulant Determination Using UV-Vis Spectra with ANNs

ANNs were used to build the coagulant determination models for the plant doses. The absorbances of the selected nine wavelengths (250-270 nm) were also used as the model inputs and the plant alum doses were used as the model outputs. ANNs have been applied successfully for coagulant dose prediction based on water quality parameters [1, 2, 31, 32]. A Multi-Layer Perceptron (MLP) ANNs, equipped with the feed-forward back-propagation algorithm was used for building ANN models. Back-propagation is a widely used algorithm for training feedforward neural networks to speed up the convergence rate and its robustness [50]. Feedforward ANN provides a flexible way for generalizing linear regression and non-linear functions. Dataset of the selected variables and their corresponding plant alum doses was randomly shuffled before ANNs training to avoid the seasonality effect. There is no precise approach to obtain the optimal number of hidden layers of MLP. A few hidden layers of ANNs have been proven to be sufficient for modelling coagulant dosage based on the reported studies [18, 51, 52]. The optimal number of hidden layers was determined by the trial-and-error method [53]. The best ANNs model is selected for its lowest RMSE with one hidden layer and 3 nodes, as shown in Figure 5-4. Thus, the best ANN architecture for plant dose determination was obtained with one input layer with 9 neurons (nodes), one hidden layer with 3 nodes, and one output layer with a single node.

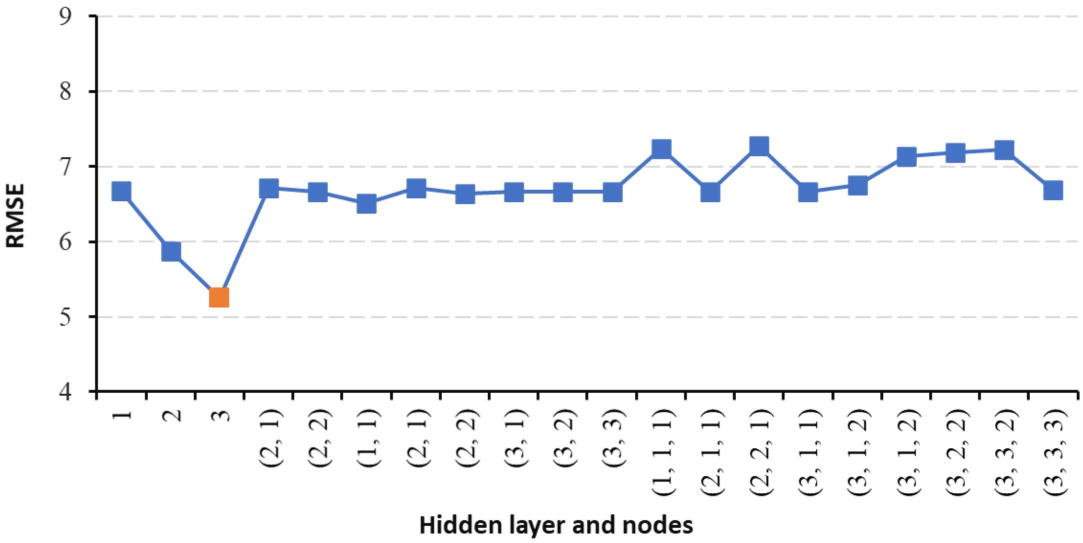

Figure 5-4 Optimal number of hidden layer and nodes.

ANNs of the coagulant model had RMSE of 5.25 mg/L and 5.26 mg/L for train and test datasets. The best ANN showed satisfactory R^2 of 0.75 for both train and test datasets. The RMSE of optimal ANN performance indicates the small discrepancies between the predicted and actual alum doses as the actual alum doses were between 40 and 90 mg/L. B1 and B2 in Figure 5-5 are two stages of biases. The bias of B2 to O1, B1 to H1, B1 to H2, B1 to H3 is -2.32, 4.58, 3.45, 2.17, respectively, which are small errors. These indicate the viability of using ANNs to predict alum doses for WTPs using UV-Vis spectral data.

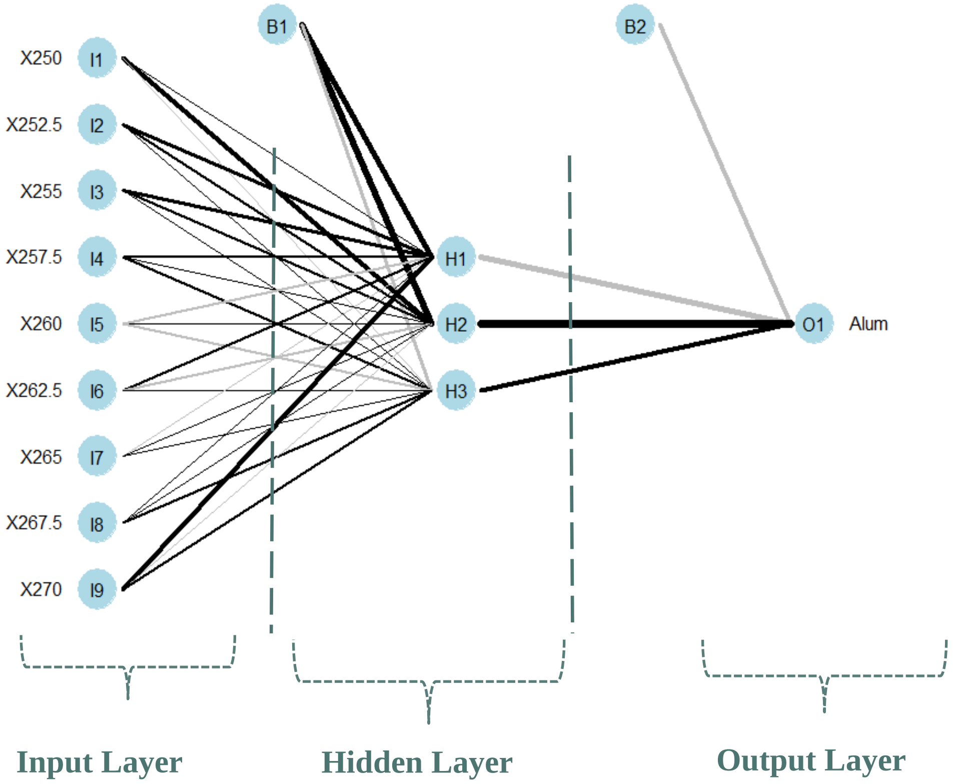

Figure 5-5 Optimal ANNs architecture for alum dose prediction.

ANNs have been applied to predict coagulant doses for WTPs by other researchers based on raw water quality parameters [7, 50-52, 54]. It is a well-known pattern recognition technique for solving complex problems. ANNs was used to determine alum doses for surface water treatment based on physio-chemical parameters of the raw water [15, 19]. There are also software sensors using ANNs for online prediction of coagulant doses with the raw water quality parameters [7, 11]. A study incorporated the operators' experience in coagulant dose determination using a time consistent mode [9]. All the above support that UV-Vis combined with ANNs could mimic the operators' experience in the determination of coagulant dose for WTPs under the optimal pH condition to achieve target DOC level of less than 5 mg/L for the treated water quality.

5.3.5 Assess Coagulant Determination Model Performance

Three modelling techniques, MLR, PLS and ANNs were applied to determine the alum dose using the selected UV spectra (250-270 nm) of raw water at HV WTP. According to the modelling performance indicators (RMSE and R^2), as shown in Figure 5-2, all three methods can be used to predict plant alum doses with the UV-Vis spectra. The use of UV-Vis spectra combined with PLS or ANNs has been studied for the determination of TOC, DOC and water quality index [20, 21, 55]. ANNs are the most commonly used technique to predict coagulant dose with the employment of the water quality parameters [7, 9, 15, 18] as inputs. Our results revealed that ANNs may not be the best modelling tool for alum dose predictions with the UV-Vis spectral data. MLR and PLS methods showed almost identical performance in terms of prediction of plant alum doses with small values of RMSE and high R^2. MLR and PLS had better performance with smaller RMSE and high R^2 values than ANNs in modelling of alum dose using UV-Vis spectra. MLR is a simple method that can directly define the coefficient of each parameter for coagulation determination. The developed three coagulant dose determination models can well adapt to the variations in raw water quality (Figure S5-2 in SI). The results indicate that the utilisation of UV-Vis spectra of raw water combined with MLR or PLS can mimic operator decisions in the selection of alum doses. There is a potential for using a portable UV-Vis spectrophotometer combined with chemometrics (MLR and PLS) to assist operators for real-time coagulant dose prediction, especially when there is an unexpected change in raw water quality.

Coagulant doses for water treatment were typically determined by the operators based on multiple factors for process control. This study shows that coagulant doses can be determined for a WTP using only the UV-Vis spectra of raw water under the optimal pH condition to achieve the target DOC level for the treated water quality and comparable results were achieved. This study may be the first that directly utilises online UV-Vis spectra of raw water quality to determine plant doses. The combination of online UV-Vis spectra of raw water and coagulation dose determination models will allow better control of the coagulation process, particularly for sudden water quality change events such as heavy rainfalls. Potentially, an online submersible instrument combined with a chemometric model (MLR or PLS) can predict coagulant doses and provide decision support information for coagulation process control at WTPs.

5.4 Conclusion

This study may be the first that present plant doses model can be built based on online UV-Vis spectra of raw water quality. Modelling techniques with different levels of complexity, including MLR, PLS and ANNs, and variable selection methods were employed to build coagulant doses models for the HV WTP. Important variables that influence the modelling of the alum dose determination were selected using VIP, SR and R methods from the UV-Vis spectra of raw water. The selected variables were determined as nine wavelengths within 250 -270 nm which revealed that the determination of coagulant doses of the HV WTP is mainly characterized in the UV region. The selected variables were used as inputs and plant doses were used as the outputs for modelling coagulant dose determinations.

Results show that all three techniques can model the alum dose prediction with the selected variables. MLR and PLS methods had an almost identical performance in predicting plant alum doses with small RMSE and high R^2. This study shows the feasibility of predicting coagulant doses based on the UV-Vis spectral data of raw water combined with a chemometric model and the ability to mimic the operator decisions in selecting the appropriate doses for process control, under the optimal pH condition to achieve a target DOC level of less than 5 mg/L for the treated water quality. It is concluded that a submersible UV-Vis spectrophotometer combined with a chemometric model (MLR or PLS) has the potential to support operators effectively for real-time determination of coagulant doses for process control, under the fluctuation of the raw water quality.

5.5 References

1. Matilainen, A., Gjessing, E.T., Lahtinen, T., Hed, L., Bhatnagar, A. and Sillanpää, M., *An overview of the methods used in the characterisation of*

natural organic matter (NOM) in relation to drinking water treatment. Chemosphere, 2011. **83**(11): p. 1431-1442.

2. Bratby, J., *Coagulation and flocculation in water and wastewater treatment*. 3rd ed. 2016, UK: IWA publishing.
3. Jiang, J.Q., *The role of coagulation in water treatment.* Current Opinion in Chemical Engineering, 2015. **8**: p. 36-44.
4. Aiswarya, A.S., Nithya, k. and Nittin, J. J., *ANN-Based modelling for coagulant dosage in drinking water treatment plant.* International Research Journal of Engineering and Technology, 2019. **06**(05): p. 6158-6144.
5. Li, L., Rong, S., Wang, R. and Yu, S., *Recent advances in artificial intelligence and machine learning for nonlinear relationship analysis and process control in drinking water treatment: A review.* Chemical Engineering Journal, 2021(405): p. 126673.
6. Li, J., Tong, Y., Guan, L., Wu, S. and Li, D., *A turbidity compensation method for COD measurements by UV–vis spectroscopy.* Optik, 2019. **186**: p. 129-136.
7. Lamrini, B., Benhammou, A., Le Lann, M.V. and Karama, A., *A neural software sensor for online prediction of coagulant dose in a drinking water treatment plant.* Transactions of the Institute of Measurement and Control, 2005. **27**(3): p. 195-213.
8. Shi, Z., Chow, C.W., Fabris, R., Zheng, T., Liu, J. and Jin, B., *Determination of coagulant dosages for process control using online UV-Vis spectra of raw water.* Journal of Water Process Engineering, 2022. **45**: p. 102526.
9. Liu, Y., He, Y., Li, S., Dong, Z., Zhang, J. and Kruger, U., *An Auto-Adjustable and Time-Consistent Model for Determining Coagulant Dosage Based on Operators' Experience.* IEEE Transactions on Systems, Man, and Cybernetics: Systems, 2019.
10. Adebayo, I.O., Olukowi, O.O., Zhiyuan, Z. and Zhang, Y., *Comparisons of coagulation efficiency of conventional aluminium sulfate and enhanced composite aluminium sulfate/polydimethyldiallylammonium chloride coagulants coupled with rapid sand filtration.* Journal of Water Process Engineering, 2021. **44**: p. 102322.

11. Mussared, A., Chow, C., Holmes, M., Van Leeuwen, J. and Kaeding, U., *Implementation of predictive alum dose control systems*, in *77th Annual WIOA Victorian Water Industry Operations Conference and Exhibition*. 2014: Bendigo Exhibition Centre.
12. Heddam, S., Bermad, A. and Dechemi, N., *ANFIS-based modelling for coagulant dosage in drinking water treatment plant: a case study*. Environmental Monitoring and Assessment, 2012. **184**(4): p. 1953-1971.
13. Kim, C.a.P., M., *Prediction of settled water turbidity and optimal coagulant dosage in drinking water treatment plant using a hybrid model of k-means clustering and adaptive neuro-fuzzy inference system.* Applied Water Science, 2017. **7**(7): p. 3885-3902.
14. Ellis, G.W., Collins, A.G., Ge, X. and Ford, C.R., *Chemical dosing of small water utilities using regression analysis.* Journal of environmental engineering 1991. **117**(3): p. 308-319.
15. Van Leeuwen, J., Chow, C.W.K., Bursill, D. and Drikas, M., *Empirical mathematical models and artificial neural networks for the determination of alum doses for treatment of southern Australian surface waters.* Journal of Water Supply: Research and Technology—AQUA, 1999. **48**(3): p. 115-127.
16. Bello, O., Hamam, Y. and Djouani, K., *Control of a coagulation chemical dosing unit for water treatment plants using MMPC based on fuzzy weighting.* Journal of Water Process Engineering, 2014. **4**: p. 34-46.
17. Jayaweera, C.D., Othman, M.R. and Aziz, N., *Improved predictive capability of coagulation process by extreme learning machine with radial basis function.* Journal of Water Process Engineering, 2019. **32**: p. 100977.
18. Maier, H.R., Morgan, N. and Chow, C.W., *Use of artificial neural networks for predicting optimal alum doses and treated water quality parameters.* Environmental Modelling & Software, 2004. **19**(9): p. 485-494.
19. dos Santos F.C.R., L., A.F.H., Dias, C.G. and Rodrigues, S.G., *Intelligent system for improving dosage control.* Acta Scientiarum. Technology, 2017. **39**(1): p. 33-38.
20. Vallet, A., Moiroux, F., and Charlier, J.B, *Optimization of high-resolution monitoring of nutrients and TOC in Karst waters using a Partial Least-Squares*

regression model of a UV–Visible spectrometer, in *Advances in Karst Science*. 2020, Springer, Cham: Eurokarst 2018, Besançon.

21. Li, J., Tong, Y., Guan, L., Wu, S. and Li, D., *Optimization of COD determination by UV–vis spectroscopy using PLS chemometrics algorithm.* Optik, 2018. **174**: p. 591-599.
22. Lourenço, N.D., Menezes, J.C, Pinheiro, H.M. and Diniz, D., *Development of PLS calibration models from UV-Vis spectra for TOC estimation at the outlet of a fuel park wastewater treatment plant.* Environmental Technology, 2008. **29**(8): p. 891-898.
23. Rathnaweera, S., Ratnaweera, H., and Lindholm, O., *Multi-parameter based dosing control as an efficient tool for improved phosphate removal by coagulation-experiences from Beijing,* in *International Forum on Environment Simulation and Pollution Control*. 2009: Beijing. p. 14.
24. Colton, J., *A method of calculating a water treatment chemical dose*. 2009.
25. Zhou, M. and F. Meng, *Aluminum-induced changes in properties and fouling propensity of DOM solutions revealed by UV–vis absorbance spectral parameters.* Water research, 2016. **93**: p. 153-162.
26. Shi, Z., Chow, C.W., Fabris, R., Liu, J., Jin, B., *Alternative particle compensation techniques for online water quality monitoring using UV–Vis spectrophotometer.* Chemometrics and Intelligent Laboratory Systems, 2020. **204**(104074).
27. Drikas, M., Chow, C.W., House, J. and Burch, M.D., *Using coagulation, flocculation, and settling to remove toxic cyanobacteria.* Journal-American Water Works Association, 2001. **93**(2): p. 100-111.
28. Shi, Z., Chow, C.W., Fabris, R, Zheng., T, Liu, J. and Jin, B., *Evaluation of the impact of suspended particles on the UV absorbance at 254 nm (UV 254) measurements using a submersible UV-Vis spectrophotometer.* Environmental Science and Pollution Research, 2021. **28**(10): p. 12576-12586.
29. R Core Team, *R: A language and environment for statistical computing.* Foundation for Statistical Computing, 2019.
30. Farrés, M., Platikanov, S., Tsakovski, S. and Tauler, R,, *Comparison of the variable importance in projection (VIP) and of the selectivity ratio (SR)*

methods for variable selection and interpretation. Journal of Chemometrics, 2015. **29**(10): p. 528-536.

31. Li, L., Lin, D., Wang, J., Yang, L. and Wang, Y., *Multivariate Analysis Models Based on Full Spectra Range and Effective Wavelengths Using Different Transformation Techniques for Rapid Estimation of Leaf Nitrogen Concentration in Winter Wheat.* Frontiers in Plant Science, 2020. **11**: p. 755.
32. Xu, D., Fan, W., Lv, H., Shan, Y,, Liang, Y,, Li, G,, Yang, Z,, and Yu, L., *Simultaneous determination of traces amounts of cadmium, zinc, and cobalt based on UV–Vis spectrometry combined with wavelength selection and partial least squares regression.* Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 2014. **123**: p. 430-435.
33. Mehmood, T., Liland, K.H., Snipen, L., and Sæbø, S., *A review of variable selection methods in partial least squares regression.* Chemometrics and Intelligent Laboratory Systems, 2012. **118**: p. 62-69.
34. Rieger, L., Langergraber, G., Thomann, M., Fleischmann, N. and Siegrist, H., *Spectral in-situ analysis of NO2, NO3, COD, DOC and TSS in the effluent of a WWTP.* Water Science and Technology, 2004. **50**(11): p. 143-152.
35. Mevik, B., Ron Wehrens, R. and Liland, K. H, *pls: Partial Least Squares and Principal Component Regression.* R package version 2.7-2, 2019.
36. Jawad, J., Hawari, A.H. and Zaidi, S.J, *Artificial Neural Network Modeling of Wastewater Treatment and Desalination Using Membrane Processes: A Review.* Chemical Engineering Journal, 2021: p. 129540.
37. Fritsch, S., Guenther, F. and Wright, M., *neuralnet: Training of Neural Networks.* R package version 1.44.2, 2019.
38. Guo, Y.L., C; Ye, R. and Duan, Q., *Advances on Water Quality Detection by UV-Vis Spectroscopy.* Applied Sciences, 2020. **10**(19): p. 6874.
39. Chen, B., Wu, H. and Li, S.F.Y., *Development of variable pathlength UV–vis spectroscopy combined with partial-least-squares regression for wastewater chemical oxygen demand (COD) monitoring.* Talanta, 2014. **120**: p. 325-330.
40. Kim, C., Eom, J.B., Jung, S. and Ji, T., *Detection of organic compounds in water by an optical absorbance method.* Sensors, 2016. **16**(1): p. 61.

41. Edzwald, J.K.a.K., G.S., *A practical method for water plants to select coagulant dosing.* Journal of the New England Water Works Association, 2009. **123**(1): p. 15.

42. Mehmood, T., Sæbø, S. and Liland, K.H., *Comparison of variable selection methods in partial least squares regression.* Journal of Chemometrics, 2020. **34**(6): p. 3226.

43. Li, X., Sha, J. and Wang, Z.L., *A comparative study of multiple linear regression, artificial neural network and support vector machine for the prediction of dissolved oxygen.* Hydrology Research, 2017. **48**: p. 1214-1222.

44. Abyaneh, H.Z., *Evaluation of multivariate linear regression and artificial neural networks in prediction of water quality parameters.* Journal of Environmental Health Science and Engineering, 2014. **12**(1): p. 1-8.

45. Heddam, S., *Extremely randomized tree: a new machine learning method for predicting coagulant dosage in drinking water treatment plant.* Water Engineering Modeling and Mathematic Tools, 2021: p. 475-489.

46. Vo, A.T., Pham, N.T., Huynh, Q.H., Nguyen, P.T.D., Phan, D.X.V. and Hoang, C.D., *Using iron alum in surface water treatment.* In IOP Conference Series: Materials Science and Engineering,IOP Publishing, 2020. **869**: p. 042001.

47. Ghaitidak, D.M.a.Y., K.D., *Effect of coagulant in greywater treatment for reuse: selection of optimal coagulation condition using analytic hierarchy process.* Desalination and Water Treatment, 2015. **55**(4): p. 913-925.

48. Avagyan, A., Runkle, B.R and Kutzbach, L., *Application of high-resolution spectral absorbance measurements to determine dissolved organic carbon concentration in remote areas.* Journal of Hydrology, 2014. **517**: p. 435-446.

49. Nilsson, S.a.H., F., *Quicker response to Quality changes in incoming water with decision support for coagulant dosage at görväln drinking water plant.* Journal of Water Management and Research, 2015(71): p. 183-190.

50. Kim, C.M., and Parnichkun, M., *MLP, ANFIS, and GRNN based real-time coagulant dosage determination and accuracy comparison using full-scale data of a water treatment plant.* Journal of Water Supply: Research and Technology—AQUA, 2017. **66**(01): p. 49-61.

51. Baouab, M.H.a.C., S., *Prediction of the optimal dose of coagulant for various potable water treatment processes through artificial neural network.* Journal of Hydroinformatics, 2018. **20**(6): p. 1215-1226.

52. Haghiri, S., Daghighi, A. and Moharramzadeh, S., *Optimum coagulant forecasting by modeling jar test experiments using ANNs.* Drinking Water Engineering and Science, 2018. **11**(1): p. 1-8.

53. Kote, A.S.a.W., D.V., *Modeling of Chlorine and Coagulant Dose in a Water Treatment Plant by Artificial Neural Networks.* Engineering, Technology & Applied Science Research, 2019. **9**(3): p. 4176-4181.

54. Wu, G.D.a.L., S.L., *Predicting real-time coagulant dosage in water treatment by artificial neural networks and adaptive network-based fuzzy inference system.* Engineering Applications of Artificial Intelligence, 2008. **21**(8): p. 1189-1195.

55. Alves, E.M., Rodrigues, R.J., dos Santos Corrêa, C., Fidemann, T., Rocha, J.C, Buzzo, J.L.L., de Oliva Neto, P., and Núñez, E.G.F., *Use of ultraviolet–visible spectrophotometry associated with artificial neural networks as an alternative for determining the water quality index.* Environmental Monitoring and Assessment, 2018. **190**(6): p. 1-15.

5.6 Supporting Information

Table 5S-1 Trial and error (examples) of determination of the best wavelength range for modelling plant does using the UV-Vis spectral data.

Wavelength range	**Train data**		**Test data**	
	RMSE	R^2	RMSE	R^2
250-260	5.96	0.81	5.89	0.81
250-262.5	5.38	0.84	5.42	0.84
250-270	**2.80**	**0.96**	**2.80**	**0.96**
250-275	4.11	0.92	4.23	0.92
250-280	4.21	0.92	4.13	0.92
250-305	4.31	0.92	4.26	0.91

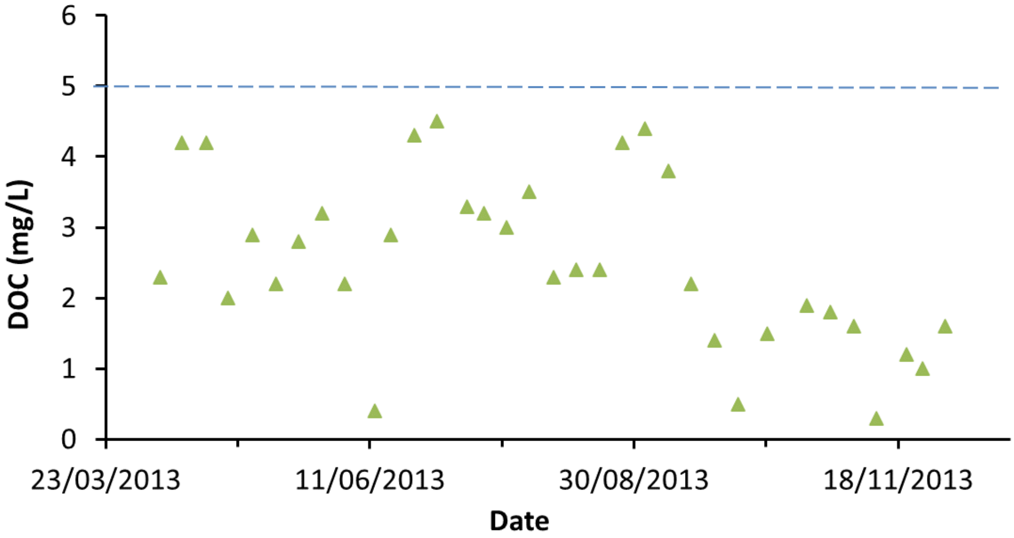

Figure 5S-1 DOC level of treated water quality of the HV WTP based on grab sampling (data was extracted from the internal database of the water utility).

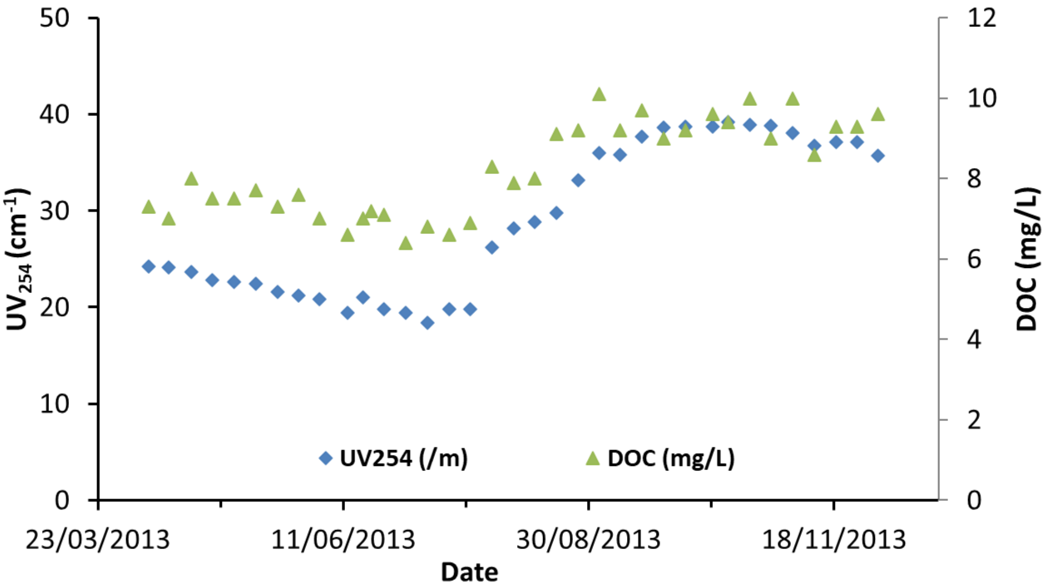

Figure 5S-2 Raw water quality data of HV WTP based on grab sampling (data was extracted from the internal database of the water utility).

Chapter 6 Conclusions and Perspectives

- Alternative compensation techniques may improve the reliability and usability of online instruments
- Developed models could be used as an additional tool for decision making at water treatment plants for process control
- Future research is needed on integration of early warning and real-time process control systems for water quality management

6.1 Conclusions

This thesis provides an overview of using online UV-Vis instruments for drinking water quality monitoring and process control. A summary of this thesis has been published, as shown in Appendix F. It also highlights the challenges and potential solutions of real-time applications of online UV-Vis spectrophotometers for the management of drinking water supplies. A study of particle impact on the measurements of a submersible UV-Vis spectrophotometer was conducted under laboratory-controlled conditions. The performance of the instrument built-in particle compensation technique was assessed. In-depth knowledge of the online measurements of UV-Vis instruments was obtained to the understand the influence of different types and various levels of concentrations of particles in the water on the UV-Vis measurements. The relationships between particle types and concentrations and the UV-Vis measurements were revealed. It also explained why the built-in generic compensation algorithms of the submersible UV-Vis spectrophotometer may generate under-compensated or over-compensated measurements for various source water.

Novel software compensation models were developed, including single wavelength compensation, linear regression compensation and multiplicative scatter correction method, using time series UV-Vis spectra data from water treatment plants in South Australia. The results show that these particle compensation techniques can improve the reliability of the UV-Vis sensors for online water quality monitoring. It also demonstrated the benefits of using software compensation methods to establish site-specific calibration models instead of relying on the instrument built-in generic calibrations. Furthermore, simple UV-Vis instruments with a single wavelength or a short wavelength band could be employed in the field to monitor water quality instead of using sophisticated full-spectrum UV-Vis instruments. The use of alternative compensation techniques may allow less maintenance of the instruments and possibly improve the reliability and usability in real-time by water treatment plant operators.

The utilisation of time series UV-Vis spectra was further explored by developing coagulant dose determination models. Modelling techniques with different levels of complexity, including multiple linear regression, partial least squares, and artificial neural works, were employed to build coagulant doses models for a water treatment plant in South Australia. Results show the feasibility of predicting coagulant doses based on the UV–Vis spectral data of raw water combined with a chemometric model. This model enables mimics operators' decisions in the determination of coagulant doses with a pH target of 6 to achieve a target DOC level of less than 5 mg/L for treated water quality. It is concluded that a submersible UV–Vis spectrophotometer combined with a chemometric model has the potential to be a decision support tool for real-time determination of coagulant doses for process control, under the fluctuation of the raw water quality.

Statement of Authorship

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Principal Author

Name of Principal Author (Candidate)	Zhining Shi		
Contribution to the Paper	Conceptualization, Methodology, Writing - Original draft preparation		
Overall percentage (%)	100		
Certification:	This paper reports on original research I conducted during the period of my Higher Degree by Research candidature and is not subject to any obligations or contractual agreements with a third party that would constrain its inclusion in this thesis. I am the primary author of this paper.		
Signature		Date	26th March 2022

6.2 Perspectives

This research and the outcomes show that the accuracy of the surrogate parameters, UV_{254}, can be obtained from the UV-Vis spectra of water by applying different particle compensation methods. Future research on the validations of this work can be done through implementing the developed methods for real-time measurements of water quality at a water treatment plant. The performance of the online UV-Vis instrument combined with software compensation techniques could be assessed by comparing it with the laboratory analytical methods to have a side-by-side field trial. The suitability of the software compensation techniques can be tested for real-time water quality monitoring through the direct comparison of online measurements and the laboratory results of the same water. In addition, this project also shows the feasibility of predicting coagulant doses based on the UV–Vis spectral data of raw water combined with a chemometric model. Future work is needed on implementing the developed coagulant models in a water treatment plant for real-time predictions of coagulant doses to evaluate the performance of the models. Accuracies and reliability of the developed models can be tested for the coagulation process control, ideally, over a period of 12 months. The online instruments can be located at raw water intake and linked to the supervisory control and data acquisition system for trailing direct online coagulation control.

Moreover, future research can be on the development of more surrogate parameters for water quality measurements using the UV-Vis spectra of water. Various surrogates of water quality measurements can be developed based on the correlations between the UV-Vis spectra and the standard laboratory measurements such as DOC, TOC and chlorine demand. Methods including PCA, PLS, ANNs could be employed to develop surrogate parameters for water quality measurements [1-3]. Future research also needs to work towards the integration of early warning and real-time water process control systems for water quality management. Figure 2 shows the integration of early warning for water quality anomaly detection and process control for water treatment plants. Online UV-Vis sensors can be placed at different locations of a water treatment plant to monitor water quality, particularly at the inlet to monitor source water quality.

Online UV-Vis measurements of water quality from the sensors connect to the Supervisory Control and Data Acquisition (SCADA) system. Particle compensation of the online UV-Vis measurements may be performed automatically using a selected technique such as a single wavelength compensation to remove the particle effects [4]. Then, the online UV-Vis measurements can be analysed to detect any unusual measurements based on the magnitude of the variations in the spectra and provide an early warning of rapidly changing water quality [5, 6]. In addition, coagulant doses can be determined and predicted using the combination of online UV-Vis measurements and chemometrics in real-time [7]. It can support operators for real-time determination of coagulant doses for water treatment process control when water quality change events occur.

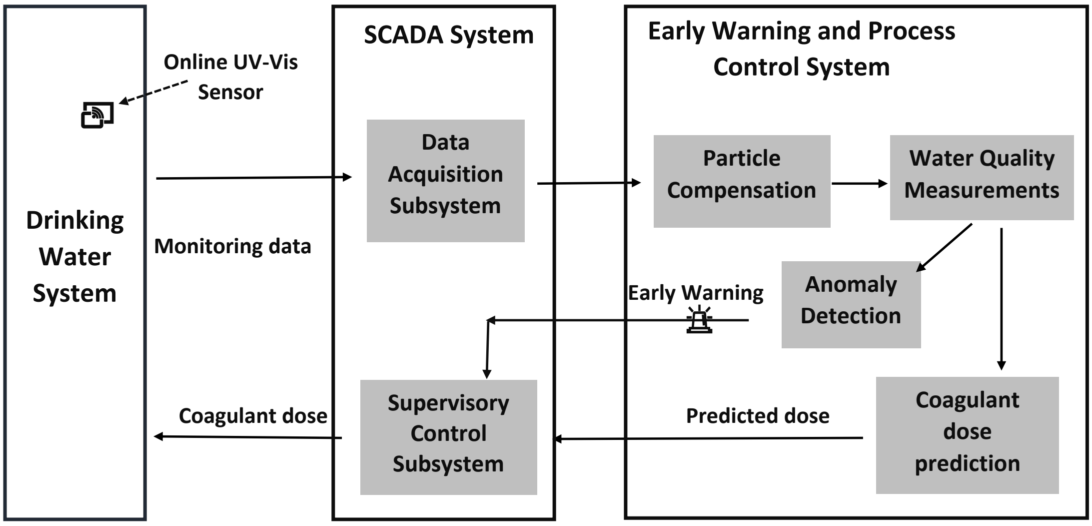

Figure 0-1Integration of early warning of water quality anomaly detection and water treatment process control.

6.3 References

1. Korshin, G.V., Sgroi, M. and Ratnaweera, H., *Spectroscopic surrogates for real time monitoring of water quality in wastewater treatment and water reuse.* Current Opinion in Environmental Science & Health, 2018. **2**: p. 12-19.
2. Fitzgerald, F., Chow, C.W. and Holmes, M., *Disinfectant demand prediction using surrogate parameters–a tool to improve disinfection control.* Journal of Water Supply: Research and Technology—Aqua, 2006. **55**(6): p. 391-400.
3. Miguntanna, N.S., Egodawatta, P., Kokot, S. and Goonetilleke, A., *Determination of a set of surrogate parameters to assess urban stormwater quality.* Science of the Total Environment, 2010. **408**(24): p. 6251-6259.
4. Shi, Z., Chow, C.W., Fabris, R., Liu, J., Jin, B., *Alternative particle compensation techniques for online water quality monitoring using UV–Vis spectrophotometer.* Chemometrics and Intelligent Laboratory Systems, 2020. **204**(104074).
5. Kim, C., Eom, J.B., Jung, S. and Ji, T., *Detection of organic compounds in water by an optical absorbance method.* Sensors, 2016. **16**(1): p. 61.
6. Arnon, T.A., S. Ezra, and B. Fishbain, *Water characterization and early contamination detection in highly varying stochastic background water, based on Machine Learning methodology for processing real-time UV-Spectrophotometry.* Water Research, 2019. **155**: p. 333-342.
7. Shi, Z., Chow, C.W., Fabris, R., Zheng, T., Liu, J. and Jin, B., *Determination of coagulant dosages for process control using online UV-Vis spectra of raw water.* Journal of Water Process Engineering, 2022. **45**: p. 102526.

Appendices

Appendix A Stormwater monitoring using on-line UV-vis spectroscopy, published in Environmental Science and Pollution Research

Appendix B Application of online UV-Vis spectrophotometer for drinking water quality monitoring and process control: a review, accepted by Sensors

Appendix C Evaluation of the impact of suspended particles on the UV absorbance at 254 (UV_{254}) measurements using a submersible UV-Vis spectrophotometer, published in Environmental Science and Pollution Research

Appendix D Alternative particle compensation techniques for online water quality monitoring using UV-Vis spectrophotometer, was published in Chemometrics and Intelligent Laboratory Systems

Appendix E Determination of coagulant dosages for process control using online UV-Vis spectra of raw water, was published in Journal of Water Process Engineering

Appendix F Online Water quality monitoring and process control using UV-Vis sensors, was accepted by the Water e-Journal

Appendix A

Environmental Science and Pollution Research
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RESEARCH ARTICLE

Stormwater monitoring using on-line UV-Vis spectroscopy

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Abstract

Stormwater runoff contains a myriad of pollutants, including faecal microbes, and can pose a threat to urban water supplies, impacting both economic development and public health. Therefore, it is a necessity to implement a real-time hazard detection system that can collect a substantial amount of data, assisting water authorities to develop preventive strategies to ensure the control of hazards entering drinking water sources. An on-line UV-Vis spectrophotometer was applied in the field to collect real-time continuous data for various water quality parameters (nitrate, DOC, turbidity and total suspended solids) during three storm events in Mannum, Adelaide, Australia. This study demonstrated that the trends for on-line and comparative laboratory-analysed samples were complimentary through the events. Nitrate and DOC showed a negative correlation with water level, while turbidity and total suspended solids indicated a positive correlation with water level during the high rainfall intensity. The correlations among nitrate, DOC, turbidity, total suspended solids and water level are the opposite during low rainfall intensity. Nitrate, one of the main pollutants in stormwater, was investigated and used as a surrogate parameter for microbial detection. However, the microbiological data (*Escherichia coli*) from captured storm events showed poor correlations to nitrate and other typical on-line parameters in this study. This is possibly explained by the nature of the stormwater catchment outside of rain events, where the sources of bacteria and nutrients may be physically separated until mixed during surface runoff as a result of rainfall. In addition, the poor correlations among the microbiological data and on-line parameters could be due to the different sources of bacteria and nutrients that were transported to the stormwater drain where sampling and measurement were conducted.

Keywords Stormwater · Real-time monitoring · UV-vis spectrophotometer · Surrogate parameter · Nitrate · *E. coli*

Introduction

Access to a safe and reliable water supply is necessary for economic development and public health. Water-borne diseases, including cholera, amoebic dysentery, typhoid and paratyphoid fevers, are commonly found and reported in the less-developed areas of the world (Bricker 2007, Petney and Taraschewski 2011, WHO 2006). Wastewater is one of the main pollutants of water resources and sources of enteric diseases (Petney and Taraschewski 2011). With increasing populations, the availability of good quality freshwater in urban areas is becoming an urgent issue (Hamilton et al. 2005, Thayanukul et al. 2013). Additionally, expanding urbanisation has caused significant changes in local hydrological conditions, generated urban runoff and led to the degradation of ecosystems (Göbel et al. 2007). Strong correlations were found between urbanisation, stormwater and wastewater discharges, the transfer of pollutants and the quality of natural surface and ground waters (Göbel et al. 2007). Increase in population and water demand is making stormwater an important resource. Thus, stormwater quality monitoring will need to be developed as a component

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of integrated water resource management to minimise both environmental and public health risks.

In Australia, many policies have been developed to regulate wastewater discharges, but the same is not true for stormwater, and stormwater has remained as one of the main sources of pollution to urban freshwaters. Urban stormwater contains dissolved, colloidal and solid constituents in a heterogeneous mixture, which includes nutrients, heavy metals and organic and inorganic compounds (Bricker 2007, Gnecco et al. 2005). Additionally, urban stormwater runoff has been shown to contain large quantities of faecal microbes, such as *Escherichia coli* (*E. coli*) (Selvakumar and Borst 2006). Stormwater Quality Improvement Devices (SQIDs) have been applied to trap rubbish and pollutants that end up in stormwater drains, preventing large quantities of pollutants entering the stormwater drainage system (Hamilton et al. 2005). However, SQIDs are not effective in removing all contaminants; for instance, soluble nutrients, heavy metals, organics, suspended solids and faecal microbes can still flow from streets and gutters into creeks, streams and rivers, contaminating the surface water and posing a threat to our urban water supply (Eriksson et al. 2007, Greenway et al. 2002).

Microbial fate and transport in aquatic environments can be affected by various physical, chemical and biological factors, which include season, temperature, nutrient availability, adsorption/desorption processes, hydrologic processes, predation and others (Ferguson et al. 2003, McCarthy et al. 2007, Selvakumar and Borst 2006). The fate and transport of these contaminants, especially those microbiological, have received high attention recently due to public health concern. Studies have shown an increased concentration of microorganisms during storm flows, indicating a relationship between flow magnitude and microorganism transport (Davis et al. 1977, Olivieri 1977). Other studies presented a significant relationship between microbes and the incidence of rainfall and rainfall intensity (Davies and Bavor 2000, Haydon and Deletic 2006, Kelsey et al. 2004). Davis et al. (1977) presented the correlations between microorganisms and both discharge and suspended solids for stormwater runoff. Duncan (1999) reported that faecal coliforms were strongly correlated with some stormwater quality parameters, such as total phosphorus and turbidity. Kelsey et al. (2004) and Mallin et al. (2009) evaluated the relationships between land use and faecal coliform bacterial pollution. However, most of these studies have been conducted in streams, rivers and/or estuaries (Ferguson et al. 2003, Kelsey et al. 2004, Mallin et al. 2009, Selvakumar and Borst 2006). Also, analyses are mainly performed on single grab samples, which tend to have a relatively low resolution to identify the inter-event trends (Mallin et al. 2009, McCarthy et al. 2012, McCarthy et al. 2007, Selvakumar and Borst 2006). Therefore, an alternative monitoring technique that can capture real-time data, such as nutrients, dissolved organic carbon, turbidity and total suspended solids, for stormwater will provide a better understanding of variations in microbe concentrations related to different water quality parameters. This information will be useful for decision-making to perform rapid corrective actions regarding water management and public health.

On-line monitoring systems have been identified as useful tools with the introduction of UV spectroscopic techniques for wastewater and stormwater quality monitoring, such as total suspended solids and turbidity (Brito et al. 2014, Carreres-Prieto et al. 2020, Gruber et al. 2006, Ly et al. 2019, Moin 2021, Torres and Bertrand-Krajewski 2008). Additionally, the application of UV spectroscopic techniques for qualitative and quantitative analyses of organic pollutants has been extensively investigated, although it may be limited for the survey of non-absorbing compounds, i.e. saturated hydrocarbons and carbohydrates, and almost all mineral species except oxyanions such as nitrite and nitrate (El Khorassani et al. 1998). Mrkva (1975) suggested that the UV absorbance at a certain wavelength is proportional to the content of dissolved organic matter present in the surface waters and in some types of effluents with predominant organic compounds of aromatic character. This is based on a basic interaction between UV light and unsaturated ionic or molecular structures (chromophores) (Thomas et al. 1999). For instance, the absorbance value at 254 nm has long been used for the estimation of non-specific parameters, i.e. COD and BOD_5, in water and wastewater (Briggs and Melbourne 1968, Brito et al. 2014, Lepot et al. 2016, Torres and Bertrand-Krajewski 2008), while the presence of nitrate was found to increase absorbance intensity for wavelengths around 210 nm etc. (Causse et al. 2017, van den Broeke 2007).

South Australia depends heavily on the River Murray water as a source water supply. The 60-km-long Mannum–Adelaide Pipeline (MAPL) is one of the major pipelines supplying raw water from Mannum (a country town along the River Murray) to Adelaide, a city of over 1 million residents. Stormwater from the Mannum township enters the River Murray close to the pipeline intake with consequent potential water quality risks. In addition, there are other potential hazards, such as agricultural activities from upstream of the intake. It is, therefore, a necessity to implement a real-time hazard detection system and use this system to collect a substantial amount of data, helping water authorities to develop preventive strategies to ensure the control of hazards potentially entering downstream drinking water sources (Chow et al. 2009).

This paper describes a stormwater monitoring study using an on-line UV-Vis spectrophotometer in the Mannum township near the Mannum–Adelaide Pipeline (MAPL). A key component of this study was to investigate the use of on-line monitoring technique to identify the chemical and microbiological signatures of water samples using on-line spectral data with the aims of determining the relationships among various parameters, during rainfall events. The knowledge gained will be used to evaluate the feasibility of implementing future early warning systems to develop hazard analysis and critical control point (HACCP) approach for water quality incidents (including stormwater runoff) as part of a decision support system for water supply operations.

Materials and methods

On-line monitoring instrumentation and sampling system

An on-line UV-Vis spectrophotometer, s::can spectro::lyser, with optical path length of 0.5 cm was installed in a stormwater drain at the Mannum township (population c. 2,500), a residential area on the west bank of the Murray River in South Australia, equipped with an automatic carousel sampler (24 samples) with a flow proportional campsite sampling (FPCS) system. The autosampler was programmed to capture event samples. Spectro::lyser with different path lengths can be purchased; a path length of 0.5 cm was selected from previous stormwater measurement experience for the balance between sensitivity and dynamic range. This spectrophotometer was designed based upon the principle of a photodiode array (PDA) spectrophotometer, which has no moving parts and has the advantage of reagent-free operation. Full spectrum absorbance (200–720 nm) was measured, and calculated equivalents, such as nitrate (NO_3^-), dissolved organic carbon (DOC), turbidity and total suspended solids (TSS), were determined.

The spectrophotometer was set up to record the full spectrum every 5 min, along with corresponding parameter values (calculated equivalents). During rain events, the level sensor was used to measure the water level in the stormwater drain at 5-min intervals, the autosampler was triggered by the flow condition; the collection of water samples was initiated by the FCPS system when the water level was above a threshold of 25 mm which is designed to collect individual samples during an event based upon the flow. The samples were collected based on representative distribution across the flow profile of the stormwater event, obtained from the storm drain water level sensor. Samples were collected more frequently at larger fluctuations of water level changes or during rapid changes of water level and less frequently at smaller fluctuation. Samples from the three storm events, (1) July 29th, 2010 (18 samples); (2) August 19th, 2010 (13 samples); and (3) November 25th, 2010 (24 samples), were captured and analysed. The collected water samples were kept at less than 4 °C while being transported to the laboratory and filtered within 24 h for microbiological analysis. The first event (Event 1) and the second event (Event 2) were conducted during the wet season (July to September) in South Australia (supported by rainfall data in 2010 provided by the Bureau of Meteorology). The last event (Event 3) was carried out to capture the stormwater quality after a period of the dry season to study the impact of seasonal change. The three events reported in this study were thus carefully selected to obtain the maximum amount of relevant information.

Laboratory analytical methods

Chemical

To validate the accuracy of the calculated equivalent results from the on-line UV-Vis instrument, 18, 13 and 24 grab water samples collected by the autosampler from Events 1, 2 and 3, respectively, at corresponding times, were analysed in the laboratory for NO_3^-, DOC and turbidity. NO_3^- was analysed using a discrete analyser according to the standard method (Federation and APH Association 2007). DOC was determined using a total organic carbon analyser (900, Sievers Instruments Inc., USA) with the standard method (Federation and APH Association 2007). Turbidity was measured in NTU without physical filtration using a turbidimeter (2100AN, Hach, USA).

Microbiological

According to the results of water quality parameters from the autosampler, samples (9, 10 and 9 samples from Event 1, 2 and 3, respectively) with differences were selected for *Escherichia coli* measurement. *E. coli* numbers were estimated using Colilert-18 (Defined Substrate Technology, IDEXX Laboratories Pty. Ltd., Sydney) as previously described (Adcock and Saint, 1997, AS 4276.21-2005).

Statistical analyses

Statistical analyses were performed using Microsoft Excel and SPSS Statistics 24 (IBM). Differences between the on-line and laboratory measurement for various water quality parameters were tested using Passing–Bablok regression. Pearson correlation was applied to evaluate any correlations among water quality parameters, water level and *E. coli*. Both correlation factor (r) and probability (p) values were used to determine significance.

Results and discussion

Validation of on-line stormwater quality monitoring

Several water quality parameters (NO_3^-, DOC, turbidity and TSS) were determined by the on-line spectrophotometer during the three rainfall events using partial least square method (Shi et al. 2020). The grab samples were also collected by the autosampler from the three events at corresponding times and analysed in the laboratory (Event 1, 18 samples; Event 2, 13 samples; and Event 3, 24 samples). NO_3^-, DOC and turbidity were measured in the laboratory. In the case of TSS, a volume of 300–500 mL of water sample is required for analysis, and the autosampler was not able to provide sufficient volume for all the analyses. The TSS calculated equivalent value was used as an alternative. The other calculated equivalent results from the on-line spectrophotometer were compared with the laboratory results. These parameters have been validated previously for surface water samples, in good agreement with results obtained from laboratory analyses (Chow et al. 2007, Chow et al. 2008), but have not been validated for stormwater samples. Part of this study was to validate these parameters for stormwater samples. The calculated equivalent parameters were determined using the built-in algorithms with raw spectral data of water quality provided by an acquisition software, ana::pro, with a global calibration. The built-in algorithms of this acquisition software were built with the partial least squares regression based on hundreds of water sources.

In this study, the numerical values (concentrations) of stormwater quality parameters were obtained from both the on-line spectrophotometer and laboratory measurements. Passing–Bablok regression was used to compare the two methods. The results from Table 1 showed that the slope values (*b* values) from NO_3^- data were close to 1 and most of the intercept values (a values) were close to 0, indicating the on-line and laboratory measurements were comparable within the investigated concentration range. For turbidity results, the intercept values were negative and far from 1, while the slope values were close to 1 except for Event 2, indicating there is a systematic difference (the on-line spectrophotometer overestimated the results) but no proportional difference between the two methods. However, neither the intercept values or slope values for DOC was close to 1, indicating the systematic and proportional difference between the two methods. This difference could be caused due to several reasons. One is due to the aromatic substances in stormwater. Aromatic substances have strong absorption in low wavelength region, especially below 220 nm, which could cause interference for the DOC measurement. The second reason is we only applied global calibration in this study. The project team did not conduct local calibration during the monitoring period. This procedure requires entering the laboratory result of a sample to the on-line spectrophotometer control unit, and then the software adjusts the calibration by matching the on-line spectral signature of that sample with laboratory results. If the local calibration was conducted, it would allow the determination of the concentrations of stormwater quality using the spectrophotometer in real-time. Instead, a post data analysis on the collected data was conducted for the evaluation to determine the feasibility of applying the on-line instrument as a routine monitoring tool.

Table 1 Differences and correlations between the on-line and laboratory measurements

	Water quality parameters	Passing–Bablok regression ($y = a + bx$)	Pearson correlation coefficients (r)
Event 1	NO_3^-	$y = 0.9377 + 1.015x$	0.789**
	DOC	$y = -5.009 + 0.6887x$	0.971**
	Turbidity	$y = -75.81 + 1.071x$	0.835**
Event 2	NO_3^-	$y = x$	0.990**
	DOC	-	0.259
	Turbidity	$y = -466.9 + 3.999x$	0.603*
Event 3	NO_3^-	$y = x$	1.00**
	DOC	$y = -3.157 + 0.6483x$	0.985**
	Turbidity	$y = -99.38 + 1.047$	0.941**

Although differences were shown for the on-line and laboratory measurements, good correlations of the water quality parameters were observed across all the events (Table 1). The Pearson correlation coefficients were also applied, and the results showed significantly positive correlation between the two measurements (on-line and laboratory), with the *r* values ranging from 0.603 to 1 and most $p < 0.05$ except DOC for Event 2. Overall, the calculated equivalent parameters obtained via the on-line UV-Vis instrument showed comparable results with the laboratory analyses of stormwater samples for NO_3^-, DOC and turbidity. These results provide support for the application of the real-time monitoring system for detecting chemical contaminants present in stormwater discharges (Richter and Tränckner 2019).

Passing–Bablok regression, *y* scale is for laboratory grab sample and *x* scale is for on-line sample. Pearson correlation coefficients, ** means the correlation is significant at $p < 0.01$ level. * means the correlation is significant at $p < 0.05$ level

Evaluation of correlation among on-line and lab surrogate parameters for storm events

The detailed information of on-line surrogate parameters during rainfall events are presented in Figures 1, 2 and 3, and the monitored storm events are summarised in Table 2.

The data obtained from the Bureau of Meteorology contained total rainfall, rainfall duration and antecedent dry period. Table 2 showed that Events 1 and 2 happened during the wet and winter season in Adelaide, and Event 3 was conducted during the dry and summer season.

Event 1 was captured after a long antecedent dry period of 14 days, while both Event 2 and 3 were captured after 7

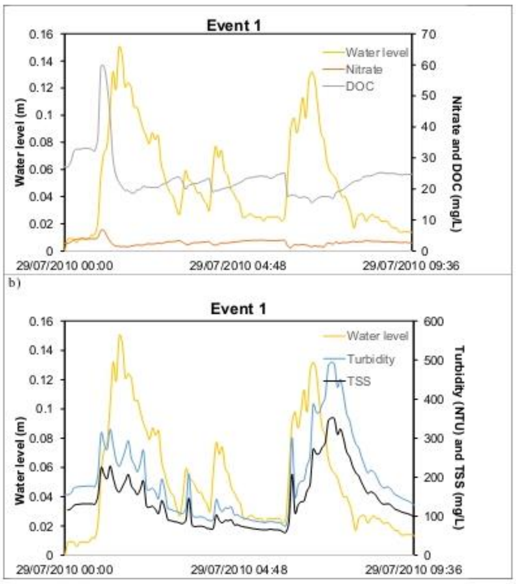

Figure 1 Water level and stormwater on-line data for **a** nitrate and DOC and **b** turbidity and TSS for Event 1

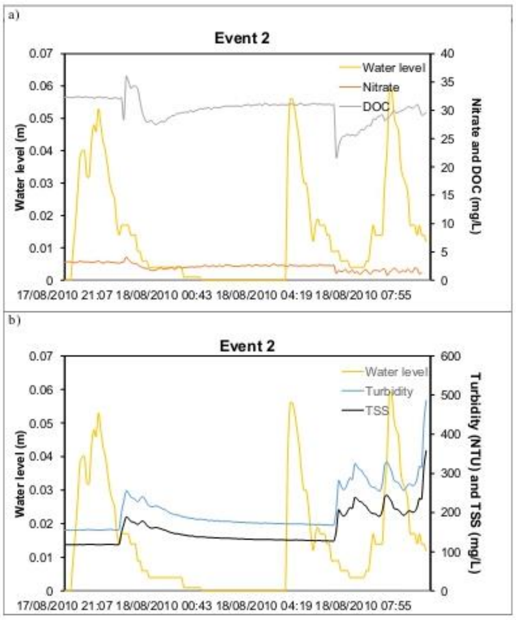

Figure 2 Water level and stormwater on-line data for **a** nitrate and DOC and **b** turbidity and TSS for Event 2

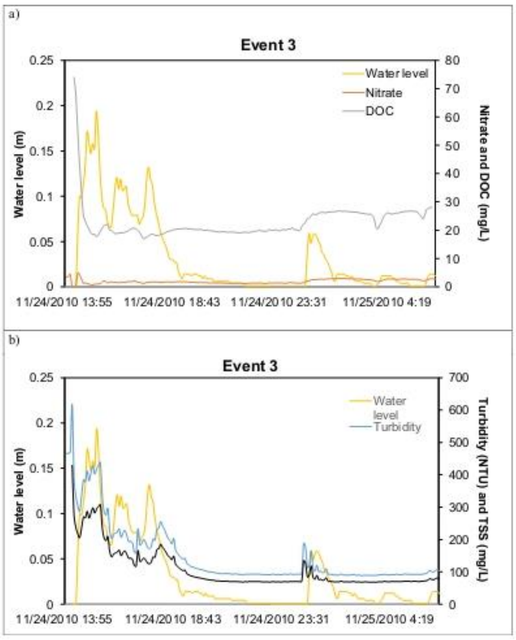

Figure 3 Water level and stormwater on-line data for **a** nitrate and DOC and **b** turbidity and TSS for Event 3

Table 2 Summary of monitored storm events (modified from Huang et al. (2016))

Rainfall event (m/day)	Rainfall (mm)	Rainfall duration (min)	Antecedent dry period (days)
Event 1 (29/07)	10	420	14
Event 2 (19/08)	8	755	7
Event 3 (25/11)	14	655	7

days of dry period. Additionally, the data shows that Event 3 had the highest rainfall of 14 mm and medium rainfall duration of 655 min, Event 1 had medium rainfall of 10 mm and the shortest duration of 420 min, and Event 2 had the lowest rainfall of 8 mm and the longest rainfall period of 755 min (Huang et al. 2016).

Figures 1, 2, and 3 show the changes of water levels in the drain during each event. As can be seen, water levels for Event 1 ranged from 9 to 150 mm with an average value of 48 ± 37 mm. The water levels for Event 2 were from 0the water levels in to 59 mm with the average result of 14 ± 16 mm and Event 3 had the widest range for water levels from 1 to 194 mm with an average water level of 32 ± 44 mm. Although Event 3 had the highest water level which was up to 194 mm, Event 1 had the highest average water level.

This is because the rainfall intensities from Event 3 became lower after the halfway mark of the event, leading to the lower average water level for Event 3. Overall, Event 1 and 3 had higher rainfall intensity and presented larger dynamic changes of the water flow conditions, while Event 2 had lower rainfall intensity and a more stable and lower flow.

Pearson correlation was applied to evaluate if any correlations existed among water quality parameters and water level (Table 3) during the events. The results show that there is a strong negative correlation between NO_3^- and water level for Event 1 and 3 which had higher rainfall intensities. Event 2, which had low rainfall intensity and flow rate, presented a strong positive correlation to NO_3^-. In this study, high rainfall intensity could lead to decreased NO_3^- concentration in the drain as the water level increased, while low rainfall intensity resulted in increased NO_3^- concentration when the water level was subsiding. The decrease in NO_3^- concentration in the stormwater drain could be due to the dilution effect from the high rainfall intensity. Another possible reason why a negative correlation is shown between NO_3 concentrations and water level is because there is a time delay between the two factors. McCarthy et al. (2012) reported that rainfall intensity needed to be adjusted to capture the time of concentration for each event. In MaCarthy's study, the measured hydrologic data was "shifted" (by ± 15 min) to capture the inherent variability in the timing of pollutographs with respect to hydrologic pattern (McCarthy et al. 2012). The result from this study is different from other studies but not contradictory. For instance, Mallin et al. (2009) presented that there was not a corresponding positive correlation between rainfall and NO_3^-. Dillon and Chanton (2005) reported that NO_3^- concentrations were elevated in stormwater relative to rainwater in an urbanised coastal environment, but this trend was not statistically significant. In addition, the NO_3^- results from Events 1 and 3 indicate that the NO_3^- levels were high in the sump water before the event started, which could be due to the impact of the fertiliser runoffs from farming activities. Furthermore, NO_3^- showed a significantly positive correlation with DOC, indicating NO_3^- and DOC were discharged into the system at the same time during the rainfall events. Moreover, NO_3^- indicated strong negative correlations with turbidity and TSS through all events, although Nebbache et al. (2001) revealed no clear correlation between turbidity and NO_3^- concentration, whether positive or negative during the rainfall event. These negative correlations can suggest different sources for NO_3^-, turbidity and TSS.

Additionally, there is a strong positive correlation between water level and turbidity and TSS except Event 2 which indicates a weak negative relationship. In this study, high rainfall intensity led to increased turbidity and TSS in the drain as the water level increased, while low rainfall intensity and flow rate resulted in increased turbidity and TSS when the water level decreased. Mallin et al. (2009) reported that turbidity was significantly higher during rain events compared to non-rain periods and a positive correlation occurred between rainfall and turbidity. Other studies also discovered a significantly positive correlation between the rainfall intensity and TSS concentrations (Mallin et al. 2009, McCarthy et al. 2012). Furthermore, turbidity was an indication of the concentration of colloids and suspended particulates (Huang et al. 2016). Our study indicated a significantly positive relationship between turbidity and TSS during the events. Furthermore, the correlations between the water level and DOC were similar to NO_3^-. Event 2 with the lowest rainfall showed a strong positive correlation

Table 3 Pearson correlation coefficients among water quality parameters and water level

		NO_3^-	DOC	Turbidity	TSS	Water level
Event 1	NO_3^-		0.828**	−0.211*	−0.194*	−0.572**
	DOC	0.828**		−0.046	−0.039	−0.263**
	Turbidity	−0.211*	−0.046		0.999**	0.435**
	TSS	−0.194*	−0.039	0.999**		0.408**
	Water level	−0.572**	−0.263**	0.435**	0.408**	
Event 2	NO_3^-		0.811**	−0.757**	−0.760**	0.165*
	DOC	0.811**		−0.193**	−0.190**	0.251**
	Turbidity	−0.757**	−0.514**		1.000**	−0.052
	TSS	−0.760**	−0.510**	1.000**		−0.049
	Water level	0.165*	0.251**	−0.052	−0.049	
Event 3	NO_3^-		0.362**	−0.328**	−0.364**	−0.206**
	DOC	0.362**		0.119	0.122	0.085
	Turbidity	−0.328**	0.119		1.000**	0.816**
	TSS	−0.364**	0.122	1.000**		0.814**
	Water level	−0.206**	0.085	0.816**	0.814**	

* means $p < 0.05$, and ** means $p < 0.01$

with DOC and Event 1 with the highest rainfall intensity indicated a strong negative correlation with DOC, although a weak positive correlation for Event 3. Other studies indicated that there was a significant increase in DOC concentrations during storm events (Dalzell et al. 2005, Vidon et al. 2008). In addition, DOC also presents negative relationships with the turbidity and TSS except for Event 3. Once again, these negative correlations can suggest different origins between DOC, turbidity and TSS.

The study indicated that the chemical and physical parameters were characteristic of changing water quality through the drain that was not just related to the velocity of the flow. The factors that are affecting the response of NO_3^-, turbidity and TSS in this study are clearly more complex than just the velocity of water passing through the sump. These changes could include the rainfall intensity and the distance from the stormwater drain affecting the time at which the peak levels arrived at the detectors, time required to re-suspend particles, the nature of the catchment area and the size and character of the particles (clay, sand, soot, etc.).

Assessment of correlation among microbiological and chemical parameters

Figure 4a, b and c show the water levels in the stormwater monitoring sump overlaid with the sample points analysed for *E. coli* with counts as the most probable number (MPN) per 100 mL. The results indicated the highest average concentrations of *E. coli* (93166 ± 89283 count) were found at Event 3, followed by Event 2 with 6442 ± 3850 counts, and Event 1 had the lowest average *E. coli* concentration of 4687 ± 5684 counts. This could be due to a more intense rainfall that occurred during the first 8 h of Event 3, introducing a larger amount of *E. coli* into the drain. Furthermore, temperature was another important factor for the *E. coli* numbers. In Adelaide, the temperature was higher in the dry season than in the wet season, and *E. coli* could be persisting or growing in the aquatic environments during periods of warmer temperature, contributing to higher initial concentrations and peaks during subsequent runoff events. But this is also different from Mallin et al. (2009) where the authors reported that wet-period faecal coliform bacteria counts were significantly higher than dry period counts (no rainfall in the previous 72 h) for the individual creek in Hanover County, North Carolina, USA, although the effect of temperature was not discussed between the wet (defined as any rainfall) and dry periods.

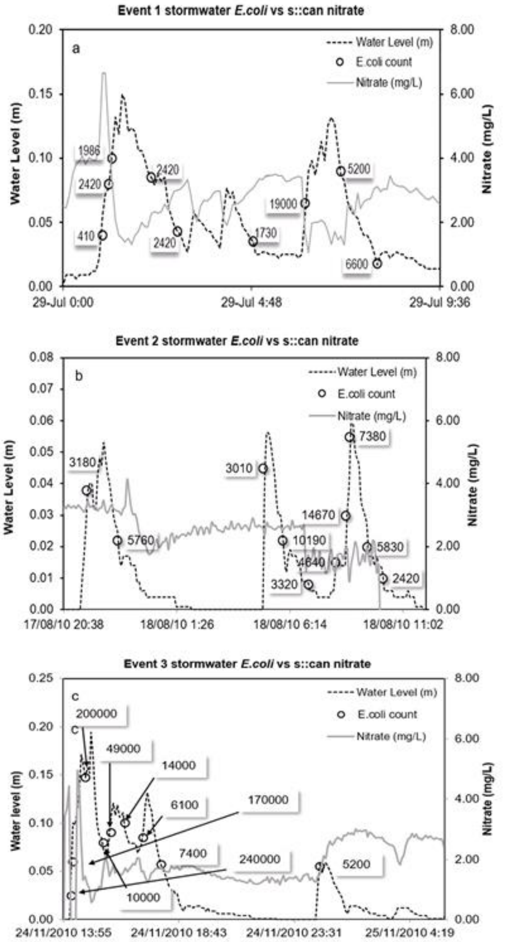

Figure 4 *E. coli* counts (cfu/100mL) versus nitrate in stormwater determined as calculated equivalents in grab samples, **a** Event 1, **b** Event 2 and **c** Event 3

In the cases of Events 1 and 2, the distribution indicates that bacterial numbers did not correlate with the water level, with the highest values detected late in the event with no increase due to water level rises. Other studies reported that the incidence of rainfall and rainfall intensity were highly significantly correlated with faecal coliform bacteria (Davies and Bavor 2000, Haydon and Deletic 2006, Kelsey et al. 2004, Mallin et al. 2009). At the same time, McCarthy et al. (2012) also reported *E. coli* was less correlated to hydrologic parameters, such as rainfall and runoff variables, for urban runoff. Event 3, with a different, more intense onset, did exhibit the highest *E. coli* numbers with the first flush. Additionally, most of the timing of peak *E. coli* concentrations was randomly scattered with respect to the timing of the peak water level, indicating that *E. coli* did not consistently experience a first flush and that concentrations were probably not affected solely by rainfall or catchment depletion processes. Many researchers have reported that pollutants can exhibit higher levels in the first flush of a stormwater runoff event, but these strategies may be deficient as the first flush of typical stormwater pollutants, such as sediment, nutrients and others, is not always observed in urban runoff (Duncan 1995, McCarthy 2009). McCarthy (2009) determined that cumulative mass versus volume curves related to the first flush phenomenon was not consistently present; the presence and magnitude of a first flush varied considerably between each site and poor consistent correlations were shown between *E. coli* and the first flush effect. This could also explain the contradiction to the chemical parameter observations and introduces the likelihood that different mechanisms of transport are operating in the stormwater drain. Furthermore, while the chemical parameters potentially enter the stormwater by rapid dissolution or dilution of a concentrated source, bacterial transport may require re-suspension before subsequent flows can flush the cells from the catchment to the stormwater drain.

Table 4 Pearson correlation coefficients (r) among water quality parameters and *E. coli*

	Event 1	Event 2	Event 3
NO_3^-	−0.535	−0.143	−0.608
DOC	−0.470	−0.119	0.572
Turbidity	−0.284	0.007	0.916**
TSS	−0.286	0.010	0.913**
Water level	−0.163	0.186	0.257

* means $p < 0.05$ and ** means $p < 0.01$

NO_3^- is the logical choice for surrogate microbial detection, as it is a representative of nutrient content (Whitehead and Cole 2006) and therefore possible raw sewage contamination. In addition, NO_3^- is detected in the low wavelength (< 220 nm), high-energy region giving excellent sensitivity to changes and the lowest detection limits. Thus, calculated equivalent NO_3^- concentration was the most likely candidate as a surrogate for microbial numbers. The monitored NO_3^- concentrations during the captured flow events in July, August and November are shown in Figure 4a, b and c, respectively. Our study indicated a negative correlation between NO_3^- and *E. coli* numbers through all the events, but this relationship was not significant (Table 3). To confirm the relationships with *E. coli*, other calculated equivalent parameters (DOC, turbidity and TSS) from the time scale of the sample collection from all the captured events were also plotted against *E. coli* counts. Correlation factors were very low in almost all cases indicating very little potential for relating these parameters to stormwater microbial loadings (Table 4). A strong correlation was found with turbidity ($r = 0.916$, $p < 0.01$) and TSS turbidity ($r = 0.913$, $p < 0.01$) but only within Event 3 indicating this relationship may not be reproducible, although faecal bacteria were found frequently associated with turbidity and/or TSS (Mallin et al. 2009). With NO_3^-, the direction of the trend also indicated that if a relationship existed, it was the reduction of the parameter that encouraged *E. coli* proliferation which is counter-intuitive if its role as a surrogate for growth nutrients is considered. The possible reasons for this lack of correlation are believed to be related to the nature of the stormwater catchment rather than any failing of the instrumentation or procedures. The water quality parameters from the laboratory-analysed grab samples were also plotted against *E. coli* counts within the three events. The disparity of trends between the chemical parameters (NO_3^-, DOC and turbidity) and *E. coli* counts was visually apparent, and the poor correlations were also present except for Event 3 (Table 2). Compared to calculated equivalent, limited results were provided by the grab samples, and the strong correlations among *E. coli* counts and NO_3^-, DOC and turbidity for Event 3 might be coincident. Unlike a permanent water body where solutes and nutrients are constantly accessible to water-borne organisms, the stormwater catchment is typically dry until the onset of a rain event. As a result, the bacteria and chemical nutrients are likely to be spatially separated until they come into contact during the event, and detection of either would therefore be unrelated. In addition, while NO_3^- does promote bacterial proliferation, it is not usually a growth-limiting nutrient, and its absence does not preclude the detection of significant bacterial numbers. Furthermore, faecal microbial contamination in urban and peri-urban areas could come from various sources, including livestock and domestic animals and urban wildlife including pets, waterfowl, pigeons, rats and others (McCarthy 2009). Additionally, NO_3^- concentrations could be influenced by non-point sources, especially for agriculture runoffs. The complicated sources from the urban and peri-urban areas could contribute to a weak correlation between NO_3^- and *E. coli* (James and Joyce 2004).

Furthermore, temporal variations were apparent for the detection of parameters in the stormwater flow events, with the dissolved chemical parameters peaking early in the first flush and decreasing rapidly throughout the monitored event. Microbiological parameters such as *E. coli* count were lower in the early period of the event and peaked during subsequent increases in water flow, indicating that different mechanisms of transport are exerting influence. It is believed that while chemical species are easily dissolved and carried with the primary flow, microorganisms require re-suspension from solid substrates before the later flow increases can transport them through the catchment area and into the stormwater drain (Etheridge et al. 2019). In addition, this can be because the bacterial comes from animal faeces that slowly dissolve in fields and on roads before entering the stormwater system rather than an overflow of a domestic sewerage system where it would be expected the presence of *E. coli* and nitrate would be concomitant.

Conclusion

This study has applied an on-line UV-Vis spectrophotometer in the field to collect real-time continuous data for various water quality parameters (nitrate, DOC, turbidity and total suspended solids) during three storm events in Mannum, Adelaide, Australia. This study demonstrated that the trends for on-line and comparative laboratory-analysed samples were complimentary through the events. The study not only investigated the correlations among various water quality parameters (nitrate, DOC, turbidity and TSS) and water levels, but also investigated the potential correlations among water quality parameters and *E. coli*. The results showed that water levels had a strong negative correlation with NO_3^- and DOC and a strong positive correlation with turbidity and TSS during high rainfall intensity, while water levels presented a positive correlation with NO_3^- and DOC and negative correlation with turbidity and TSS during low rainfall intensity. Microbiological parameter — *E. coli* counts, was lower in the early period of the event and peaked during subsequent increases in water flow, indicating that different mechanisms of transport are exerting influence. Our study also indicated that NO_3^-, DOC, turbidity, TSS and water level did not show strong correlations with *E. coli*. The poor correlations among the microbiological data and on-line parameters can be due to the nature of the stormwater catchment outside of rain events or due to the different sources of bacteria and nutrients that end up in the stormwater drain. This case study represented a trial of technologies in a prototype self-contained monitoring station for the ability to act as a hazard detection tool for stormwater inputs into drinking water sources. While solutions to a number of issues could not be resolved within the duration of the project, the monitoring should be continued to collect more valuable data which will help guide its future implementation for routine on-line monitoring of stormwater.

Author contribution Jianyin Huang, data analysis and manuscript writing. Christopher W. K. Chow, experimental design, data analysis and manuscript writing. Zhining Shi, data analysis and manuscript writing. Rolando Fabris, experimental design and data analysis. Amanda Mussared, experimental design and data analysis. Gary Hallas, experimental design and data analysis. Paul Monis, experimental design, data analysis and manuscript writing. Bo Jin, experimental design and data analysis. Christopher P. Saint, experiment design, data analysis and manuscript writing.

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Declarations

Ethics approval Not applicable.

Consent to participate Not applicable.

Consent for publication Not applicable.

Competing interests The authors declare no competing interests.

References

Adcock PW, Saint C (1997) Trials of Colliert System. Water-Melbourne then Artamon 24:22–28

Bricker SB (2007) Effects of nutrient enrichment in the nation's estuaries: a decade of change: National Estuarine Eutrophication Assessment update

Briggs R, Melbourne K (1968) Recent advances in water quality monitoring. Water Treat. Exam 17:107–120

Brito RS, Pinheiro H, Ferreira F, Matos JS, Lourenço N (2014) In situ UV-Vis spectroscopy to estimate COD and TSS in wastewater drainage systems. Urban Water J 11:261–273

Carreres-Prieto D, García JT, Cerdán-Cartagena F, Suardiaz-Muro J (2020) Wastewater quality estimation through spectrophotometry-based statistical models. Sensors 20:5631

Causse J, Thomas O, Jung A-V, Thomas M-F (2017) Direct DOC and nitrate determination in water using dual pathlength and second derivative UV spectrophotometry. Water Res 108:312–319

Chow C, Dexter R, Sutherland-Stacey L, Fitzgerald F, Fabris R, Drikas M, Holmes M, Kaeding U (2007): UV spectrometry in drinking water quality management. WATER-MELBOURNE THEN ARTARMON- 34, 63

Chow C, Fabris R, Dixon M (2008): Case studies using S:: CAN on-line monitoring system. Adelaide

Chow C, Sweet V, Adams K, Mosisch T, Shephard M, R D (2009): Implementation of a real time early warning system for water quality incidents, OzWater 09, AWA, Melbourne Convention and Exhibition Centre, Melbourne

Dalzell BJ, Filley TR, Harbor JM (2005): Flood pulse influences on terrestrial organic matter export from an agricultural watershed. J Geophys Res Biogeosci 110

Davies C, Bavor H (2000) The fate of stormwater-associated bacteria in constructed wetland and water pollution control pond systems. J Appl Microbiol 89:349–360

Davis E, Casserly D, Moore J (1977) Bacterial relationships in stormwaters 1. J Am Water Resour Assoc 13:895–906

Dillon KS, Chanton JP (2005) Nutrient transformations between rainfall and stormwater runoff in an urbanized coastal environment: Sarasota Bay, Florida. Limnol Oceanogr 50:62–69

Duncan H (1995): A review of urban stormwater quality processes.

Duncan H (1999): Urban stormwater quality: a statistical overview. CRC for Catchment Hydrology

El Khorassani H, Theraulaz F, Thomas O (1998) Application of UV spectrophotometry to the study of treated wastewater discharges in rivers. Acta Hydrochim Hydrobiol 26:296–299

Eriksson E, Baun A, Scholes L, Ledin A, Ahlman S, Revitt M, Noutsopoulos C, Mikkelsen PS (2007) Selected stormwater priority pollutants—a European perspective. Sci Total Environ 383:41–51

Etheridge JR, Randolph M, Humphrey C (2019) Real-time estimates of Escherichia coli concentrations using ultraviolet-visible spectrometers. J Environ Qual 48:531–536

Federation WE, APH Association (2007) Standard methods for the examination of water and wastewater. American Public Health Association (APHA), Washington, DC

Ferguson C, Husman AMdR, Altavilla N, Deere D, Ashbolt N (2003) Fate and transport of surface water pathogens in watersheds. Crit Rev Environ Sci Technol 33:299–361

Gnecco I, Berretta C, Lanza L, La Barbera P (2005) Storm water pollution in the urban environment of Genoa, Italy. Atmos Res 77:60–73

Göbel P, Dierkes C, Coldewey W (2007) Storm water runoff concentration matrix for urban areas. J Contam Hydrol 91:26–42

Greenway M, Le Muth N, Jenkins G (2002): Monitoring spatial and temporal changes in stormwater quality through a series of treatment trains. A case study—Golden Pond, Brisbane, Australia, Global Solutions for Urban Drainage, pp. 1-16

Gruber G, Bertrand-Krajewski J-L, Beneditis JD, Hochedlinger M, Lettl W (2006): Practical aspects, experiences and strategies by using UV/VIS sensors for long-term sewer monitoring. Water Practice and Technology 1

Hamilton AJ, Boland A-M, Stevens D, Kelly J, Radcliffe J, Ziehrl A, Dillon P, Paulin B (2005) Position of the Australian horticultural industry with respect to the use of reclaimed water. Agric Water Manag 71:181–209

Haydon S, Deletic A (2006) Development of a coupled pathogen-hydrologic catchment model. J Hydrol 328:467–480

Huang H, Chow CW, Jin B (2016) Characterisation of dissolved organic matter in stormwater using high-performance size exclusion chromatography. J Environ Sci 42:236–245

James E, Joyce M (2004) Assessment and management of watershed microbial contaminants. Crit Rev Environ Sci Technol 34:109–139

Kelsey H, Porter D, Scott G, Neet M, White D (2004) Using GIS and regression analysis to evaluate relationships between land use and fecal coliform bacterial pollution. J Exp Mar Biol Ecol 298:197–209

Lepot M, Torres A, Hofer T, Caradot N, Gruber G, Aubin J-B, Bertrand-Krajewski J-L (2016) Calibration of UV/Vis spectrophotometers: a review and comparison of different methods to estimate TSS and total and dissolved COD concentrations in sewers, WWTPs and rivers. Water Res 101:519–534

Ly DK, Maruéjouls T, Binet G, Bertrand-Krajewski J-L (2019) Application of stormwater mass–volume curve prediction for water quality-based real-time control in sewer systems. Urban Water J 16:11–20

Mallin MA, Johnson VL, Ensign SH (2009) Comparative impacts of stormwater runoff on water quality of an urban, a suburban, and a rural stream. Environ Monit Assess 159:475–491

McCarthy D, Mitchell V, Deletic A, Diaper C (2007) Escherichia coli in urban stormwater: explaining their variability. Water Sci Technol 56:27–34

McCarthy D (2009) A traditional first flush assessment of E. coli in urban stormwater runoff. Water Sci Technol 60:2749–2757

McCarthy D, Hathaway J, Hunt W, Deletic A (2012) Intra-event variability of Escherichia coli and total suspended solids in urban stormwater runoff. Water Res 46:6661–6670

Moin S (2021) Evaluating the benefits of near-continuous monitoring, real-time control, and SCM visibility in performance of stormwater control measures

Mrkva M (1975) Automatic UV-control system for relative evaluation of organic water pollution. Water Res 9:587–589

Nebbache S, Feeny V, Poudevigne I, Alard D (2001) Turbidity and nitrate transfer in karstic aquifers in rural areas: the Brionne Basin case-study. J Environ Manage 62:389–398

Olivieri VP (1977) Microorganisms in urban stormwater, 1. Environmental Protection Agency, Office of Research and Development

Petney T, Taraschewski H (2011) Waterborne parasitic diseases: hydrology, regional development, and control

Richter B, Tränckner J (2019) Balancing of COD, TSS and NO3-N loads in an urban streams by high resolution online monitoring. Novatech

Selvakumar A, Borst M (2006) Variation of microorganism concentrations in urban stormwater runoff with land use and seasons. J Water Health 4:109–124

Shi Z, Chow CW, Fabris R, Liu J, Jin B (2020) Alternative particle compensation techniques for online water quality monitoring using UV–Vis spectrophotometer. Chemometr Intell Lab Syst 204:104074

Thayanukul P, Kurisu F, Kasuga I, Furumai H (2013) Evaluation of microbial regrowth potential by assimilable organic carbon in various reclaimed water and distribution systems. Water Res 47:225–232

Thomas O, El Khorassani H, Touraud E, Bitar H (1999) TOC versus UV spectrophotometry for wastewater quality monitoring. Talanta 50:743–749

Torres A, Bertrand-Krajewski J-L (2008) Partial least squares local calibration of a UV–visible spectrometer used for in situ measurements of COD and TSS concentrations in urban drainage systems. Water Sci Technol 57:581–588

van den Broeke J (2007): On-line and in situ UV/Vis spectroscopy. AWE International March, 55-59

Vidon P, Wagner LE, Soyeux E (2008) Changes in the character of DOC in streams during storms in two Midwestern watersheds with contrasting land uses. Biogeochemistry 88:257–270

Whitehead R, Cole J (2006) Different responses to nitrate and nitrite by the model organism Escherichia coli and the human pathogen Neisseria gonorrhoeae. Portland Press Limited

WHO (2006) guidelines for drinking water quality, World Health Organisation, Geneva, Switzerland

Appendix B

This is an early access version, the complete PDF, HTML, and XML versions will be available soon.

Applications of Online UV-Vis Spectrophotometer for Drinking Water Quality Monitoring and Process Control: A Review

by **Zhining Shi** [1], **Christopher W. K. Chow** [2,3,*], **Rolando Fabris** [4], **Jixue Liu** [5] and **Bo Jin** [1]

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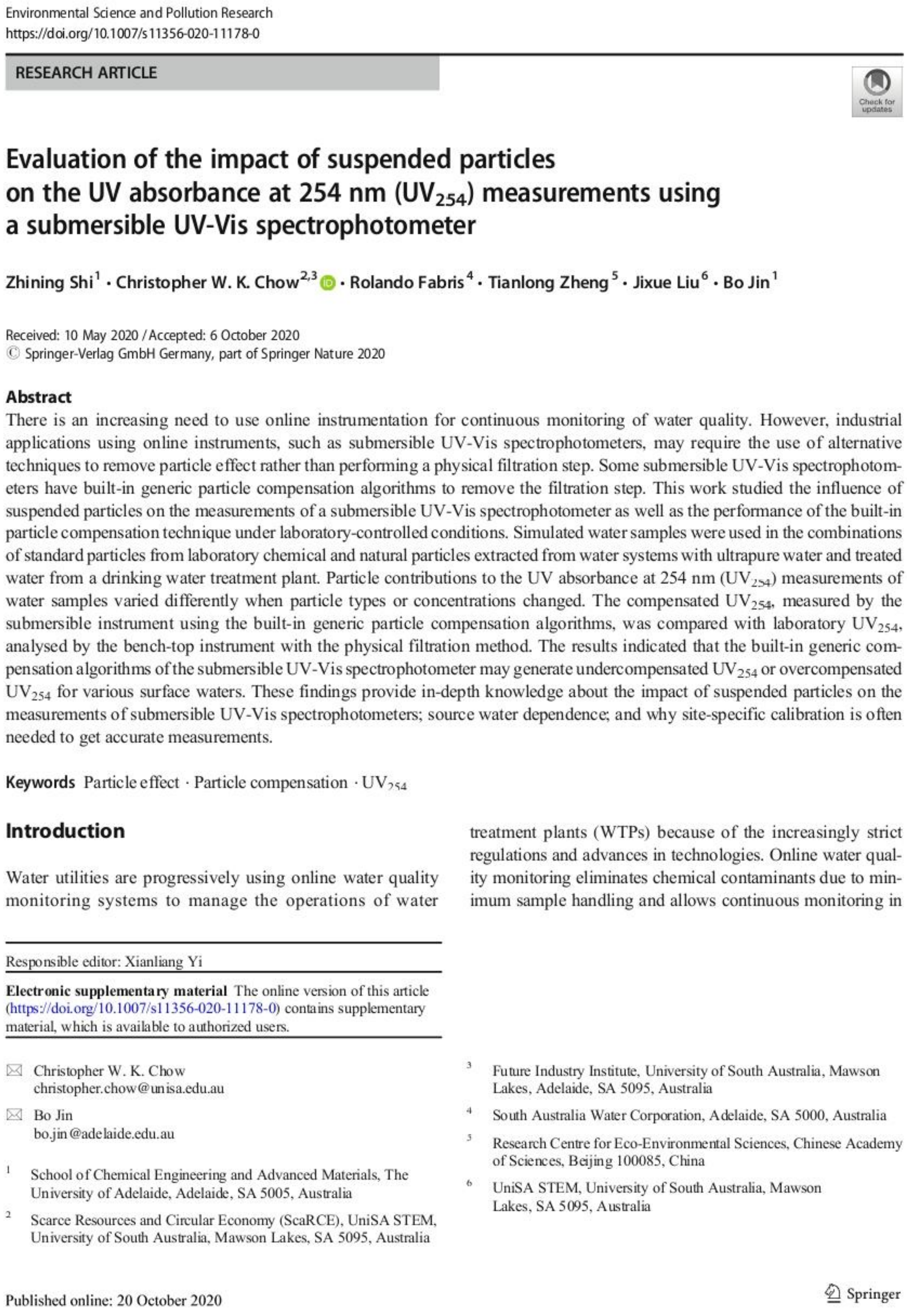
Abstract

Water quality monitoring is an essential component of water quality management for water utilities for managing the drinking water supply. Online UV-Vis spectrophotometers are becoming popular choices for online water quality monitoring and process control, as they are reagent free, do not require sample pre-treatments and can provide continuous measurements. The advantages of the online UV-Vis sensors are that they can capture events and allow quicker responses to water quality changes compared to conventional water quality monitoring. This review summarizes the applications of online UV-Vis spectrophotometers for drinking water quality management in the last two decades. Water quality measurements can be performed directly using the built-in generic algorithms of the online UV-Vis instruments, including absorbance at 254 nm (UV_{254}), colour, dissolved organic carbon (DOC), total organic carbon (TOC), turbidity and nitrate. To enhance the usability of this technique by providing a higher level of operations intelligence, the UV-Vis spectra combined with chemometrics approach offers simplicity, flexibility and applicability. The use of anomaly detection and an early warning was also discussed for drinking water quality monitoring at the source or in the distribution system. As most of the online UV-Vis instruments studies in the drinking water field were conducted at the laboratory- and pilot-scale, future work is needed for industrial-scale evaluation with ab appropriate validation methodology. Issues and potential solutions associated with online instruments for water quality monitoring have been provided. Current technique development outcomes indicate that future research and development work is needed for the integration of early warnings and real-time water treatment process control systems using the online UV-Vis spectrophotometers as part of the water quality management system.

Keywords: online UV-Vis spectrophotometer; real-time measurement; online water quality monitoring; drinking water

Figure A-1 Early access version of the review paper, entitled ‘application of online UV-Vis spectrophotometer for drinking water quality monitoring and process control: a review’, published by Sensors, MDPI.

Appendix C



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RESEARCH ARTICLE

Evaluation of the impact of suspended particles on the UV absorbance at 254 nm (UV_{254}) measurements using a submersible UV-Vis spectrophotometer

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Abstract

There is an increasing need to use online instrumentation for continuous monitoring of water quality. However, industrial applications using online instruments, such as submersible UV-Vis spectrophotometers, may require the use of alternative techniques to remove particle effect rather than performing a physical filtration step. Some submersible UV-Vis spectrophotometers have built-in generic particle compensation algorithms to remove the filtration step. This work studied the influence of suspended particles on the measurements of a submersible UV-Vis spectrophotometer as well as the performance of the built-in particle compensation technique under laboratory-controlled conditions. Simulated water samples were used in the combinations of standard particles from laboratory chemical and natural particles extracted from water systems with ultrapure water and treated water from a drinking water treatment plant. Particle contributions to the UV absorbance at 254 nm (UV_{254}) measurements of water samples varied differently when particle types or concentrations changed. The compensated UV_{254}, measured by the submersible instrument using the built-in generic particle compensation algorithms, was compared with laboratory UV_{254}, analysed by the bench-top instrument with the physical filtration method. The results indicated that the built-in generic compensation algorithms of the submersible UV-Vis spectrophotometer may generate undercompensated UV_{254} or overcompensated UV_{254} for various surface waters. These findings provide in-depth knowledge about the impact of suspended particles on the measurements of submersible UV-Vis spectrophotometers; source water dependence; and why site-specific calibration is often needed to get accurate measurements.

Keywords Particle effect · Particle compensation · UV_{254}

Introduction

Water utilities are progressively using online water quality monitoring systems to manage the operations of water treatment plants (WTPs) because of the increasingly strict regulations and advances in technologies. Online water quality monitoring eliminates chemical contaminants due to minimum sample handling and allows continuous monitoring in

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real-time. Online water quality monitoring may provide decision-making information for early warning responses (Dong et al. 2015; Hou et al. 2013). Online UV-Vis spectrophotometer is a popular choice for water utilities to monitor water quality as it does not require sample pretreatment or chemical reagents (Zhang et al. 2017). There are several commercially available systems, such as submersible UV-Vis spectrophotometers. Some submersible instruments provide generic calibrations with built-in particle compensation algorithms (Langergraber et al. 2003). These algorithms were developed using advanced computing techniques, such as partial least squares, to establish the relationship between UV-Vis spectra and laboratory measurements of water samples. They extracted information from the spectra to determine measurements of certain water quality parameters such as UV_{254}, colour and dissolved organic carbon (DOC). The algorithms were developed based on hundreds of datasets containing both UV-Vis spectra and reference laboratory data (Langergraber et al. 2003). However, the details of the algorithms are proprietary and are not provided by the manufacturers.

Peer-reviewed studies have documented various methods of compensating particle effect on the UV-Vis measurements of water quality using the submersible UV-Vis spectrophotometer. Algorithms were built based on the chemical compositions and the morphology features of UV-Vis spectra obtained from wastewater samples, which were used to eliminate measurement derivation (Hu and Wang 2017). The fourth derivative spectrum was used to eliminate the interference of particles in the measurements of total organic carbon for seawater (Hu et al. 2016). Additionally, partial least squares regression was employed to eliminate the particle effect on measuring water quality in urban drainage system (Torres and Bertrand-Krajewski 2008). Moreover, a multiple linear regression method was adapted to remove the particle effect on the UV-Vis spectra of brackish water for rapid measurements of multiple material concentrations (Etheridge et al. 2014).

Some research findings showed that particle compensation of submersible UV-Vis spectrophotometers are source water dependent and site-specific calibrations were often required to obtain accurate measurements (Avagyan et al. 2014; Drolc and Vrtovšek 2010; Huebsch et al. 2015; Jeong et al. 2012; Langergraber et al. 2003; Strohmeier et al. 2013). A study on the determination of water quality for wastewater samples concluded that the calibration of the submersible instrument needs to be matched with the specific wastewater type in some situations (Drolc and Vrtovšek 2010). Comparable water quality results were gained from a study on monitoring water quality of surface waters in the field using a submersible instrument with a multilinear calibration method. It was found that the calibration was water matrix dependent and recommended to use site-specific calibration to improve the accuracy of the quantification. Another field study using submersible UV-Vis spectrophotometers to monitor groundwater revealed that the significant fluctuations of water quality could affect the accuracy of the water quality measurements and long-term monitoring could be limited by particle compensation (Huebsch et al. 2015). A customised calibration was conducted for a submersible spectrophotometer to measure water quality in a forested catchment, and comparable results were achieved (Strohmeier et al. 2013). A site-specific calibration was performed for a submersible instrument using the built-in compensation algorithms to measure the water quality of stream water, but concentrations were overestimated because of inaccurate turbidity compensation (Jeong et al. 2012). Thus, accurate site-specific calibration is important for water quality monitoring.

To obtain accurate water quality measurements using submersible UV-Vis spectrophotometers can be challenging, and it depends on their application, particularly for real-time monitoring and process control. Submersible UV-Vis spectrophotometers have been implemented at some water utilities to monitor water quality online for the assistance of water treatment process control (Banna et al. 2014; Byrne et al. 2014; Chow et al. 2007). However, measurement issues often occur to the submersible instruments when water quality changes dramatically or water source changes (Waterra 2017). Industrial applications of the submersible instruments have encountered particle compensation issues such as under-compensation or overcompensation or even failure to generate reasonable measurements (Chow et al. 2007; Chow et al. 2017; Hu and Wang 2017; Lepot et al. 2016; Waterra 2017). Industrial experience and peer-reviewed studies show that the impact of particles is source water specific and generic calibrations could not adequately account for the differences in large water quality changes or between different types of water (Caradot et al. 2014; Chow et al. 2017; Leigh et al. 2019; Lepot et al. 2016; Meyer et al. 2019).

Even though there are studies on improving the accuracies of submersible UV-Vis spectrophotometers with site-specific calibrations, the studies of characterised particle impact on the measurements are limited. There is only one reported studies of particle effect on the measurements of an UV spectrophotometric nitrate sensor (Snazelle 2016; Van Eerdenbrugh et al. 2011)). This paper provides a systematic study utilising six types of stimulated water samples with both artificial and natural water particles for each type of water. The aim was to study the particle effect on the measurements of a submersible UV-Vis spectrophotometer. This work also determines whether the built-in compensation method can generate comparable measurements as the physical filtration method or not under lab-controlled conditions.

Materials and methods

Materials

Three types of particles were chosen including, kaolin clay (P_1), Myponga silt (P_2), and Hope Valley silt (P_3). P_1 particles are clay minerals (Chem-Supply Pty Ltd, Australia) which were chosen because they are standardised particles. P_2 particles are silica-based and were collected from the catchment of the Myponga Reservoir in South Australia (SA). P_2 particles were selected as they represented the typical particles from an enclosed water catchment of reservoirs in SA. P_3 particles are clay-based, which were sediment from Hope Valley WTP in SA. P_3 particles were selected as they represented particles of a surface water catchment of a chain of reservoirs in SA. P_2 and P_3 were dried in an oven at 40 °C overnight before use.

Two types of water, Mill-Q water (W_1) and Myponga-treated water (W_2), were selected as water bases for making up the simulated water samples. W_1 was collected from a Milli-Q Gradient system (Millipore, France) with a conductivity of 0.10 μS/cm at 25 °C. Myponga WTP utilises dissolved air flotation and filtration process (DAFF) with free chlorine disinfection, to treat source water into drinking water. W_2 was collected from Myponga WTP after the filtration process and before the chlorination process. W_1 was pure water which was used to eliminate interference from other solutes. W_2 contains residual UV-absorbing material. It was used to assess any additional matrix effects that may confound accurate particle compensation.

Preparation of water samples

Six types of concentrated stock solutions were prepared: 5 g of P_1, P_2 and P_3 particles were suspended in 1 L of W_1 water base, respectively; 5 g of P_1, P_2 and P_3 particles were also suspended in 1 L of W_2 water base, respectively. Each type of the stock solution was diluted with W_1 or W_2 water base to generate five different levels of turbidity to make up 1 L of each sample, which was defined as A, B, C, D, and E. The turbidity of the water samples was within 2–110 NTU, which was based on the turbidity range of water sources in SA (SA Water 2016). Six types of water samples, which were made up with three kinds of particles (P_1, P_2 and P_3) and two types of waters (W_1 and W_2), are defined as P_1W_1, P_2W_1, P_3W_1, P_1W_2, P_2W_2, and P_3W_2 based on their combinations. The water samples were organised into unfiltered and filtered water samples. Water samples with P_1 were considered the control as P_1 particles were composed of pure inorganics. Water samples with P_2 and P_3 were simulated natural surface waters, containing both organic and inorganic solids.

The selected six types of simulated water samples, in the combinations of different particles and water bases, represent different types of water quality. All measurements of water samples were made in triplicate and averaged. Water samples containing P_1 were used as reference samples as they were highly reproducible. The simulated water samples with P_2 or P_3 type particles were used to represent local surface source waters.

Sample analysis

Water quality parameter, particle size distribution, and inorganic chemical analysis were conducted in laboratories accredited by the National Association of Testing Authorities (NATA), Australia. All the water samples were analysed at room temperature.

Water quality

Turbidity was measured in NTU without physical filtration using a turbidimeter (2100AN, Hach, USA). Prior to UV_{254}, colour at wavelength 456 nm (true $colour_{456}$) and dissolved organic carbon (DOC) measurements, water samples were filtered through 0.45 μm polyethersulfone (PES) membrane filters (ANPEL Laboratory Technologies, China) to remove all the nondissolved particles under a constant vacuum. One hundred milliliter of water samples were filtered each time to minimise the effects of membrane fouling (Drikas et al. 2017). UV_{254} and $colour_{456}$ were analysed with a bench-top UV-Vis spectrophotometer (Evolution 60, Thermo Scientific, USA) using a standard method (Rice et al. 2007). DOC was determined using a total organic carbon analyser (900, Sievers Instruments Inc., USA) with a standard method (Rice et al. 2007).

Particle size distribution

Particle size distributions of the three types of particles in the Milli-Q water were analysed using a LISST-Portable particle counter (Sequoia, USA). Particle size distribution data were collected by following the operational instruction of the manufacturer. The particle distributions were analysed as particle volume concentration based on the particle size increment.

Inorganic chemicals

Chemical compositions of three types of particles in Milli-Q water (2 g/L) including metals and silica were analysed using inductively coupled plasma–mass spectrometer (Agilent ICP-MS, 7500cx) instruments following the standard method (Rice et al. 2007). Nitrogen as nitrate and nitrite were analysed using a discrete analyser according to the standard method (Rice et al. 2007).

Submersible UV-Vis spectrophotometer analysis

A submersible UV-Vis spectrophotometer (spectro::lyser; s::canGmbH, Austria) with a 35-mm path length was used to analyse the unfiltered and filtered water samples. The water samples were measured within a range of 200–750 nm with 2.5-nm intervals. The submersible UV-Vis spectrophotometer was connected to a controller (con::stat) which had an installed data processing software (ana::pro). The submersible UV-Vis spectrophotometer could measure the unfiltered water samples directly as the software has built-in generic particle compensation algorithms. The software can also convert the UV-Vis spectrum into water quality parameters such as compensated UV_{254}. Zero or baseline check was performed using Milli-Q water before use. The water samples were measured by filling the sample waters in the measurement port of the submersible instrument. The port and lens were cleaned before each measurement to make sure that progressive fouling, and sample carryover did not impact on the measurements. The outputs of the submersible instrument were stored in the controller and contained uncompensated UV-Vis spectra and derived water quality parameters.

Data processing

Particle contribution is the amount of particle impact on the measurements, using a submersible UV-Vis spectrophotometer, which needs to be compensated to get accurate measurements. The particle contribution to UV_{254} measurement of the submersible instrument was calculated as a subtraction between the absorbance of unfiltered and filtered for the same water samples. Particle contribution to the UV-Vis spectrum of the submersible instrument was also calculated as a subtraction between the absorbance of a spectrum for unfiltered and filtered water samples. An illustration of the calculation of the particle contribution is shown in Fig. 1.

The UV_{254} measurements of the filtered water samples using a bench-top spectrophotometer were defined as lab UV_{254}. The UV_{254} of unfiltered water samples measured by the submersible instrument with the built-in generic calibration were referred to as compensated UV_{254}. The compensated UV_{254} was compared with the lab UV_{254} to evaluate the performance of built-in generic algorithms of the submersible instrument.

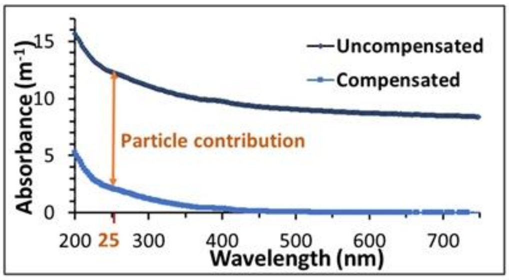

Fig. 1 An illustration of particle contribution to the spectrum of a water sample

Results and discussion

Characteristics of particle type and water samples

Particle size distribution and chemical compositions of P_1, P_2 and P_3, in Milli-Q water, were analysed, and the results are shown in Table 1 and Fig. 2. Each type of particle had distinguishable particle size distribution. P_1 type particles had the smallest mean particle size of 2.20 μm among the three types of particles. Ninety percent of the P_1 particle size was 0.85–8.65 μm. P_2 type particles had the largest mean size of 14.6 μm and the majority (90%) of P_2 type particle size was from 2.27 to 103.72 μm. P_3 had a mean size of 7.6 μm and 90% of the particles were between 2.30 and 32.55 μm. Thus, natural particles (P_2, P_3) generally had larger particle sizes than the standard particle (P_1).

The inorganic chemistry content of the particles in Milli-Q water is shown in Table 2. Each type of particle had the same particle concentration of 2 g/L as prepared. For metal content, P_1 type particles contain only 0.03 mg/mg of Al. P_2 type particles did not have any reportable amount of metals. P_3 type particles contain low levels of Al, Ca and Fe which were less than 0.10 mg/mg. The nitrogen content of total nitrogen of nitrate and nitrite for all three types of particles was below the detection limit. The low level of nitrogen content is common in SA water sources (SA Water 2016). Metal and nitrogen contents were analysed because high concentrations of inorganic species such as iron and nitrate could interfere with the UV absorbance of water (Weishaar et al. 2003). However, there was no evidence that metal and nitrogen at very low concentration in the water samples can affect the UV measurements in this work. Both water samples with P_1 particles and water samples with P_2 particles had low alkalinity as $CaCO_3$ (< 50 mg/L), while water sample with P_3 particles had the highest alkalinity (200 mg/L). A previous study using the UV-Vis spectrophotometric method to determine water quality and achieved comparable results. The instrument was robust in the high alkalinity condition with water alkalinity up to 459 mg/L (Bowker 2011). Therefore, the alkalinity of the water samples containing P_1, P_2 or P_3 could not affect the measurements of UV-Vis spectrophotometers.

The water quality parameters include turbidity, lab UV_{254}, true $colour_{456}$, DOC and pH, of all simulated water samples were analysed using the laboratory standard methods, and the results are shown in Table 3. In general, all six types of simulated water samples had different lab UV_{254} response. The

Table 1 Particle size of Kaolin (P_1), Myponga (P_2) and Hope Valley (P_3) particles in the water

Particle type	Mean size (μm)	Std of particle size (μm)	Size range (μm)	90% size (μm)
P_1	2.2	21.8	0.37–14.22	0.85–8.65
P_2	14.6	54.2	1.19–237.35	2.27–103.72
P_3	7.6	16.2	1.01–63.11	2.3–32.55

lab UV_{254}, true colour$_{456}$ and DOC of P_1W_1 water samples were close to zero as P_1 is purely clay mineral. All the P_1W_2 samples had constant values of lab UV_{254}, true colour$_{456}$, and DOC as W_2 water-base containing natural organics.

All the simulated natural water samples with P_2, P_3 contain organics. Lab UV_{254} measurements of P_2W_1, P_3W_1, P_2W_2 and P_3W_2 samples were from 0.1 to 5.3 m^{-1}, 0.0 to 1.0 m^{-1}, 11.2 to 13.6 m^{-1} and 11.4 to 12.5 m^{-1}, respectively. Water samples with W_2 water base had higher values of lab UV_{254}, true colour$_{456}$ and DOC than the water samples with W_1 water base. Myponga-treated water was employed as the W_2 water base, which had a high DOC content which was in line with the historical data (Fabris et al. 2012).

Water quality results in Table 3 indicate that the pH of all the water samples was within a range of 5.5 to 8.3, which is similar to the reported pH range (6 to 8.5) of most surface water in SA (SA Water 2016). There was no significant influence of water sample pH on the lab UV_{254}. Thus, the pH of the water samples was not adjusted. Weishaar et al. (2003) reported that the minor pH effect on UV absorbance measurements was observed for river water samples. A study also concluded that only relatively high or low pH had impacted on the UV absorbance of the lake water samples (Pace et al. 2012).

Relationships between water quality parameters and UV measurements

Particle compensation is also called turbidity compensation for the measurements of water quality using UV-Vis spectrophotometers. Turbidity measures light scattering which is interactions between light and suspended particles. Suspended particles can cause light scattering and affect the light absorption of the water samples. Accordingly, turbidity has a major and direct connection to the measurements of UV-Vis spectrophotometers. UV_{254} is commonly used as a surrogate to determine the concentration of organic matter in water. Therefore, to understand the UV response of water samples, we investigated relationships between water quality parameters, such as turbidity and DOC and UV_{254} measurements using a bench-top UV-Vis spectrophotometer.

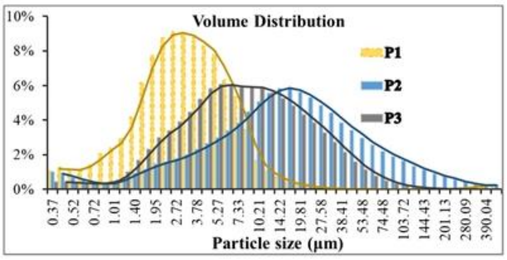

Fig. 2 Particle size distributions of Kaolin, Myponga, and Hope Valley particles in the Milli-Q water

Lab UV_{254} is plotted as a function of turbidity for all six types of simulated natural water samples which is shown in Fig. 3a and b. As the increase in turbidity of P_1W_1 and P_1W_2 water samples, lab UV_{254} measurements were constant (Table 3). P_1 particles were purely inorganics and insoluble in water which can be removed by physical filtration. There were statistically robust linear relationships between turbidity and lab UV_{254} for P_2W_1, P_2W_2, P_3W_1 and P_3W_2 water samples with $R^2 \geq 0.99$. As the turbidity level increased, the lab UV_{254} of the water samples increased linearly. The slopes and intercepts of the water samples with P_2 type particles were different from that of water samples with P_3 type particles. For water samples with P_2 and P_3 particles, water samples with W_1 water base had intercepts of almost 0 m^{-1}, whereas the intercepts of water samples with the W_2 water base were around 11 m^{-1}. It was because the W_2 water base contains high levels of dissolved organics.

UV_{254} is also plotted against DOC for all the water samples, shown in Fig. 3c and d. The relationship between DOC and UV_{254} of P_1W_1 and P_1W_2 water samples was not taken into consideration, as P_1 type particles do not contain any organics. For all P_2W_1 and P_2W_2 water samples, an increase in DOC leads to an increase in UV_{254}. DOC had linear correlations with the UV_{254} for P_2W_1, P_2W_2, P_3W_1 and P_3W_2 water samples with R^2 of 1.00 and 0.99, respectively, with different slope and intercept for each water type. The slopes of water samples containing particle type P_3 were lower than the water samples containing particle type P_2, which could be explained by the UV of supracolloidal particles has lower slopes than fine colloidal particles (Vaillant et al. 2002). Thus, different types of simulated natural waters had different linear relationships between DOC and UV_{254}.

Overall, different natural water samples had different lab UV_{254} responses using a bench-top UV-Vis spectrophotometer combined with a physical filtration method. The UV response of the turbidity for the filtered water samples was caused by DOC. In general, particle characters that affect

Table 2 Inorganic chemistry of particles in Milli-Q water: Kaolin (P_1), Myponga (P_2) and Hope Valley (P_3)

Particle type	Metal (mg/mg)		N as ($NO_2^- + NO_3^-$) (mg/mg)	Alkalinity as $CaCO_3$ (mg/L)
P_1	Al	0.03	0.00	20
	Ca	0.00		
	Fe	0.00		
	P	0.00		
	Na	0.00		
	Mg	0.00		
P_2	Al	0.00	0.00	40
	Ca	0.00		
	Fe	0.00		
	P	0.00		
	Na	0.00		
	Mg	0.00		
P_3	Al	0.07	0.00	200
	Ca	0.01		
	Fe	0.03		
	P	0.00		
	Na	0.00		
	Mg	0.00		

measurements of bench-top UV-Vis spectrophotometers are mainly DOC. There were linear relationships between turbidity and UV_{254} as well as DOC and UV_{254} of surface catchments water in SA, such as river water and reservoir water. The findings were supported by two reported studies. Mamane et al. (2006) reported that with the increase of particle concentration in the water, the associated UV absorbance increase linearly. UV_{254} measured by the bench-top UV-Vis instrument was changed directly with the change of DOC in the river waters (Volk et al. 2005).

Particle contribution to measurements of a submersible UV-Vis spectrophotometer

Particle contribution was calculated based on the measurements of a submersible UV-Vis spectrophotometer as mentioned in the "Data processing" section. According to the results present in SI Fig. 1, the turbidity of all six types of water samples increased when the particle concentrations increased. The particle contribution to UV-Vis spectra and UV_{254} for the six types of water samples with five different turbidity levels (A, B, C, D, E) are shown in Fig. 4, and SI Figs. 2 and 3. As water turbidity increased, the particle contributions in P_1W_1 also increased. Similarly, an increase in turbidity was associated with the increase in the particle contributions to P_2W_1, P_3W_1, P_1W_2, P_2W_2, and P_3W_2 water samples. Thus, an increase in the turbidity of water samples can lead to an increase in particle contribution. P_3 particle had the highest contribution to the UV-Vis spectra, and P_2 had the least particle contribution, among the three types of particles, for each turbidity level of water samples: turbidity level A to turbidity level E.

For UV_{254} measurement, particle contribution of each water sample was distinguished according to their absorbance values in Fig. 4b and SI Fig. 3. At the same turbidity level in the water samples with W_1 water base, P_3 type particles had the largest particle contribution to UV_{254} measurements, while P_2 particle had the lowest particle contribution to the UV_{254} measurements. Interestingly, in the water samples prepared with W_2 water base, P_1 particles were found to demonstrate a slightly higher particle contribution to the UV_{254} measurements than P_3 particles. The difference between P_2 had the lowest particle contribution to the UV_{254} measurements. Thus, the influence of the particle contributions on the UV_{254} measurements could be dependent on the water matrix.

Overall, the particle contribution to the UV-Vis measurements is dependent on the particle type and particle concentration. As particle concentration increases, suspended particles in the water cause light scattering. Particle contributions caused by the light scattering of the suspended particles are common in natural waters. Light scattering could significantly affect the UV-Vis measurements, which can be influenced by the particle concentration, particle type and particle size (Bohren and Huffman 2008; Mamane et al. 2006; Volk et al. 2005). For small particles, light scattering has a linear relationship with particle concentration. Thus, an increase in the particle concentration leads to an increase of particle contribution to the UV-Vis measurement. Particle type influences

Table 3 Water quality characteristics of six types of simulated water samples that were made up of three types of particles (P_1, P_2, and P_3) and two base-waters (W_1 and W_2)

Water samples	Sample level	Particle conc.	Turbidity (NTU)		Lab UV_{254} (m^{-}1)		True $colour_{456}$ (m^{-}1)		DOC (mg/L)		pH	
		mg/L	Unfiltered		Filtered		Filtered		Filtered		Unfiltered	
			Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
W_1	-	0	< 0.1	0	< 0.1	0	< 0.1	0	< 0.1	0	7.0	0
P_1W_1	A	2.5	2.3	0.2	0.1	0	< 1	0	0.1	0	5.6	0
	B	25	21	0.1	0.1	0	< 1	0	0.1	0	5.6	0.1
	C	50	43	0.9	0.1	0	< 1	0	0.1	0	5.5	0.1
	D	100	85	0.6	0.1	0	< 1	0	0.1	0	5.6	0.1
	E	125	105	1.0	0.1	0	< 1	0	0.1	0	5.6	0.1
P_2W_1	A	25	2.3	0.1	0.1	0	< 1	0	0.2	0	6.5	0.1
	B	250	21	0.5	1.1	0	3	0.1	0.4	0	6.3	0.1
	C	500	44	0.4	2.2	0	4	0.1	0.7	0	6.2	0.1
	D	1000	86	1.1	4.3	0	7	0.1	1.2	0	6.1	0.1
	E	1300	107	1.0	5.3	0	11	0.2	1.5	0	6.0	0.1
P_3W_1	A	5	2.4	0.1	0.0	0	<1	0	0.2	0	8.0	0
	B	50	21	0.6	0.1	0	<1	0	0.3	0	8.2	0.1
	C	100	43	0.7	0.3	0	2	0.1	0.5	0	8.3	0.1
	D	200	85	1.1	0.8	0	3	0.1	0.7	0	8.2	0.1
	E	250	106	1.0	1.0	0	5	0.2	0.8	0	8.3	0.2
W_2	-	0	0.2	0.0	10.7	0	6	0	5.1	0	7.1	0
P_1W_2	A	5	2.3	0.0	11.3	0	6	0	5.2	0	7.1	0
	B	50	21	0.3	11.3	0	6	0	5.2	0	7.1	0.1
	C	100	44	0.5	11.3	0	6	0	5.2	0	7.2	0.1
	D	175	86	0.4	11.3	0	6	0	5.3	0	7.1	0.1
	E	225	107	1.0	11.3	0	6	0	5.2	0	7.1	0
P_2W_2	A	25	2.4	0.1	11.2	0	7	0.1	5.2	0	6.7	0.1
	B	250	21	0.2	11.6	0	8	0	5.3	0	6.6	0.1
	C	500	43	0.7	12.1	0	9	0.2	5.4	0	6.8	0.1
	D	875	85	0.5	13.1	0	10	0.1	5.7	0	6.7	0.1
	E	1125	106	0.8	13.6	0	11	0.	5.8	0	7.0	0.1
P_3W_2	A	5	2.3	0.1	11.4	0	7	0.1	5.2	0	7.1	0.1
	B	50	21	0.3	11.6	0	7	0.1	5.3	0	7.2	0.1
	C	100	44	0.7	11.8	0	8	0.1	5.5	0	7.3	0.1
	D	175	86	0.9	12.3	0	8	0.1	5.8	0	7.3	0.1
	E	225	107	0.8	12.5	0	9	0.2	5.9	0	7.2	0.1

Measurement error was shown as standard deviation (SD)

the light scattering which can, in turn, affect the particle contribution. Particle size could largely affect the intensity of the scattering light. Increase of the small particle size, the intensity of the scattered light is likely to increase. P_1 particle type was pure clay, P_2 particle type was silica-based, and P_3 particle type was clay-based. Both P_2 and P_3 particles were collected from the natural surface source water. Clay particle has 50% of light scatter away, and particles from natural waters have 20–30% light scatter away (Volk et al. 2005). The differences in particle sizes and particle types contribute to the different light scattering effect, in turn, lead to the difference in their particle contribution. These can be explained that P_1 and P_3 had much higher particle contribution to the UV-Vis measurements than P_2.

Understanding the particle contribution caused by the particle types and concentrations, which assist to discover the built-in compensation behaviour of submersible UV-Vis spectrophotometers. The particle contribution to the measurements of water samples could be determined by particle compensation, which can be conducted to remove the particle

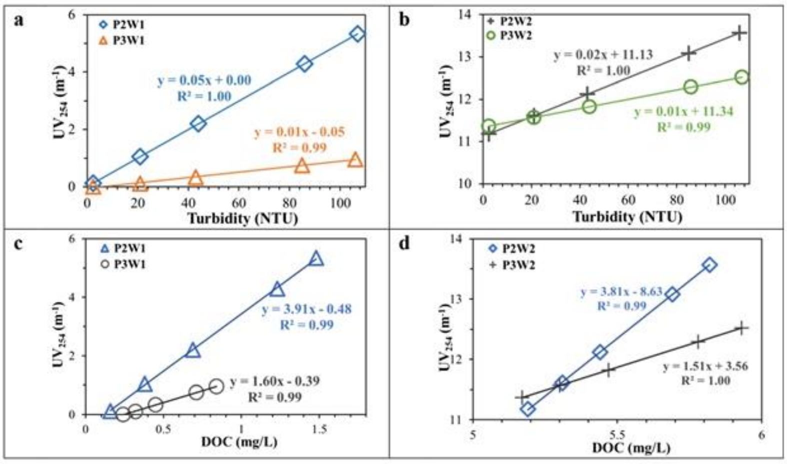

Fig. 3 **a**, **b** Correlations between turbidity and lab UV_{254} of simulated natural water samples; **c**, **d** relationships between DOC and lab UV_{254} of simulated natural water samples. P_2W_1, P_2W_2, P_3W_1 and P_3W_2 were simulated water samples that were made up of two types of particles (P_2 and P_3), and two types of water bases (W_1 and W_2), respectively

interference on the measurements of water quality (Hu et al. 2016). The particle contributions can be varied with the water sources type and concentration, thus leading to corresponding changes of measurements of a submersible UV-Vis spectrophotometer. Thus, a universal particle compensation is not always effective.

Evaluation of the performance of a submersible UV-Vis spectrophotometer

The performance of the built-in generic particle compensation algorithms of the submersible instrument was evaluated in an offline mode, by comparing it with the bench-top instrument.

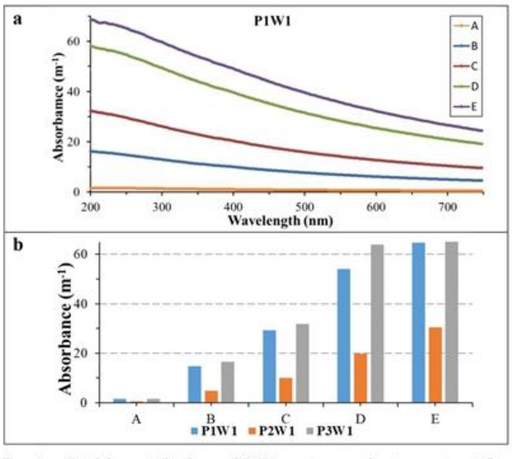

Fig. 4 **a** Particle contributions of P_1W_1 water samples to spectra at five different concentration levels; **b** Particle contribution of different types of waters to UV_{254} measurements. Particle concentration levels were from low to high (water sample A to water sample E)

The UV_{254} of water samples measured by the submersible instrument were compensated for the particle effect using the built-in generic calibration (compensated UV_{254}). The lab UV_{254} of the same water samples measured by the bench-top spectrophotometer was used as references. Compensated UV_{254} and lab UV_{254} of all the water samples were plotted as a bar chart and are shown in Fig. 5 and SI Fig. 4. UV_{254} was used as it is an essential absorbance-based water quality parameter for the concentrations of organic matter and disinfection byproduct precursors in the water.

According to SI Fig. 4, the compensated UV_{254} was much lower than the lab UV_{254} for P_1W_1 and P_1W_2 water samples. The compensated UV_{254} of P_1W_1 and P_1W_2 water samples were highly overcompensated by the built-in generic compensation algorithms, which was probably because the P_1 contained purely inorganics. The built-in compensation algorithms were based on hundreds of natural water samples, which may not suitable for compensating water contains purely inorganics. For P_2W_1 water samples, the compensated UV_{254} was slightly lower than the lab UV_{254} as shown in Fig. 5, which indicates the submersible instrument slightly overcompensated the UV_{254} measurements. For P_2W_2 water samples, the compensated UV_{254} seemed close to the values of lab UV_{254}. This finding was agreed with the conclusion that the submersible instrument was effective in compensating the particle effect on the measurements (Snazelle 2016). It was found that the compensated UV_{254} had strong linear correlations with lab UV_{254} with a slope of 1.34 and 1.71 and R^2 of 0.99 for P_2W_1 and P_2W_2 (SI Fig. 5). It is interesting to note that the compensated UV_{254} was higher than lab UV_{254} for some types of water samples whereas was lower than lab UV_{254} for other types of water samples. There are also linear relationships between compensated UV_{254} and lab UV_{254} for water samples with P_5. An increasing linear relationship was

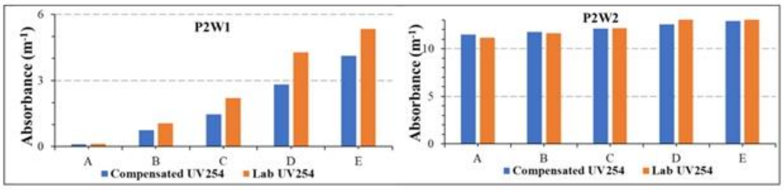

Fig. 5 Comparisons between UV_{254} measurements of submersible and bench-top UV-Vis instruments. Compensated UV_{254} is obtained from the outputs of a submersible UV-Vis spectrophotometer. Lab UV_{254} is measured using a bench-top UV-Vis spectrophotometer. P_2W_1 and P_2W_2 were water samples made up of P_2 type particles and W_1 or W_2 water bases

found for P_3W_1 water samples whereas a decreasing linear relationship was found for P_3W_2 water samples.

Overall, there were linear relationships between compensated UV_{254} and lab UV_{254} for all the simulated natural water samples with P_2 or P_3 particles. The built-in compensation algorithms of a submersible UV-Vis spectrophotometer could not always generate comparable compensated UV_{254} for natural water samples as the bench-top UV-Vis instrument. For natural waters, the built-in generic particle compensation methods may generate either under or overcompensated measurements. A previous study also reported that the incomparable measurements of UV measurements of the built-in generic algorithms for waters (Drolc and Vrtovšek 2010). This work shows that particle compensation is source water specific and the site-specific particle compensation should be performed when using the submersible instrument to measure water quality. Some scientists also believed that particle compensation based on the water matrix needs to be considered to achieve comparable measurements using the submersible instrument (Avagyan et al. 2014; Hu and Wang 2017; Jeong et al. 2012; Langergraber et al. 2003; Shi et al. 2020; Torres and Bertrand-Krajewski 2008). Industrial applications of using the submersible instrument to monitor water quality had experienced that the generic compensation algorithms were unable to generate accurate measurements for some water sources (Byrne et al. 2014; Chow et al. 2007; Chow et al. 2017; Hu and Wang 2017; Lepot et al. 2016; Waterra 2017). Particle compensation is one of the barriers for online instrument implement in industry application. It is essential to perform site-specific particle compensation and establish the frequency of the compensation to achieve accurate measurements (Chow et al. 2014; Langergraber et al. 2004; Liu et al. 2014; Mussared et al. 2014). Therefore, it is recommended that the evaluation of the accurate measurements of the submersible instrument is conducted before using it to monitor water quality.

Conclusion

Laboratory-scale investigations were conducted to understand relationships between turbidity and UV_{254}, DOC and UV_{254}, and particle compensation behaviour of a submersible UV-Vis spectrophotometer. Six kinds of simulated waters, in the combinations of artificial standard particles, natural water particles, ultrapure water and treated water from a drinking WTP. Both turbidity and DOC were linearly correlated with UV_{254} measurements with $R^2 \geq 0.99$. Different type of simulated water samples had different UV absorbance response. Particle contributions to the UV-Vis measurements not only vary when particle types changes but also particle concentrations change. The compensated UV_{254}, measured by a submersible instrument with the build-in generic particle compensation algorithms, were compared with the lab UV_{254}, tested by the bench-top instrument with the physical filtration method. The results showed that the built-in generic calibration compensation algorithms of the submersible instrument tend to generate undercompensated or overcompensated UV_{254} for surface waters. These findings provide evidence that the particle influence on the measurements of the submersible instrument is source water dependent. It helps users to understand the behaviour of submersible UV-Vis spectrophotometers and why the built-in generic calibration often does not generate comparable results in many cases.

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Authors' contributions Conceptualization: Zhining Shi and Christopher W.K. Chow, Methodology: Christopher W.K. Chow and Rolando Fabris, Formal analysis and investigation: Zhining Shi, Tianlong Zheng and Jixue Liu, Writing—original draft preparation: Zhining Shi; Writing—review and editing: Christopher W.K. Chow, Rolando Fabris and Bo Jin, Funding acquisition: [nil], Resources: Rolando Fabris, Supervision: Bo Jin.

Data availability The datasets used and/or analysed during the current study are available from the corresponding author on reasonable request.

Compliance with ethical standards

Competing interests The authors declare that they have no competing interests.

Ethics approval and consent to participate Not applicable.

Consent for publication Not applicable.

References

Avagyan A, Runkle BR, Kutzbach L (2014) Application of high-resolution spectral absorbance measurements to determine dissolved organic carbon concentration in remote areas. J Hydrol 517:435–446

Banna MH, Imran S, Francisque A, Najjaran H, Sadiq R, Rodriguez M, Hoorfar M (2014) Online drinking water quality monitoring: review on available and emerging technologies. Crit Rev Environ Sci Technol 44:1370–1421

Bohren C, Huffman DR (2008) Absorption and scattering of light by small particles. John Wiley & Sons

Bowker JD (2011) The robustness of a simple UV-Vis spectrophotometric. In: Partnership AADA (Hrsg.), Method to Determine the Concentration of Eugenol in Water. U.S. Fish & Wildlife Service

Byrne AJ, Brisset T, Chow CWK, Lucas J, Korshin GV (2014) Development of online surrogate parameters using UV-Vis spectroscopy for water treatment plant optimisation. Aust Water Assoc Water J 41:94–100

Caradot N, Sonnenberg H, Rouault P, Gruber G, Hofer T, Torres A, Pesci M, Bertrand-Krajewski J (2014) Influence of local calibration on the quality of on-line wet weather discharge monitoring: feedback from five international case studies. 13th International Conference on Urban Drainage, Sarawak, Malaysia, 7–12 September 2014

Chow C, Dexter R, Sutherland-Stacey L, Fitzgerald F, Fabris R, Drikas M, Holmes M, Kaeding U (2007) UV spectrometry in drinking water quality management. J Aust Water Assoc 34:63

Chow C, Saint C, Zappia L, Henderson R, Roeszler G, Dexter R, Nguyen T, Stuetz R, Byrne A, Trolio R, Lucas J (2014) Online water quality monitoring: the voice of experience. Water J Aust Water Assoc 41:60

Chow C, Van Leeuwen J, Mussared A, Holmes M, Kaeding U (2017) UV spectrometry in drinking water quality management, OZwater'17, Australian Water Association, pp. 63

Dong J, Wang G, Yan H, Xu J, Zhang X (2015) A survey of smart water quality monitoring system. Environ Sci Pollut Res 22:4893–4906

Drikas M, Kapralos C, Kozlik E, Fabris R (2017) Getting the right result. Australian Water Association Water E-journal

Drolc A, Vrtovšek J (2010) Nitrate and nitrite nitrogen determination in waste water using on-line UV spectrometric method. Bioresour Technol 101:4228–4233

Etheridge JR, Birgand F, Osborne JA, Osburn CL, Burchell MR, Irving J (2014) Using in situ ultraviolet-visual spectroscopy to measure nitrogen, carbon, phosphorus, and suspended solids concentrations at a high frequency in a brackish tidal marsh. Limnol Oceanogr Methods 12:10–22

Fabris R, Chow CW, Drikas M (2012) Comparison of coagulant type on natural organic matter removal using equimolar concentrations. J Water Supply Res Technol AQUA 61:210–219

Hou D, Song X, Zhang G, Zhang H, Loaiciga H (2013) An early warning and control system for urban, drinking water quality protection: China's experience. Environ Sci Pollut Res 20:4496–4508

Hu Y, Wang X (2017) Application of surrogate parameters in characteristic UV–vis absorption bands for rapid analysis of water contaminants. Sensors Actuators B Chem 239:718–726

Hu Y, Wen Y, Wang X (2016) Detection of water quality multi-parameters in seawater based on UV-Vis spectrometry, OCEANS 2016-Shanghai. IEEE, pp. 1-4

Huebsch M, Grimmeisen F, Zemann M, Fenton O, Richards KG, Jordan P, Sawarieh A, Blum P, Goldscheider N (2015) Field experiences using UV/VIS sensors for high-resolution monitoring of nitrate in groundwater. Hydrol Earth Syst Sci 19:1589–1598

Jeong JJ, Bartsch S, Fleckenstein JH, Matzner E, Tenhunen JD, Lee SD, Park SK, Park JH (2012) Differential storm responses of dissolved and particulate organic carbon in a mountainous headwater stream, investigated by high-frequency, in situ optical measurements. J Geophys Res Biogeosci 117

Langergraber G, Fleischmann N, Hofstaedter F (2003) A multivariate calibration procedure for UV/VIS spectrometric quantification of organic matter and nitrate in wastewater. Water Sci Technol 47: 63–71

Langergraber G, Fleischmann N, Hofstaedter F, Weingartner A (2004) Monitoring of a paper mill wastewater treatment plant using UV/VIS spectroscopy. Water Sci Technol 49:9–14

Leigh C, Alsibai O, Hyndman RJ, Kandanaarachchi S, King OC, McGree JM, Neelamraju C, Strauss J, Talagala PD, Turner RD, Mengersen K (2019) A framework for automated anomaly detection in high frequency water-quality data from in situ sensors. Sci Total Environ 664:885–898

Lepot M, Torres A, Hofer T, Caradot N, Gruber G, Aubin J, Bertrand-Krajewski J (2016) Calibration of UV/Vis spectrophotometers: a review and comparison of different methods to estimate TSS and total and dissolved COD concentrations in sewers, WWTPs and rivers. Water Res 101:519–534

Liu X, Zhang Y, Shi K, Zhu G, Xu H, Zhu M (2014) Absorption and fluorescence properties of chromophoric dissolved organic matter: implications for the monitoring of water quality in a large subtropical reservoir. Environ Sci Pollut Res 21:14078–14090

Mamane H, Ducoste JJ, Linden KG (2006) Effect of particles on ultraviolet light penetration in natural and engineered systems. Appl Opt 45:1844–1856

Meyer A, Klein C, Fünfrocken E, Kautenburger R, Beck HP (2019) Real-time monitoring of water quality to identify pollution pathways in small and middle scale rivers. Sci Total Environ 651:2323–2333

Mussared A, Chow C, Holmes M, Van Leeuwen J, Kaeding U (2014) Implementation of predictive alum dose control systems. 77th Annual WIOA Victorian Water Industry Operations Conference and Exhibition, Bendigo Exhibition Centre

Pace ML, Reche I, Cole JJ, Fernández-Barbero A, Mazuecos IP, Prairie YT (2012) pH change induces shifts in the size and light absorption of dissolved organic matter. Biogeochemistry 08:109–118

Rice EW, Baird RB, Eaton AD, Editors (2007): Standard methods for the examination of water and waste water. American public health association (APHA), Federation, Water Environment, American Public Health Association,Washington, DC, USA

SA Water (2016) Drinking Water Quality Report, Government of South Australia

Shi Z, Chow CW, Fabris R, Liu J, Jin B (2020): Alternative particle compensation techniques for online water quality monitoring using UV–Vis spectrophotometer. Chemom Intell Lab Syst, 104074

Snazelle TT (2016) The effect of suspended sediment and color on ultraviolet spectrophotometric nitrate sensors, US Geological Survey

Strohmeier S, Knorr KH, Reichert M, Frei S, Fleckenstein JH, Peiffer S, Matzner E (2013) Concentrations and fluxes of dissolved organic carbon in runoff from a forested catchment: insights from high frequency measurements. Biogeosciences 10:905–916

Torres A, Bertrand-Krajewski JL (2008) Partial least squares local calibration of a UV-visible spectrometer used for in situ measurements of COD and TSS concentrations in urban drainage systems. Water Sci Technol 57:581–588

Vaillant S, Pouet MF, Thomas O (2002) Basic handling of UV spectra for urban water quality monitoring. Urban Water 4:273–281

Van Eerdenbrugh B, Alonzo DE, Taylor LS (2011) Influence of particle size on the ultraviolet spectrum of particulate-containing solutions: implications for in-situ concentration monitoring using UV/Vis fiber-optic probes. Pharm Res 28:1643–1652

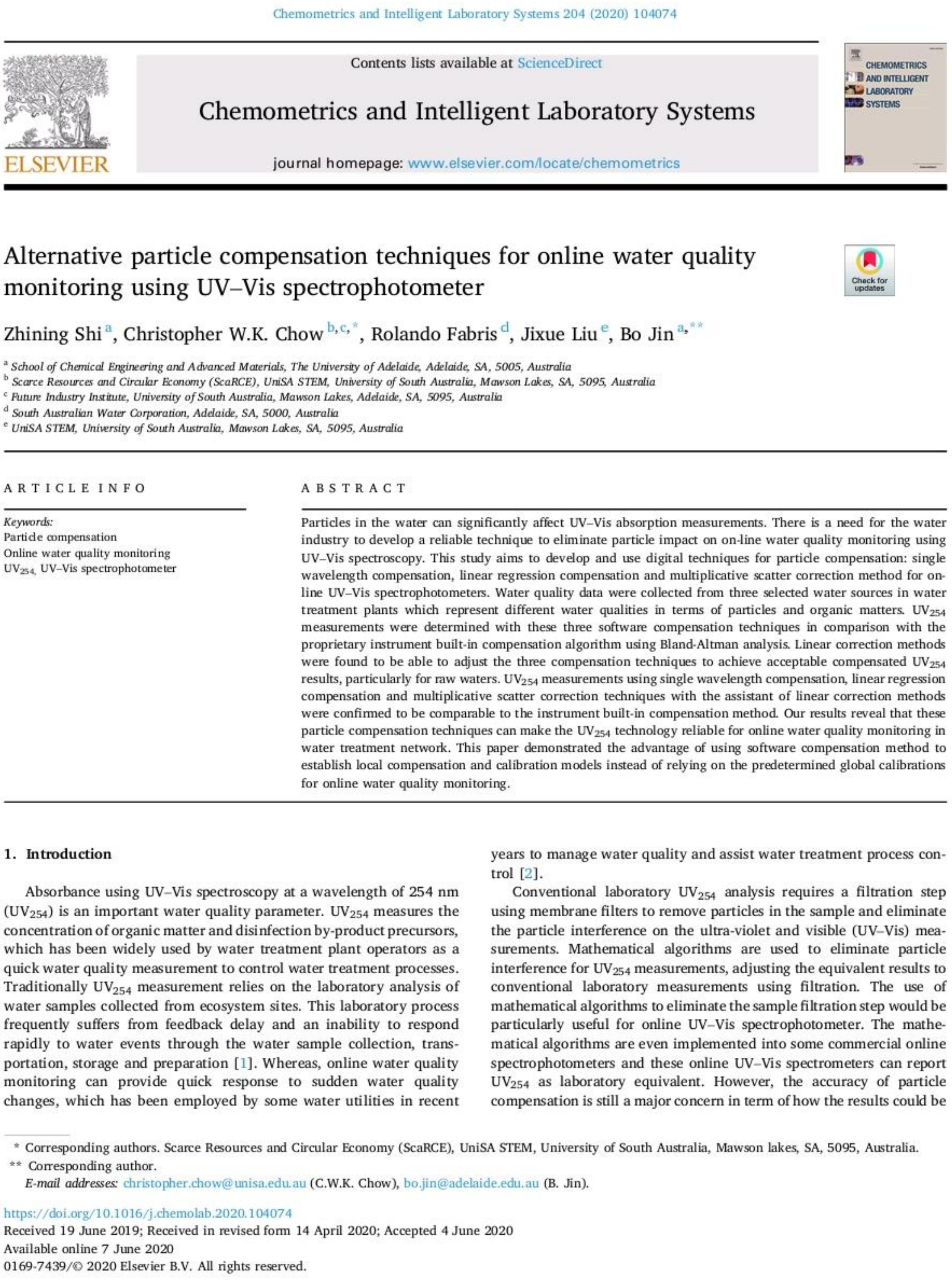
Volk C, Kaplan LA, Robinson J, Johnson B, Wood L, Zhu HW, LeChevallier M (2005) Fluctuations of dissolved organic matter in river used for drinking water and impacts on conventional treatment plant performance. Environ Sci Technol 39:4258–4264

Waterra (2017) Optimisation of existing instrumentation to achieve better process performance. 1075, Water research Australia

Weishaar J, Aiken GR, Bergamaschi BA, Fram MS, Fujii R, Mopper K (2003) Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. Environ Sci Technol 37:4720–4708

Zhang J, Hou D, Wang K, Huang P, Zhang G, Loáiciga H (2017) Real-time detection of organic contamination events in water distribution systems by principal components analysis of ultraviolet spectral data. Environ Sci Pollut Res 24:12882–12898

Appendix D



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Alternative particle compensation techniques for online water quality monitoring using UV–Vis spectrophotometer

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ABSTRACT

Particles in the water can significantly affect UV–Vis absorption measurements. There is a need for the water industry to develop a reliable technique to eliminate particle impact on on-line water quality monitoring using UV–Vis spectroscopy. This study aims to develop and use digital techniques for particle compensation: single wavelength compensation, linear regression compensation and multiplicative scatter correction method for on-line UV–Vis spectrophotometers. Water quality data were collected from three selected water sources in water treatment plants which represent different water qualities in terms of particles and organic matters. UV_{254} measurements were determined with these three software compensation techniques in comparison with the proprietary instrument built-in compensation algorithm using Bland-Altman analysis. Linear correction methods were found to be able to adjust the three compensation techniques to achieve acceptable compensated UV_{254} results, particularly for raw waters. UV_{254} measurements using single wavelength compensation, linear regression compensation and multiplicative scatter correction techniques with the assistant of linear correction methods were confirmed to be comparable to the instrument built-in compensation method. Our results reveal that these particle compensation techniques can make the UV_{254} technology reliable for online water quality monitoring in water treatment network. This paper demonstrated the advantage of using software compensation method to establish local compensation and calibration models instead of relying on the predetermined global calibrations for online water quality monitoring.

1. Introduction

Absorbance using UV–Vis spectroscopy at a wavelength of 254 nm (UV_{254}) is an important water quality parameter. UV_{254} measures the concentration of organic matter and disinfection by-product precursors, which has been widely used by water treatment plant operators as a quick water quality measurement to control water treatment processes. Traditionally UV_{254} measurement relies on the laboratory analysis of water samples collected from ecosystem sites. This laboratory process frequently suffers from feedback delay and an inability to respond rapidly to water events through the water sample collection, transportation, storage and preparation [1]. Whereas, online water quality monitoring can provide quick response to sudden water quality changes, which has been employed by some water utilities in recent years to manage water quality and assist water treatment process control [2].

Conventional laboratory UV_{254} analysis requires a filtration step using membrane filters to remove particles in the sample and eliminate the particle interference on the ultra-violet and visible (UV–Vis) measurements. Mathematical algorithms are used to eliminate particle interference for UV_{254} measurements, adjusting the equivalent results to conventional laboratory measurements using filtration. The use of mathematical algorithms to eliminate the sample filtration step would be particularly useful for online UV–Vis spectrophotometer. The mathematical algorithms are even implemented into some commercial online spectrophotometers and these online UV–Vis spectrometers can report UV_{254} as laboratory equivalent. However, the accuracy of particle compensation is still a major concern in term of how the results could be

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comparable to analytical data using the conventional laboratory method for the variable water samples under different conditions.

Particle compensation is called either solid compensation by some instrument manufacturers or turbidity compensation, as turbidity measures light scattering which is the interaction of light and suspended solids in the water. Suspended particles affect the light absorption and consequently influence the whole UV–Vis spectrum that leads to attenuation of the transmitted light intensity . Studies show that there are two types of particle compensation algorithms which can be used to remove the particle effect on the UV–Vis: compensation/subtraction technique and empirical modelling technique [3]. Compensation technique is defined as direct subtraction of absorbance of the single wavelength characterised by the particles in the water [4,5]. Tang et al. concluded that individual single wavelengths including 275 nm, 350 nm, and 550 nm could be utilised to characterise the particles and successfully applied the compensation technique to remove particle effect [6]. Compensation technique by correcting the turbidity after correlating with the blue shift was also reported as an option to eliminate the deviation and improve the accuracy of UV–Vis measurement in wastewaters [3].

Empirical modelling approaches can also be used as an alternative to the compensation technique to obtain the laboratory equivalent results using the measured parameters and the corresponding spectra. Hu and Wang developed surrogate parameters based on the integration of spectra for different functional groups of compounds and then eliminated the turbidity impact by deducting the turbidity component from surrogate parameters [7]. Dynamic partitioning algorithm was used based on the fourth-order derivative spectrum to analyse and predict the groups of contaminants. Hu et al. analysed the impact of chemical compositions in wastewater samples and extracted the morphology features of their absorptive spectra to eliminate the measurement derivation [8]. Partial least square (PLS) calibration models have been computed with the fourth derivative UV–Vis spectrum to remove the particle effect on the detection of water quality multi-parameter in artificial seawater [9]. Torres and Bertrand-Krajewski employed the partial least square to eliminate the particle effect on measuring chemical oxygen demand and total particles in urban drainage systems using Matlab software [10]. They commented that further tests for the application of the PLS method are needed to evaluate the robustness and variation of the regression. Empirical modelling using a multiple linear regression from the 'lars' package in the R software was adapted to remove the particle effect on the UV–Vis spectra of brackish water for rapid measurement of multiple material concentrations [11]. This study indicated that site-specific compensation should be developed individually for future applications. Besides, instrument built-in compensation algorithm of some commercial UV–Vis spectroscopy software is developed based on PLS to link the spectra and laboratory data [4]. However, the details of the built-in algorithm method and technique for these commercial online spectrophotometers are not accessible to the users. Most of the reported compensation methods are relatively complex and may need long processing time to conduct the analysis, making these techniques unsuitable for online water quality monitoring [7]. Due to the complexity and poor adaptability of the aforementioned methods, a simple and easy technique for particle compensation is needed for online water quality monitoring using UV–Vis spectrometry.

In this study, software compensation techniques include single wavelength (single point) and linear regression (multiple points) models were developed to remove the particle effect on the UV_{254} measurements. In addition, a well-established software compensation technique was also used to reduce the particle effect as comparison. Online UV–Vis measurement systems were set up in two industrial water treatment plants with three water sources. The accuracies of the three compensation techniques were assessed through comparison with the instrument built-in compensation method. Bland-Altman analysis, a statistical analysis technique, was used to determine the agreement limits of the three compensation techniques as a comparison against the built-in algorithms.

2. Material and methods

2.1. Water sources

Water quality data were provided by two Water Treatment Plants (WTPs), Anstey Hill WTP and Happy Valley WTP in South Australia for this study. Both WTPs employ conventional water treatment practice comprising coagulation, flocculation, sedimentation and filtration to produce drinking water for South Australia. Anstey Hill WTP plant has switchable water source system, taking water from Millbrook Reservoir or River Murray water (via the Mannum-Adelaide pipeline). Happy Valley WTP has a single water source from the Happy Valley Reservoir with water originating from both the River Murray and local catchment areas. These two WTPs were selected because of the differences in the water quality of the water sources. Three natural water matrices including Anstey Hill raw water (RW1), Happy Valley raw water (RW2) and Happy Valley treated water (TW), were selected as they represent different water qualities in terms of particle concentrations as determined by turbidity (NTU) and dissolved organic content (DOC). RW1 contained high turbidity (10–93 NTU) and moderate DOC (3.8–8.4 mg/L); RW2 had moderate turbidity (2–10 NTU) and high DOC (6.4–10.1 mg/L), and TW had low concentrations of both turbidity (0.1–0.8 NTU) and DOC content (0.3–4.5 mg/L). Turbidity and DOC ranges represent seasonal and water source variations between April and December 2013.

2.2. Instrument and monitoring locations

Three s:can spectro::lysers (s:can Messtechnik GmbH, Austria) were installed at three locations in the two selected WTPs to monitor the real-time water quality of RW1, RW2 and TW. The s:can spectro::lyser comprises a double beam photodiode array 256 pixel UV–Vis spectrometer and uses a Xenon lamp as a light source. It measures a UV–Vis spectrum at a wavelength range of 200–720 nm with a selectable optical path length range between 5 and 100 mm for different applications based on the required sensitivities. The installation locations were at the inlet of Anstey Hill WTP and both inlet and outlet of Happy Valley WTP. Path length of the spectro::lyser used was 5 mm, 5 mm and 100 mm for the inlet of Anstey Hill WTP (RW1), the inlet of Happy Valley WTP (RW2) and outlet of Happy Valley WTP (TW), respectively. The instruments were first zero checked/baseline adjusted with ultrapure water to ensure a zero baseline. The spectro::lysers were equipped with automatic cleaning using compressed air before each measurement. Scheduled maintenance (manual cleaning) of the instruments was conducted fortnightly to ensure the cleanliness of the lens to eliminate drifting caused by fouling and that the sample lines were unobstructed. The three water quality monitoring locations were also used as sampling points for routine water quality monitoring (grab sampling), including inlet at Anstey Hill WTP, inlet and outlet of Happy Valley WTP.

2.3. Water quality monitoring period

The three water sources were monitored between April and December 2013. Online spectro::lyser data and standard laboratory UV absorbance at 254 nm (UV_{254}) data were utilised in this work. The spectro::lyser was set to monitor water quality at a 2-min interval. Grab samples of raw water were collected for laboratory analyses on a weekly basis and fortnightly for the treated water. Water quality parameters of grab samples for routine monitoring including UV_{254}, colour at 456 nm, turbidity, and DOC were utilised to characterise the water quality. Prior to measuring UV_{254}, colour and DOC, the water samples were filtered using 0.45 μm PES membrane filters (ANPEL Laboratory Technologies, China). UV_{254} and colour were determined with a UV–Vis spectrophotometer (Evolution 60, Thermo Scientific, USA) using the method described in published work [12]. Turbidity was measured using a turbidity meter (2100AN, Hach, USA) and DOC using a total organic carbon analyser (900, Sievers Instruments Inc., USA) and determined using the methods described in Standard Methods [12][].

2.4. Data acquisition and processing

The UV–Vis spectra were acquired by the s:can spectro::lyser, with the full UV–Vis spectral data saved as fingerprint (FP) files stored in the instrument hard-drive. FP files contain time series data of spectral absorbance values which has a timestamp column (first column) to record the time of each measurement for wavelengths ranged from 200 to 720 with a 2.5 nm interval. FP files contain raw non-compensated data. Initial data pre-treatment was guided by the instrument integrated data diagnostic status (a column in the data stream to flag instrument issues). Those UV–Vis spectral data caused by known instrument issues or failure were manually eliminated. Further data pre-treatment was conducted by a time resolution optimisation algorithm using R and R-Studio [14,15]. From the initial studies, the hourly average of the FP data did not reduce the resolution. Thus, the hourly average was used in this work to reduce the data volume for easier comparisons and without losing resolution. R scripts (codes) were developed to handle the large volume of UV–Vis spectral data generated by the spectro::lyser and perform the required compensation calculations and statistical analysis.

2.5. Particle compensation techniques

Four particle compensation techniques were used to remove particle effect on the UV_{254} for online water quality monitoring of three water sources: RW1, RW2 and TW.

1. Ana::pro is the acquisition software supplied for the s:can spectro::lyser by the manufacturer (s:can Messtechnik, Austria). The compensation can be conducted by the instrument integrated ana::pro software in real-time or offline standalone PC version. It contains algorithms using PLS based on the results of hundreds of water sources [16]. In this work, ana::pro was used in offline mode to process the raw spectral data (FP files) according to the procedures from the manual [17]. FP files of the three selected water sources were imported separately into the ana::pro software (offline mode) to generate compensated UV_{254} as an output parameter.
2. The single wavelength compensation (SWC) is a direct subtraction method. However, as s:can spectro:lyser has a 2.5 nm resolution and absorbance of UV_{254} was not given in the raw FP, an interpolate algorithm (R-script) was first applied to generate the spectral data in 1 nm resolution. Then the compensated UV_{254} was determined by subtracting the absorbance between 254 nm and 550 nm.
3. The linear regression compensation (LC) technique is based on the visible region of 380–750 nm which is the most impacted by particles given responses occurs [9]. As explained previously, 1 nm resolution spectra (FPs) were generated first then an R algorithm was used to perform the calculations. For each spectrum, a linear regression (linear fit) was performed using a wavelength range of 550–580 nm as x-axis and their corresponding absorbance as y-axis. The obtained linear equation was then used to determine the particle absorbance at 254 nm. Compensated UV_{254} was a subtraction between UV_{254} and particle contribution of UV_{254}.
4. The multiplicative scatter correction (MSC) method is a normalization technique to correct particle effect (light scattering) on spectra. MSC method can correct the spectra by changing the scale and the offset based on the reference spectrum which is the mean of the spectra [18]. The hourly averaged UV–Vis spectra were processed for MSC using the unscrambler X software (version 10.4, CAMO). Then compensated UV_{254} were extracted from the spectra for analysis purposes.

A brief illustration of removing particle effect on the UV_{254} using different compensation methods is shown in Fig. 1. Detailed explanations of these compensation techniques are shown in the results and discussion.

2.6. Local calibrations

The instrument built-in compensation algorithm (B) was developed using PLS based on hundreds of water samples. This technique is also considered as a generic method (average compensation) which may require a local calibration using grab samples [19]. The compensated UV_{254} of the built-in compensation method for the three water sources were calibrated using a simulated local calibration method which conducted the offline calibration using the laboratory grab sample measurements based on the linear model. Similarly, the compensated UV_{254} of three particle compensation techniques were also conducted local calibrations based on the linear modes.

2.7. Statistical analysis

Data sets in this work were assumed to be generated from a large number of water samples from which the water quality data tend to follow normal distribution regardless of the shape of the data [20]. The bland-Altman analysis was used to assess the comparability of single wavelength, linear regression compensation techniques and multiplicative scatter correction method against the instrument built-in algorithm

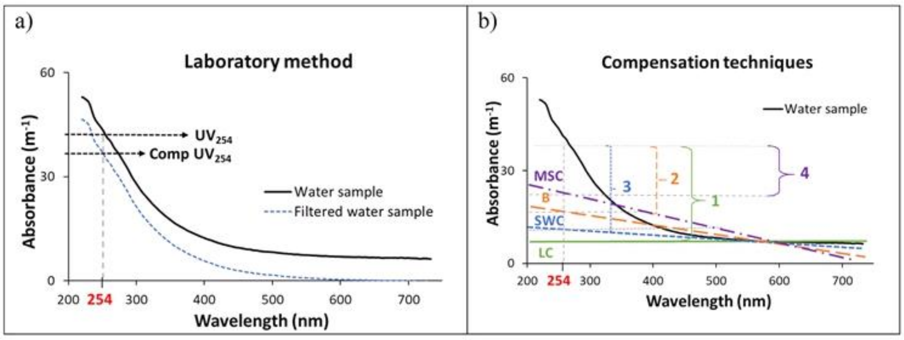

Fig. 1. Illustration of particle compensation of UV_{254} using a) laboratory method and b) compensation techniques, i. single wavelength compensation (SWC), ii. instrument built-in compensation algorithm (B), iii. linear regression compensation (LC), and iv. multiplicative scatter correction (MSC) method. 1, 2, 3 and 4 in Fig. 1b represents the compensated (Comp) UV_{254} of SWC, B, LC and MSC, respectively.

for UV_{254} of RW1, RW2 and TW. Bland-Altman analysis studies the difference of the compensation techniques by constructing the limits of agreement, which is determined by the bias (mean of the differences) of UV_{254} plus and minus 1.96 times its standard deviation of the differences between the two compensation methods [21]. It defines that 95% of data points lie within the limits of agreements. In this work, the differences between the two techniques were plotted as percentages. Percentage differences were calculated using the difference between the two methods divided by the means of the two methods then multiplying by 100%. The Bland-Altman method only defines the intervals of agreements and does not indicate whether the limits are acceptable or not. Therefore, the acceptable limits need to be defined and compared with the limits of agreement generated by the Bland-Altman analysis. The limit of the acceptable percentage difference of UV_{254} (compensated) was defined as plus/minus 10% of the instrument built-in compensation method. A flowchart of the data analysis procedure of particle compensation techniques is shown in Fig. 2.

3. Results and discussion

3.1. Instrument built-in compensation and calibration

UV–Vis spectral data of RW1, RW2 and TW monitored from April to Dec 2013, were processed using the ana::pro software. It should be noted that the water source for Anstey Hill WTP was switched from Millbrook Reservoir water to River Murray water in May and June 2013 as indicated on Fig. 3. The three sets of data were compensated using the built-in compensation algorithms in offline mode. The compensated UV_{254} and calibrated UV_{254} (after calibrations using laboratory UV_{254} measurements) were plotted against time for the three water sources as shown in Figs. 3 and 1S in Supplementary Information (SI). The plots of the built-in compensation for RW1 and RW2 water are shown in Fig. 3.

The water quality profiles as measured by UV_{254}, turbidity and DOC are shown in Fig. 4a indicates that the turbidity of RW1 was dramatically increased when the source water was switched from Millbrook Reservoir water to River Murray water. The built-in compensation method was unable to generate the compensated UV_{254} measurements when the turbidity is higher than 60 NTU for Anstey Hill raw water, which may be beyond the compensation limit. Therefore, this result indicates that it is important and necessary to seek alternative particle compensation methods for online water quality measurements using UV–Vis spectroscopy, especially in highly variable water sources.

Large differences were observed between the compensated UV_{254} and the UV_{254} of the grab samples for RW1 when the water source was switched from Millbrook Reservoir water with turbidity level less than 40 NTU to River Murray water with turbidity level over 40 NTU. After the local calibration was applied (in simulated mode), the calibrated and laboratory analytical UV_{254} data were well matched with each other. It indicates the results of the built-in compensation method is not comparable with laboratory filtration method for water such as RW1 with large turbidity changes. However, with the adjustment of the local calibration, the built-in compensation is comparable with laboratory filtration method even when large turbidity changes occur. Similar observations were obtained from the RW2 according to Fig. 3. There was a gradual increase in turbidity of the RW2 from July to October 2013, during which much larger deviations between the UV_{254} of the built-in compensation method and that of the laboratory method at medium turbidity level over 5 NTU could be observed. Yet, after having performed the calibration, a good match between the calibrated and laboratory analytical UV_{254} data was found for RW2. A similar observation can also be seen for the TW with low turbidity level and low DOC content (Fig. 1S in SI). The DOC remained quite stable for all three water sources in which the turbidity changed significantly for raw waters. Therefore, the built-in compensation method with local calibration is comparable with the laboratory filtration method. Local calibrations have been conducted by other researchers to improve the accuracy of the online measurements of UV–Vis spectrometers [10] [22,23]. Therefore, our results reveal that with proper calibration, the built-in compensation method can perform the same particle compensation as the laboratory filtration. Our results reveal that the particle compensation techniques can assist the online UV

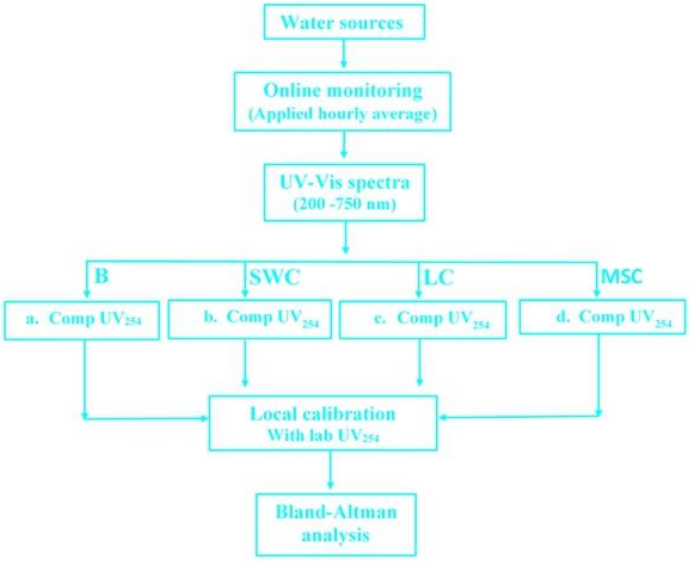

Fig. 2. Flow chart to show the comparison procedures of single wavelength compensation (SWC), linear regression compensation (LC) and multiplicative scatter correction (MSC) techniques against the instrument algorithm (B) for UV_{254}.

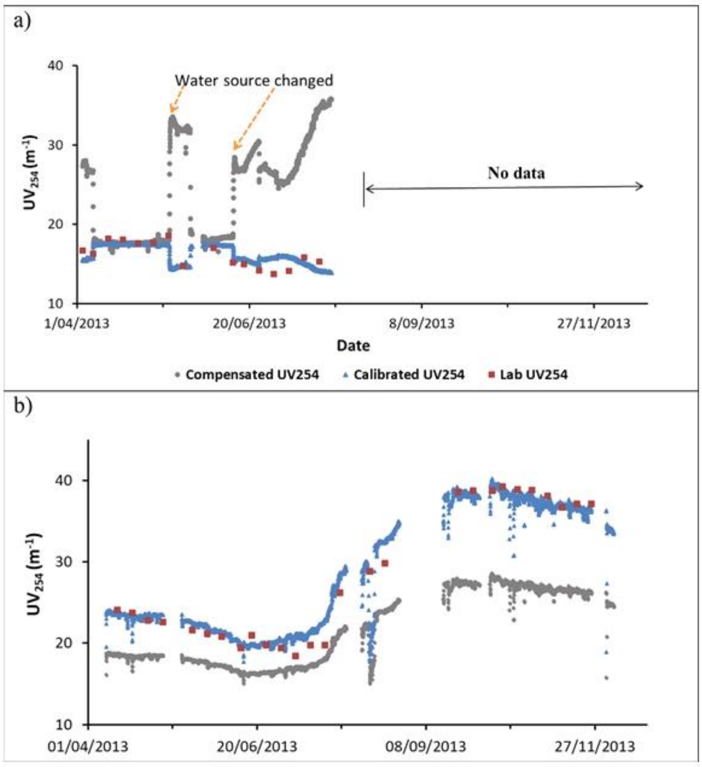

Fig. 3. Comparisons between compensated UV_{254} and calibrated UV_{254} measurements against laboratory UV_{254} for a) Anstey Hill raw water (RW1) and b) Happy Valley raw water (RW2). Note: no data was recorded after August 2013 (Fig. 3a), the instrument software could not perform the calculation for compensated UV_{254} due to the high turbidity of the water.

measurements to provide acceptable water quality results for raw water with high turbidity and medium DOC content, raw water with medium turbidity and high DOC content and treated water with low turbidity and low DOC content. The built-in compensation method was used as a reference method to assess the two developed compensation methods and a well-established compensation techniquein this work.

3.2. *Software compensation techniques and correction methods*

Nephelometric turbidity units (NTU) have been widely used as a surrogate measure of suspended particles. Turbidity signal was determined by selecting the wavelength range from 380 to 750 nm to eliminate the particle effects on the UV–Vis absorbance measurements of water samples. Studies have shown that the wavelength at 550 nm is the best for turbidity compensation in drinking water samples and has often been used in conjunction with UV_{254} measurements [24]. Absorbance at 546 nm was reported to eliminate the particle effect on the DOC for river water [25]. Mrkva used wavelength 545 nm in an automatic UV analyser to deduct the absorbance of particles for surface and wastewaters [26]. Some commercial instruments including HACH UV probe [27] and Burkert spectral absorption coefficient sensors compensate particle effect using a reference measurement at 550 nm [28]. Shimadzu UV instruments include UV-probe Type LXG 139 and type LXG 144, which also compensate particle effect through a reference measurement at 550 nm. Thus, the single wavelength compensation (SWC) technique in this study was developed by direct subtraction between the absorbance of wavelength at 254 nm and 550 nm. The second compensation method developed in this study was linear regression compensation (LC) technique. It is based on the characteristic of particles between 550 and 580 nm to remove the particle effect on the UV–Vis spectra. A wavelength range of 550–580 nm was used in the LC technique as it represents the visible region most impacted by particles given responses occurs within the wavelength range of 380–750 nm [9]. The third particle compensation method, multiplicative scatter correction (MSC), is a well-documented technique. The MSC is a transformation method to compensate for the particle effect in spectral data. MSC method can be used to reduce the particle effect by separating the chemical light absorption from the physical light scatter [29]. MSC technique is a commonly used method for processing NIR spectral data, however, it has not been widely used for processing UV–Vis spectra data. Studies have shown the MSC method can reduce the particle effect on the spectra [30–32].

SWC, LC, and MSC techniques were applied to determine UV_{254} by removing the particle effect for RW1, RW2 and TW. It was observed that in a similar way as the built-in compensation behaviour, SWC, LC and MSC have different compensated results for different waters (Table 2S in SI) because of the different particle contents. Since the compensation is water source dependent, local calibration to compensate the background water matrix is required. Well-fitted linear relationships are found between the compensated UV_{254} obtained from the compensation

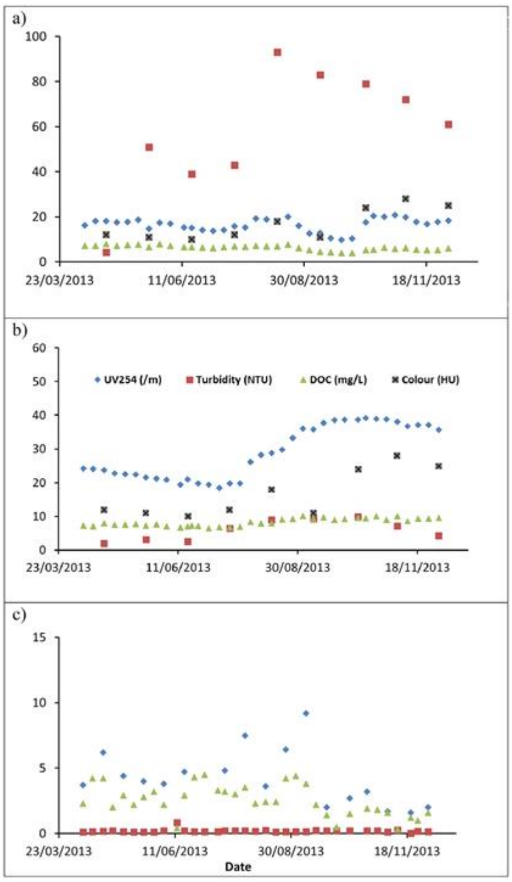

Fig. 4. Laboratory results of water quality parameters of a) Anstey Hill raw water (RW1) and b) Happy Valley raw water (RW2) and c) Happy Valley treated water (TW) from April 2013 to December 2013.

techniques and laboratory UV_{254} measurements for all three water sources using the three compensation techniques, except for TW using the MSC. There was no linear correlation between the compensated UV_{254} and lab UV_{254} after conducting MSC could because of all the compensated UV_{254} were very close to each other for different data. MSC may not be suitable for compensating UV spectral data of clean water such as treated water. This is because that it was designed to remove large particle effects on spectra. Linear regression has been commonly used as a calibration method to improve the measurement accuracy for analytical methods and has been used for spectroscopy [33]. The spectro::lyser also uses a linear calibration mode. Thus, the compensated UV_{254} readings were corrected based on the linear relationships between the compensated UV_{254} of the developed techniques and laboratory UV_{254}. After adjustment, the corrected UV_{254} were plotted with their closest corresponding laboratory UV_{254} measurements, the slopes, y-intercepts and the coefficient of determination (R^2) from the linear regression line were determined for comparisons. A linear plot of the corrected UV_{254} of SWC compared to laboratory UV_{254} for RW2 is shown in Fig. 5. According to the trend, the slope between the corrected UV_{254} and laboratory UV_{254} is 1.00 and y-intercept is 0.00 with R^2 of 0.93, which means that SWC can generate the same compensated UV_{254} as the reference laboratory method. The linear regression line of the calibrated UV_{254} of LC and laboratory UV_{254} has a slope of 1, intercept of close to zero and R^2 of 0.96 for RW2. It indicates that SWC can also generate the same compensated UV_{254} as the laboratory method. After adjustment, all the compensation methods include SWC, LC and MSC are comparable to the laboratory filtration method for RW2. Similar interpretations can also be stated for RW1 and TW according to Fig. 2S in SI. The results reveal that linear regression models can be used to correct the compensation methods. The stable level of DOC in each of the three water sources which may contribute to the success of using linear calibration to adjust the compensation techniques. Linear regression methods have been employed by Torres and Bertrand-Krajewski to calibrate the particle compensation method of online UV–Vis spectrophotometer for different water matrices [10]. Another study showed the linear curve fit was able to optimise the performance of UV–Vis spectrophotometers [34]. Linear regression is proven as a robust and sustainable adjustment method of UV–Vis spectrophotometers to estimate concentrations of water quality parameters [35].

3.3. *Evaluation of particle compensation methods*

In this work, SWC, LC and MSC techniques were investigated in comparison with the instrument built-in compensation method using the Bland-Altman analysis, which was used to assess the accuracies of the three techniques for raw (natural water quality) and treated waters (drinking water quality).

3.3.1. *Assessment of single wavelength compensation technique*

The SWC technique was assessed for the performance of compensating the particle effects on the UV_{254}, for RW1, RW2 and TW, against the instrument built-in algorithm using Bland-Altman analysis. After adjustments of compensated UV_{254} measurements (calibrated UV_{254}) from SWC technique and the built-in algorithm, the percentage differences between corrected UV_{254} of these two methods were plotted against the mean of the two methods, as Bland-Altman plots, for the three waters, respectively. Bias (mean of percentage difference) is represented by the space between the x-axis and the zero percentage differences in the Bland-Altman plots. The analytical results of the Bland-Altman analysis are shown in Table 1.

The bias between the corrected UV_{254} of SWC technique and built-in compensation was determined as 1.71% for RW1. Agreement limits of the corrected UV_{254} between the two methods varied in a range of −6.21% and 9.62%. Compared to the pre-defined acceptable agreement limits of the interval from −10% to 10% of the differences, SWC technique is comparable to the built-in compensation algorithm for compensating the particle effect on UV_{254} for RW1. For RW2 as shown in Fig. 6, the bias between corrected UV_{254} of SWC technique and that of built-in compensation were −1.14%. Agreement limits between corrected UV_{254} of the two methods were found in the range of −7.32% and 5.04% for RW2. The percentage differences between corrected UV_{254} using two methods varied from −7.32% to 5.04% when the average of the corrected UV_{254} of these two methods increased. Compared to the pre-defined acceptable agreement limits, the SWC technique can generate good results as those using the built-in compensation algorithm for RW2. Similarly, for TW the agreement limits between these two methods were relatively small and varied within the range of the interval of −10%–10% of the UV_{254} (Fig. 3S in SI). The SWC technique generated similar compensated UV_{254} measurements compared to that of the built-in compensation algorithm for RW2. Statistically, it can be 95% confident that the SWC technique is comparable to the built-in compensation method for removing the particle effect on the UV_{254} of raw and treated waters if the percentage differences between the two methods are acceptable within the plus/minus 10% .

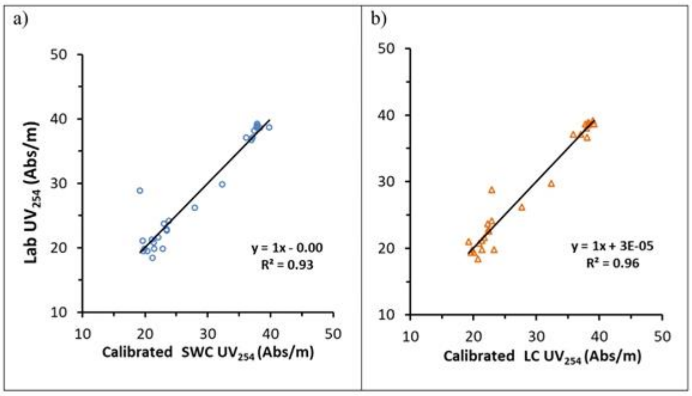

Fig. 5. Comparison of calibrated UV_{254} of a) single wavelength compensation (SWC) and b) linear regression compensation (LC) with laboratory UV_{254} for Happy Valley raw water (RW2).

Table 1
Bland-Altman analysis of assessing single wavelength (SWC), linear regression compensation (LC) and multiplicative scatter correction (MSC) techniques against the built-in algorithm (B) for Anstey Hill (RW1) and Happy Valley raw waters (RW2), and Happy Valley treated water (TW).

Water sources	Methods	Bland-Altman Analysis			
	after adjustment	Mean of difference(%)	Limit of agreement(%)	Acceptable limit of agreement(%)	Agreement between two methods
RW1	SWC vs. B	1.71	[-6.21, 9.62]	[-10, 10]	Yes
	LC vs. B	1.45	[-5.37, 8.28]	[-10, 10]	Yes
	MSC vs. B	−0.94	[-8.33, 6.45]	[-10, 10]	Yes
RW2	SWC vs. B	−1.14	[-7.32, 5.04]	[-10, 10]	Yes
	LC vs. B	−0.77	[-5.18, 3.65]	[-10, 10]	Yes
	MSC vs. B	−1.52	[-9.81, 6.77]	[-10, 10]	Yes
TW	SWC vs. B	0.25	[-6.10, 6.67]	[-10, 10]	Yes
	LC vs. B	0.30	[-5.82, 6.68]	[-10, 10]	Yes
	MSC vs. B	–	–	–	–

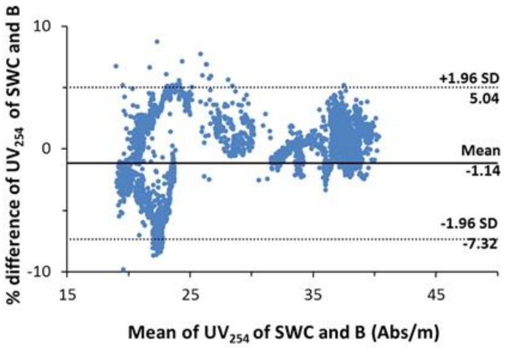

Fig. 6. Bland-Altman plot of UV_{254} after application of single wavelength compensation technique (SWC) and the built-in algorithm (B) for Happy Valley raw water (RW2). The solid line represents the mean of percentage differences in UV_{254} of the two methods. Horizontal dotted lines indicate upper (+1.96SD) and lower (−1.96SD) limits of agreement of the two methods.

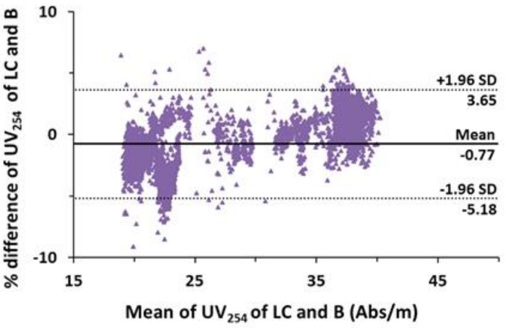

Fig. 7. Bland-Altman plot of UV_{254} after application of linear regression compensation technique (LC) and the built-in algorithm (B) for Happy Valley raw water (RW2). The solid line represents the mean of percentage differences in UV_{254} of the two methods. Horizontal dotted lines indicate upper (+1.96SD) and lower (−1.96SD) limits of agreement of the two methods.

3.3.2. Assessment of linear regression compensation technique

After adjustments, the LC technique was evaluated in comparison with the built-in algorithm in terms of the performance of compensating the particle effects on the UV_{254}, using Bland-Altman analysis for RW1, RW2 and TW. The differences between corrected UV_{254} measurements using the LC technique and that of the built-in algorithm were plotted against the mean of corrected UV_{254} of the two methods, as Bland-Altman plots, for three waters, respectively (Table 1).

Bias between the corrected UV_{254} of LC technique and the built-in compensation was 1.45% for RW1. Agreement limits between the two methods varied from −5.37% to 8.28%, which is within the acceptable limit of intervals. Hence the LC technique is comparable to the built-in compensation method for RW1. For both RW2 and TW, the bias between the corrected UV_{254} of LC technique and that of built-in compensation was less than 1% in Figs. 7 and 4S (SI). Agreement limits between corrected UV_{254} of the two methods were within the acceptable limit agreement. Therefore, the LC technique generated similar compensated UV_{254} compared to that of built-in compensation algorithm for RW1, RW2 and TW. Statistically, there is 95% certainty that the LC technique is comparable to the built-in compensation method of raw and treated waters within a plus/minus 10% difference between the two methods.

Along with adjustments, LC has similar particle compensation behaviour as the built-in compensation method on the UV_{254} for different water sources. The LC technique considers particle contribution on the UV_{254} within a wavelength range of 550–580 nm. Similar to the SWC technique, the LC technique is also water source dependent and linear adjustment methods can improve the accuracies of compensating the particle effect on UV_{254} of raw and treated waters.

3.3.3. *Assessment of multiplicative scatter correction technique*

After performed local calibration of multiplicative scatter correction (MSC) method, the performance of the MSC method was evaluated by comparing with the instrument built-in algorithm for RW1 and RW2, using the Bland-Altman analysis. The percentage difference between the calibrated UV_{254} of MSC were plotted against the mean of the two methods as shown in the Bland-Altman plots for RW1 and RW2 (Fig. 5S in SI). The mean difference between the calibrated UV_{254} of MSC and the built-in compensation methods was −0.94% and −1.52% for RW1 and RW2, respectively. Limit of agreement between the two methods was within the intervals of acceptance limit. Hence, the MSC technique is comparable to the built-in compensation method for RW1 and RW2. However, MSC is not comparable to the built-in compensation method for TW. This could be because the nature of MSC is to correct light scattering of the particle in the water. TW contained a very low particle content. It should be pointed out that MSC is commonly used for turbid solutions such as wine and solid materials such as meat [18,29].

In the case of comparison of SWC, LC and MSC with the built-in compensation method, all three particle compensation methods had the different particle compensation behaviour when compared to the built-in compensation method on UV_{254} for different water types. SWC, LC and MSC techniques need to be adjusted for individual waters to remove the particle effect. It shows that particle compensation is water source dependent. This finding is in agreement with the previous studies [35]. This is probably because compensation techniques often cannot directly handle the large change of water quality, particularly turbidity character changes [5,7]. Water quality characteristics are different for individual water sources. Variation of the water quality, particularly turbidity can affect the compensation ability of the compensation method on the UV_{254}. Reported studies showed that it is difficult to compensate for the particle effect when there is a large variation of turbidity [5,7]. Industrial experience of monitoring water quality also shows that compensating particle effect on the UV–Vis absorbance measurement is difficult when water turbidity is fluctuating or the water source changes [36].

Provided linear correction (local calibration) method with acceptable error, the developed single wavelength compensation and linear regression compensation techniques could be used as alternative methods to eliminate the particle effect on the UV_{254} measurements for raw and treated waters. Also, multiplicative scatter correction technique could be used as alternative particle compensation method to remove the particle effect for raw waters.

Overall, our results reveal that SWC, LC and MSC techniques with the linear adjustment can be applied in practice for online water quality monitoring. SWC is a relatively simple method to remove particle effect on the UV_{254} in the water. Simple UV–Vis instruments with a single wavelength in the visible region (550 nm) could be employed in the field to monitor water quality instead of using sophisticated full-spectrum UV–Vis instruments. These findings can assist water treatment plant operators to monitor water quality more effectively because the utilization of software compensation methods and local calibrations allow more accurate and reliable UV–Vis readings. Further research is necessary to investigate how these compensation methods can be applied to the situation of real-time water quality monitoring.

4. Conclusion

Our results reveal that after applying local calibration methods, instrument built-in compensation methods can be comparable to the reference laboratory methods for the UV_{254} measurements of raw and treated waters from two drinking water WTPs. In the same way as the built-in compensation method, the developed SWC and LC techniques as well as multiplicative scatter correction method are also water source dependent. Linear correction methods as local calibrations are based on the linear relationships of compensated UV_{254} of the three techniques and the laboratory UV_{254} measurements of the grab samples. It could be applied for the development of techniques to improve the accuracies of online measurements of water quality monitoring. The bland-Altman analysis was employed to assess the calibrated UV_{254} using developed SWC and LC as well as MSC techniques. The compensated UV_{254} generated from these three methods were found to be comparable with that of the built-in compensation method using online UV–Vis spectral data from drinking water treatment plants. According to the Bland-Altman analysis, with the assistant of the linear correction (local calibration) method, both SWC and LC had very similar compensation behaviours on the UV_{254} as the built-in compensation algorithm for varied raw and treated waters. MSC was comparable to the built-in compensation method for raw waters. Potentially, along with the linear correction method, both the single wavelength and the linear regression compensation, as well as the multiplicative scatter correction methods could be used as alternatives to remove the particle effect on the UV_{254} for online water quality monitoring. The use of the alternative compensation techniques may allow less maintenance of the instrument and possibly improve the reliability and usability in online mode by WTP operators. Moreover, simple UV–Vis instruments with a single wavelength in the visible region (550 nm) could be employed in the field to monitor water quality instead of using sophisticated full-spectrum UV–Vis instruments.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Zhining Shi: Conceptualization, Methodology, Writing - original draft. **Christopher W.K. Chow:** Conceptualization, Supervision, Writing - review & editing. **Rolando Fabris:** Supervision, Methodology, Writing - review & editing. **Jixue Liu:** Software, Visualization, Writing - review & editing. **Bo Jin:** Supervision, Writing - review & editing.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemolab.2020.104074.

References

[1] M.H. Banna, S. Imran, A. Francisque, H. Najjaran, R. Sadiq, M. Rodriguez, M. Hoorfar, Online drinking water quality monitoring: review on available and emerging technologies, Crit. Rev. Environ. Sci. Technol. 44 (12) (2014) 1370–1421.

[2] A. Matilainen, Mikko Vepsäläinen, Mika Sillanpää, Natural organic matter removal by coagulation during drinking water treatment: a review, Adv. Colloid Interface Sci. 159 (2) (2010) 189–197.

[3] Y. Hu, Y. Wen, X. Wang, Novel method of turbidity compensation for chemical oxygen demand measurements by using UV–vis spectrometry, Sensor. Actuator. B Chem. 227 (2016) 393–398.

[4] G. Langergraber, N. Fleischmann, F. Hofstaedter, A multivariate calibration procedure for UV/VIS spectrometric quantification of organic matter and nitrate in wastewater, Water Sci. Technol. 47 (2) (2003) 63–71.

[5] X. Wang, Z. Lin, X. Jin, Ultraviolet scanning technique for water COD measurement and its instrument development, J. Zhejiang Univ. Eng. Sci. 40 (11) (2006) 1951.

[6] B. Tang, et al., Experimental research of turbidity influence on water quality monitoring of COD in UV-visible spectroscopy, Spectrosc. Spectr. Anal. 34 (11) (2014) 3020–3024.

[7] Y. Hu, X. Wang, Application of surrogate parameters in characteristic UV–vis absorption bands for rapid analysis of water contaminants, Sensor. Actuator. B Chem. 239 (2017) 718–726.

[8] Y. Hu, C. Liu, X. Wang, Novel local calibration method for chemical oxygen demand measurements by using UV–Vis spectrometry, in: IOP Conference Series: Earth and Environmental Science, IOP Publishing., 2017, 012016.

[9] Y. Hu, Y. Wen, X. Wang, Detection of water quality multi-parameters in seawater based on UV-Vis spectrometry. OCEANS 2016-Shanghai, IEEE, 2016, pp. 1–4.

[10] A. Torres, J.L. Ertrand-Krajewski, Partial Least Squares local calibration of a UV–visible spectrometer used for in situ measurements of COD and TSS concentrations in urban drainage systems, Water Sci. Technol. 57 (4) (2008) 581–588.

[11] J.R. Etheridge, F. Birgand, J.A. Osborne, C.L. Osburn, M.R. Burchell, J. Irving, Using in situ ultraviolet-visual spectroscopy to measure nitrogen, carbon, phosphorus, and suspended solids concentrations at a high frequency in a brackish tidal marsh, Limnol Oceanogr. Methods 12 (1) (2014) 10–22.

[12] American Public Health Association, American Water Works Association, Water Environment Federation, Standard methods for the examination of water and wastewater, American Public Health Association (APHA): Washington, DC, USA. (2005).

[14] R Core Team, A Language and Environment for Statistical Computing, R Foundation for Statistical Computing, 2013.

[15] RStudio Team, *RStudio: Integrated Development for R*. RStudio, Version 1.0.143, Inc., Boston, MA, 2015.

[16] J. Van den Broeke, G. Langergraberb, Weingartnera, Andreas., *On-line and in-situ UV/vis spectroscopy for multi-parameter measurements: a brief review*, Spectrosc. Eur. 18 (4) (2006).

[17] s::can Messtechnik GmbH, Spectrometer probe V2, Manual (2011).

[18] S. Preys, J.M. Roger, J.C. Boulet, Robust calibration using orthogonal projection and experimental design. Application to the correction of the light scattering effect on turbid NIR spectra, Chemometr. Intell. Lab. Syst. 91 (1) (2008) 28–33.

[19] R. Fabris, C. Chow, R. Dexter, J. Colton, J. Knoblauch, M. Drikas, Feed-forward coagulant control using online UV/Vis monitoring, Water Sci. Tech- W. Sup. 13 (2) (2013) 420–426.

[20] A.C. Elliott, W.A. Woodward, Statistical Analysis Quick Reference Guidebook with SPSS Examples, first ed., Sage Publications, London, 2007.

[21] D. Giavarina, Understanding bland altman analysis, Biochem. Med. 25 (2) (2015) 141–151.

[22] R.S. Brito, H.M. Pinheiro, F. Ferreira, J.S. Matos, N.D. Lourenço, In situ UV-Vis spectroscopy to estimate COD and TSS in wastewater drainage systems. Urban Water J. 11 (4) (2014) 261–273.

[23] A. Mussared, C. Chow, M. Holmes, J. Van Leeuwen, U. Kaeding, Implementation of predictive alum dose control systems, in: 77th Annual WIOA Victorian Water Industry Operations Conference and Exhibition, Bendigo Exhibition Centre, 2014.

[24] B.M. Saunier, Robert E. Selleck, R Rhodes Trussell, Preozonation as a Coagulant Aid in Drinking Water Treatment, American Water Works Association, 1983, pp. 239–246.

[25] Y. Zhao, Y. Li, Y. Zhen, Y. Fang, A novel monitoring system for COD using optical ultraviolet absorption method, Procedia Environ. Sci. 10 (2011) 2348–2353.

[26] M. Mrkva, Automatic UV-control system for relative evaluation of organic water pollution, Water Res. 9 (5–6) (1975) 587–589.

[27] HACH, UVAS Sc. HACH User Manual, HACH Company, 2014.

[28] Burkert, Miniaturised SAC Measurement for Continuous Monitoring of Water Quality, Burkert fluid control systems, 2015.

[29] P. Geladi, D. MacDougall, H. Martens, Linearization and scatter-correction for near-infrared reflectance spectra of meat, Appl. Spectrosc. 39 (3) (1985) 491–500.

[30] Y. Wu, S. Peng, Q. Xie, Q. Han, G. Zhang, H. Sun, An improved weighted multiplicative scatter correction algorithm with the use of variable selection: application to near-infrared spectra, Chemometr. Intell. Lab. Syst. (185) (2019) 114–121.

[31] Z. Huang, W. Tao, J. Fang, X. Wei, Y. Du, Multivariate calibration of on-line enrichment near-infrared (NIR) spectra and determination of trace lead in water, Chemometr. Intell. Lab. Syst. 98 (2) (2009) 195–200.

[32] Z. Kovacs, G. Bázár, M. Oshima, S. Shigeoka, M. Tanaka, A. Furukawa, A. Nagai, M. Osawa, Y. Itakura, R. Tsenkova, Water spectral pattern as holistic marker for water quality monitoring, Talanta 147 (2016) 598–608.

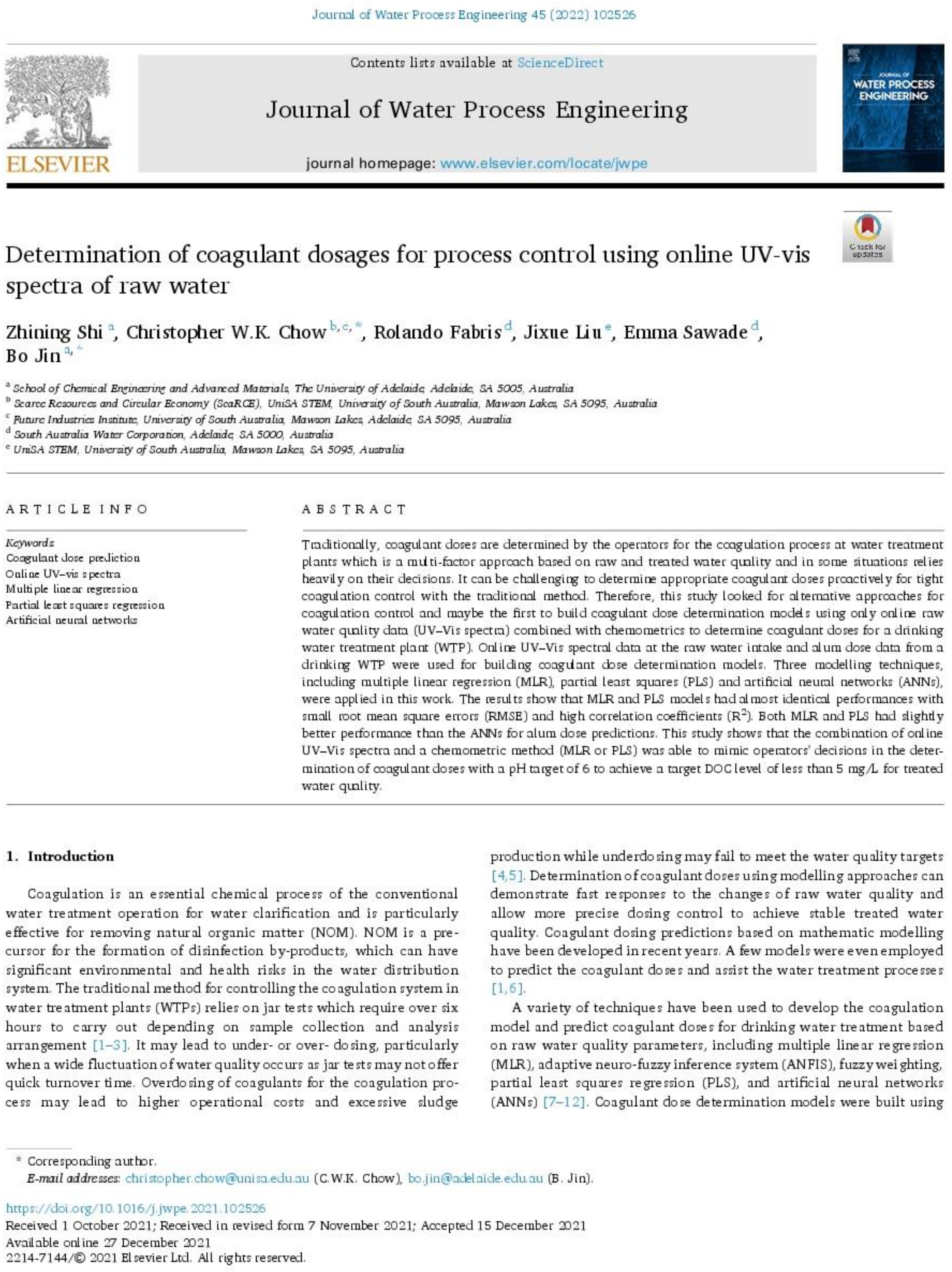
[33] J. Boulet, S.D. Brown, J. Roger, A simple, projection-based geometric model for several linear pretreatment and calibration methods, Chemometr. Intell. Lab. Syst. 138 (2014) 48–56.

[34] C.E. Adeeyinwo, N.N. Okorie, G.O. Idowu, Basic calibration of UV/visible spectrophotometer, Int. J. Sci. Technol. 2 (3) (2013).

[35] M. Lepot, A. Torres, T. Hofer, N. Caradot, G. Gruber, J. Aubin, J. Bertrand-Krajewski, Calibration of UV/Vis spectrophotometers: a review and comparison of different methods to estimate TSS and total and dissolved COD concentrations in sewers, WWTPs and rivers, Water Res. 101 (2016) 519–534.

[36] C. Chow, John Van Leeuwen, A. Mussared, M. Holmes, U. Kaeding, UV spectrometry in drinking water quality management, Ozwater 17 (2017) 63.

Appendix E



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Determination of coagulant dosages for process control using online UV-vis spectra of raw water

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ABSTRACT

Traditionally, coagulant doses are determined by the operators for the coagulation process at water treatment plants which is a multi-factor approach based on raw and treated water quality and in some situations relies heavily on their decisions. It can be challenging to determine appropriate coagulant doses proactively for tight coagulation control with the traditional method. Therefore, this study looked for alternative approaches for coagulation control and maybe the first to build coagulant dose determination models using only online raw water quality data (UV–Vis spectra) combined with chemometrics to determine coagulant doses for a drinking water treatment plant (WTP). Online UV–Vis spectral data at the raw water intake and alum dose data from a drinking WTP were used for building coagulant dose determination models. Three modelling techniques, including multiple linear regression (MLR), partial least squares (PLS) and artificial neural networks (ANNs), were applied in this work. The results show that MLR and PLS models had almost identical performances with small root mean square errors (RMSE) and high correlation coefficients (R^2). Both MLR and PLS had slightly better performance than the ANNs for alum dose predictions. This study shows that the combination of online UV–Vis spectra and a chemometric method (MLR or PLS) was able to mimic operators' decisions in the determination of coagulant doses with a pH target of 6 to achieve a target DOC level of less than 5 mg/L for treated water quality.

1. Introduction

Coagulation is an essential chemical process of the conventional water treatment operation for water clarification and is particularly effective for removing natural organic matter (NOM). NOM is a precursor for the formation of disinfection by-products, which can have significant environmental and health risks in the water distribution system. The traditional method for controlling the coagulation system in water treatment plants (WTPs) relies on jar tests which require over six hours to carry out depending on sample collection and analysis arrangement [1–3]. It may lead to under- or over- dosing, particularly when a wide fluctuation of water quality occurs as jar tests may not offer quick turnover time. Overdosing of coagulants for the coagulation process may lead to higher operational costs and excessive sludge production while underdosing may fail to meet the water quality targets [4,5]. Determination of coagulant doses using modelling approaches can demonstrate fast responses to the changes of raw water quality and allow more precise dosing control to achieve stable treated water quality. Coagulant dosing predictions based on mathematic modelling have been developed in recent years. A few models were even employed to predict the coagulant doses and assist the water treatment processes [1,6].

A variety of techniques have been used to develop the coagulation model and predict coagulant doses for drinking water treatment based on raw water quality parameters, including multiple linear regression (MLR), adaptive neuro-fuzzy inference system (ANFIS), fuzzy weighting, partial least squares regression (PLS), and artificial neural networks (ANNs) [7–12]. Coagulant dose determination models were built using

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ANNs and regression equations for surface water treatment with raw water quality parameters, including dissolved organic carbon (DOC), UV absorbance at 254 nm (UV_{254}), turbidity, alkalinity, dissolved oxygen and pH [2,10,13,14].

Some studies have utilised PLS combined with UV–Vis spectral data to predict water quality parameters in water [15,16] and wastewater [17,18]. Most of the reported prediction models for coagulant doses are operated based on the water quality results provided from laboratory analysis. There were very few reported studies using PLS to predict coagulant doses. PLS can extract information from a large volume of data matrix which is suitable to apply when the matrix has more independent variables than dependent variables and there is multicollinearity among the independent variables. In comparison with PLS, ANNs is a popular prediction model for coagulant dose prediction. ANNs can also handle large datasets, detect complex relationships, learn patterns and make decisions based on similar situations. Most of the prediction models rely on the raw water quality data of grab samples as inputs to predict the coagulant doses. It is unlikely to capture the rapid variations of the water quality to get correct predictions based on the data of grab samples when water quality changes as there are significant delays in obtaining the laboratory data. However, predictions based on the online UV–Vis spectral data could be a promising approach, which can use continuous water quality data to predict doses, with the ability to capture the rapid variations of water quality to get the correct predictions. Colton [19] reported a unique method using the online UV–Vis spectra to predict coagulant doses for WTPs. However, this was an indirect method that first needs to quantify the water quality (turbidity, UV_{254} and DOC) of the raw water using the spectra and then utilised the quantified water quality data as inputs for an exponential model to determine the coagulant doses. Zhou and Meng [20] conducted a lab-based study to use spectral data from a bench-top UV–Vis instrument to determine optimal coagulant doses for the removal of dissolved organic matter from a combined coagulation and ultrafiltration system. The optimal doses were determined in their study based on the correlations between spectral data and fouling behaviour.

This study was to establish an in-situ coagulation dosing prediction and control method integrated with the online UV–Vis spectra monitoring technique. We employed online UV–Vis spectral data of raw water from a municipal drinking WTP to build coagulant dose determination models and to determine coagulant doses for coagulation process control. This study also aimed at directly using raw water UV–Vis spectra to mimic operators' decisions in the determination of coagulant dose for process control. Three different models with different levels of complexity were evaluated, including multiple linear regression (MLR), partial least squares (PLS) and artificial neural networks (ANNs).

2. Methods and materials

2.1. Water treatment plant

Happy Valley (HV) WTP in South Australia was selected for this study. The HV WTP employs conventional water treatment practices comprising coagulation, flocculation, sedimentation, and filtration units. This WTP provides drinking water across the metropolitan area in the capital city of South Australia (SA). The raw water for the WTP is provided by the Happy Valley Reservoir with water originating from both the River Murray and local catchment areas. The raw water is characterised by moderate turbidity (0.1 to 10 NTU) and high DOC ranging from 6 to 10 mg/L. Turbidity and DOC ranges represented seasonal variations between April and December 2013. The HV WTP was selected as the source water is the representation of enclosed surface water catchment of a reservoir in SA.

2.2. Monitoring location and instrument

The inlet of HV WTP was the sample point for real-time water quality monitoring with a submersible UV–Vis spectrophotometer. The instrument, s::can spectro::lyser (s::can Messtechnik GmbH, Austria), is a double beam photodiode array 256 pixel UV-vis spectrometer with an optical path of 5 mm and spectral resolution of 2.5 nm. The online instrument measures the absorbance of wavelengths within 220-720 nm. The details of the instrument and the maintenance can be found in the previous study [21].

2.3. Data source

The water source was monitored between April and December 2013. Raw UV–Vis spectra in the range of 220–720 nm were acquired from the submersible instrument at two-minute intervals. The plant alum dose record in the same period was also obtained for this study. Alum, aluminium sulphate [$Al_2(SO_4)_3.18H_2O$)], was used as the primary coagulant. WTP alum doses were determined by the operators, to achieve treated water with DOC less than 5 mg/L, under pH conditions of 6 (plant record). The WTP alum doses were determined by WTP operators mainly based on jar tests of raw water and operators' experience, in some water quality event situations such as heavy rainfalls, the operators may refer to the WTC-Coag software and the treated water quality [22]. Jar tests of raw water were conducted once every two months or when there were sudden changes in the water quality. WTC-Coag is a mathematical model for real-time prediction of optimal alum dose, which has been used in metropolitan WTPs in SA for over 10 years including the HV WTP [6]. This software requires UV_{254}, colour, and turbidity of raw water as inputs to generate predicted alum doses. The operators can select certain % removal of the total coagulable DOC and choose to refer to the coagulant doses determined based on the 80–90% DOC removal using the WTC-Coag software when they were deciding the dose levels.

Overall, UV–Vis spectral data of raw water quality and plant dose data of the HV WTP were utilised in this study. The UV–Vis spectral data were collected from the online instrument. The data of plant doses were extracted from an internal operational database of SA Water Corporation (SA Water) with hourly extrapolation.

2.4. Data pre-treatment

Initial data pre-treatment was based on the instrument operation status. The online UV–Vis spectra related to the instrument issues and non-operational period of WTP were excluded. Further data pre-treatment was conducted using a time resolution optimisation algorithm and hourly average [21]. Particles in the water can affect the online UV–Vis measurements [23]. Thus, the averaged UV–Vis spectra were processed using a particle compensation method to remove particles. The baseline correction method was based on the absorbance of particles is at a wavelength of 550 nm. Particle compensation of source water using UV_{550} has been proved to be an effective method to remove the particle effect on the online UV–Vis measurements [21].

2.5. Data processing

The data pre-treatment and processing were conducted in the workspace of R and R-Studio [24]. Fig. 1 shows a flow chart of modelling development and validation of coagulant dose determinations. The online UV–Vis spectra of raw water quality data of the HV WTP were utilised to determine the coagulant dose. Important wavelengths of the online UV–Vis spectra were selected using variable selection methods. The absorbances of the selected wavelengths were used as model inputs to predict plant alum doses. The plant doses determined by operators were utilised as the model output. The DOC level of treated water during the same period was under 5 mg/L (Fig. S1 in SI) which met the drinking water quality target. It indicates that the plant doses were accurate for the coagulation control.

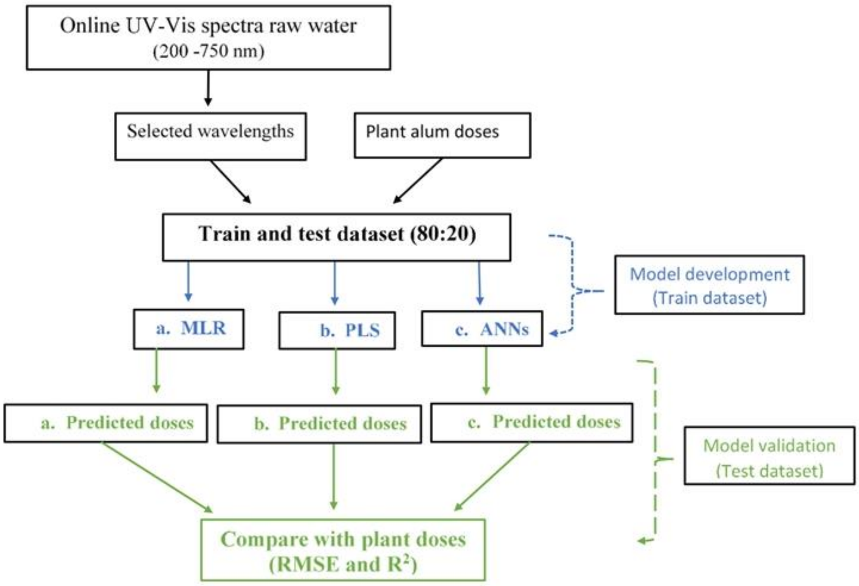

Fig. 1. Flow chart of modelling development and validation of coagulant dose determinations.

2.5.1. *Input variable optimisation methods*

Three variable optimisation methods: Variable Importance in Projections (VIP), Selectivity Ratio (SR) and correlation coefficient (R) were used to select the most important wavelengths that influence the coagulant dose prediction models. These methods are frequently used for variable selections in chemometrics [25]. These methods for X variable (input) importance related to the explanation of Y variance (output) are useful for prediction. The optimisation of spectral wavelengths (variables) can enhance the predictive ability of the full spectrum [26–28]. First, the full spectra of 220–720 nm were screened down to 250–600 nm as the absorbance at these wavelengths show characteristics that indicate the matrix of water quality [29]. Organic and turbidity in the water are represented by the wavelengths between 250 and 370 nm and 370–600 nm.

VIP scores were obtained from the construction of the initial PLS model. A higher VIP score indicates that the wavelength is more important to predict the alum doses, while the wavelength having a lower VIP score has less impact on the prediction [25]. VIP scores select the variables that contribute the most to the Y variance explanation. Generally, the threshold score of a VIP is defined as 1.0. The threshold score can be higher if the number of variables is large [25]. SR associates the statistical significance based on target projections for variable selection. SRs are based on the calculations of the ratio of explained to the residual variance of X obtained variance. An F-test (95%) has been chosen to define the threshold value of SR with a F-value to determine the significance. The pair-wise correlation coefficients (R) were the correlation between absorbances of wavelengths for the raw water and alum doses of HV WTP.

2.5.2. *Development methods of coagulant dose prediction*

Three model development methods: multiple linear regression (MLR), partial least squares (PLS) and artificial neural networks (ANNs) were used to determine alum doses. MLR is used to model the linear relationship between a dependent variable and independent variables which can directly define the coefficient of each parameter, while PLS can indirectly reveal the functional relationships and define the coefficient of each parameter. ANNs learns to recognise patterns in data between inputs and outputs. These modelling methods were applied to capture and incorporate the operators' decisions in selecting the alum doses using the spectral data of the raw water quality.

PLS constructs components (latent variables) by projecting the predictor variables to a new space. The observation variables are also projected. Then the linear regression models were built between new predictors and responses. PLS regression is particularly suitable to use when the matrix of predictors has more variables than observed variables and there is multicollinearity among the predictors. PLS can easily extract relevant information from a large data matrix and generate reliable models. Therefore, PLS was used to develop the coagulant prediction model in this study. Package 'pls' was used in the R and R-Studio for the calculations of PLS models [30]. PLS was analysed with leave-one-out cross-validation to avoid under- or over- fitting of the model. The optimal number of components (minimum number of latent variables) is 6 for PLS.

ANNs are computational techniques based on biological neurons which can learn complex patterns among the variables through training. ANNs employ a learning process that is similar to the human brain process to solve problems [31]. One of the commonly used ANNs is Multi-Layer Perceptron (MLP). MLP consists of three layers: the input layer, hidden layer and output layer. The input layer contains the input parameters. The hidden layer processes the data. And the output layer extracts the results. Package 'neuralnet' is used for modelling alum dose predictions with MLP ANNs [32]. The best ANNs architecture for this study is with one input layer, one hidden layer and 3 nodes, and one output layer. The number of hidden layers and the nodes are determined by the trial-and-error method.

The whole set of data, containing online UV–Vis spectral data of the raw water and their corresponding plant alum dose data, was divided into train and test datasets using a randomization method with a ratio of 80:20 to develop and validate the developed models for coagulant dose determination. The datasets were scaled to '0 to 1' using the formula: x_i -

minimum/(maximum - minimum) before they were used to develop PLS and ANNs models.

2.6. Evaluation of coagulation determination model performance

Coefficient of determination (R^2) and root mean square error (RMSE) are commonly used to evaluate the performance of models. R^2 is commonly used to assess the 'goodness of fit' for regression models. R^2 close or equal to 1 is an indicator of a good model. RMSE is commonly used to measure the differences between the predicted values and the actual values. RMSE value is considered the most important criterion for prediction model fit. The smaller the RMSE, the better the model. Another common way of using RMSE to assess the developed model is to compare the RMSE values of models for both train and test data; the model is good if the values are similar. RMSE and R^2 were used to evaluate the performance of the models.

3. Results and discussion

3.1. Optimisation of input variables

The best representative wavelengths of the pre-processed UV–Vis spectral data of HV raw water that impact on the alum determination models were evaluated by three variable optimisation methods, VIP, SR and R. The high-dimensional data of original spectra contain a proportion of redundant and irrelevant information for building coagulant models. This is because parts of the spectra collect unnecessary water quality information and the absorbance measured at some wavelengths may represent noise rather than the real water quality. Optimisation of input variables reduces the complexity and calculation time for modelling while enhancing the extraction of essential information [33]. Wavelength optimisation methods have been used by other researchers to determine the water quality parameters using UV–Vis spectra [16,27,34]. Application of these variable selection methods before modelling could lead to better and less complex prediction models [29].

VIP and SR were performed with partial least squares regressions. Online UV–Vis spectral data of wavelength range from 250 to 600 nm were X variables (model input) and the corresponding alum doses were Y variables (model output). Both variables were normalised from 0 to 1 to make sure they had an equal influence on the model. An initial PLS regression model was built with leave-one-out cross-validation. VIP scores and SR values were obtained from the results of the PLS regression model. Pair-wise correlation coefficients (R) between the absorbances of the UV–Vis spectra for the raw water quality and alum doses for the WTP with their level of significance (p-value) were calculated. The results of wavelength optimisation from the online UV–Vis spectra using VIP, SR and R approaches are presented in Table 1.

First, important wavelengths were selected based on VIP and SR, and R for modelling alum dose determination associated with the spectral data as X variables (inputs) and plant alum doses as Y variables (outputs). Due to a large number of filtered variables and the strength of influence of the variables, a trial-and-error method was also applied. The most important wavelengths were determined based on the overlapping variables of the three selection methods and the trial-and-error method. The trial-and-error results showed that wavelengths within 250–270 nm are the most important variables that influence the modelling of the plant coagulant dose determination and lead to the improved prediction performance of the models. More detailed results are given in Table S1 in Supplementary Information (SI). The selected wavelengths are determined in a range of 250–270 nm with a 2.5 nm interval, including nine wavelengths: 250, 252.5, 255, 257.5, 260, 262.5, 265, 267.5 and 270 nm. The corresponding thresholds of the selected wavelengths were 1.82 and 1.48 for VIP scores and SR (F-test, 95%). When the correlation coefficient of X variables and Y variables were considered, variables with R of 0.76–0.77 were the same as the variable selected by the VIP and SR methods.

The nine selected wavelengths were considered to have significant contributions to the model development for alum dose determinations for the HV WTP. All the important wavelengths are in the UV spectral region. It is shown that the determination of coagulant doses of HV WTP is mainly characterised in the UV region. A major purpose of coagulation is to remove the natural organic matter from the raw water. The natural organic matter of the raw water is characterised within a wavelength range of 250–300 nm [27,35], In addition, UV_{254} is a preferred indicator for selecting alum dosing for WTPs [6,36]. The selected wavelengths in this study also contained UV_{254} for modelling coagulant dose determination. These studies supported that the selected wavelengths are the important variables that influence the modelling of the alum dose determinations and results in improved model interpretation and performance [25,28,37]. Literature has shown that the variable selections can extract the most important variables and led to enhanced performance of models [16,29,33].

3.2. Coagulant determination using UV–Vis spectra with MLR

The absorbances of selected nine wavelengths were also used as inputs to build MLR determination models of plant doses for the HV WTP. MLR has been used to predict water quality [38,39] and coagulant dose using water quality parameters [9,10]. A train dataset was used to build the calibration MLR. Then a test dataset was used to validate the developed model.

The results of MLR were shown in Fig. 2. The coefficients of the MLR model were obtained and the MLR model can expressed as below:

Table 1
Selection of important variables for models using three methods, including VIP, SR and R.

Model input	Model output	Variables	VIP scores	SR			Correlation coefficient	
				scores	F-value	Significant	R	p-value
Online UV-Vis Spectra	Plant dose	250	2.42	1.51	1.06	Yes	0.77	<0.001
		252.5	2.34	1.50			0.77	
		255	2.13	1.51			0.77	
		257.5	2.05	1.52			0.77	
		260	2.01	1.51			0.77	
		262.5	1.93	1.50			0.77	
		265	1.86	1.49			0.76	
		267.5	1.84	1.49			0.76	
		270	1.82	1.48			0.76	
		272.5	1.77	1.47			0.76	
		275	1.71	1.46			0.76	
		277.5	1.67	1.45			0.76	
		280	1.65	1.44			0.76	

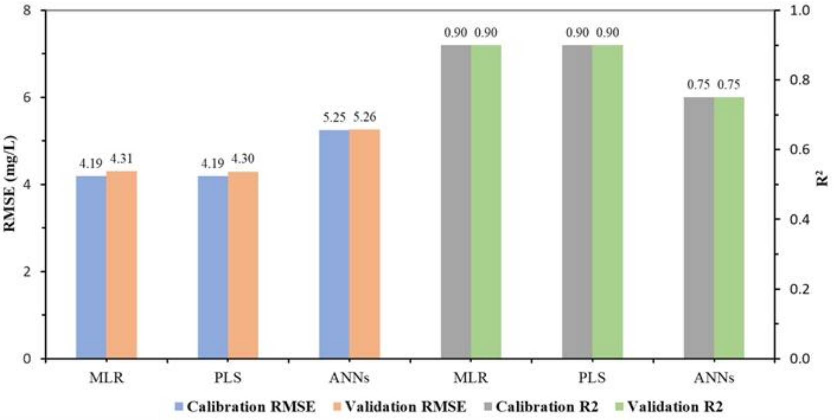

Fig. 2. Summary of the best models developed for alum dose determination using UV–Vis spectra of raw water.

$$Y\,(\text{alum dose}) = 200.69*X250-335.33*X252.5-58.91*X255 +185.27*X257.5+12.68*X260+140.26*X262.5-154.85*X265 +312.20*X267.5-305.24*X270-34.41$$

In the MLR model equation, X refers to the absorbance at a certain wavelength. For instance, X250 indicates the absorbance at wavelength 250 nm. According to R^2 and RMSE of MLR presented in Fig. 2, the predicted alum doses of MLR and actual plant doses were strongly correlated. For the calibration model, RMSE and R^2 for plant alum doses were 4.19 mg/L and 0.90, respectively. For the validation model, RMSE and R^2 for plant alum doses were 4.31 mg/L and 0.90, respectively. RMSE values of the MLR were small compared to that the plant alum doses were between 40 and 90 mg/L. It is confirmed that the MLR model with online UV–Vis spectral data as inputs can be used to determine the alum doses for WTPs.

Modelling results shown in Fig. 2 reveal a minor difference between the predicted alum doses using the MLR method and their corresponding observed (plant) alum doses. MLR can be used to model the alum dose determination using online UV–Vis spectral data because the correlations are high between the variables and the alum doses. This indicates that the determination of alum doses using online UV–Vis spectral data combined with MLR is comparable to the plant dose determination method (jar tests and operator experience). MLR results could mimic the operator decisions in selecting the appropriate alum doses. This seems contradictory to an argument that MLR is unable to provide a high-level relation between water quality variables and coagulant doses because of the high nonlinearity and the multiple factors affecting the coagulation process [40]. However, MLR has been used to predict coagulant doses with physico-chemical water quality parameters and was recognised as an appropriate approach to predict coagulant doses to assist water [9,10,41] and wastewater treatment operations [42]. In this work, the online UV–Vis spectra instead of water quality parameters of raw water were used to build a coagulant dose prediction model with MLR under the optimal coagulation pH of 6 to achieve a target DOC level of less than 5 mg/L for treated water quality.

3.3. *Coagulant determination using UV–Vis spectra with PLS*

PLS was also used to build the coagulant determination models for the HV WTP using the selected wavelengths in the UV range of 250–270 nm of raw water. PLS is a popular modelling method for spectral analysis which also has been used to generate water quality parameters [16,17,43] and coagulant dose prediction [44]. The absorbances of the 9 wavelengths were used as model inputs and plant alum doses of HV WTP were used as model outputs. The optimal number of components (minimum number of latent variables) of the PLS model was established by the cross-validation, leaving one sample at a time, to avoid under- or over- fitting of the model.

The RMSE of the PLS model was plotted against the rank of the number of the components, as shown in Fig. 3. The optimal number of components for the model is that the lowest number of components gives the lowest RMSE. The results indicate that 6 was the optimal number component for the PLS calibration model. The established PLS model was assessed with the test dataset. The PLS results for plant alum determination using train and test datasets are shown in Fig. 2. RMSE of the PLS based on the train dataset was 4.19 mg/L and the corresponding R^2 was 0.90. The RMSE of the validation was 4.30 mg/L and the corresponding R^2 was 0.90. Both RMSE values of the PLS models are small compared to the alum doses which ranged from 40 to 90 mg/L. Therefore, a good PLS model of determination of plant alum doses was obtained based on the online spectral data of a submersible UV–Vis instrument. Our results reveal that UV–Vis spectral data can be used to determine the alum doses and model the operators' decisions in the selection of the suitable doses using PLS.

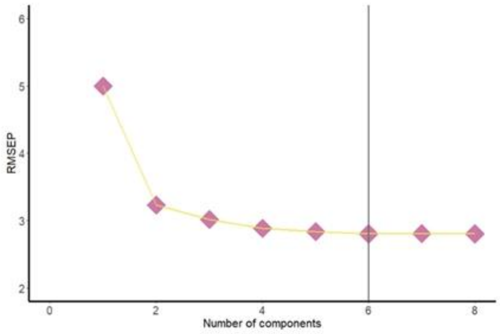

Fig. 3. Optimal number of components for PLS model with UV–Vis spectra to predict alum doses.

Our results reveal that PLS is effective in modelling alum doses using the UV–Vis spectra and is capable of capturing the operator experience in the determination of alum dose. This statement is supported by the following two reasons. Firstly, PLS was used to develop coagulant dosage predictions with water quality parameters as inputs. PLS regression analysis was used for the development of coagulant dosage prediction models using water quality parameters to remove phosphate from wastewater. PLS was proven to be an efficient tool for coagulant dose prediction [18]. PLS was also used to develop a decision support system for control of the coagulant dosage at a drinking WTP, using water quality parameters including UV, colour, chemical oxygen demand, TOC and conductivity. Thus, PLS could be recognised as a promising and useful estimation tool for coagulant dosing prediction [44]. Furthermore, PLS combined with UV–Vis spectra has also been employed to determine water quality parameters such as TOC in Karst water [15], TOC in wastewater [17] and COD in water [16]. Therefore, UV–Vis spectra of the raw water combined with PLS is able to determine the coagulant dose in the WTPs under the optimal pH of 6 to achieve a target DOC level of less than 5 mg/L for the treated water quality.

3.4. *Coagulant determination using UV–Vis spectra with ANNs*

ANNs were used to build the coagulant determination models for the plant doses. The absorbances of the selected nine wavelengths (250–270 nm) were also used as the model inputs and the plant alum doses were used as the model outputs. ANNs have been applied successfully for coagulant dose prediction based on water quality parameters [1,2,31,32]. A Multi-Layer Perceptron (MLP) ANNs, equipped with the feed-forward back-propagation algorithm was used for building ANN models. Back-propagation is a widely used algorithm for training feed-forward neural networks to speed up the convergence rate and its robustness [45]. Feedforward ANN provides a flexible way for generalizing linear regression and non-linear functions. Dataset of the selected variables and their corresponding plant alum doses was randomly shuffled before ANNs training to avoid the seasonality effect. There is no precise approach to obtain the optimal number of hidden layers of MLP. A few hidden layers of ANNs have been proven to be sufficient for modelling coagulant dosage based on the reported studies [13,46,47]. The optimal number of hidden layers was determined by the trial-and-error method [48]. The best ANNs model is selected for its lowest RMSE with one hidden layer and 3 nodes, as shown in Fig. 4. Thus, the best ANN architecture for plant dose determination was obtained with one input layer with 9 neurons (nodes), one hidden layer with 3 nodes, and one output layer with a single node.

ANNs of the coagulant model had RMSE of 5.25 mg/L and 5.26 mg/L for train and test datasets. The best ANN showed satisfactory R^2 of 0.75 for both train and test datasets. The RMSE of optimal ANN performance indicates the small discrepancies between the predicted and actual alum doses as the actual alum doses were between 40 and 90 mg/L. B1 and B2 in Fig. 5 are two stages of biases. The bias of B2 to O1, B1 to H1, B1 to H2, B1 to H3 is −2.32, 4.58, 3.45, 2.17, respectively, which are small errors. These indicate the viability of using ANNs to predict alum doses for WTPs using UV–Vis spectral data.

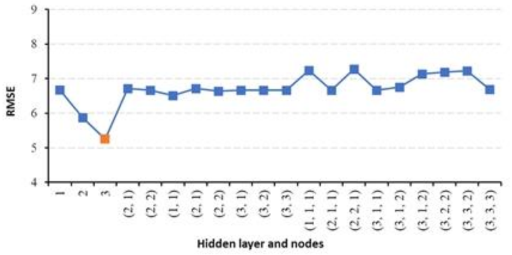

Fig. 4. Optimal number of hidden layer and nodes.

ANNs have been applied to predict coagulant doses for WTPs by other researchers based on raw water quality parameters [1,45–47,49]. It is a well-known pattern recognition technique for solving complex problems. ANNs was used to determine alum doses for surface water treatment based on physio-chemical parameters of the raw water [10,14]. There are also software sensors using ANNs for online prediction of coagulant doses with the raw water quality parameters [1,6]. A study incorporated the operators' experience in coagulant dose determination using a time consistent mode [2]. All the above support that UV–Vis combined with ANNs could mimic the operators' experience in the determination of coagulant dose for WTPs under the optimal pH condition to achieve target DOC level of less than 5 mg/L for the treated water quality.

3.5. *Assess coagulant determination model performance*

Three modelling techniques, MLR, PLS and ANNs were applied to determine the alum dose using the selected UV spectra (250–270 nm) of raw water at HV WTP. According to the modelling performance indicators (RMSE and R^2) as shown in Fig. 2, all three methods can be used to predict plant alum doses with the UV–Vis spectra. The use of UV–Vis spectra combined with PLS or ANNs has been studied for the determination of TOC, DOC and water quality index [15,16,50]. ANNs are the most commonly used technique to predict coagulant dose with the employment of the water quality parameters [1,2,10,13] as inputs. Our results revealed that ANNs may not be the best modelling tool for alum dose predictions with the UV–Vis spectral data. MLR and PLS methods showed almost identical performance in terms of prediction of plant alum doses with small values of RMSE and high R^2. MLR and PLS had better performance with smaller RMSE and high R^2 values than ANNs in modelling of alum dose using UV–Vis spectra. MLR is a simple method that can directly define the coefficient of each parameter for coagulation determination. The developed three coagulant dose determination models can well adapt to the variations of raw water quality (Fig. S2 in SI). The results indicate that the utilisation of UV–Vis spectra of raw water combined with MLR or PLS can mimic operator decisions in the selection of alum doses. There is a potential of using a portable UV–Vis spectrophotometer combined with chemometrics (MLR and PLS) to assist operators for real-time coagulant dose prediction, especially when there is an unexpected change in raw water quality.

Coagulant doses for water treatment were typically determined by the operators based on multiple factors for process control. This study shows that coagulant doses can be determined for a WTP using only the UV–Vis spectra of raw water under the optimal pH condition to achieve the target DOC level for the treated water quality and comparable results were achieved. This study may be the first that directly utilities online UV–Vis spectra of raw water quality to determine plant doses. The combination of online UV–Vis spectra of raw water and coagulation dose determination models will allow better control of the coagulation process, particularly for sudden water quality change events such as heavy rainfalls. Potentially, an online submersible instrument combined with a chemometric model (MLR or PLS) can predict coagulant doses and provide decision support information for coagulation process control at WTPs.

4. Conclusion

This study may be the first that model plant doses based on online UV–Vis spectra of raw water quality. Modelling techniques with different levels of complexity, including MLR, PLS and ANNs, and variable selection methods were employed to build coagulant doses models for the HV WTP. Important variables that influence the modelling of the alum dose determination were selected using VIP, SR and R methods from the UV–Vis spectra of raw water. The selected variables were

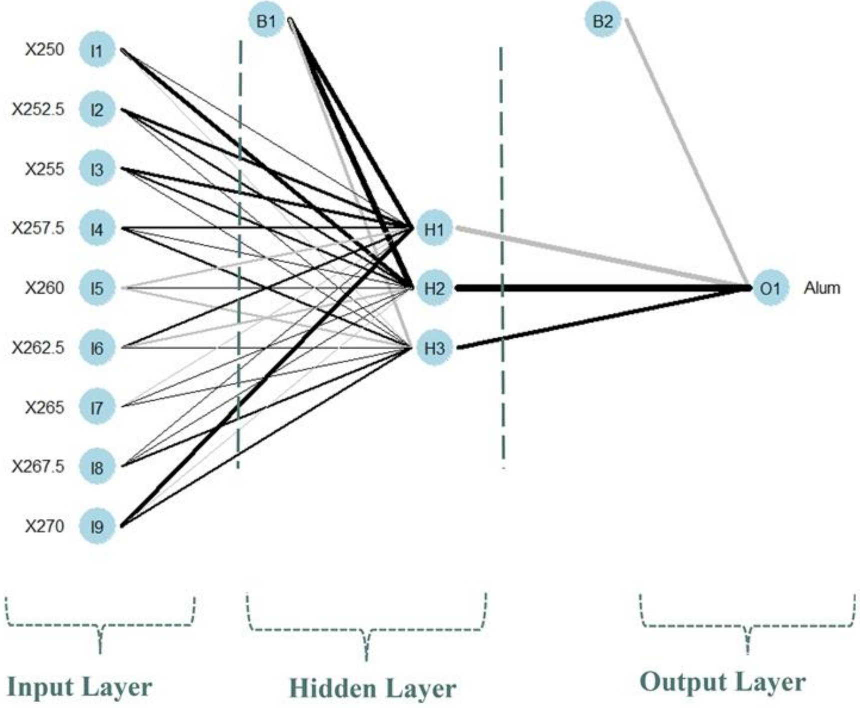

Fig. 5. Optimal ANNs architecture for alum dose prediction.

determined as nine wavelengths within 250–270 nm which revealed that the determination of coagulant doses of the HV WTP is mainly characterised in the UV region. The selected variables were used as inputs and plant doses were used as the outputs for modelling coagulant dose determinations.

Results show that all three techniques can model the alum dose prediction with the selected variables. MLR and PLS methods had an almost identical performance of predicting plant alum doses with small RMSE and high R^2. This study shows that the feasibility of predicting coagulant doses based on the UV–Vis spectral data of raw water combined with a chemometric model and the ability to mimic the operator decisions in selecting the appropriate doses for process control, under the optimal pH condition to achieve a target DOC level of less than 5 mg/L for the treated water quality. It is concluded that a submersible UV–Vis spectrophotometer combined with a chemometric model (MLR or PLS) has the potential to support operators effectively for real-time determination of coagulant doses for process control, under the fluctuation of the raw water quality.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jwpe.2021.102526.

References

[1] B. Lamrini, A. Benhammou, M.V. Le Lann, A. Karama, A neural software sensor for online prediction of coagulant dose in a drinking water treatment plant, Trans. Inst. Meas. Control. 27 (3) (2005) 195–213.

[2] Y. Liu, Y. He, S. Li, Z. Dong, J. Zhang, U. Kruger, An auto-adjustable and time-consistent model for determining coagulant dosage based on Operators' experience, IEEE Trans. Syst. Man Cybernet.: Syst. 51 (9) (2019) 5614–5625.

[3] I.O. Adebayo, O.O. Olukowi, Z. Zhiyuan, Y. Zhang, Comparisons of coagulation efficiency of conventional aluminium sulfate and enhanced composite aluminium sulfate/polydimethyldiallylammonium chloride coagulants coupled with rapid sand filtration, J. Water Process Eng. 44 (2021), 102322.

[4] A.S. Aiswarya, K. Nithya, J.J. Nittin, ANN-Based modelling for coagulant dosage in drinking water treatment plant, International Research Journal of Engineering and Technology 06 (05) (2019), 6138-6144.

[5] L. Li, S. Rong, R. Wang, S. Yu, Recent advances in artificial intelligence and machine learning for nonlinear relationship analysis and process control in drinking water treatment: a review, Chem. Eng. J. 405 (2021), 126673.

[6] A. Mussared, C. Chow, M. Holmes, J. Van Leeuwen, U. Kaeding, Implementation of Predictive Alum Dose Control Systems in 77th Annual WIOA Victorian Water Industry Operations Conference and Exhibition, Bendigo Exhibition Centre, 2014.

[7] S. Heddam, A. Bermad, N. Dechemi, ANFIS-based modelling for coagulant dosage in drinking water treatment plant: a case study, Environ. Monit. Assess. 184 (4) (2012) 1953–1971.

[8] C.A.P. Kim, check <check>M., Prediction of settled water turbidity and optimal coagulant dosage in drinking water treatment plant using a hybrid model of k-means clustering and adaptive neuro-fuzzy inference system, Applied Water, Science 7 (7) (2017) 3885–3902.

[9] G.W. Ellis, A.G. Collins, X. Ge, C.R. Ford, Chemical dosing of small water utilities using regression analysis, J. Environ. Eng. 117 (3) (1991) 308–319.

[10] J. Van Leeuwen, C.W.K. Chow, D. Bursill, M. Drikas, Empirical mathematical models and artificial neural networks for the determination of alum doses for treatment of Southern Australian surface waters, J. Water Supply: Res. Technol.—AQUA 48 (3) (1999) 115–127.

[11] O. Bello, Y. Hamam, K. Djouani, Control of a coagulation chemical dosing unit for water treatment plants using MMPC based on fuzzy weighting, J. Water Proc. Eng. 4 (2014) 34–46.

[12] C.D. Jayaweera, M.R. Othman, N. Aziz, Improved predictive capability of coagulation process by extreme learning machine with radial basis function, J. Water Proc. Eng. 32 (2019), 100977.

[13] H.R. Maier, N. Morgan, C.W. Chow, Use of artificial neural networks for predicting optimal alum doses and treated water quality parameters, Environ. Model Softw. 19 (9) (2004) 485–494.

[14] F.C.R. dos Santos, A.F.H. Librantz, C.G. Dias, S.G. Rodrigues, Intelligent system for improving dosage control, Acta Scientiarum. Technology 39 (1) (2017) 33–38.

[15] A. Vallet, F. Moiroux, J.B. Charlier, Optimization of high-resolution monitoring of nutrients and TOC in Karst waters using a Partial Least-Squares regression model of a UV–Visible spectrometer, in: Advances in Karst Scienc, Springer, Cham, 2020. Eurokarst 2018, Besançon.

[16] J. Li, Y. Tong, L. Guan, S. Wu, D. Li, Optimization of COD determination by UV–vis spectroscopy using PLS chemometrics algorithm, Optik 174 (2018) 591–599.

[17] N.D. Lourenço, J.C. Menezes, H.M. Pinheiro, D. Diniz, Development of PLS calibration models from UV-vis spectra for TOC estimation at the outlet of a fuel park wastewater treatment plant, Environ. Technol. 29 (8) (2008) 891–898.

[18] S. Rathnaweera, H. Ratnaweera, O. Lindholm, Multi-parameter based dosing control as an efficient tool for improved phosphate removal by coagulation-experiences from Beijing, in: International Forum on Environment Simulation and Pollution Control, 2009, p. 14. Beijing.

[19] J. Colton, A, Method of Calculating a Water Treatment Chemical Dose, 2009.

[20] M. Zhou, F. Meng, Aluminum-induced changes in properties and fouling propensity of DOM solutions revealed by UV–vis absorbance spectral parameters, Water Res. 93 (2016) 153–162.

[21] Z. Shi, C.W. Chow, R. Fabris, J. Liu, B. Jin, Alternative particle compensation techniques for online water quality monitoring using UV–Vis spectrophotometer, Chemom. Intell. Lab. Syst. 204 (104074) (2020).

[22] M. Drikas, C.W. Chow, J. House, M.D. Burch, Using coagulation, flocculation, and settling to remove toxic cyanobacteria, J. Am. Water Works Assoc. 93 (2) (2001) 100–111.

[23] Z. Shi, C.W. Chow, R. Fabris, T. Zheng, J. Liu, B. Jin, Evaluation of the impact of suspended particles on the UV absorbance at 254 nm (UV 254) measurements using a submersible UV-Vis spectrophotometer, Environ. Sci. Pollut. Res. 28 (10) (2021) 12576–12586.

[24] R Core Team, R, A Language and Environment for Statistical Computing, Foundation for Statistical Computing, 2019.

[25] M. Farrés, S. Platikanov, S. Tsakovski, R. Tauler, Comparison of the variable importance in projection (VIP) and of the selectivity ratio (SR) methods for variable selection and interpretation, J. Chemom. 29 (10) (2015) 528–536.

[26] L. Li, D. Lin, J. Wang, L. Yang, Y. Wang, Multivariate analysis models based on full spectra range and effective wavelengths using different transformation techniques for rapid estimation of leaf nitrogen concentration in winter wheat, Front. Plant Sci. 11 (2020) 755.

[27] D. Xu, W. Fan, H. Lv, Y. Shan, Y. Liang, G. Li, Z. Yang, L. Yu, Simultaneous determination of traces amounts of cadmium, zinc, and cobalt based on UV–Vis spectrometry combined with wavelength selection and partial least squares regression, Spectrochim. Acta A Mol. Biomol. Spectrosc. 123 (2014) 430–435.

[28] T. Mehmood, K.H. Liland, L. Snipen, S. Sæbø, A review of variable selection methods in partial least squares regression, Chemom. Intell. Lab. Syst. 118 (2012) 62–69.

[29] L. Rieger, G. Langergraber, M. Thomann, N. Fleischmann, H. Siegrist, Spectral in-situ analysis of NO2, NO3, COD, DOC and TSS in the effluent of a WWTP, Water Sci. Technol. 50 (11) (2004) 143–152.

[30] B. Mevik, R. Ron Wehrens, K.H. Liland, pls: Partial Least Squares and Principal Component Regression, 2019. R package version 2.7-2.

[31] J. Jawad, A.H. Hawari, S.J. Zaidi, Artificial neural network modeling of wastewater treatment and desalination using membrane processes: a review, Chem. Eng. J. 419 (2021), 129540.

[32] S. Fritsch, F. Guenther, M. Wright, neuralnet: Training of Neural Networks, 2019. R package version 1.44.2.

[33] Y.L. Guo, R. Ye, Q. Duan, Advances on water quality detection by UV-Vis spectroscopy, Appl. Sci. 10 (19) (2020) 6874.

[34] B. Chen, H. Wu, S.F.Y. Li, Development of variable pathlength UV–vis spectroscopy combined with partial-least-squares regression for wastewater chemical oxygen demand (COD) monitoring, Talanta 120 (2014) 325–330.

[35] C. Kim, J.B. Eom, S. Jung, T. Ji, Detection of organic compounds in water by an optical absorbance method, Sensors 16 (1) (2016) 61.

[36] J.K.A. Edzwald, G.S. Kaminski, A practical method for water plants to select coagulant dosing, J. New Engl. Water Works Assoc. 123 (1) (2009) 15.

[37] T. Mehmood, S. Sæbø, K.H. Liland, Comparison of variable selection methods in partial least squares regression, J. Chemom. 34 (6) (2020) 3226.

[38] X. Li, J. Sha, Z.L. Wang, A comparative study of multiple linear regression, artificial neural network and support vector machine for the prediction of dissolved oxygen, Hydrol. Res. 48 (2017) 1214–1222.

[39] H.Z. Abyaneh, Evaluation of multivariate linear regression and artificial neural networks in prediction of water quality parameters, J. Environ. Health Sci. Eng. 12 (1) (2014) 1–8.

[40] S. Heddam, Extremely randomized tree: a new machine learning method for predicting coagulant dosage in drinking water treatment plant, Water Eng. Model. Mathemat. Tools (2021) 475–489.

[41] A.T. Vo, N.T. Pham, Q.H. Huynh, P.T.D. Nguyen, D.X.V. Phan, C.D. Hoang, Using iron alum in surface water treatment, in: IOP Conference Series: Materials Science and Engineering, IOP Publishing, 2020, p. 042001, 869.

[42] D.M.A. Ghaitidak, K.D. Yadav, Effect of coagulant in greywater treatment for reuse: selection of optimal coagulation condition using analytic hierarchy process, Desalinat. Water Treat. 55 (4) (2015) 913–925.

[43] A. Avagyan, B.R. Runkle, L. Kutzbach, Application of high-resolution spectral absorbance measurements to determine dissolved organic carbon concentration in remote areas, J. Hydrol. 517 (2014) 435–446.

[44] S.A.H.F. Nilsson, Quicker response to Quality changes in incoming water with decision support for coagulant dosage at görväln drinking water plant, J. Water Manag. Res. 71 (2015) 183–190.

[45] C.M. Kim, M. Parnichkun, MLP, ANFIS, and GRNN based real-time coagulant dosage determination and accuracy comparison using full-scale data of a water treatment plant, J. Water Supply: Res. Technol.—AQUA 66 (01) (2017) 49–61.

[46] M.H.A.C.S. Baouab, Prediction of the optimal dose of coagulant for various potable water treatment processes through artificial neural network, J. Hydroinformat. 20 (6) (2018) 1215–1226.

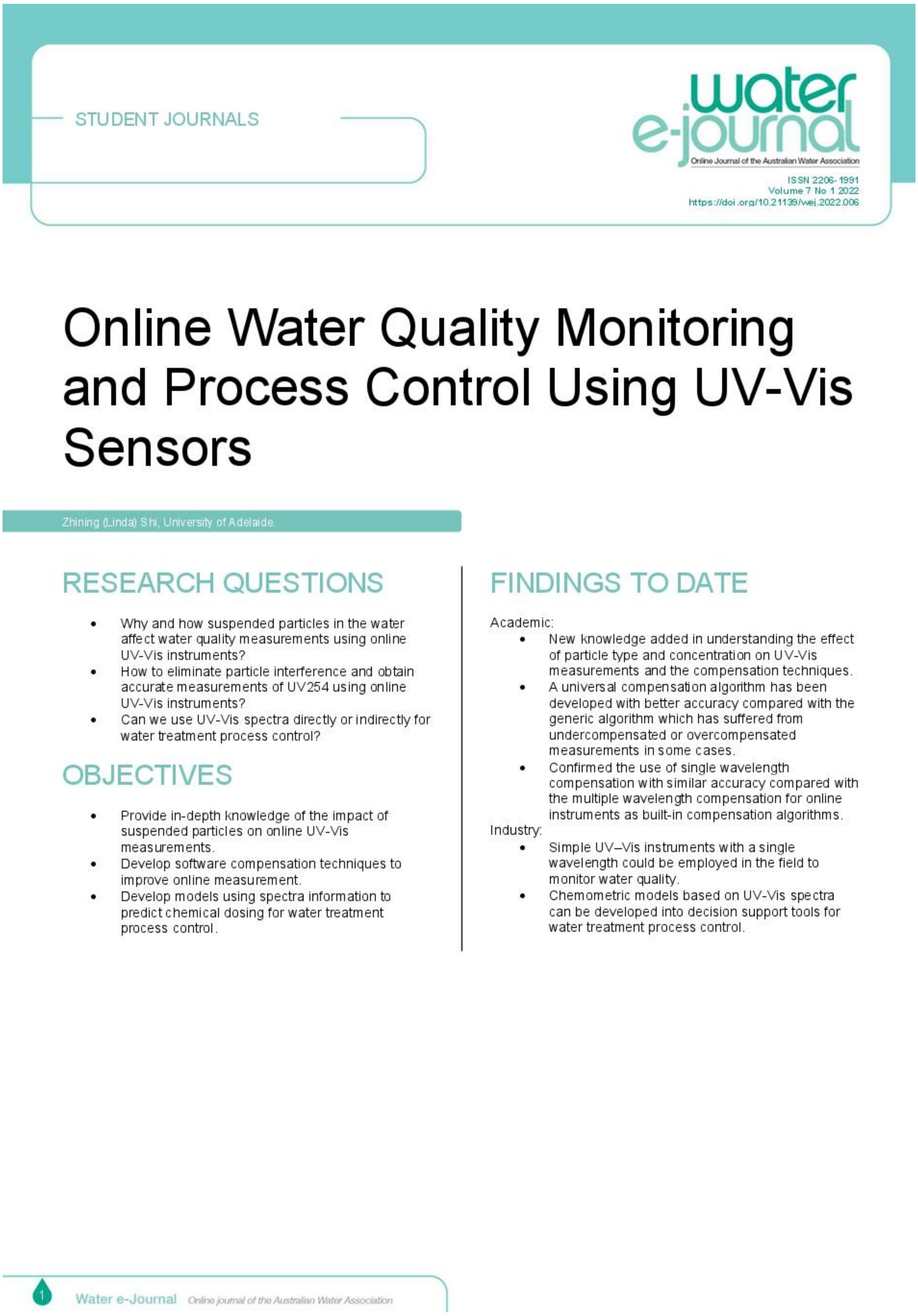
[47] S. Haghiri, A. Daghighi, S. Moharramzadeh, Optimum coagulant forecasting by modeling jar test experiments using ANNs, Drinking Water Eng. Sci. 11 (1) (2018) 1–8.

[48] A.S.A. Kote, D.V. Wadkar, Modeling of chlorine and coagulant dose in a water treatment plant by artificial neural networks, Eng. Technol. Appl. Sci. Res. 9 (3) (2019) 4176–4181.

[49] G.D.A.L. Wu, S. Lo, Predicting real-time coagulant dosage in water treatment by artificial neural networks and adaptive network-based fuzzy inference system, Eng. Appl. Artif. Intell. 21 (8) (2008) 1189–1195.

[50] E.M. Alves, R.J. Rodrigues, C. dos Santos Corrêa, T. Fidemann, J.C. Rocha, J.L. L. Buzzo, P. de Oliva Neto, E.G.F. Núñez, Use of ultraviolet–visible spectrophotometry associated with artificial neural networks as an alternative for determining the water quality index, Environ. Monit. Assess. 190 (6) (2018) 1–15.

Appendix F



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Online Water Quality Monitoring and Process Control Using UV-Vis Sensors

Zhining (Linda) Shi, University of Adelaide.

RESEARCH QUESTIONS

- Why and how suspended particles in the water affect water quality measurements using online UV-Vis instruments?
- How to eliminate particle interference and obtain accurate measurements of UV254 using online UV-Vis instruments?
- Can we use UV-Vis spectra directly or indirectly for water treatment process control?

OBJECTIVES

- Provide in-depth knowledge of the impact of suspended particles on online UV-Vis measurements.
- Develop software compensation techniques to improve online measurement.
- Develop models using spectra information to predict chemical dosing for water treatment process control.

FINDINGS TO DATE

Academic:

- New knowledge added in understanding the effect of particle type and concentration on UV-Vis measurements and the compensation techniques.
- A universal compensation algorithm has been developed with better accuracy compared with the generic algorithm which has suffered from undercompensated or overcompensated measurements in some cases.
- Confirmed the use of single wavelength compensation with similar accuracy compared with the multiple wavelength compensation for online instruments as built-in compensation algorithms.

Industry:

- Simple UV–Vis instruments with a single wavelength could be employed in the field to monitor water quality.
- Chemometric models based on UV-Vis spectra can be developed into decision support tools for water treatment process control.