Current Online Water Quality Monitoring Methods and Their Suitability for the Western Corridor Purified Recycled Water Scheme

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The Urban Water Security Research Alliance (UWSRA) is a $50 million partnership over five years between the Queensland Government, CSIRO's Water for a Healthy Country Flagship, Griffith University and The University of Queensland. The Alliance has been formed to address South-East Queensland's emerging urban water issues with a focus on water security and recycling. The program will bring new research capacity to South-East Queensland tailored to tackling existing and anticipated future issues to inform the implementation of the Water Strategy.

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Description: Current system configuration of six self-contained sensing probes
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FOREWORD

Water is fundamental to our quality of life, to economic growth and to the environment. With its booming economy and growing population, Australia's South-East Queensland (SEQ) region faces increasing pressure on its water resources. These pressures are compounded by the impact of climate variability and accelerating climate change.

The Urban Water Security Research Alliance, through targeted, multidisciplinary research initiatives, has been formed to address the region's emerging urban water issues.

As the largest regionally focused urban water research program in Australia, the Alliance is focused on water security and recycling, but will align research where appropriate with other water research programs such as those of other SEQ water agencies, CSIRO's Water for a Healthy Country National Research Flagship, Water Quality Research Australia, eWater CRC and the Water Services Association of Australia (WSAA).

The Alliance is a partnership between the Queensland Government, CSIRO's Water for a Healthy Country National Research Flagship, The University of Queensland and Griffith University. It brings new research capacity to SEQ, tailored to tackling existing and anticipated future risks, assumptions and uncertainties facing water supply strategy. It is a $50 million partnership over five years.

Alliance research is examining fundamental issues necessary to deliver the region's water needs, including:

- ensuring the reliability and safety of recycled water systems.
- advising on infrastructure and technology for the recycling of wastewater and stormwater.
- building scientific knowledge into the management of health and safety risks in the water supply system.
- increasing community confidence in the future of water supply.

This report is part of a series summarising the output from the Urban Water Security Research Alliance. All reports and additional information about the Alliance can be found at http://www.urbanwateralliance.org.au/about.html.

C. Davis

Chris Davis
Chair, Urban Water Security Research Alliance

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EXECUTIVE SUMMARY

This report forms part of the Water Quality Monitoring Technology and Information Collection System research project jointly undertaken by CSIRO and Griffith University under the Urban Water Security Research Alliance. The report presents a broad overview of the current state of online water quality monitoring systems from both research and commercial perspectives. It provides a summary of commercially available methods, and details the strengths and limitations of existing online monitoring technology for the purpose of real-time water quality monitoring within different treatment barriers of the Western Corridor Recycled Water (WCRW) scheme. There has been a shift towards online water quality monitoring in the WCRW scheme because of the new Queensland Recycled Water Guidelines (QRWG), which specify that continuous or online analysers are preferred to discrete or grab sampling at critical control points (CCPs) to mitigate health hazards associated with the PRW scheme.

The report briefly describes why online water quality monitoring is important to guarantee a consistent supply of PRW, and also gives an overview of uses and applications of online monitoring tools for the WCRW project that can identify particular hazards and provide early warning of treatment failure or a decline in system performance. A summary of water quality parameters that are required to be monitored at each treatment barrier is presented, along with details of ideal online analyser requirements to obtain continuous, reliable water quality information.

It was found that obtaining reliable low maintenance continuous online analysers for Barriers 1 and 2 is problematic, and is a real challenge for commercial systems currently available due to the difficult nature of the measurement environment.

In addition, due to the geographic separation of the PRW components and the diversified measurement conditions associated with each treatment barrier, a large number of widely separated instruments are required. Consequently, to obtain reliable online water quality information, it is recommended that online analysers must be capable of autonomous operation, especially at Barriers 1, 6 and 7. They must also be capable of maintaining their calibration status for lengthy periods and have acceptable (low) maintenance costs. The analysers must be resistant to biofouling, signal drift and blockages. In addition, the analytical performance must not be significantly affected by matrix interferences, so that the results can be directly used to optimise operational management procedures. For Barriers 1 and 2, biofouling and blockages are likely to be a major issue due to the harsh nature of the measurement environment. For Barriers 5-7 the analysers must have the resolution required to ensure compliance of the parameters measured with the Australian Drinking Water Guidelines (ADWG) and Australian Recycled Water Guidelines (ARWG).

During the review it became evident that most online analysers have difficulty obtaining continuous, accurate and cost-effective water quality information, as most were based on direct adaptations of standard laboratory-based methods, which were not originally designed for field applications. Consequently, the online monitoring techniques/analysers available generally suffer from more problems than when used for laboratory-based analysis. Online systems require frequent calibration and maintenance, and may be prone to matrix interferences, biofouling, blockages and signal drift, as they must operate in variable non-ideal measurement environments. Therefore, there are significant economic and logistics costs associated with maintaining the equipment, especially for remote monitoring locations. These factors have greatly limited the widespread application of online instrumentation, especially for large-scale remote water quality monitoring, since there is no cost effective online monitoring technology currently available that can operate autonomously for extended periods of time.

In light of this, it is recommended that when selecting online analysers for the PRW system, special care should be taken to ensure that the analysers employed are appropriate for their intended use.

The report describes current approaches and technological advances associated with improving the performance of online monitoring systems. It was found that there is not one single approach that can resolve the problems associated with improving existing online monitoring performance.

More selective sensors have been developed, but it is very difficult to apply these successfully for online applications, where there are often significant fluctuations in measuring environments and sample matrices. This is particularly the case for Barriers 1, 2 and 6, which are subject to the most variable sample matrix conditions. This could also be a factor at Barrier 7 for online analysers located within the distribution network, when potable water from desalination, PRW and different conventional water sources are blended together as part of the SEQ Water Grid.

Although lab-on-chip technology shows promise, it is still prone to blockages, and requires fixed internal measurement environments and regular calibration to compensate for signal drift. Therefore these devices are not suitable for large-scale water quality monitoring applications in their current form.

Methods such as interference ion compensation and customised standards have been developed to improve online sensor performance to matrix interferences, but there are still significant drawbacks with these techniques which make them non-viable for changeable real world measurement environments.

Most field analysers currently available still require regular maintenance to guarantee their reliability. Therefore, there is a definite need to develop cost-effective online water quality monitoring technology that can maintain its calibrated status for prolonged periods of time and operate reliably irrespective of environmental or sample matrix conditions. It is also highly desirable that the instruments should use limited or no reagents, so that they are viable for large-scale remote monitoring applications. In addition, membrane fouling, signal drift and matrix interferences still need to be addressed and improved, to make online water quality monitoring economically and logistically viable for large-scale applications such as the Western Corridor Recycled Water (WCRW) Project.

The report reviews a number of commercial sensors potentially suited to the WCRW scheme and showcases a range of online analysers produced by key market players and details their suitability for each treatment barrier, based on key water quality parameters that are required to be monitored in the PRW closed loop system.

It was evident that there are online analysers available for most organic load indicators, nutrients, physicochemical parameters and inorganic ions. However, it should be noted that their performance can be impaired in the field if employed for continuous monitoring purposes. It was also found that manufacturers' specifications sometimes do not adequately reflect the actual performance of analysers in continuous, real world measurement environments. It is strongly recommended that water utilities should independently investigate the operation and performance of any analysers selected to ensure that they are in fact suitable for the intended use.

Online heavy metal analysis is becoming more important because of the requirement to mitigate risks associated with the WCRW scheme. The review indicated that there is a pressing need for the development of new cost-effective techniques, because direct adaptations of conventional laboratory-based methods such as AAS or ICP-MS are unsuitable as online monitoring tools due to separation and extraction costs. It was found that Electronic tongues (E-tongues) or voltametric measurement principles that are currently being investigated may offer an alternative and cost effective approach.

Rapid microbial analysis is also essential for the WCRW project to mitigate risks associated with the three main classes of pathogens - viruses, bacteria and protozoa. The review highlighted that surrogate indicators such as turbidity or free chlorine are the only commercially available online tools for monitoring pathogens. Although biosensors show promise, there are no commercially available sensors which have reliable performance equivalent to that of equivalent chemical sensors (e.g. pH). Electronic tongues or software sensors may offer promise in this area, so long as the appropriate microbial sensing surfaces can be determined and manufactured. However it should be noted that this is a rapidly developing field, especially for monitoring toxicity. In light of this information, it is recommended that online microbial analysis tools that are robust, sensitive and require limited maintenance should be developed for the WCRW system, especially for monitoring the three main classes of pathogens.

For pesticides, EDCs, Pharmaceuticals, THMs, NDMA and VOCs, there are no commercially and economically viable online monitoring systems available for the WCRW project. However, it was noted in the research and development section that software sensors such as E-tongues and E-noses could offer some potential in the future if further developed. They have the potential to reduce the number of analysers required whilst maximising the number of water quality parameters that can be determined, thereby reducing reagent costs and maintenance associated with online monitoring.

It was also found that at present there are a number of important water quality parameters that cannot be monitored in real-time. As it is difficult for operators and grid managers to mitigate risks of which they are not aware, it is highly desirable that early warning systems should be implemented using surrogate measures that can indicate deviations from baseline water quality, irrespective of seasonal, diurnal and temporal variations. Such systems could be used to alert to an abnormal condition, or to indicate situations such as a hazard threatening to overwhelm the treatment process.

1. AIM OF THE REVIEW

The aim of this report is to review methods currently available for online monitoring of environmental water quality, with specific applications to wastewater, fresh water and purified recycled water (PRW). This report addresses:

- Water quality monitoring and sensing requirements for the PRW closed loop system;
- Current online water quality monitoring methods;
- Commercially available sensors and their suitability for the seven barrier approach; and
- Current developments in online water quality technology that may have potential applications in the WCRW project to further strengthen the baseline water quality monitoring practices.

2. OVERVIEW OF THE PRW SYSTEM

The Western Corridor Recycled Water (WCRW) Scheme is designed to supplement the traditional South East Queensland (SEQ) freshwater supplies with purified recycled water (PRW). It is Australia's largest recycled water project and the Advanced Water Treatment Project is considered the third largest project of its kind in the world. The WCRW project will deliver up to 232 ML/day of PRW to power stations, industry, agriculture and the Wivenhoe Dam, which will be achieved using a multi-barrier treatment process to mitigate the hazards associated with water recycling. The closed loop PRW system will process raw wastewater from 6 sewer catchments through a seven-barrier treatment process to produce PRW to supplement existing freshwater resources at Wivenhoe Dam (Figure 1). The WCRW project will form part of the SEQ water grid (see Figure 2).

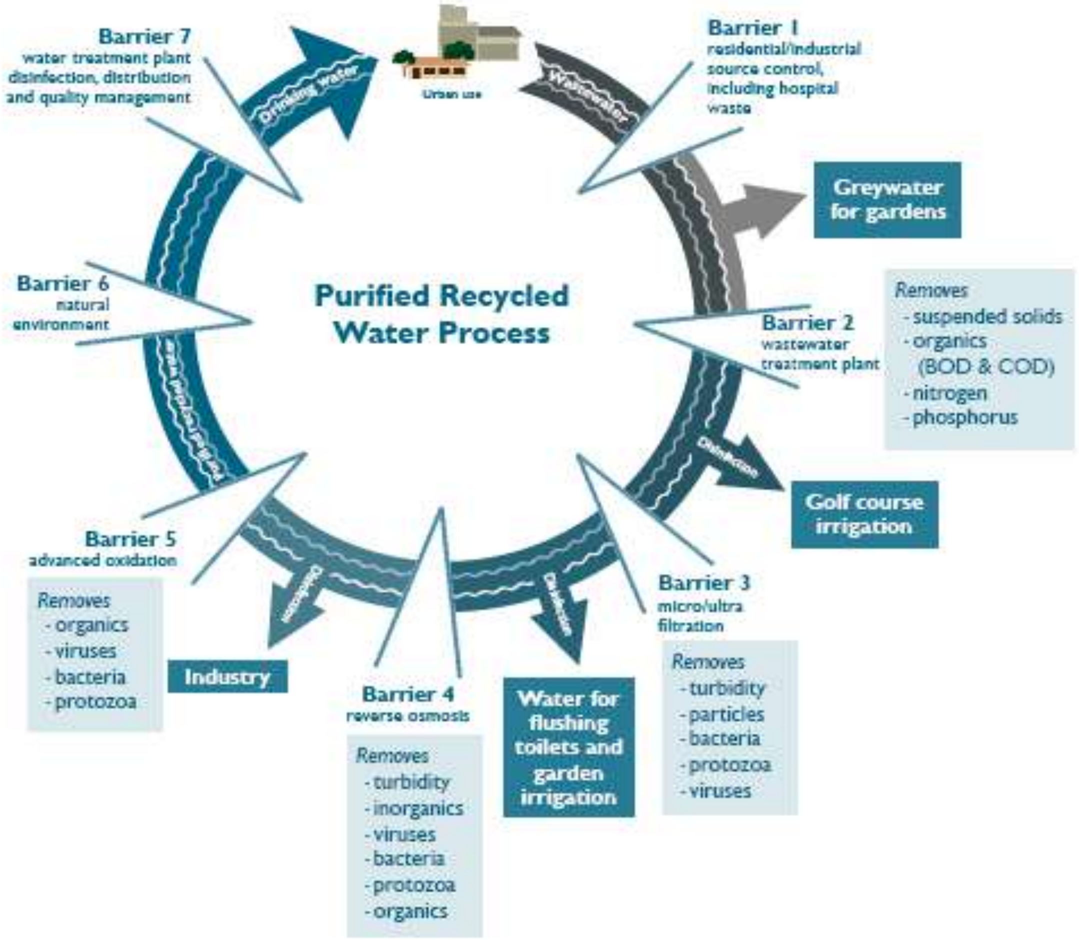

Figure 1 Schematic diagram of the Seven-Barrier treatment process employed in the WCRW Project (source: Queensland Water Commission Fact Sheet 4[1])

The multi-barrier treatment process employed for the PRW scheme can only be effective when timely information is available to determine if the water quality is fit for its intended use prior to it being released to the next treatment barrier. This is to ensure that the treated water produced within each barrier of the supply chain complies from both a human health and environmental health perspective, under the *Water Supply (Safety and Reliability) Act 2008*[3], to ensure a consistent safe supply of PRW.

It is therefore essential that each stakeholder operating within each treatment barrier obtains the appropriate water quality information in real-time, to ensure the integrity of each barrier can be maintained according to a Hazard Analysis Critical Control Point (HACCP) based management approach[3]. To achieve this, the Queensland Recycled Water Guidelines (QRWG) recommend online or continuous analysers be employed for operational monitoring, in preference to discrete or grab samples for Critical Control Points (CCPs), Quality Control Points (QCP) and Critical Measures (CM) that have been identified through HACCP[3]. This is to ensure that the recycled water produced within each barrier is of a quality specified for its intended use, and to shift to a more preventative management approach for the PRW system. If the monitoring is not continuous and non-conformance is detected, the corrective action will have to be applied to all non-conforming recycled water since the last sample was taken[3]. Therefore, a consistent supply of PRW can only be achieved effectively when continuous, real-time, accurate water quality information is employed for operational monitoring purposes.

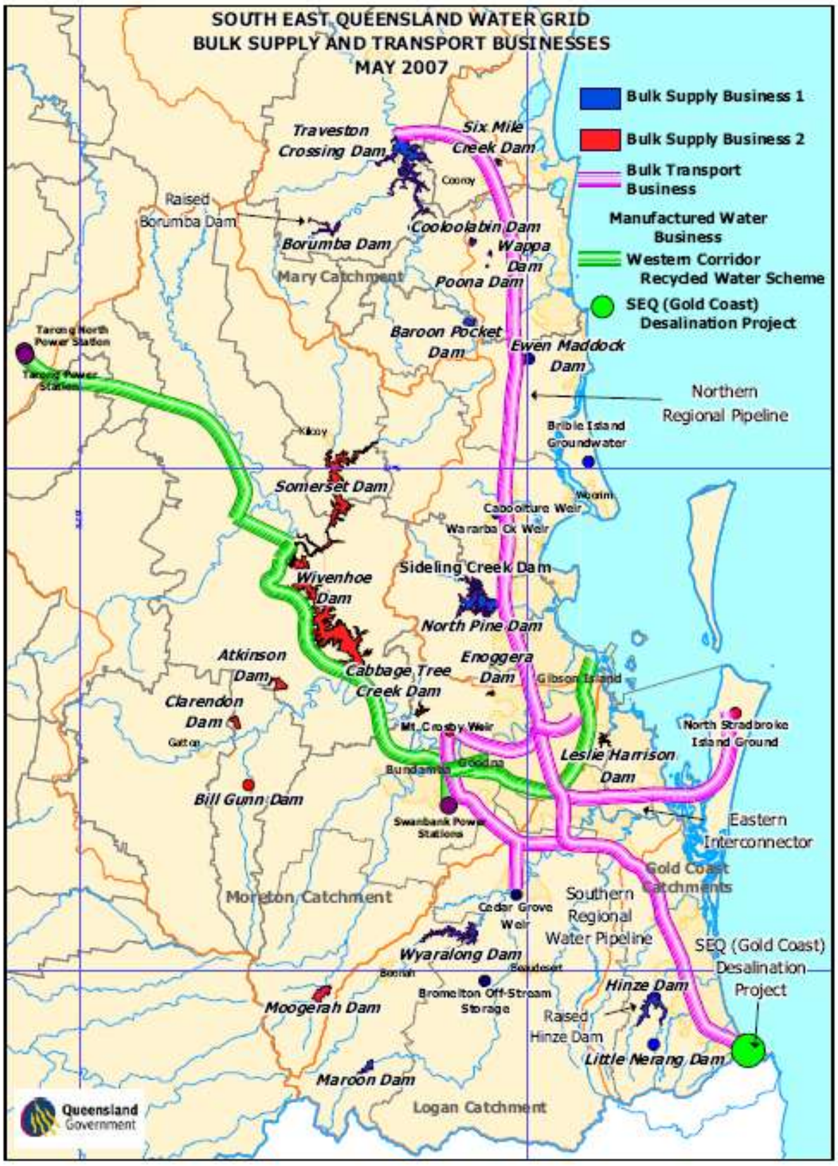

Figure 2 Schematic diagram of the South East Queensland (SEQ) Water Grid, which will include the WCRW project. (Urban Water Supply Arrangement in South East Queensland[2])

3. ONLINE WATER QUALITY REQUIREMENTS FOR THE WCRW SCHEME

As the quality of PRW produced within the WCRW project should be consistent, irrespective of seasonal, diurnal and temporal variations[3], there are a number of water quality parameters that must be monitored operationally to assess the treatment performance of each barrier. This means that reliable online measurements of critical water quality parameters that cover its microbial, physical and chemical properties are of high importance. They would also improve baseline water quality monitoring strategies and assist operators and grid managers to maintain the integrity of each barrier. Online water quality monitoring tools are required that assist operators to:

- Identify non-conformance and implement corrective actions;
- Identify if particular hazards are compromising the system;
- Provide early warning identification of hazards that may cause system failure;
- Indicate CCP and Critical Operation Points (COP), or can be used as surrogate indicators. COP are used to control water quantity hazards, whereas CCP are used for controlling the quality associated with a health based hazard;
- Provide real-time trend analysis to indicate a decline in system performance;
- Identify false positive and false negative errors;
- Optimise treatment processes according to diurnal, seasonal and temporal variations, given that there may be a lack of suitable historical information available to operators;
- Identify cross connection or infiltration problems; and
- Assist trade waste operators to identify and track illegal discharges.

In the transition to a closed loop PRW system, over 360 Indirect Potable Reuse (IPR) contaminants of concern have been identified, in addition to conventional parameters of importance. These can be classified into the following categories:

- Organic Loads (with emphasis on BOD and COD)
- Suspended Solids
- Total Nitrogen
- Total Phosphorus
- Inorganics
- Heavy metals
- Physicochemical parameters
- Microbiological contaminant indicators, such as E. Coli
- Pesticides
- Endocrine Disrupting Compounds (EDCs)
- Radioactive materials
- Volatile Organic Carbons (VOC) and Trihalomethanes (THM)
- Haloacetic acids (HAA)
- Nitrosamines
- Pharmaceuticals.

These parameters were identified based on a number of factors:

- Review of current scientific literature on reuse applications;
- Sewer catchment characterisation;
- Those which may affect the treatment processes within the Wastewater Treatment Plant (WWTP) or the Advanced Water Treatment Plant (AWTP);
- Those which could be produced during the treatment processes;
- Those intentionally or incidentally designed to be removed within each barrier; and
- Those that may impair the quality of product water produced if the contaminants exceed the Australian Drinking Water Guidelines[4] or Australian Recycled Water Guidelines[5].

The number of parameters per category that are required to be measured within each barrier to ensure that treatment efficiency can be maintained is shown in Table 1.0. While it is difficult to monitor for all parameters, especially IPR contaminants of concern, it is highly recommended that specific hazards which may influence the final quality should be monitored continuously. In addition, online sensors that could be used as surrogate parameters for important contaminants that cannot be currently measured in real-time would also be highly desirable. Therefore it is recommended that where possible, online monitoring of treated water should be instituted for all contaminants or indicators that pose a human health risk[3].

The following section briefly describes each treatment barrier within the WCRW scheme and details ideal online analyser requirements.

Barrier 1

Barrier 1 focuses on the control of industrial, commercial and residential source wastewater entering the sewer catchment from a significant number of entry points. It is one of the most important barriers and it must be controlled effectively[3], as production of high quality PRW is dependent on the quality of source water obtained from the sewer catchment.

Therefore, online water quality monitoring technology required for Barrier 1 must be capable of operating:

- Reliably and accurately for prolonged periods of times;
- Robustly in a range of harsh measurement environments from industrial, commercial and residential sources, without being affected by matrix interferences; and
- Continuously and reliably in highly turbid environments where suspended solids concentrations are high. Hence, online analysers employed in this barrier must be resistant to biofouling, signal drift and blockages.

It should be noted that obtaining reliable, low maintenance, continuous online analysis at this barrier is a real challenge using currently available commercial systems due to the complex nature of the measurement environment.

Barrier 2

The WWTPs are responsible for the treatment processes associated with Barrier 2. These are existing infrastructure and have been primarily designed for the removal of suspended solids, organic matter and nutrients. Treatment effectiveness has traditionally been monitored using parameters such as Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Total Nitrogen and Total Phosphorous. Although there is only one entry and exit point to the WWTP, the measurement environment is still considered extreme and harsh for online analysers[6] due to the complexity of the sample matrix[7]. In addition, the treatment processes are exposed to ambient conditions and as a consequence the analysers may also be influenced by environmental factors such as temperature and humidity[8].

To enable reliable and continuous online water quality information at this treatment barrier, online analysers must:

- Function in raw sewage influents of heterogeneous and variable compositions, with high and variable turbidity, nutrients, COD, BOD and suspended solids concentrations.
- Function in a treated wastewater sample matrix, which has a significantly lower turbidity, COD, BOD, suspended solids and nutrient concentration.
- Function reliably irrespective of seasonal, diurnal and temporal variations, including wide variations in hydraulic flow.
- Be resistant to sensor biofouling and signal drift to ensure that calibration can be maintained. Calibration intervals must be at most daily, however longer periods of time would be preferred.
- Must be able to function adequately irrespective of sample matrix conditions, to reduce measurement errors.

Therefore online analysers that are prone to fouling, blockages, matrix interferences and signal drift may not be suitable for this measurement barrier due to high costs associated with maintaining instruments to obtain reliable data.

Barrier 3

Barrier 3 will use Micro-Filtration (MF), which is designed for the removal of viruses, bacteria and protozoa with a minimum log removal efficiency of 3 Log 10. If treatment is successful, it will then be used as the feed water to Barrier 4, Reverse Osmosis (RO). Online analysers used in Barrier 3 must operate reliably in a relatively closed measurement environment with one defined entry and exit point. The online analysers will have to function reliably at the inlet where there may be source water variations, and after subsequent pre-treatment steps will operate in a more controlled measurement environment than at Barrier 2.

At Barrier 3, online analysers must have the following characteristics:

- Function reliably at the raw water inlet, in addition to the MF raw water and permeate. This is especially important for Bundamba AWTP that will receive raw water from four WWTPs within the scheme.
- Maintain their calibrated status irrespective of sample matrix conditions. For example, at the Bundamba AWTP, analysers must be capable of functioning accurately in a changeable measurement environment, as the raw source water is derived from four different WWTPs.
- Operate reliably at low concentration levels.

It is preferable for maintenance and calibration to be minimal, particularly as there are a number of online monitoring systems employed at this treatment barrier.

Barrier 4

Barrier 4 involves treatment using RO, which is designed to remove turbidity, organics, viruses, bacteria, and protozoa from the feed water through a molecular size exclusion process[9]. Once the RO permeate is treated to the required specification it will be subject to Advanced Oxidation (AO) in Barrier 5 for the purpose of producing Class A^+ PRW. The online analysers operating in this measurement environment must be capable of reliable, high sensitivity measurements in a relatively consistent measurement environment, with one defined entry and exit point.

Online analysers must have the following capabilities:

- Operate reliably in a high purity water matrix.
- Have adequate sensitivity for low level contaminants.
- It is imperative that sensors can function accurately and are capable of providing reliable information that can detect a decline in treatment performance or identify if a hazard is compromising the system.
- Preferable for maintenance and calibration requirements to be minimal, as large numbers of online analysers are employed for operational monitoring purposes.

Barrier 5

Barrier 5 uses AO to produce water of a higher quality than conventional water treatment processes, and will remove trace organics, pathogens, viruses, and protozoa in addition to NDMA and 1,4-dioxane. The treatment process has one defined entry and exit point. Once the PRW has been treated and the water stabilised and disinfected, it will be transported through the western corridor pipeline for treatment in the natural environment (Barrier 6). It is very important for Barrier 5 to maintain its integrity, and online analysers must be capable of reliable, continuous measurements to monitor the quality of PRW produced before it is released to Barrier 6.

Online analysers operating within this barrier must have the following capabilities:

- They must function accurately and reliably so that they can adequately maintain barrier integrity and detect failure before PRW is released into the natural environment.
- Analysers used for pH dosing, disinfection and water stabilisation must be reliable and insensitive to matrix interferences, to ensure that effective dosing is maintained.
- Must be robust enough to operate reliably in a low ionic strength environment, irrespective of environmental conditions.
- Preferable if maintenance and calibration requirements are minimal, as a large number of online analysers are employed for operational monitoring purposes.

Barrier 6

This comprises the second largest barrier within the supply chain of PRW in the WCRW project. Approximately 50-100 ML/day of PRW from 3 AWTPs will be delivered to Wivenhoe dam for a period of natural treatment. This treatment process involves retention in the dam for extended periods which will provide an additional environmental buffer to ensure the water is suitable for drinking purposes. The treatment barrier is open to the natural environment with a number of entry points, with PRW comprising one of the entry points. Hence the source water quality may vary depending on the inlet and environmental conditions such as high rainfall events.

Online analysers in this barrier should be capable of the following:

- Capable of functioning autonomously for prolonged periods of time in remote, unattended locations.
- Capable of functioning accurately and reliably irrespective of sample matrix conditions, as there are many sources of entry and the PRW will be blended with existing variable freshwater resources.
- As many of the sensors employed may be in situ, they need to maintain their calibrated status for extended periods.
- Sensors must be capable of operating reliably in high nutrient environments, especially in high rainfall events, without being prone to sensor fouling, signal drift or failure.

Barrier 7

The water treatment plant is the last treatment process in the PRW closed loop system. It will involve filtration, pH adjustment and disinfection of blended PRW prior to distribution to residential, industrial and commercial entities in SEQ. Once the water has been used, it will be discharged into Barrier 1 and the treatment process will commence once again. Online analysers must be capable of reliable measurements to ensure the potable water produced is fit for human consumption according to ADWG. In addition, if online analysers are installed in the distribution network, they must be capable of functioning:

- Autonomously for prolonged periods of time, as the distribution network covers an extended geographic area.
- Capable of responding accurately irrespective of climatic or environmental conditions such as temperature or changes in sample matrix.
- Must be able to maintain calibration in situ or online for prolonged periods of time with limited maintenance.
- Must have minimal occurrence of false positive and false negative events.
- Provide early warning on deteriorations in water quality irrespective of seasonal and diurnal trends.

Due to the wide geographic spread of the PRW project and diversified measurement conditions, a large number of widely separated instruments are required. Consequently any online analysers must be capable of autonomous, reliable and accurate measurements, their calibration status must be maintained at each barrier and they must have acceptable (low) maintenance costs.

4. REVIEW OF EXISTING ONLINE MONITORING ANALYSERS

Online water quality monitoring is a rapidly advancing field due to a number of strong drivers including those associated with global freshwater shortages. The scope of this review provides a broad overview of the current status of online monitoring systems from both a commercial and research perspective for the context of WCRW project. The following issues are discussed and addressed:

- Current performance of online analysers for continuous water quality monitoring;
- Future research directions and requirements to improve online analyser performance;
- Review of currently available commercial analysers and their suitability for each treatment barrier; and
- Review of current research and development pertaining to key water quality indicators.

The review has aimed to evaluate the commercial sensors currently available from the key major players based on their suitability for each barrier. Sensors have been classified according to their ability to address the analytical requirements for each barrier outlined as follows, based on the current manufacturers' specifications:

- Ability to operate in the relevant sample matrix and environmental conditions;
- Ability to achieve the level of sensitivity required to monitor the treatment processes within each barrier;
- Calibration and maintenance requirements for each barrier; and
- Type of method and its suitability for each barrier.

It should be noted that the manufacturers' specifications sometimes do not adequately reflect the actual performance of analysers in continuous, real-world measurement environments. Therefore, this evaluation is based on the ideal performance characteristics of the analysers, as presented by the manufacturers. However, the common experience is that commercially available online analysers require frequent calibration and maintenance to enable continuous, reliable measurements over prolonged periods of time. Consequently, it is recommended that when water utilities are selecting analysers for specific water quality monitoring purposes, they should thoroughly investigate the operation and performance of the instruments to ensure that they are suitable for their intended use based on the following factors:

- Economic costs associated with maintenance and calibration;
- Robustness to reliably and continuously operate in non-ideal environmental conditions;
- Ability to be linked with a centralised Supervisory Control and Data Acquisition (SCADA) system; and
- Ability to process data in real-time and provide accurate water quality information.

It is recommended that water utilities should also engage with other water utilities that have employed particular online analysers to obtain honest feedback on the instruments performance and reliability.

Table 1 Number of water quality parameters required at each barrier to verify the treated water is of a specified quality for its intended use

Water Quality Indicators Classes	Barrier 1	Barrier 2	Barrier 2/ 3	Barrier 3	Barrier 4 (RO Feed and Permeate)	Barrier 5	Barrier 6	Barrier 7
Microbiological		4				4		7
Inorganic Disinfection By-Products						5		
Metals		26	24		10	21		10
Inorganic Anions		5	7		5	5		
Radionuclides			1			3		
Nutrients	5	8	5		5	4		3
Organics	2	4	2		1	1		
Physical Parameters	4	8	5		1	5		6
Physical Parameters Online Monitored	1	1	5	5	6 (ROF) and 1 ROP	7		
Phenolics					16 (ROF)	16		
Herbicides/Pesticides by LCMS			19			19		
Pesticides, Phenoxyacid Herbicides, Dalapon			11			11		
Pesticides - Glyphosate			2			2		
Pesticides - Haloacetic Acids					6	6		
Trihalomethanes					5	5		1
Nitrosamines			5		5	5		
EDTA			1			1		
Endocrine Disrupting Compounds			12			12		
Pharmaceuticals			50			50		
PCBs and Dioxins			7					
Organochlorine Pesticides			32					
Pesticides, Organophosphorous			17					
Flow	1 (inlet)	1						

ROF = Reserves Osmosis Feed Water; ROP = Reverse Osmosis Permeate
Please note that for Barrier 6 the information was not made available to the project at the time the report was written.

4.1 Current Online Water Quality Monitoring System Performance

In recent years online water quality monitoring technology has been rapidly expanding, with the specific purpose of providing accurate and continuous water quality information for the protection of natural and man made fresh water supplies. For example, there are already commercially available systems on the market for parameters such as Fluoride[10], Sodium[11], pH[12], Conductivity[13], Redox[14], Ammonia[15], Ammonium[16], Chlorine[15, 17], TOC[18], Nitrate[19] and Dissolved Oxygen[20]. Some methods are based on electrochemical detection[10, 11, 21, 22], with specific emphasis on voltametric and amperometric techniques, as well as Ion-Selective Electrodes (ISE)[23, 24] for parameters such as Fluoride[10], pH[12]and Sodium[11]. Other online monitoring systems are based on optical detection techniques[20] such as UV adsorption[15, 19, 25] with the majority employing colorimetric detection principles [15, 25] (e.g. COD[25], Ammonia[15] and Chlorine[15, 17]).

Online monitoring systems have the advantage over traditional laboratory-based and portable field methods in that they are capable of obtaining continuous measurement data autonomously for periods of time, at the monitoring site of interest, without skilled staff being required to perform the analyses[26]. This is because sample collection and laboratory bench processes such as sample pre-treatment, calibration, reagent addition and sample analyses procedures have all been automated[26-30]. The water quality information is usually transmitted to the water authority through their existing SCADA systems. This eliminates the need for sample collection, preservation and transportation, and hence reduces costs.

Real-time continuous measurements can be acquired by two main methods: online; and inline or *in-situ*[30]. Online measurements are in most cases based on automated laboratory-based measurement techniques. The sample is usually injected using rotation valves or peristaltic pumps into the instrument using Flow Injection Analysis (FIA)[29] or Sequential Flow Injection (SIA) techniques[29], via a separate analytical line which is connected to the main process stream[29, 30]. The sample is then extracted, pre-treated if required and presented to the analytical instruments for the analyses required. This system can be either calibrated online automatically, or off-line by a skilled operator[30]. Online analysers usually require a suitable temperature and pressure, fixed background measurement conditions and frequent calibration to obtain analytically valid results[30].

In-line analysers are simpler in design and can measure directly in the process line, using a probe that is reasonably chemically insensitive[30]. However they are more susceptible to physical and chemical interferences from the sample matrix, as measurement backgrounds are more changeable and they usually require ex-situ calibration.

However, despite the ability to acquire continuous, real-time data, their widespread application has been limited due to an inability to reliably obtain accurate, cost-effective water quality data[24, 26, 28, 31-33]. Online monitoring suffers from more problems than laboratory-based methods[8, 24, 28, 32] because to date, the majority of online monitoring technologies developed are direct adaptations of traditional, laboratory-based analytical methods[10-12, 15, 17, 23, 24, 34], which were not originally designed for field applications. Instead they are required to operate in extreme and variable measurement environments whilst still obtaining accurate and reproducible results [8, 26, 35]. Consequently, these methods require frequent calibration and maintenance [8, 23, 24, 26, 28, 33, 36] and often consume large quantities of chemical reagents[26, 28, 37, 38]. They often require reagents such as standards and buffers which produce secondary forms of pollution that require safe disposal. In addition the analysers often suffer from cross responses due to matrix variations between the standards and samples analysed, as the measurement conditions are not controlled. There are also significant economic and logistics costs associated with maintaining remote equipment, as it is difficult for operators and grid managers to detect problems such as sensor fouling.

Another issue is that online analysers usually do not include a data processing element to provide a measurement context for making decisions. For instance, this could incorporate:

- Hydraulic models, in order to understand the dynamics of the water system and relationships between different water quality environments;

- Additional background information (referred to as metadata) to provide a measurement context, such as information concerning known changes in system performance including public holidays, major system failure, calibration and maintenance events; and
- Historical information to assist in discerning what might have caused short-term or long-term changes.

If the online analysers are not capable of acquiring reliable, continuous water quality information, it can lead to the following problems:

- Increased likelihood of false positive and false negative events;
- Decreased likelihood of detecting short and long-term deviations from baseline monitoring conditions; and
- Large volumes of redundant data being produced but not being useable for optimising operational processes.

The problems associated with conventional online analysers stem from the fact that univariate linear calibration models derived from Gauss's theory of least squares are employed to determine unknown concentrations[36,39]. Therefore, the samples and standards must be measured with equal care, under the same measurement conditions, to obtain reproducible and accurate results[36, 39]. Seeing that consistent measurement conditions are rarely present in the field, this invalidates the operating conditions required for reliable performance, and causes a high degree of unreliability in the results from online instrumentation. Consequently, many water authorities need to frequently validate their online results with laboratory based or portable field instruments[24]. Therefore, it is recommended that care be taken when using these results to make critical management decisions.

The cost associated with maintaining these conventional instruments has also greatly limited their widespread application, especially in regards to large-scale remote water quality monitoring in places like the European Union (EU)[31, 33, 40]. For example, the EU Water Framework Directive (WFD) is probably the most significant piece of water protection legislation to be introduced on an international scale for many years[31, 40]. This directive takes a broad view of water management, and its key objective is the prevention of further deterioration of all water bodies. The successful implementation of the WFD will rely heavily on the monitoring programme, but will only achieve its full potential when the online monitoring data is reliable, accurate and cost effective [31, 33].

The major problem with such water quality initiatives is that there is no cost effective online monitoring technology currently available that can operate autonomously for extended periods of time[26, 28, 32, 33, 41]. Consequently, the WDF has not mandated any particular monitoring method. It simply provides a framework listing of water parameters that should be monitored[31, 33], because there are no agreed international standards or methods developed that allow for large-scale, online, reliable and cost-effective water quality information to be obtained[31, 33, 40].

In light of this, it is recommended that when selecting online analysers for the PRW system, special care should be taken to ensure the analysers employed are appropriate for their intended use.

4.2 Overview of Measuring Principles of Commercially Available Online Monitoring Systems

Photometric Sensors

Photometric sensors are among the most commonly used measurement principles for online analysers. These methods are based on measuring the interaction of light with the sample and the measurement principle is usually based on Beer's Law[7, 42-44]. They are often employed because of their simplicity and rapid response. The majority of commercially available photometric sensors fall into three main categories: Colorimetric; UV Absorption; and UV-Visible Absorption. Optical sensors, such as non-destructive sensor arrays, also have the advantage over ISE (ion-selective electrodes) for water quality monitoring in that gross fouling and potential problems or contamination can be detected by colour changes in the sample[45].

Colorimetric

These are largely based on direct adaptations of APHA standard methods[103], which use reagents to obtain desired complex ion formation to quantify the concentration at a specific wavelength. They require regular calibration with standard reagents using Beer's law to maintain their calibrated online status.

UV absorption

The measurement principle is based on the specific absorption at a specified wavelength in the ultraviolet range. They require conventional calibration according to Beer's Law and standard reagents. For example, they include some turbidity sensors as well as a new type of Dissolved Oxygen (DO) sensor[20] which employs a Light Emitting Diode (LED) to measure the DO concentration instead of using a conventional membrane based sensor.

UV-Vis absorption

This is based on semi-quantitative/selective information obtained from UV-Visible spectra. The methods usually employ pattern recognition techniques (PRT) to quantify the absorption profile and convert it to an equivalent concentration for the particular water quality parameter of interest. It should be noted that this method is only suitable for water quality parameters that have suitable UV-absorption bands (e.g. nitrate). Usually these methods do not require sample pre-treatment or daily calibration at the monitoring site of interest. They are employed mainly because samples can be analysed with very little sample preparation, no chemicals are required, and they have low operational costs. Such methods have been developed for monitoring Chemical Oxygen Demand (COD), Total Organic Carbon (TOC), Biochemical Oxygen Demand (BOD) and Nitrate.

Ion Selective Electrodes (ISE)

ISEs are commonly employed as online sensors due to their speed and simplicity, as well as low maintenance and purchase costs. With careful use, frequent calibration and ideal measurement conditions being maintained, they can achieve accuracy and precision in the order of ± 2-3%. Hence, in theory the configuration and embodiment of an ISE makes itan ideal sensing probe for on-site, real-time monitoring applications.

Data obtained from online ISE measurements, although continuous, is usually semi-quantitative in nature. This is because the analytical signal of the ISE is known to be affected by matrix interferences, drift, contamination (e.g. by organic molecules), nonlinear responses at the lower end of detection, and temperature in non-ideal measurement conditions. These factors in turn cause measurement errors. To improve its reliability, especially in the field, an ISE must be regularly calibrated with standards (e.g. every two hours) and samples should be analysed according to prescribed measurement conditions. However, the economic costs associated with calibration, especially for instruments that require ex-situ calibration with skilled personnel, have greatly limited its adoption. This is especially the case in the water industry.

4.3 Desirable Autonomous Water Quality Monitoring of WCRW Scheme

Ideally, operators and grid managers require water quality instruments that are capable of operating autonomously for prolonged periods of time. They should also be easy to operate and maintain, and use limited reagents, so that they are cost effective to implement for large-scale water quality monitoring purposes[24, 26, 28, 32, 33, 40]. It is crucial that they are able to produce analytically valid results and can flag sensor faults[8, 24, 26]. This is required so that they can competently detect real system problems, and so that the data is useful for managing water resources across large geographic areas[8, 24, 26, 32, 33], as is the case for the PRW scheme in SEQ. Hence, as the distribution networks of Barriers 1 and 7 are very large, prolonged autonomous operation (i.e. for approximately 6 months) would be preferred.

The instruments should be robust and rugged, so that they are capable of operating in variable and extreme measurement conditions, whilst still maintaining their calibrated status[24, 26, 33, 41]. This is especially important in Barriers 1 and 2 as the measurement environments are extreme. Therefore, sensors that are stable slow to drift and maintain their calibration are required. This is also the case for Barriers 6 and 7 as they can be still prone to sample matrix interference, signal drift and sensor fouling that can produce measurement errors, despite the treated water being of a higher quality[23, 24, 30]. It is crucial that the instruments are able to provide analytically valid results, so that any harmful events can be accurately detected, and the data is useful for managing water resources across large geographic locations[26, 28, 33, 46]. They should also be easy to operate and maintain and use limited reagents, so that they are cost effective to implement for large-scale water quality monitoring purposes[26, 28, 33, 37]. Essentially, online/*in situ* water quality monitoring sensors should be sufficiently robust to cope with changing environmental conditions and matrix interferences. They should also be capable of adequately monitoring changes in baseline performance that may indicate deterioration in water quality.

4.4 Advanced Approaches to improve the suitability of Online Instruments for their intended purpose

Advances in materials science, microelectronics, miniaturisation, electro-optics, data analysis and computing power over the last two decades have enabled development of more robust and reliable online water monitoring systems[47]. In the following sections, approaches and advances associated with improving the performance of current online monitoring systems based on traditional analytical principles are discussed.

Improving Sensor Selectivity

One of the traditional approaches commonly employed to improve the reliability and accuracy of online water quality monitoring systems is to develop and synthesize more selective sensors[48-50]. This is because the majority of sensing surfaces suffer cross responses from interferences or are altered by the sample matrix composition. This in turn affects the output of the sensing system and hence its accuracy[23, 28]. Accordingly, research scientists and technologists have focused on developing novel sensing materials[51], colorimetric detection principles[43, 52] and even new measurement principles[22]. However, as research outcomes have indicated, it has been very difficult to develop an entirely selective sensor that can operate in a diverse range of measurement conditions such as the WCRW project. This is because the majority of new methods still require regular calibration according to traditional analytical practice.

Improving Stability and Consumption of Reagents

An integral part of current online monitoring systems is the use of standard reagents to ensure accurate field calibration[24, 26, 36]. However, the lack of stability, volume of reagent consumption and economic costs associated with these methods has greatly limited their widespread application[26, 32, 33, 40]. For example, reagents that contain sodium hypochlorite are unstable and require constant replenishing[37]. Hence, to address these issues and make current online instruments more economically viable, research and commercial endeavours have focused on improving the stability and reducing consumption requirements of reagents.

For long-term applications, researchers have developed more stable reagents[26, 28, 37]. For example, Sequeira and Diamond (1997) devised a technique to improve the reagent stability from two weeks to one year[37] in the indophenols method used for the analysis of ammonia. Alternatively, to reduce reagent consumption a significant portion of research has centred on the miniaturisation of analytical devices[22, 27, 28, 41]. These devices are commonly referred to as "lab-on-chips"[26, 27], "lab-on-cables"[27], "Micro Total Analytical Systems (μTAS)"[47] or "Micro Electro Mechanical Systems (MEMS)"[47], that operate on micro- and nanometre scales. They enable complex bench processes such as sampling, reagent addition, calibration, temperature control and analysis, to be incorporated into compact, low powered devices with fixed internal environments[26, 27]. Some examples are ammonia[37, 53] and ORP[54]. However, although they are beneficial in terms of reagent consumption, they are still prone to blockages[28] and the sensors must be continually calibrated to compensate for signal drift.

Overcoming Matrix Interferences

Because of the difficulty in developing highly selective online analysers, many suffer cross responses from matrix interferences that can affect accuracy in the field. To overcome this problem, research and commercial endeavours have developed a number of new methods for coping with matrix interferences in the field[23, 28, 36, 55, 56]. This has been achieved through sample pre-treatments such as filtration, distillation, or the use of reagents for complexing and buffering the sample. Alternative approaches have tried to eliminate sample pre-treatment, which would make the methods more robust and cost-effective for applications such as the WCRW project. One example is ISEs that use major ion-interference compensation in an attempt to reduce sample pre-treatment costs and improve their accuracy[49, 57, 58]. This approach has been successfully demonstrated using ISE for Nitrate[49], Ammonium[57, 59], Potassium[57, 60, 61], Sodium[57, 60], Chloride[62], Bromide[62], Hydroxide[62] and Fluoride[62], with commercially available sensors such as Ammonium[34] and Nitrate[63] introduced to the market in late 2006. Although the method shows considerable potential as a simple means to cope with cross-responses from interferences, it should be noted that in all examples strictly defined physicochemical measurement backgrounds were required to obtain analytically valid results on synthetic samples[48, 49, 57, 58, 60]. The performance of the method on real samples has not been adequately demonstrated in the literature, with few examples of real sample analysis[49, 64, 65]. In addition, to compensate for signal drift, the sensors still require regular calibration in the field, which can increase maintenance costs.

A contrasting approach that has been commercially implemented to improve the reliability and performance of online monitoring instruments has been to use standards designed to replicate the composition of the samples being measured. Successful commercial applications have already been developed for fluoride[66]. This approach is effective because, as previously stated, most online monitoring techniques require consistent measurement conditions between the standards and samples measured. However, as the standard solutions replicate samples being measured, the technique is very location (matrix) specific and not suitable for process applications where the matrix is constantly changing (as is the case for Barriers 1, 2, 6 and 7). Hence, it may not be an economically viable approach for the WCRW applications, given the number of locations and the range of parameters required, especially when considering that the quality of raw sewage, treated wastewater and surface water may vary greatly due to seasonal, temporal and geographic factors[64].

Simplification of Calibration

To improve the operation and maintenance of the instruments and to increase their economic viability, research endeavours have focused on simplifying calibration methodologies. For example, one approach has been to reduce the number of points required for automatic calibration, resulting in a reduction in reagent consumption and labour costs. However, this may not be readily adapted to existing instruments as they are normally pre-programmed and most systems cannot autonomously detect signal drift to determine when recalibration is required. Alternatively, a recent commercial advance has seen the development of sensors with disposable pre-calibrated cartridges that can be replaced half yearly or yearly[34, 67]. An example of this is the Hach-Lange dissolved oxygen (DO) sensor[67].

However, despite the attempts to improve their economically viability by simplifying calibration, online analysers are still fundamentally affected by sample matrix effects, which can make it difficult to obtain continuous, reliable measurements in the field. Therefore, most field analysers still require regular maintenance to guarantee their reliability.

Reducing Sample Pre-Treatment

In recent years, an alternative and promising approach to reduce requirements for sample pre-treatment has emerged in the development of Software Sensors[55, 68] such as Electronic Tongues (E-Tongues)[59, 64, 69, 70], Electronic Noses (E-Noses)[56, 64, 71], or Spectral Finger Printing[7, 44, 65, 72-74]. These software sensors use a signal obtained from a readily available, fast and reliable device such as a UV-Visible Spectrophotometer or an electrochemical sensor and then determine the water quality parameter of interest (e.g. BOD_5 or COD) using mathematical signal processing tools such as partial least squares[44, 75, 76] or Artificial Neural Networks (ANNs)[44, 73, 76]. This has been made possible by the massive increase in cheap computing power. The most significant advantage of a software sensor is that it can handle more than one response, which is not the case for traditional online analysers based on simple linear regression. E-tongues are the most common software sensor employed in water quality monitoring. They are based on an array of semi-selective or non-selective sensors that when measured simultaneously can be used to classify and in some cases quantify complex aqueous samples using pattern recognition techniques (PRT)[47, 49, 64, 65, 77]. This method is unique in that it tries to avoid the need to separate the analyte from the complex sample matrix before it is analysed. The software sensor approach diverges from the traditional analytical concept in which one, highly-selective sensor is used to indicate change in one parameter in a complex aqueous sample.

Sensor Fouling and Failure

The ability to overcome sensor fouling and detect sensor failure is extremely important to ensure that continuous and reliable water quality information can be obtained. It also can assist to reduce the number of false positive and false negative events recorded by the sensor. Methods for overcoming fouling include:

- Self cleaning sensors;
- Frequent maintenance;
- Positioning of sensor and online analyser design; and
- Flow rate.

Methods for overcoming failure include:

- Employing multiple sensors;
- Signal processing techniques; and
- Operator maintenance checks.

Other Issues

To ensure that online analysers will be a valuable operational process and control tool for the PRW closed loop system, it is imperative that the information obtained is accurate so it can be used to assist operators/grid managers in optimising and improving water quality management strategies. A recent review by O'Halloran *et al.* (2008) highlights that online water quality information must also encompass a measurement context to be effective for management purposes[8]. The report raised the following points that should be incorporated to improve current online water quality monitoring practices used by the water industry:

- Metadata Information. It is important to collect additional background information (referred to as metadata) concerning other factors that will affect the PRW system and sensors. This would include information on system-wide events such as public and school holidays, major system upsets, severe weather events, major changes in water source or treatment, as well as information related to individual sensors such as maintenance and calibration. This metadata would need to be supplied and regularly updated by the relevant authorities. This information aids in the identification, detection and assessment of events and also ensures that the online information can be stored and retrieved correctly[8].
- Hydraulic information. Hydraulic flow information is important to assess how water quality might be changing between online sampling locations, to detect potential problems and optimise dosing procedures[8].

5. COMMERCIALLY AVAILABLE SENSORS – SUITABILITY FOR WCRW PROJECT

A number of commercial sensors potentially suited to the WCRW project have been reviewed in the following sections. This list is by no means comprehensive, however it showcases a range of commercially available online analysers produced by key market players and details their suitability for each treatment barrier (see Appendix 1). As evident from the literature review, the field of online water quality monitoring is rapidly expanding and still requires further advancements. The following assessment is based on the manufacturers' guidelines and does not necessarily reflect the instruments' reliability for continuous water quality monitoring within each barrier in the PRW system. It only provides recommendations based on researchers' and industry experience with online analysers.

5.1 Organic Load Indicators

Online parameters that can indicate the organic load of the water source are essential to ensure the integrity of all barriers within the PRW closed loop system. This is primarily because the PRW is designed to remove organic matter from the wastewater to produce high purity drinking water. In addition, organic levels in Barriers 6 and 7 can cause disinfection by-product formation, and their presence is also used as a surrogate to indicate microbial contamination[4, 78].

Table 2 Organic parameters or indicators required to be measured at each barrier to indicate organic loadings

Parameter	B1	B2	B3	B4	B5	B6	B7	Commercially Available
BOD_5	√	√						Yes
COD	√	√						Yes
TOC		√	√		√			Yes
DOC						√	√	Yes
Suspended Solids	√	√	√			√		Yes
Turbidity	√	√	√	√	√	√	√	Yes

Commercially Available Sensors

Table 2 lists the parameters required to be measured at each barrier to indicate organic loadings. Currently there are online sensors available for monitoring all of these parameters; however their suitability for Barriers 1, 2 and 2/3 is questionable due to the variability in the matrix composition (see Appendix 1 for more information).

BOD_5

There are a number of instruments commercially available: those which use various means to measure the oxygen respiration rate of sewage sludge, and those based on chemometric algorithms to estimate BOD from UV-visible absorption. Some examples are given below:

AppliTek Ra-BOD® On-line BOD analyzer

Direct BOD measurement using respiration rate (mgO_2/l.h) of sludge from the WWTP

Endress+Hauser Biox-1010

This rapidly measures BOD_5 from the dilution factor required to keep the DO level constant in a small online bioreactor fed by wastewater diluted with air saturated water.

Advantages:

- Has a high measuring range; and
- Does not require chemicals.

Disadvantages:

- Requires sample conditioning.

s::can; Endress+Hauser Stipscan

These employ UV-Vis absorption and chemometric algorithms to quantify BOD_5 non-destructively in real-time. They use the spectral absorbance values around 250-380 nm to indirectly quantify BOD using UV-Vis absorption patterns.

Advantages:

- Sample acquired in-line with limited pre-treatment; and
- Can rapidly determine concentrations in a non-destructive manner.

Disadvantages:

- Method is not direct and hence is matrix dependent. This can lead to measurement errors if matrix changes substantially; and
- May require frequent calibration if matrix composition continually changes e.g. every two weeks if system has not been developed on monitoring site in question. Works best if the monitoring site of interest has been incorporated into its data training base, and has turbidity < 150 NTU for unfiltered samples[7].

Suitability:

- Barrier 1, 2 for all analysers and in addition Barrier 6 for the s::can and Stipscan, as organics are not in trace quantities. Techniques such as s::can are based on the absorption pattern of organics in the UV region, and hence sufficient levels of organics are required to obtain adequate sensitivity.

COD

There are three companies making commercial systems: Endress+Hauser, s::can and Aqua Diagnostic.

s::can; Endress+Hauser Stipscan

These instruments use UV-Vis absorption patterns and chemometric algorithms. These methods are based on using the spectral absorbance profiles to indirectly determine COD values through semi-quantitative/qualitative analysis employing pattern recognition and computationally intelligent techniques. Most organics absorb strongly in the UV region and an absorbance profile is more conducive to characterising the complex nature of heterogeneous samples[7].

Advantages:

- Sample acquired in-line, rapidly with limited pre-treatment.

Disadvantages:

- Method is not direct and hence is matrix dependent. This can lead to measurement errors if matrix changes substantially. May require frequent calibration if matrix composition continually changes to obtain accurate measurements, e.g. every two weeks if system has not be developed on monitoring site in question.

Endress+Hauser: The Phoenix 1010 analyser uses ozone to oxidise the organic content of effluent, with differential ozone sensors used to measure how much is required to break down the organic load. The Phoenix Thermcat uses high temperature catalytic oxidation instead of ozone.

Advantages:

- Sample can be acquired with limited sample pre-treatment;
- Rapidly determines concentration; and
- Automatic calibration.

Disadvantages:

- Requires a pre-filter which may block.

Aqua Diagnostic Pty Ltd: have recently launched a new COD analyser - the PeCOD™ (Photoelectrochemical Oxygen Demand). It uses photochemical oxidation at a titanium electrode and quantifies COD directly by measuring the number of electrons in an external circuit using Faraday's Law[22].

Advantages:

- Sample can be acquired with limited sample pre-treatment;
- Rapidly determines concentration on very small sample aliquots; and
- Very accurate compared to standard method, especially below 20 mg/L.

Disadvantages:

- It employs measurements in a microfluidic environment. Therefore the sample chamber may be prone to blockages. This may be especially for Barriers 1, 2 and 6, which are more heterogeneous and variable in nature.

Suitability:

- Barrier 1, 2, 6 – s::can, Stipscan, Phoenix.
- Barrier 2 at clarifier, Barriers 3, 4, 5, 7- PeCOD, Phoenix.

Total Organic Carbon (TOC) (including dissolved organic carbon, DOC)

There are a number of online TOC analysers available, for example:

- Hach: High temperature oxidation;
- Greenspan: Non-dispersive IR;
- Endress+Hauser:
  - EZ TOC uses UV- supported low temperature oxidation;
  - STIP-toc uses high temperature catalytic oxidation;
  - STIP-scan uses UV-Vis Spectral absorbance patterns combined with chemometric algorithms;
- Mettler Toledo: UV oxidation; and
- s::can: uses UV-Vis Spectral absorbance patterns combined with chemometric algorithms.

All methods are suitable for analysing samples continuously as long as the sample is relatively consistent and is not too turbid. Most calibration is performed either automatically or off-line. If the matrix constantly changes the analyser may require more frequent calibration, consume more reagents and require more maintenance to ensure valid measurements are obtained. This is because apart from s::can and STIP-scan, the TOC analysers have been based on laboratory methods that have been modified for online applications. Therefore they are best employed after sample pre-treatment to minimise maintenance and labour costs associated with the analysers that may be affected by a changeable sample matrix.

Recommended: Barriers 3, 4, 5 and 7.

Turbidity

There are many commercially available turbidity analysers on the market that are suitable for monitoring in most barriers of a closed loop PRW system (see Appendix 1 for more information). However, as turbidity measurements are based on optical principles, the current *in situ* sensors may be prone to fouling in the more extreme and changeable conditions at barriers such as 1 and 2. Therefore, the sensor position, type of sensor, flow cell design and signal drift and calibration will need to be addressed for these more difficult barriers.

Recommended: Barriers 3, 4, 5, 6 and 7 in its current form.

Suspended Solids

There are a number of commercially available sensors for monitoring suspended solids that are suitable for the PRW system, e.g:

- Hach: LED probe.
- Endress+Hauser: UV-Vis spectral absorbance sensor.
- Greenspan: Photometric sensor.

These sensors are once again based on the non-destructive interaction of light[7] with the sample and use optical measurement principles. However the sensors still require regular calibration to control signal drift. As the sensors are optically based, they may be prone to fouling in the more extreme and variable barriers such as 1 and 2. Therefore, the sensor position, type of sensor, calibration requirements and flow cell design will need to be addressed for these more difficult barriers.

Recommended: Barriers 3, 4, 5, 6 and 7 in their current form.

5.2 Nutrients

The reduction of nutrients from the sewer catchment source water is of primary importance to ensure production of high quality PRW. Therefore, it is necessary to measure the reduction of these compounds through Barriers 1-5 to ensure treatment processes are meeting design specifications as well as complying with the license agreements of the WWTP and AWTP. This can only be achieved if continuous monitoring of nutrients is included, as they have been identified as a PRW contaminant of concern. This is especially important at Barrier 6, to ensure nutrient levels in the PRW are discharged at a rate that can be assimilated by the natural environment in Lake Wivenhoe.

Table 3 sets out the nutrient parameters that must to be measured at each barrier in the WCRW project. There are a number of commercially available sensors on the market that are claimed to measure these parameters accurately.

Table 3 Nutrient parameters or indicators required to be measured at each barrier in the WCRW project

Parameter	B1	B2	B3	B4	B5	B6	B7	Commercially Available
Total Nitrogen	√	√	√	√	√	√		Yes
Total Phosphorus	√	√	√	√	√	√		Yes
Nitrate	√	√	√	√	√		√	Yes
Nitrite	√	√	√	√	√		√	Yes
Orthophosphorus			√	√	√	√		Yes
Organic Nitrogen	√	√						Yes
Ammonia		√	√	√	√		√	Yes

Nitrogen

Greenspan: total nitrogen - Colorimetric; Nitrate - Ion-selective Electrode.

Hach: Nitrogen/ammonia – colorimetric.

Endress+Hauser: Nitrate – UV-Vis.

YSI: Nitrate - Cadmium Reduction/Diazotization.

s::can: Nitrate – UV-Vis.

From the review of commercially available online sensors:

- The colorimetric, ISE and Cadmium Reduction/Diazotization methods require frequent calibration and consume reagents. The reagents are usually only stable for ca. 1 month before they require replacement.
- ISE membranes may by be prone to fouling in Barrier 1-2 (especially if PVC based) due to high nutrient content of water compared to drinking water. This may also be the case in Barrier 6 due to the number of other water inlets to Wivenhoe dam.
- UV-Vis measurements can be performed without sample pre-treatment. However, optical-based measurements will be prone to measurement errors in Barriers 1 and 2 due to changes in turbidity levels. For example, a study by Fogelman *et al.* (2006)[7], found measurements of sewage influent can be impaired if turbidity > 150 NTU.

Overall, the assessment of these online sensors indicated that most are suitable for use in the PRW system after the clarification step in Barrier 2. However, as most online measurements are based on direct adaptations of standard methods, frequent calibration and maintenance will be required to ensure that reliable measurements are obtained. The frequency will depend on the nature of the sample and its complexity and the stability and reliability of each sensor in the measurement environment.

Recommended: For Barriers 3, 4, 5 and 7.

Note: care should be taken to ensure that maintenance and calibration requirements are considered for each particular measurement environment. It must also be economically viable to implement in remote areas to make online monitoring cost-effective for the WCRW project.

Phosphorus

- Hach: Orthophosphate-Colorimetric.
- Endress+Hauser: Phosphorus- Colorimetric.
- Greenspan: Colorimetric.

The online analysers used to monitor phosphorus are based on direct adaptations of the standard laboratory-based analytical methods. Therefore, they require frequent calibration as well as a regular supply of reagents to form the complex ion required for detection. The stability of the reagents and maintenance requirements of the instruments must also be determined to ensure they are economically viable to implement and maintain. If frequent calibration is required, the instrument will consume more reagents, especially in changeable and complex measurement environments such as at Barriers 1, 2 and 2/3.

Recommended: For Barriers 2/3; and with care for 4, 5 and 6.

Ammonia

Ammonia is an important parameter as it is an indicator of treatment efficiency. If NH_3 concentrations are higher than the operational design specification, it can indicate possible contamination with raw sewage and high microbial levels. This is of paramount importance in Barrier 7 to ensure continuous safe supply of IPR to SEQ residents. The ADWG guideline requirement is 0.5 mg/L, and in Barrier 2/3 a specification of less than 7.5 mg/L is required.

Currently there are few commercially available sensors on the market that can reliably achieve the sensitivity required for these treatment design specifications.

- Hach: Ammonia/Nitrogen – Colorimetric; Ammonia/Ammonium – Colorimetric.
- YSI: Ammonia – Ion Selective Electrode.
- Endress+Hauser: Ammonia- Colorimetric.
- Greenspan: Ammonia- Ion-Selective Electrode.
- s::can: Ammonia- Ion-Selective Electrode.

All of these analysers are suitable for Barriers 2/3. If the detection limit required is below the 0.5 mg/L ADWG value, it is recommended Hach or Endress+Hauser be used. This is because the instrument specifications are more sensitive and ammonia is often used as a surrogate to indicate the presence of microbial or sewage contamination[4]. However, care should be taken with these analysers for the following reasons:

- Ammonia/Ammonium ISE are PVC membrane based sensors that are prone to fouling. In addition they require additional reagents for sample pre-treatment. Therefore frequent calibration with standard reagents may be required to maintain accurate field measurements.
- Colorimetric methods work well, however there are reagent stability issues for those that use indophenols, as the hypochlorite ion is unstable[37]. Therefore it increases the maintenance costs associated with the method.
- Sensors need to operate autonomously in changeable measurement environments.

5.3 Inorganic parameters

There are a number of inorganic ions that are required to be monitored in the PRW system to ensure that its integrity is maintained. For example, fluoride is measured because it is an IPR contaminant of concern and may pose a health risk if not treated appropriately, whereas alkalinity needs to be monitored as it is a COP point in Barrier 5 for water stabilisation and a critical point that may have an impact on Barrier 6. There are also additional parameters that need to be measured for compliance monitoring purposes. The inorganic parameters required to be measured at each treatment barrier within the WCRW project are listed in Table 4.

Table 4 Inorganic parameters required at each treatment barrier within the WCRW project.

Parameter	B1	B2	B3	B4	B5	B6	B7	Commercially Available
Sodium		√	√	√			√	Yes
Potassium		√	√	√	√			Yes
Fluoride						√	√	Yes
Calcium		√	√	√	√			Yes
Iodide			√	√	√			
Silica			√	√	√			
Cyanide					√			
Alkalinity			√	√	√	√		Yes
Sulphate			√	√	√		√	
Chloride			√	√			√	Yes

Currently there are online commercially available sensors for most of these parameters, e.g:

- Hach: Alkalinity - colorimetric; sodium - ISE; Hardness ($CaCO_3$) – colorimetric; Fluoride ISE.

There are other companies that also produce these online sensors. However it should be noted that currently they are all based on standard laboratory methods. Therefore, these systems require frequent calibration and regular maintenance, especially in Barriers 2, 3, 6 and 7 where the sample matrix can be more changeable. Barrier 1 may also be problematic due to the nature of the sewer network and highly turbid nature of the samples.

Recommended: - Sodium analyser for Barriers 4 and 5.
- Fluoride analyser for Barriers 5 and 7 (when fluoride is introduced into the SEQ water grid).

Research and Development

Electronic tongues offer a potential option for monitoring inorganic ions simultaneously and may eliminate the need for multiple analysers. For example, Rudnitskyaya *et al.* (2001)[58] demonstrated the feasibility of using an electronic tongue based on non-specific potentiometric sensors to determine sodium, chloride and calcium in addition to some heavy metals such as copper and zinc, with limited sample pre-treatment being required. Guttierrez *et al.* (2008)[79] demonstrated using an electronic tongue for measuring calcium, sodium and potassium, in addition to ammonium and nitrate ions. This could be an option for online analysis in the future, which would reduce the number of analysers whilst maximising the number of parameters that could be determined. This approach could significantly reduce the costs and maintenance presently associated with online monitoring. However, issues associated with membrane fouling, signal drift and matrix interferences may still need to be addressed, as the PRW system encompasses a diverse range of monitoring environments.

5.4 Heavy Metals

Because the WCRW project is producing PRW from treated wastewater, the need for rapid and continuous online sensors for heavy metal analysis is becoming more important. To mitigate the risks associated with a PRW closed loop system, a number of heavy metal IPR contaminants have been identified that must be monitored to ensure the quality of recycled water produced in each treatment phase meets the required standard (Table 5). In addition, from Barrier 3 onwards the levels of IPR heavy metals are recommended to be below, and after Barrier 5 must be below, AWDG and ARWG limits[80]. Therefore, this means that online sensors must have an adequate range and sensitivity for heavy metal concentrations found in Barrier 2, and sufficient sensitivity to detect changes below 1 mg/L in Barriers 5-7.

Table 5 Heavy metal parameters required to be measured at each treatment barrier within the WCRW project

Parameter	B1	B2	B3	B4	B5	B6	B7
Arsenic		√	√		√	√	√
Antimony		√	√		√		√
Barium		√	√	√		√	√
Beryllium		√	√		√		
Boron		√	√	√	√	√	√
Cadmium		√	√		√		√
Chromium		√	√		√		√
Cobalt		√	√		√		
Copper		√	√		√		√
Lead		√	√		√		√
Lithium		√					
Magnesium		√	√	√	√		
Manganese		√	√	√	√	√	√
Nickel		√	√		√		√
Selenium		√	√		√	√	√
Silver		√					
Strontium		√	√	√	√		
Zinc		√	√		√		√
Tin		√					
Mercury		√	√		√	√	√
Molybdenum		√	√		√		√
Vanadium		√	√		√		
Aluminium		√	√	√	√		√
Iron		√	√	√	√	√	√

The majority of analytical methods which are used to measure heavy metals are only suitable for laboratory use: Atomic Absorption Spectroscopy (AAS); Inductively Coupled Plasma Mass Spectrometry (ICP-MS); Graphite Furnace Atomic Adsorption Spectroscopy (GFAAS); and Neutron Activation Analysis (NAA)[81]. The high costs associated with maintenance, separation and extraction make these techniques unsuitable as online monitoring tools.[82]

There are only a few online techniques available that can measure heavy metals in a continuous and cost-effective manner that would be suited to the WCRW project:

- Hach: Copper- Colorimetric.
- AppliTek: Zinc, Cadmium, Lead, Arsenic, Mercury, Iron and Chromium - Anodic Stripping Voltammetry.
- SensAqua A/S: Copper, Zinc, Mercury, Iron, Lead, Cadmium - Voltammetry.

The AppliTek and SensAqua A/S are relatively new on the market, and these analysers are still in the process of being fully commercialised. Alternatively, Hach copper analysers can be used and give satisfactory results, provided that they are calibrated and maintained regularly.

Research and Development

To further develop this field, research into *in situ* measurements of heavy metals is becoming a high priority[82]. Once again, as it is not economically feasible to monitor for every heavy metal required, development of an online analytical tool that could measure several key heavy metals or which could indicate other key contaminants would be highly desirable. Currently, there are two main research approaches available that may be suitable for the WCRW project.

Voltammetric sensors are promising candidates for real-time, simultaneous measurements, as they can acquire continuous information with minimal or limited sample pre-treatment[82]. For example, Xie *et al* (2004) used microelectrode E-tongue arrays based on voltammetry to determine heavy metals in water; the sensor array was based on non-selective sensors to develop a pattern[83]. Zhu *et al.* (2006) used a microelectrode array to determine Zn^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+}, Fe^{3+}, Cr^{3+} [84]. From the literature review, there were several potentiometric sensors and biosensors that may also be viable alternatives[85, 86].

However, the following factors should be taken into account when developing electronic tongues or biosensors for the WCRW project.

- Need for rugged reference electrodes that reduce the risk of contamination from diffusion through liquid junctions[82]. This is important if the sensors will be used *in situ*, to mitigate any risk associated with contamination especially if the sensors may contain IPR contaminants of concern (e.g. mercury).
- Biofouling of membranes may impair the analytical signal obtained. This is a major concern in Barriers 1, 2 and 6, where the sample matrix is constantly variable. In addition the wastewater in Barrier 1 and at the sample inlet to Barrier 2 has very high microbial and organic loads, which make membrane based sensors extremely vulnerable to biofouling.
- Because E-tongues are based on multiple sensor arrays, signal drift is difficult to overcome, as the algorithms or patterns developed by the sensor arrays are represented in a higher dimensional search space. Therefore, improved data analysis techniques to make them suitable for long-term deployment would be highly valuable.
- There is a requirement to account for environmental variations to correct changes in sensor signal attributed to matrix interferences. Sensors that are calibrated based on traditional analytical principles require fixed measurement conditions, which are usually not obtained in field measurements.
- Minimise consumption requirements of reagents, so that they can be suitable for remote monitoring. The economic costs associated with reagent stability, calibration and maintenance will greatly limit their widespread application.
- Incorporate hydraulic and metadata information into data processing for online systems to ensure that water quality information collected in real-time has a measurement context, which can be used to improve/optimise management decisions.

5.5 Physicochemical Sensors

For a closed loop PRW system to be effective, there are a number of physicochemical parameters that need to be measured and controlled to ensure adequate treatment efficiencies. This is required to ensure the source water entering and being released from a treatment barrier within the scheme can meet the design specifications. For example, source quality is of paramount importance to ensure that RO membrane treatment can be effective in Barrier 4. Hence, as there are a number of IPR contaminants that must be measured in the validation phase, selected physicochemical parameters can often be used as the first indicators of a deterioration or potential failure in treated water quality[4]. Currently there are a number of these physicochemical sensors that are commercially available from a range of manufacturers (see Table 6 and Appendix 1). The suitability of physicochemical sensors for the closed loop PRW system will be dependent on:

- The robustness of the sensor;
- Sample matrix;
- Maintenance required;
- Sampling location;
- Fouling of the sensor; and
- Calibration.

Table 6 Physicochemical parameters required to be measured at each barrier

Parameter	B1	B2	B3	B4	B5	B6	B7	Commercially Available
Temperature	√	√	√	√	√	√	√	Yes
pH	√	√	√	√	√	√	√	Yes
Conductivity	√	√	√	√	√	√	√	Yes
Dissolved Oxygen	√	√				√	√	Yes
Suspended Solids		√	√			√		Yes
Turbidity		√	√	√	√	√	√	Yes

- Eutech Instruments: pH - ISE; Conductivity - Resistance; DO - Amperometric; Temperature – Thermistor.
- Hach: pH-ISE; Conductivity - Inductive; Turbidity - LED; DO - Polarographic or amperometric.
- Endress+Hauser: pH - ISE; Turbidity - LED/UV-Vis.
- YSI: Conductivity - Resistance; DO - Optical; pH - ISE; Temperature – Thermistor.
- Hanna Instruments: pH - ISE; Temperature – Thermistor.
- Mettler Toledo: Temperature - Thermistor; pH - ISE; DO – Galvanic.
- Greenspan: Conductivity - Resistance; DO - Galvanic; pH - SE; Temperature - Thermistor; Turbidity – Photometric.

As online sensors are required to operate continuously, they must withstand extreme and/or variable conditions, especially at Barriers 1, 2, 3 and 6, whilst still maintaining their calibrated status if they are to be an effective operational tool for operators and grid managers. Clearly, more commercial sensors should be suitable for operation in Barriers 3, 4 and 5, as the matrix is more consistent and the treated product water is of a higher quality compared to Barriers 1, 2, 6 and 7. For example, it is highly recommended that photometric DO probes be employed for Barriers 1, 2, and 6, rather than relying on membrane based sensors. This is because the sensors are required to operate in more variable and extreme matrix conditions, and those based on permeable membranes may be more prone to fouling and produce inaccurate measurements.

For Barriers 1, 6 and 7 where the monitors will be distributed over wide geographic areas, it is recommended that more robust sensors be employed to reduce the maintenance costs associated with the measurements. Most sensors require maintenance at least monthly, but as they are required for operational and control purposes, it is important that signal drift and calibration is controlled. Maintenance costs could be cost prohibitive if sensors cannot function unattended for prolonged periods. Clearly autonomous *in situ* sensors are preferable to labour intensive ones. For Barriers 1, 2, 6 and 7, it is also important that sensors can be compensated for environmental variations and signal drift.

5.6 Microbial Contaminants

The presence of micro-organisms poses the highest risk in PRW due to health risks associated with potentially infectious diseases, because in the WCRW project potable water is being produced from an impaired water resource (sewage effluent)[87]. Therefore, it is vitally important that the treatment processes employed in the WCRW project are capable of meeting their design specifications for the effective removal of the three main classes of pathogens; namely viruses, bacteria and protozoa. It would be preferable if continuous real-time information could be obtained on these three microbial classes to validate that the treatment processes were effective and that the required level of removal is achieved consistently.

Table 7 presents the microbial parameters that must be measured for each barrier. Presently there are no commercially available direct online measurements that can be used to analyse the key microbiological parameters, especially for Barriers 5 and 7.

Table 7 Microbial parameters required to be measured in PRW closed loop system for each barrier

Parameter	B1	B2	B3	B4	B5	B6	B7
Faecal Coliforms		√					
F-RNA Phages					√		
Somatic coliphages					√		
Escherichia Coli					√	√	√
Total Coliforms							√
Clostridium perfringens						√	
Giardia						√	
Cryptosporidium						√	
Cyanobacteria						√	
Algal Counts						√	

The development of reliable and rapid online microbiological monitoring tools would further strengthen existing baseline monitoring strategies and reduce costs currently associated with microbial assays. The only online sensors commercially available that can be used as surrogates to indicate the presence of microbial contamination are indicators such as turbidity, suspended solids and free chlorine. For Barrier 7, it is highly recommended that free available chlorine is monitored in conjunction with turbidity and temperature to ascertain if the conditions within the distribution system may be conducive to microbiological activity[4]. For example, if the free chlorine levels are low and turbidity is increasing, then that risk may be potentially increasing. As turbidity and temperature analysers have been discussed previously, this section will deal with online analysers for monitoring chlorine.

- Hach: Free chlorine- amperometric; Ammonia/monochloramine - colorimetric.
- Endress+Hauser: Free chlorine – amperometric.
- YSI: Chlorine – cadmium reduction ionisation.
- Hanna: Chlorine - amperometric.

Monochloramine is a suitable disinfectant for Barriers 3-4 to ensure RO membrane performance is maintained. However, it should be noted that online free chlorine analysers are only suitable for Barriers 5, 6 and 7, as they are based on direct adaptations of laboratory-based methods. Therefore they require strictly controlled measurement conditions and frequent calibration. For Barriers 2 (post clarification) and 3 there are no suitable commercially available methods with sufficient sensitivity to monitor free chlorine levels below 0.05 mg/L. This is due to the limitations of the method and nonlinear responses at the lower concentrations. As free chlorine is a CCP in Barrier 2 that may affect the performance of upstream treatment barriers, it is of paramount importance that there is online monitoring technology available that can detect in real-time if the system is approaching critical limits. In addition, reagent stability is of concern, as is signal drift.

Therefore, there is still work to be done before commercially available online sensors can be used for large-scale autonomous water quality monitoring. This is very important in Barriers 5-6 and for the distribution system in Barrier 7, as appropriate chlorine residuals must be maintained to ensure a consistent, safe supply of potable water.

As microbiological quality is the most important parameter required to ensure a safe supply of drinking water, the development of new online water quality monitoring tools that could rapidly assess the treatment process would be highly beneficial and further complement the WCRW plan. Although there have been some rapid methods developed for pathogens, e.g. flow cytometry and fluorescent in situ hybridisation (FISH), these still have several inherent drawbacks that inhibit their widespread applications, such as detection problems, the presence of large numbers of interfering species, and the requirement for highly skilled personnel[87].

Although there has been significant research in this area, viruses and protozoa are difficult to detect in fresh water due to their low concentrations. Consequently, large volumes of water are required to make a measurement with any degree of confidence. This can make analytical methods unsuitable for real-time online process control, especially within Barriers 3-7[87, 88]. Methods that require centrifugation as a pre-concentration step are also not suitable for online applications[88].

Therefore, there are still no suitable online microbial analysis tools available that have the robustness, sensitivity and limited maintenance requirements necessary to be an effective monitoring tool for the WCRW system.

Research and Development

Biosensors offer an alternative for measuring microorganisms such as pathogens, viruses and bacteria in real-time to complement existing standard monitoring practices. For example, a cell-based biosensor has been demonstrated for measuring an *E. coli* strain that was responsive to mercury. It was immobilised on a micro-well fibre array and its response to mercury was measured[86]. Alternatively, DNA hybridization microarrays have been suggested as a platform for the parallel detection of pathogenic organisms, which has potential applications in the PRW system[86]. Further development is required to improve their selectivity, durability and resistance to biofouling before they could be used in applications such as the PRW system. Stewart-Pullaro *et al. (*2006) investigated a simple, rapid and inexpensive method for monitoring F^+RNA, however no continuous, real-time methods with suitable accuracy were available[89]. Another promising development by Delahaye *et al.* (2003) has been the titration of adenosine triphosphate (ATP) using bioluminescence, which could have applications for monitoring coliforms and entercocci[90]. However despite these research advances, there are no biosensors available that have the operational performance and simplicity of comparable inorganic sensors (e.g. pH sensors) [86].

Once again electronic tongues have been suggested as an alternative tool for pathogen detection. They show some promise, as measurements can be obtained rapidly with limited sample pre-treatment being required, provided the correct sensors can be obtained to indicate microbial populations. However, sensor fouling would still be a problem, especially within Barriers 2, 6 and 7. Additionally, issues such as signal drift, reproducibility and calibration still need to be overcome to make this technique suitable for real-time continuous monitoring.

5.7 Pesticides

Currently there are no commercially available pesticide sensors that are economically feasible to implement in the WCRW project. However, there are a number of methods that have been demonstrated in the scientific literature that may be suitable if further developed.

Research and Development

Durrier *et al.* (2006) used biosensors based on chlorophyll fluorescence or enzyme inhibition to detect the presence of toxic heavy metals and pesticides in aquatic samples[91]. The technique was shown to be sensitive at low concentrations and may be suitable for online monitoring applications.

Cortina *et al.* (2007) used amperometric sensors to develop an electronic tongue for monitoring pesticides in aqueous solutions[92]. It was evaluated on river water before and after sewage treatment, with reasonable results being achieved. Solna *et al.* (2005) employed an electronic tongue based on amperometric sensors to determine pesticides and phenols such as carbaryl[93]. It could be a potential alternative for rapidly monitoring pesticides in the WCRW project.

Wang *et al.* (2007) have demonstrated the potential of using spectral fluorescence. They found that carbamate, benzoylurea and fungicides may emit strong fluorescence when excited by UV radiation under certain conditions[94].

This field is rapidly emerging and future developments may offer some potential water quality monitoring options for the WCRW project.

5.8 Endocrine Disrupting Compounds (EDCs)

Currently there are no commercially available online sensors suitable for monitoring EDCs rapidly and cost-effectively in the WCRW project. For continuous monitoring, separation processes such as chromatography should not be used as they have high costs and maintenance requirements. However, there are a number of methods that have been demonstrated in the research literature that may be suitable if further developed.

Research and Development

Rogers (2006) discussed the use of an in-line immunosensor system for measuring a wide range of EDCs and pesticides[86].

Wang *et al.* (2006) demonstrated using a bifurcated fibre optic chemical sensor for real-time monitoring of Bisphenol A[95]. It used fluorescence quenching of pyrene/dimethyl β-cyclodextrin complex immobilised in a plasticised PVC membrane as an indicator probe. This method or modifications of the measurement principle may be potential options in the future.

5.9 Trihalomethanes (THMs)

Currently there are no commercially available online sensors suitable for monitoring THMs rapidly and cost-effectively in the WCRW project. However, there are a number of methods reported in the research literature that may be suitable if further developed.

Research and Development

A promising research paper was produced by Chellam and Krasner (2001), which investigates using Dissolved Organic Carbon (DOC) and Specific UV Absorbance (SUVA) to determine disinfection by-products in nano-filtered waters[96]. There were found to be significant and positive correlations between DOC and SUVA for both THMs and Haloacetic Acids (HAA)[96]. Isaji (2003) proposed using physicochemical parameters as surrogates to indicate THM, as well as additional organic and inorganic compounds[97]. For example, conductivity can be used to provide estimations of THMs. Carvalho *et al.* (2006) used a sensor array based on conducting polymers to determine chloroform in real-time[98]. This may be the basis for a potential research option to produce a practical sensor.

5.10 Nitrosamines

To the best of our knowledge there is no available commercially technology or research that can demonstrate potential for measuring NDMA in the WCRW project cost effectively and online.

5.11 Pharmaceuticals

Currently there are no suitable and economically feasible commercial online sensors available for the WCRW project.

Research and Development

To the best of our knowledge there is limited research in the area that shows results suitable for application in the PRW system. However, Ishihara *et al.* (2005) demonstrated using an electronic tongue based on a number of parameters[99]. Caffeine was measured with an electron-cyclotron-resonance plasma (ECR) sputtered carbon electrode. Electronic tongues could be an alternative option for monitoring key IPR contaminants of concern in the WCRW project in the future.

5.12 Volatile Organic Carbon (VOC)

There are currently several commercially available systems for monitoring VOC for Barriers 1 and 2 (see examples given below). However, it should be noted that most of these systems may not be suitable for remote online monitoring applications due their high cost. Hence, they are not suitable for large-scale water quality monitoring applications within the WCRW project, but may be considered for monitoring at major treatment plants.

- ECH Elektrochemie Halle GmbH: Gas Chromatography.
- Ionicon Analytik: Proton Transfer Reaction – Mass Spectrometry (PTR-MS).
- Multisensor Systems: uses custom sensor arrays.
- RAE Systems: Photoionisation detector (Not considered fully automated online).

Research and Development

From the investigation of current research and development in the area, the use of an E-tongue may again be a potential option. This is because online sensors could be developed to indicate a number of key VOC that have been identified as IPR contaminants of concern in the PRW scheme. For example De Melo *et al.* (2005) used an electronic nose based on conducting polypyrrole chains for determining the presence of VOC[100]. The sensing system showed good sensitivity to methanol, ethanol and benzene. Kim and Yang (2007) developed an Electronic nose (E-nose) using 4 different carbon black-polymer composite sensors in addition to a temperature sensor[101]. The sensor array measured the chemoresistance of different VOC responses acquired through a voltage circuit. Hence, E-Noses offer the potential to limit the number of online monitoring analysers employed in the system, whilst increasing the number of key output parameters that can be determined. This would be a highly desirable approach for the WCRW project. However, further research and investigation is required to ensure that this is the most appropriate measurement technique available with the required sensitivity.

5.13 Early Warning Systems

Early warning systems are important for the preventative management approach requirements of the WCRW project. This is because there are a number of IPR contaminants of concern that need to be monitored continuously to ensure the treatment efficiency of each barrier. As it is not cost effective or technically feasible to measure all IPR contaminants of concern, it is important that online monitoring systems can detect excursions that may indicate that there is contamination or a gradual deterioration in water quality. This is especially important as operators and grid managers must ensure that their plants comply with PWR guidelines, but it is extremely difficult to mitigate for risks that may only become evident after serious problems have occurred.

- Hach: Event Monitor.

Recently, Hach introduced an Event Monitor that can be used for early warning. It can detect, alert and classify contaminants such as arsenic or anthrax based on computationally intelligent techniques that employ a combination of physicochemical sensors, total chlorine and TOC to monitor changes in baseline patterns. The system can be continuously updated, as it is based on fingerprint identification. However, as the system is based on intelligent software that is commercial and in confidence, it is not available for peer review. It has also been noted in the literature that the accuracy of measurement systems based on multi-parameter sensor inputs that are processed collectively is still affected by signal drift issues over time[65] if they use conventional methods of calibration. In addition, if compound identification is based on non-selective information such as physicochemical sensors, the system may also be matrix dependent. This is because non-selective sensors are used to indicate changes in the baseline sample matrix[65] or IPR contaminants of concern based on an indirect cause and effect relationship between the sample matrix and sensor system employed. Therefore it may be only valid in specific, well defined measurement conditions.

Research and Development

This research area is rapidly expanding, as the demand for rapid detection of deliberate contamination and the ability to safely recycle waters becomes more prominent. There are many approaches being used for rapid early warning, with numerous research approaches focused on developing intelligent data processing techniques for detecting a) sensor failure and b) contamination. For example, Rieger *et al.* (2004) used software techniques to detect sensor malfunctions[102]. However, this research is still in its infancy. Clearly, for the PRW system an intelligent early warning system that can collectively incorporate historical as well as online monitoring data would be highly beneficial. Currently, there is no historical data available from the Western Corridor Recycled Water scheme suitable for developing an early warning monitoring system that incorporates diurnal, seasonal and temporal variation as well as contamination events. Consequently, it is recommended that immediate steps should be taken to implement a systematic data and metadata recording scheme for the PRW scheme. This would form the basis for developing and implementing a real time early warning system.

6. CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

As became evident during the course of this review, the field of online water quality monitoring is rapidly expanding and still requires further advances to improve sensor performance, reliability and cost effectiveness. Currently, there are no broadly agreed international standards or methods developed that allow for large-scale, online, reliable and cost-effective data to be acquired, integrated and applied. There are commercially available analysers for monitoring Turbidity, Suspended Solids, Nutrients, Ammonia, organic parameters such as BOD_5, COD and TOC; as well as Inorganic and Physicochemical parameters. However, most have difficulty acquiring continuous, reliable and cost-effective water quality information in online installations. This is primarily due to the maintenance and calibration costs associated with the instrumentation, as most online analysers are based on direct adaptations of traditional laboratory-based methods. These methods require controlled measurement environments to obtain analytically valid results, which are rarely present in the field. As a consequence, online monitoring in its current form suffers from more problems than laboratory-based methods, as the methods were not originally designed for field applications. Hence, there are significant economic and logistics costs associated with maintaining online analysers of this nature, especially in remote areas, due to maintenance, calibration, blockages, matrix interferences, biofouling, signal drift and reagent consumption. In addition, it was evident that there are only a limited number of commercially available online analysers that are suitable for all measurement environments and treatment barriers required within the WCRW scheme.

It has been highlighted in the review that failure to maintain and calibrate online analysers appropriately can result in the following problems:

- Increased likelihood of false positive and false negative events;
- Decreased likelihood of detecting short and long-term trends from baseline monitoring conditions; and
- Large volumes of redundant data being produced but not being useable to optimise operational monitoring procedures.

To improve the performance of existing online systems, commercial and research endeavours have focused on improving sensor selectivity; reducing reagent consumption; overcoming matrix interferences; and simplifying calibration and sample pre-treatment requirements. However as evidenced by the review, there is not one single approach that has been implemented that can resolve most of the problems associated with improving online monitoring performance. This is especially the case for those methods that are based on direct adaptations of traditional laboratory-based methods. To overcome the logistics and economic costs associated with maintaining reliable online measurements and improve their widespread application, it is clearly evident that online technology should be redesigned to operate continuously in changeable measurement environments. Therefore, there is an urgent need to develop cost-effective online water quality monitoring technology that can maintain its calibrated status for prolonged periods of time and operate reliably irrespective of environmental or sample matrix conditions. It is also highly desirable that the instruments should use limited or no reagents, and be more resistant to fouling, signal drift and matrix interferences.

From the review of commercially available online analysers it was evident that obtaining reliable low maintenance continuous online analysers for Barriers 1 and 2 is problematic. Monitoring in these locations is currently a real challenge for commercial systems due to the complex nature of the measurement environment. In addition, many of the systems available are too expensive to allow their widespread use.

In regards to monitoring of heavy metals, online sensors must have adequate sensitivity for Barrier 2 and high sensitivity for Barriers 5-7. It was evident that a cost-effective technique is required, as direct adaptations of conventional laboratory-based methods such as AAS and ICP-MS are unsuitable online monitoring tools due to their high expense, along with separation, extraction and maintenance costs. Electronic tongues or voltametric methods may offer an alternative, and several such devices are currently being commercially developed.

With regards to online analysers for rapid microbial detection, there are at present only surrogate indicators commercially available, such as turbidity or free chlorine analysers. Although biosensors show promise, there are no commercially available sensors with equivalent performance to equivalent chemical sensors. It is possible that electronic tongues or software sensors may offer promise in this area. Therefore it is recommended that, as a high priority, robust, sensitive and low maintenance online microbial analysis tools should be developed for the WCRW system, especially to detect the three main classes of pathogens.

For Pesticides, EDCs, Pharmaceuticals, THMs, NDMA and VOCs, there are no commercially and economically viable online monitoring systems available for the WCRW scheme. E-tongues, E-noses and software sensors may offer some potential in the future if further developed. They have the potential to reduce the number of analysers required for the scheme whilst maximising the number of water quality parameters that can be determined. They would also reduce reagent costs and maintenance associated with the monitoring. However, the following should be taken into account when developing systems of this nature:

- Need rugged reference electrodes to reduce risk of contamination through liquid junctions;
- Must be resistant to biofouling especially in Barriers 1, 2 and 6;
- Improved data analysis techniques are required to make software sensors more suitable for long-term deployment applications by reducing signal drift; and
- Minimise consumption of reagents, so that they can be suitable for remote monitoring applications.

6.2 Summary of Recommendations

The following recommendations are provided from this review of current online water quality monitoring methods and commercially available online sensors.

Recommendation 1:

Priority needs to be given to sourcing or developing online analysers that are more reliable and resistant to biofouling and failure, especially for Barriers 1, 2 and 6, 7.

Recommendation 2:

Metadata needs to be recorded and incorporated into the data processing procedure to provide a measurement context to aid in the identification and assessment of events, and to ensure consistent data recording and retrieval protocols.

Recommendation 3:

There is an urgent need to develop online microbial analysis tools for the WCRW system that are robust, sensitive and require limited maintenance, especially for monitoring treatment efficiency in regards to the three main classes of pathogens.

Recommendation 4:

Hydraulic data should be incorporated with the online water quality information to help assess how water quality might be changing between online sampling locations, to identify potential problems, and to optimise chemical dosing procedures.

Recommendation 5:

If UV-Vis absorption techniques such as *s::can* that incorporate chemometric algorithms are used in the WCRW scheme, it is recommended that to ensure performance and accuracy, they should be placed in measurement environments where turbidity is below 150 NTU.

Recommendation 6:

Labour intensive online analysers such as colorimetric techniques should be employed in barriers where there are always staff present to maintain the instruments. Less labour intensive methods such as fibre optics and conductivity sensors should be used for Barrier 1, 5/6 and 7, especially if the monitoring site is remote.

Recommendation 7:

The manufacturers' specifications for online analysers sometimes do not adequately reflect the actual performance of the analyser in continuous, real-world measurement environments. It is recommended that water utilities independently investigate the operation and performances of instruments to ensure they are suitable for the intended use, based on the following criteria:

- Economic costs associated with maintenance and calibration;
- Robustness to operate continuously and reliably in non-ideal environmental conditions;
- Ability to be linked with a centralised SCADA system;
- Ability to process data in real-time and provide accurate water quality information; and
- Honest feedback on the instruments performance and reliability obtained from other water utilities that have employed the online analysers.

Recommendation 8:

Online analysers should be designed from the ground up to operate in changeable field environments, rather than to follow the current practice of modifying laboratory-based methods. The online analysers should be developed to:

- Operate in changeable measurement environments irrespective of sample matrix conditions;
- Be capable of maintaining their calibrated status for extended periods of time;
- Consume limited or no reagents;
- Be resistant to biofouling, signal drift and blockages;
- Be capable of operating reliably and accurately; and
- Minimise the number of false positive and false negative events.

Recommendation 9:

Computationally intelligent techniques should be employed for online data processing to assist grid managers in identifying any deterioration in water quality, or to alert if there is too much hazard overwhelming the system. These techniques could also be used to incorporate relevant metadata into the decision-making process, so that features in the online data record can be matched to known system events (e.g. treatment plant upsets, scheduled maintenance).

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Appendix 1: Review of Commercially Available Sensors for WCRW Project

Company Name	Website	Water Quality Parameter	Measurement Range	Matrix Suitability	Reliability and maintenance -frequency of calibration	Measurement Principle	Maintenance/ Warranty	Accreditation
Eutech Instruments	http://www.eutechinst.com/	pH Conductivity ORP Dissolved Oxygen Temperature	0-14 0- 2000 uS/cm 0-995 mV 0.04 to saturation -10 to 125°C	B 2-7 B 2-7 B 3-7 B1-7 B1-7	Frequency of calibration will vary depending on sample matrix and variability	ISE Amperometric Thermistor	1 year instrument, 6 months sensors	ISO 9001
ECH Elektrochemie Halle GmbH	www.ech.de	Hydrocarbons VOC	< 1 ppm	B 1-3	GC is online, Cal. every 6months	Gas Chromatography	1 year warranty	ECH Elektrochemie Halle GmbH
HACH	http://www.hach.com/	Alkalinity Ammonia/Nitrogen Chlorine, Free Chlorine, Total Conductivity Copper Dissolved Oxygen Dissolved Oxygen Hardness pH pH Sodium Suspended Solids (&Turbidity) TOC	0-500 mg/L 0.02-2.0 mg/L NH_3 as N 0-20 mg/L HOCL 0-2000 µS/cm 0.05-2.0 mg/L 0-80 ppm 0-40 mg/L 0.05-10 mg/L 2-12 0-14 0.01-10000 ppm 0-200 ppm 0.001-500 mg/L 0-4000 NTU 0-25 mg/L	B 3 – B 5, B4-5,B7 B3-B7 B2-B7 B2-B5,B7 B3-B7 B2, B6 B4 B4,B5 B2-B7 B4-5 B3,B6-7 B1-B7 B4,5, 7 B1-2, 6 B2-B7	Online, Auto-C Min 1/month Online, Auto-C. Min 1/month Min per 2 months Online Online, Auto- C Min 1/month Online Min 1/ year Online Online/auto Min 1/month Online Online Online Auto C, min 100 days Online Online Online	Colorimetric Colorimetric Amperometric Inductive Colorimetric polarographic Amperometric Colorimetric Potentiometric Potentiometric ISE LED High Temp. Oxidation Spectrophotometer Absorbance, Transmittance	1 month maintenance depending calibration 1/month Field proven Low maintenance Operates 1 month unattended Worry-Free Suitable for industrial applications. Field work	HACH's ISO 9001-2000 certification; Known worldwide & industrial applications

Company Name	Website	Water Quality Parameter	Measurement Range	Matrix Suitability	Reliability and maintenance -frequency of calibration	Measurement Principle	Maintenance/ Warranty	Accreditation
		UV 254 Ammonia/monochloramine Ammonia/ammonium Orthophosphate Flow Event Warning	0-20000 mg/L 0.01-3000m^{-1} 0.02-2.0 mg/L as N (0.1- 10.0 mg/L as Cl2) 0-20 mg/L 0-15 mg/L May not respond to many of the 360 IPR contaminants	B3-5,B7 B2C-3,B6 B2C-B7 B1-2, B6, B7 B2-B7	Online Online/auto-C every 3 days Online auto-C every 3 days	Colorimetric Colorimetric Colorimetric		
E+H Endress+Hauser	http://www.de.endress.com/	pH Turbidity Ammonium Nitrate Phosphate *STIP in-situ, see product information* Nitrate COD TOC Turbidity (ATU) 3 sludge parameters	0-14 0-100 NTU 1-500µg/l ; 0.2-100mg/l 0.2-30 g/l 0.1-8mg/l ;1.0-50mg/l 0.3-23 mg/l 10-2000 mg/l 4-800 mg/l 1-250 m^{-1}	B 1 – 7 B 6 – 7 B 2C – 7 B 2-7 B 2C-7 B2C B3-B7 B2	Online, fully automated Online, primary calibration less than 5 minutes online /auto-C maintenance 6 months Online /in-line Online Online, in-line Online Online Online	Electrochemical LED Colorimetric UV Photometric Colorimetric Spectroscopic Colorimetric UV Spectrometry	For drinking & wastewater For drinking & treated process water Water treatment plants & outlets activated sludge Water treatment plants & outlets Measures directly in wastewater	Accredited & marketed worldwide

Company Name	Website	Water Quality Parameter	Measurement Range	Matrix Suitability	Reliability and maintenance -frequency of calibration	Measurement Principle	Maintenance/ Warranty	Accreditation
		Free Chlorine Toxicity BOD COD	0.05-20 mg/L 0-100% 20-100000 mg/L 10-10000 mg/L	B2 B2	Online	Amperometric Biosensor Dilution ratio require to maintain oxygen consumption Ozone sensor		
YSI	https://www.ysi.com/	*Professional Plus:* Ammonia Conductivity Dissolved Oxygen Nitrate Chlorine pH Temperature TDS	Depends on application Depends on application 0-50 mg/l 0-10 mg/l 0-14 -5/+70 °C Depends on application	B2C, B6-7 B2C, B6-7 B2 B2C, B6-7 B2, B6-7 B2, B6-7 B2, B6	Online/In-line Online/In-line Online/In-line Online/In-line Online/In-line Online/In-line Online/In-line	Optical Cadmium redn. Ionisation	Tough, Smart, Versatile Warranty Instrument: 3a Field Cables: 2a Sensor: 1a	
HANNA Instruments	http://www.hannainst.com/	pH Chlorine, Free Chlorine, Total Temperature pH	0.00-14.00 0.00-5.00 mg/L 0.00-5.00 mg/L 5.0-75.0 °C 0.00-14.0	B2C, 6 – 7 B2	Online	Potentiometric Amperometric Amperometric Thermistor		Known worldwide
Mettler Toledo	www.mt.com	*Thornton 770MAX:* Dissolved Oxygen pH TOC Temperature	0-100% -1.00-15 0.05-1000 ppb -40/200 °C	B 2 – 7	Online	Galvanic Potentiometric UV oxidation Thermistor	Measures even in worst wastewater conditions	Global presence
Greenspan	http://www.tycoflowcontrol.com.au/TES_Greenspan_Analytical/products/aqualab	*AquaLab:* Nitrate Ammonia Phosphorus, Total Nitrogen, Total TOC	0.1-14 mg/L 0-14 mg/L 0.1-3 mg/L 0-7 mg/L 0-50 mg/L 0-2000 µS/cm	B6-7	Online, self-calibrating	ISE ISE Colorimetric Colorimetric Non-dispersive IR		Measurement in the Everglades

Company Name	Website	Water Quality Parameter	Measurement Range	Matrix Suitability	Reliability and maintenance -frequency of calibration	Measurement Principle	Maintenance/ Warranty	Accreditation
		Conductivity Dissolved Oxygen pH Temperature Turbidity	2-12 0-2000 NTU			Galvanic Potentiometric Photometric		
RAE Systems	http://www.raesystems.eu/	VOC (Volatile Organic Carbon)	0-15000ppm	B1-2	Real-time	Photoionization Detector (PID), MiniRae3000		
s::can	http://www.s-can.at/	Full Water Quality Monitoring Station Includes: TSS/TS/MLSS, UV 254/SAC, Colour, COD, BOD, NO3, NO2, H2S, NH4, K+, pH, ORP, O2, Conductivity, Temperature, Hydrocarbon alarm, Industrial emission alarm	Depends on the application	B 1-3, 6,7	In situ & online, global calibration	Spectral UV-VIS Spectro::lyser, ammo::lyser, fluor::lyser, oxi::lyser, free chlorine sensor, con::stat		
Aqua Diagnostic	http://www.aquadiagnostic.com/	*PeCOD P100:* COD	0.2-350 ppm Dilution< 15000 ppm	B 2-B7	Online	Photoelectrochemical		
AppliTek	http://www.applitek.com	Heavy Metals Zn, Cd, Pb, As, Hg, Fe, Cr Toxicity	0.01-100 ppm	B2 B2	Online-Auto C	Voltammetric Oxygen Sensor	-Requires reagents and calibration	
SensAqua A/S	www.sensaqua.com	Heavy Metals Cu, Pb, Zn, Cd, Fe, Hg,		B6	Online	Solid Dental Amalgam Sensor-Voltammetry	-Requires reagents and calibration	

Appendix 2: Review of Research Developments for Contaminants of Concern

Reference	Contaminants of Concern	Notes
Durrieu, C *et al. (*2006). *European Physical Journal – Applied Physics*, **36** (2): 205-209	Heavy Metals and Pesticides	Biosensors –chlorophyll fluorescence or enzyme (phosphatase and esterase) inhibition were used to detect presence of toxic heavy metals and pesticides in aquatic samples. Results with whole-cell biosensors show these devices are sensitive to heavy metals and pesticides - The system allows the cells to operate in their natural environment which favours long term stability and reflects the toxic action mechanism therefore providing an ecological interest. - Real-time detection and online monitoring possible
Zhu S *et al. (*2006). *Rare Metal Materials and Engineering*, **35:** 381-384	Heavy Metals Zn^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+}, Fe^{3+}, Cr^{3+}	Electronic tongue – uses a microelectrode array and differential pulse voltammetry with ppb level of detection.
Men H *et al. (*2005). *Sensors and Actuators B*, **110**:350-357	Heavy Metals Fe, Cr, Mn, As, Zn, Cd, Pb, Cu	Electronic tongue – made from multiple light addressable potentiometric sensors (MLAPS) and two groups of electrochemical electrodes. MLAPS are based on chalcogenide thin film for simultaneous detection of Fe (III) and Cr(VI) while two groups of electrochemical electrodes detect other heavy metals. The electrodes used in this method are non-selective. Specific standards and buffers required for measurement of different ions.
Rudnitskyaya A *et al*. (2001). *Talanta*, **55**:425-431	Heavy Metals, Inorganic ions and alkali cations Cu^{2+}, Zn^{2+} Mn^{2+}, Fe^{3+}, Ca^{2+}, Mg^{2+}, Na^{+}, Cl^{-}, SO^{2-}_{4}	Electronic tongue- array of non-specific potentiometric chemical sensors for monitoring heavy metals in ground water. 13 PVC membranes and 12 solid state membranes. No reagents used. The lowest errors of content determination (0.7% for Cu; 0.7% for Zn; 1,1% for Fe(III), 3.6% for Ca; 5.7% for Mg; 2.8% for SO4; 4.5% for Na; 4.7% for Cl) were obtained using responses of all 25 sensors in the array during signal processing.
Xie X *et al* (2004). *Sensors and Actuators B*, **97**:168-173	Heavy Metals Cd and Pb	Electronic tongue- based on iridium ultramicroelectrode arrays and square wave anodic stripping voltammetry (SWASV), trace concentration of heavy metals like Pb and Cd in aqueous solution could be successfully determined at ppb levels. Buffers and pH adjustment required for measurements. Results are reasonable for ppb detection.
Prestel H, Gahr A and Niessner R (2000). *Fresenius J Anal Chem*, **368**:182-191	Heavy Metals Cd^{2+}, Ni^{2+}, Cu^{2+}	Electronic tongue using fibre optic sensors. Developed for monitoring dissolved heavy metals in ground and surface water. The sensor consists of 5 sensing modules and measures the excitation using a Nitrogen Laser (λ = 337.1 nm) and a detection module containing a spectrograph with a CCD camera. Heavy metals need to be controlled in aqueous matrix with negligible concentration of other ionic pollutants. *Further information is required about matrix effects. This may be a problem in sewage samples or varying water matrices.*
Tercier-Waeber M *et al*. (1999). *Measurement Science and Technology*, **10**(12) :1202-1213	Heavy Metals Cu (II) Pb (II) Cd (II) Mn (II) Zn (II)	Voltammetric sensor array comprised of gel integrated microsensor array was used for *in situ* profiling measurements of surface and ground waters. It allows high spatial resolution and profile measurements at the sediment-water interface.

Reference	Contaminants of Concern	Notes
Delahaye, E *et al.* (2003). *Water Research*, 37: 3689-3698	Microorganisms Total and thermoresistant coliforms and enterococci	Presence of microorganisms can be measured rapidly using titration of adenosine triphosphate (ATP) by bioluminescence - A new extraction and titration system of bacterial ATP has been tested in the Paris drinking water distribution network. Conclusion: - There is a linear relationship between log [ATP] and log(HPC-R2A/ml) → quick method by detecting positive, microbial compounds in waste water gives evidence about water quality → This may be a potential option for PRW system; however the stability of reagents and sample pre-treatment needs to be refined for it to be viable in the field.
Stewart-Pullaro J *et al.* (2006). *Journal of Applied Microbiology*, 101: 1015 -1026	F^+RNA	Coliphages have been used as indicators for faecal contamination, sewage contamination, and enteric virus contamination in environmental waters → Use of F^+RNA coliphages typing for MST appears advantageous because it is simple, rapid and inexpensive compared to other methods → no continuous, real-time methods with suitable accuracy are currently available on the market
Rogers K (2006). *Analytica Chimica Acta*, 568: 222-231	Microbial Analyses Heavy Metals Phenols and Endocrine disrupting Compounds VOCs	A suite of biosensors have been developed that have applications suitable for the PRW system. The employ various measurement principles e.g. an in-line immunosensor system for measuring a wide range of pesticides, endocrine disrupting compounds and industrial pollutants. However biosensors in their current form still tend to suffer from biofouling and are susceptible to matrix effects. Until they have operational characteristics similar to a pH sensor in terms of durability, selectivity and concentration range, they will not be suitable for autonomous, real-time data acquisition in the context of a PRW closed loop system. This is due to high maintenance costs in their current form.
Horsburgh A *et al* (2002). *Biosensors & Bioelectronics*, **17**:495-501	Microorganisms/ Toxicity	Review of potential biosensors for online toxicity testing with applications for water quality monitoring. Discusses simple toxicity testing and more complex fingerprinting techniques. The biosensor was based on *E-coli* and was used to assess the toxicity of a range of pollutants such as Zn, Cu, 3,5 DCP, Benzene. The pollutants assessed were IPR contaminants of concern for WCRW project. Toxicity fingerprints were highly sensitive to different effluents and differently shaped profiles.
Van Poucke, S and Nelis H (2000). *Journal of Applied Microbiology*, **3**: 390-396	Bacteria *E. coli*	Describes method measuring the number of *E. coli* present in drinking water. The method is based on solid phase flow cytometry and two-step enzymatic labelling. Results were similar to those measured by epifluorescence microscopy.
Straub T and Chandler D (2003). *Journal of Microbiological Methods*, **53**: 185-197	Pathogens	Discusses potential methods that could be used for rapid detection of pathogens. Methods range from online sample processing and purification to DNA micro array technologies. Reviews challenges facing pathogen detection such as pathogen size, expected pathogen concentrations in water (e.g. require larger volume of sample for analyses), matrix effects. Before rapid pathogen analysis can be achieved require more fundamental research in improved sample extraction, purification, eliminating PCR from analytical process and optimising the sensitivity.
Rudnitskaya A and Legin A (2008). *J Ind Microbiol Biotechnol*, **35**:443-451	Microorganisms	Evaluates sensor system, electronic tongues and noses and their potential for monitoring biotechnological processes. Evaluates problems with online sensors. For example it discusses an electronic tongue based on pulsed voltammetry and potentiometric sensors for discriminating between different types of yeast and bacteria. However problems with drift, sensor fouling, stability, reproducibility and calibration need to be further addressed before the systems can become more applicable.

Reference	Contaminants of Concern	Notes
Gutirrez M *et al.* (2008). *International Journal of Environmental Analytical Chemistry*, **88**: 103-117	Inorganic parameters Potassium, sodium and chloride	Electronic tongues based on arrays of potentiometric sensors and complex data processing by artificial neural networks and data transmission by radiofrequency. Tested using a system simulating real conditions in surface water, performed simultaneous monitoring of ammonium, potassium, sodium, chloride, and nitrate ions Conclusion: - The proposed system allows assessing the effect of natural biodegradation stages for these species. - A second application was to monitor concentrations of ammonium, potassium, and sodium in the 'Ignacio Ramirez' dam (Mexico). → The electronic tongue allowed determination of K^+, Na^+, Cl^- in real samples → RF communications worked robustly, thus demonstrating the viability of the proposed systems for automated remote applications.
Brown M.A and Emmert G. (2006). *Analytica Chimica Acta*, **555** :75-85	Trihalomethanes (THMs) a) $CHCl_3$ (chloroform) b) $CHBr_3$ (bromodichloromethane) c) $CHBr_2Cl$ (chlorodibromomethane) d) $CHBr_3$ (bromoform)	Online monitoring of trihalomethane concentrations in drinking water distribution systems using capillary membrane sampling-gas chromatography with electron capture detection. - methods provide good accuracy, precision and level of precision - methods not economically feasible for continuous online monitoring Chen and Her [8] – built a continuous flow P&T-GC-mass spectrometer (MS) for monitoring THMs Wang et al. [9] used a laboratory head space unit attached to a GC-ECD Lopez-Avilia et al. [11] used membrane introduction mass spectrometry (MEVIS) to monitor THM concentrations. -ideal analytical method, needs a sampling rate of 1 per hour, operating range of 0.5 to 5 ug/L means recovery of 100+/- 5% with an RSD +/-10 %. It would exhibit minimal interference from TOC concentrations of 10-20 mg/L.
Chellam S and Krasner S (2001). *Environ.Sci.Technol*, **35**: 3988-3999	THMs Haloacetic Acids (HAAs)	Trialled DOC and SUVA to determine disinfection by-products in nanofiltered waters. There were found to be significant and positive correlations between DOC and SUVA for both THMs and HAAs. The method shows promise for filling data gaps when information is required in real-time.
Cancho B and Ventura F (2005). *Global NEST Journal*, **7** (1): 72-94	THMs	Evaluates different methods for monitoring a number of disinfection by products. The majority of methods require selective detectors for trace detection employing techniques such as gas chromatography and ion chromatography There are three methods proposed for the online monitoring of HAA. a) Nicotine-fluorescence flow injection analysis b) Anion chromatography with membrane suppressed conductivity detection c) Post-IC column NCA-Flow Most methods employ traditional methods of calibration and required skilled technicians, suitability for continuous, simple monitoring and detection is still to be determined.

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Isaji C (2003). *Water Science and Technology*, **47** (9):15-23	Physicochemical Parameters Organics and inorganics THM estimation Coliforms Hardness BOD Ammonia	Developed a method for estimating trihalomethanes for DPB control. Also suggest a number of physicochemical parameters that can be used as surrogate measures for a number of difficult to measure water quality parameters. Turbidity – an important factor for effective control of chlorine residual, also important for understanding particle removal and effectiveness of measures against chlorine resistant pathogenic protozoa e.g. Cryptosporidium Found the following correlations (t: total, d:dissolved) Water temperature – DO, d-Mn, Streptococcus Turbidity – Colour, t-Fe, d-Fe, d-Al, t-Ti, coliform group Conductivity- Ca, Na, Mg, K, HCO_3, Cl, SO_4, Hardness, Sr, Ba, Li, B, F, Si, NH_4-N, NO_2-N, BOD Items not correlated: t-Zn, t-Mn Invariable: pH, NO_3-N, NO_2-N Not detected: Trace organic substances, Heavy metals
Miro et al (2004). *Talanta*, **62**:1-15	General Water Quality Parameters Anionic Compounds, Halogenated, Sulphur and metalloid species	Investigates a number of flow injection techniques for *in situ* and online water quality analysis: pH, alkalinity, total ionic concentration, conductivity, DO, BOD and COD were good parameters for the assessment of water quality using cheap and effective analytical sensors. DO – good indicator presence or organic matter, biological treatment efficiencies and toxicity Polluting potential of organic matter - COD and BOD Conductivity – ionic strength of the sample. pH – UV-Vis through phenol red indicator. Sulphate – indicator of water pollution and acidity. Suphide – product of oxidation. Highly toxic to most aquatic organisms. *Most methods are not suitable for direct in-situ analysis without reagents or calibration. The reliability of the proposed techniques for long-term sensor deployment is also questionable.*
Moisello L, *et al.* (1998). *J. Agric.Food Chem*, **46**: 3847-3851	Pesticides Atrazine and Terbuthylazine	Require rapid and reliable methods for real-time monitoring of pesticides and other organics micropollutants in water samples →new dipstick assay for terbuthylazine and atrazine using monoclonal antibody (P6A7) - measurement principle based on reaction between pesticide and enzyme tracer for binding the membrane-coated specific monoclonal antibody and involves a change in colour intensity at 657 nm. Although results are promising, it is still designed for laboratory based measurements, and thus is not suitable for real-time process control.

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Rodriguez-Mozaz S *et al*. (2004). *Journal of Chromatography A*, **1045** :85-92	Estrogens, Pesticides and Bisphenol A	A multi-residue measurement system for classes of endocrine disrupting compounds has been developed e.g. estradiol, estrone, estriol, estradiol-17-glucuronide, estradiol diacetate, estrone-3- sulphate, ethynyl estradiol, diethylstilbestrol, atrazine, simazine, desethylatrazine, isoproturon, diuron, bisphenol A. Method uses a pre-concentrated LiChrolut RP-18 cartridge, followed by HPLC-MS analysis using APCI for pesticides and electrospray negative ionisation for estrogens and bisphenol A. It is not possible to monitor every substance in surface water; however it is necessary to define major target areas of focus for effective barrier protection. Surface water chemistry exhibits changing chemistry and composition depending on environmental conditions. A single method of analysis for different classes of selected analytes would reduce the costs and time necessary for routine water quality analysis. Within the treatment process, it was found that the concentration of bisphenol A decreased progressively through each treatment step. Study by these authors found that Bisphenol A was below the quantification limit. I*t is hypothesised that these variations also exist in the sewer catchment*
Cortina M et al (2007). *Electroanalysis*, **20** (1):54-60	Pesticides	Uses amperometric sensor array combined with ANNs to determine pesticides in aqueous solutions. It was evaluated on in river water before and after sewage treatment, and gave good results with low error. It shows potential for monitoring pesticides in the PRW system.
Eaton A and Briggs M (200x). NDMA- Analytical Methods Options for a new Disinfection By-Product, Montgomery Watson Laboratories, Pasadena, CA 91101	NDMA	-The original analytical method was developed by the Canadian Ministry of Environment (MOE) using solid phase extraction technique with an Ambersorb resin, followed by isotope dilution GCMS. However many new methods have been developed to improve its reliability, sensitivity and simplicity. However there are no methods that currently provide real-time continuous information on NDMA, which is required for the PRW system. The methods are still laboratory based and require calibration and standard reagents.
Comparison of alternative Nitrosamine analyses for water reuse samples, Cheng. R and Andrews-Tate C, Hwang C, Guo Y, Grebel J and Suffer I, Funded by Water Reuse Foundation	Nitrosamine (Including NDMA)	- Report is an interlaboratory study which evaluated 5 methods for 8 types of nitrosamines including NDMA for accuracy in different matrix types. Methods include : a) Micro Liquid-Liquid Extraction (MLLE) b) Ambersorb Solid Phase Microextraction (SPME) GC/MS c) Ambersorb Solid Phase Extraction (Amb SPE) d) Liquid-Liquid Extraction (LLE) Solid phase microextraction (SPME) is a low-cost method, however was not included in round robin testing. Results indicated that the Amb-Envi SPE and Amb SPE and traditional LLE (coupled with GC/MS) detected NDMA at the minimum level of 2 ng/L and other nitrosamines between 2 and 4 ng/L.
Davi M and Gnudi F (1999). *Water Research*, **33** (14) : 3213-3219	Phenolic Compounds	Phenolic compounds are problematic in drinking water due to their toxicity. Bisphenol A and some polychlorinated biphenyls have the ability to mimic the activity of oestradiol. Method developed by EEC 75/440 determines total phenol using condensation with 4-aminoantipyrine in the presence of potassium ferricyanide to form a coloured dye. However the method does not provide information on the nature of the phenol. Interfering substances can also affect accuracy of the analysis. HPLC or GC-MS is more accurate and allows identification of individual phenolic compounds in the water matrix at low concentration. Precision and accuracy is also desirable. Chloro- and nitro-phenols listed in the EPA Federal Register, analysed by GC-MS by single ion monitoring (SIM) have rarely been detected and if so at levels less than 1 ug/L. There are no suitable rapid means of analysis.

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Gibson R *et al.* (2007). *Journal of Chromatography A,* **1169**:31-39	Acidic Pharmaceuticals and Endocrine Disrupting Compounds	-Developed a simple extraction method for these two groups in untreated wastewaters and spring water. It is based on the separation of two classes during elution from an extraction cartridge with final analysis by GC-MS. Detection Limit – 0.005 to 1 ng/L in spring water and 0.5 to 100 ng/L for wastewater LC is well suited to polar compounds and non-volatile compounds. Methods are still not simple and require calibration. The instruments are also relatively expensive.
Hao R *et al.* (2008)*Chemosphere*, **70**: 783-790	Nonylphenol	→ Model used to describe nonylphenol accumulation in wastewater effluent used in a water recycling system based on number of recycling processes, NP removal efficiency and NP accumulation factor. It was found that NP concentrations increased with number of cycles through wastewater recycling processes – suggests there should be a maximum wastewater recycling ratio. Recommended that a study of NP accumulation should be conducted on the site. Indicates that real-time information is required.
Wang X *et al.* (2006). *Analytica Chimica Acta*, **556**:313-318	Bisphenol A	A bifurcated fibre optical chemical sensor for real-time monitoring of BPA was developed. Uses fluorescence quenching of pyrene/dimethyl β-cyclodextrin complex immobilised in a plasticised PVC membrane as a indicator probe. For continuous monitoring no separation processes such as Chromatography should be used. Therefore this method shows promise for the PRW project..
Wong K *et al. (*1997). *Biosensors and Bioelectronics*, **12** (2):125-133	Toxicity	Rapid tests are important for assessing changes in water quality, especially in regards to discharges of toxic materials. Oxygen uptake is the most acceptable parameter for monitoring the toxicity of heavy metals to activated sludge, and it has been employed online. Although DO electrode is easy to calibrate and obtains rapid response, it requires electrical connection and electrode fouling, which can cause measurement errors. An alternative is the oxygen optode based on the quenching of luminescent dyes. The method has several advantages over electrodes. It has a short response time, high sensitivity and nil consumption of oxygen. Use of fibre optics means that there is no connection between the oxygen sensing surface and the detector. It uses oxygen sensing film, LED and fibre optics, and measures the emission at 610 nm, when it is irradiated at 460 nm. Used the optode to measure DO versus time in the presence of different heavy metals. It was found that activated sludge responded with different toxicity patterns to different heavy metal concentrations.
Latif M and Licek E (2004). *Environ Toxicol* **19**:302-309	Toxicity – Microbial Tests Protoxkit F™ (Protozoa) Daphtoxit F™ magna (Microalgae) Thamnotoxkit F™ (Crustaceans) Ostracodtoxkit F™ (Higher Plant)	Investigates a number of microbial tests for assessing the toxicity of wastewater and sediments in Austria to determine which ones are more sensitive. It evaluates the potential and limitations of the microbial tests. Concludes that performing a number toxicity tests may not be practicable from a cost perspective.
Carvalho E et al (2006). *Sensor Letters*, **4**(2) :129-134	Chloroform	Interdigitated gold-coated microelectrodes were covered with various conducting polymers to develop a sensor array. Their impedance was measured at a fixed frequency of 1000 Hz, which allowed simple acquisition of information. Limit of detection 0.01 mg/L

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Bohrer F et al (2008). *J.AM.CHEM.SOC*, **130**:3712-3713	Hydrogen Peroxide	H_2O_2 vapours may be detected selectively by contrasting oxidation/reduction behaviour on nanoscale chemiresistive films of monolayer protected nanoclusters (MPC). EPR studies of optically excited ZnPc solutions revealed presence of OH radicals, suggesting homolytic cleavage of H_2O_2
Ishihara S *et al. (*2005). *Anal. Chem*, **77**:7908-7915	Caffeine and taste	Development of an electronic tongue based on determining the eight major taste-causing substances: Na^+, K^+, Cl^-, H^+, sucrose, glucose, glutamate and caffeine. Patterns were analysed using a two-phase optimized radial basis function network (RBFN). Electrodes for the sensor arrays were: capillary ISEs for Na^+, K^+, Cl^-, a Pt/IrO2 electrode for pH; PFCE modified with enzymes and HRP-Os polymer for glucose, sucrose and glutamate; and ECR-sputtered carbon electrode for caffeine.
Escher B *et al*. (2008). *Journal of Environmental Monitoring,* **10** (5): 622-631	Herbicides/non-volatile compounds	- A mode-of-action based test battery of low-complexity and in-vitro bioassays can be used as a routine monitoring tool for sewage treatment efficiency and water quality assessment - field studies were undertaken at a sewage treatment plant (STP). → Samples were collected under dry and rainy conditions → None of the bioassays gave positive results with raw water in whole effluent toxicity testing → Therefore water samples from various sites during wastewater treatment and from surface water were enriched using solid- phase extraction. → focus was on non-volatile compounds of average to moderate hydrophobicity, a range that includes most pesticides, biocides and pharmaceuticals. Conclusion: - With the bioassay data the treatment efficiency of the STP can be assessed with respect to different modes of toxic action and accordingly different groups of micropollutants - Treatment efficiency was high (typically over 90%) but varied from bioassay to bioassay (detection of different types of micropollutants), so no expectation of a common answer. → system itself is relatively complicated and expensive to commission or even modify for the AWTPs
Wang Z *et al*. (2007). *Spectroscopy and Spectral Analysis*, **27** (11) : 2321-2324	Organic Pesticides	- The molecular structures of a few common pesticides such as carbamate, benzoylurea and fungicide were analysed, and the mechanism of fluorescence generation was ascertained. - a steady-state fluorescence spectrograph was used with standard solutions of these pesticides to obtain fluorescence spectra, and their fluorescence characteristics were analysed. Conclusion: - Carbamate, benzoylurea and fungicide pesticides emit strong fluorescence when excited by UV in a particular solvent, their fluorescence spectra are distinct, and the resolution is fine. - As a result, it is feasible to carry out qualitative and the quantitative analysis of these pesticides by fluorescence spectral analysis. → Method seems capable to assure water quality monitoring, but it has to be proved whether it can be applied in AWTP

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Hu Y *et al* (2008). *Talanta*, **74** (4) :760-765	Hydroxyl Radicals	- Description of a simple method to electrochemically detect hydroxyl radicals - The (OH)-O• is generated by the Fenton reaction from iron (II) sulphate and hydrogen peroxide in a phosphate buffer solution Conclusion: - Method detects (OH)-O• with high sensitivity without any separation process - The differential pulse voltammetric responses show a linear dependence on the concentration of (OH)-O• → a simple, inexpensive and promising method
Solna, R *et al*. (2005). *Talanta,* **65** (2): 349-357	Phenols and Pesticides	- Immobilization substrates for electrodes were tyrosinase, peroxidase, acetylcholinesterase, butyrylcholinesterase → measuring inhibition by pesticides: acetylthiocholine chloride as substrate for cholinesterases → determining phenols: hydrogen peroxide as co-substrate for peroxidase Results: - detection of *p*-cresol, catechol, phenol and pesticides including carbaryl, heptenophos, fenitrothion in a flow-through and steady-state system - evaluation of effect of heavy metals (Cu^{2+}, Cd^{2+}, Fe^{3+}), fluoride (NaF), benzene and dimethylsulphoxide on cholinesterase activities - electrodes modified with hydrolases and oxidoreductases can function in the same array Conclusion: Showed that simultaneous analysis was feasible, with a small degree of cross-sensitivity. Complexity of real samples gives non-linear responses of biosensor array. Alternative data analysis using principal component analysis and other chemometric methods is a possibility. Not yet a commercial product, but could be worth trialling in PRW scheme.
Shin Kim *et al.* (2005). *Sensors and Actuators B*, **108**: 285-291	VOCs	Electronic nose for detecting VOC. It uses an array of carbon black-polymer composites and pattern recognition techniques. Was able to classify different types of whiskeys.
De Melo *et al.* (2005).*Sensors and Actuators B*, 348-354	VOC	Electronic tongue using conducting polypyrrole chains for determining the presence of VOC. The polymer mix is imbedded on conducting ITO glass substrates. The sensors exhibited good sensitivities towards methanol, ethanol, benzene and carbon tetrachloride.
Shin Kim Y and Seok Yang (2007). *Sensors and Actuators B*, **121**: 507-514	VOC	Electronic nose developed using 4 different carbon black-polymer composite sensors in addition to a temperature sensor. The sensor array measured the chemoresistive response acquired through a voltage circuit.
Kessick R and Tepper G (2006). *Sensors and Actuators B*, **117**: 205-210	VOC	Electronic nose based on electrospun polymer composite fibre arrays identify VOCs. It could quantitative determine the concentration of tow organic solvents, one alcohol and one chemical welfare agent. The method shows potential.

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