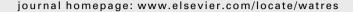


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Advances in on-line drinking water quality monitoring and early warning systems

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ABSTRACT

Significant advances have been made in recent years in technologies to monitor drinking water quality for source water protection, treatment operations, and distribution system management, in the event of accidental (or deliberate) contamination. Reports prepared through the Global Water Research Coalition (GWRC) and United States Environment Protection Agency (USEPA) agree that while many emerging technologies show promise, they are still some years from being deployed on a large scale. Further underpinning their viability is a need to interpret data in real time and implement a management strategy in response. This review presents the findings of an international study into the state of the art in this field. These results are based on visits to leading water utilities, research organisations and technology providers throughout Europe, the United States and Singapore involved in the development and deployment of on-line monitoring technology for the detection of contaminants in water.

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1. On-line monitors and early warning systems

There exists a need for better on-line monitoring of water systems given that existing laboratory-based methods are too slow to develop operational response and do not provide a level of public health protection in real time. There is a clear need to be able to rapidly detect (and respond) to instances of accidental (or deliberate) contamination, due to the potentially severe consequences to human health. Detecting this in real time is the most optimal way to ensure an appropriate and timely response. However the need for real-time monitors should be assessed on a case-by-case basis based on the requirements of an individual water management body. Water utilities worldwide therefore employ on-line monitoring tools

and early warning systems at all stages of the urban water cycle, through intake protection, treatment operations and distribution systems. Through the use of these tools water utilities have the potential to detect contaminants (either natural or artificial, and accidental or deliberate) in a drinking water system in near to real-time thus improving system management responses to events. General water quality parameters including pH, chlorine, temperature, flow and turbidity are commonly monitored using on-line instrumentation (Frey and Sullivan, 2004). These are used by operators in process control and regulatory compliance, and in some cases as early warning systems for contaminant detection.

Early warning systems (EWS) are generally an integrated system consisting of monitoring instrument technology, with an ability to analyse and interpret results in real time (Grayman

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	some advantages and limitations of various		
Sensor	Advantages	Limitations	Source
J-Mar Biosentry™	• Directly integrated into the water supply through continuous, slip-stream flow analysis	Does not provide viability data	(USEPA, 2010)
	 Process is virtually instantaneous providing for real-time detection and classification Fully automated and remotely accessible, 	 System cannot differentiate between live and dead organisms, motile or non-motile, organic 	
UV−VIS s::can spectro::lyser™	 and minimal maintenance requirements Fully submersible UV/Vis probe suitable for monitoring wide range of liquids 	 or inorganic When the instrument was installed at the intake of a treatment plant, where surface water is monitored, fouling of the flow-cell observed 	(van den Broeke, 2005, USEPA, 2010)
	 Single probe can be used to measure multiple parameters, including COD, COD-filtered, BOD, TOC, DOC, UV-254, NO3, NO2, ozone, H₂S, TSS, and turbidity 	Flow velocity determined the rate of sediment build-up	
Hach Event Monitor (Guardian Blue™)	 Distribution and plant personnel can troubleshoot remotely Programmed to recognise future occurrences of the same event and notify operations 	The instrument has little maintenance problems however has created several false alarms	(Hohman, 2007)
YSI Sonde™	Simultaneous measurement of conductivity, salinity, temp, depth, pH, dissolved oxygen, turbidity, chlorophyll and blue-green algae Provides an immediate on-site measurement	 Despite best practices sometimes not possible to clean sonde to a point where the standard is not contaminated by some small amount Depth sensor can be affected by 	(Atkinson and Mabe, 2006)
	with good sensitivity at natural levels • Ideal as early warning of algae blooms	biological fouling that grows in the water passage tube	6
Censar™	 Simultaneously measures colour, turbidity, and temperature On-line access to all sensor readings 	Limited parameters measured	(USEPA, 2009)
s::can Water Quality Monitoring Station™	 Applicable for wastewater, drinking water, and environmental water Multiple parameters measured 	 Colour measurement not highly sensitive Some issues with running system without the use of air cleaning 	(Chow et al., 2008)
TOXcontrol™ (microLAN)	Real-time assessment of microbial populations; quick response time	have been identified • Vibrio fischeri less sensitive to sodium fluoroacetate	(Zurita et al., 2007; Mons, 2008)
Algae Toximeter (BBE)	 High sensitivity of Vibrio fischeri to cyanide Precise determination of algae concentrations in water Highly sensitive with regard to detection of herbicides and their by-products 	Lag time in cultivating slow-growing algae	(de Hoogh et al., 2006; Mons, 2008)
Daphnia Toximeter™ (BBE)	Highly sensitive biological system for early detection of potentially dangerous unknown substances Low maintenance	 Not suitable for finished (chlorinated) water as <i>Daphnia magna</i> is sensitive to chlorine Adjustable high sensitivity may lead to false positive alarms in 	(de Hoogh et al., 2006; Jeon et al., 2008; Mons, 2008)
ToxProtect™ (BBE)	Rapid detection of toxic substances in water Capable of detecting law laws of grapids.	 some cases Incapable of detecting considerably high levels of fluoroacetate 	(van der Gaag and Volz, 2008;
	 Capable of detecting low levels of cyanide High toxic response relation between fish and humans exists 	Maintenance time, size required to house fish stocks	Mons, 2008)
Fish Activity Monitoring System (FAMS)	Round-the-clock monitoring of fish activity for continuous water quality monitoring Quicker response time after event occurrence	Maintenance time, size required to house fish stocks	(van der Gaag and Volz, 2008; Mons, 2008)
Surface enhanced Raman spectroscopy	Non-invasive and reagentless Highly specific microbial identification	Spectral deviations caused by metabolic or environmental factors needs to be smaller than spectral deviation between strains	(Sengupta et al., 2006; van der Gaag and Volz, 2008)
Laser tweezer Raman spectroscopy	Allows discrimination between different strains if bacteria and single Bacillus spores Bacteria selected from random growth phases can be classified	Associated biochemical and biomolecular methods required at same time to confirm effectiveness of Raman spectral method	(Xie et al., 2005; van der Gaag and Volz, 2008)
Surface acoustic wave (SAW) devices	 Highly specific and low-cost Array-based sensors and data processing schemes provide increased utility 	Reduced sensitivity and stability suggests they are not ready to fully replace analytical methodologies	(van der Gaag and Volz, 2008)

et al., 2001, USEPA, 2005a). The goal of an EWS is to identify lowprobability/high-impact contamination events in sufficient time to be able to safeguard the public. EWS should provide a fast and accurate means to distinguish between normal variations, contamination events and differences in quality due to biochemical and physical interactions. EWS should be able to detect deliberate as well as accidental contamination events and ideally should be reliable, with few false positives and negatives, inexpensive, easily maintainable and easily integrated into network operations (Brussen, 2007). A new generation of on-line monitoring tools based on sensor technology has emerged in recent years. Effective implementation of these tools however has not been realized for a number of reasons, least of which (i) they do not meet practical utility needs, (ii) their cost, reliability and maintenance are unsatisfactory, and (iii) data handling and management and an ability to produce meaningful operational information is yet to be realized (van der Gaag and Volz, 2008).

There is a need, however, to better understand the opportunities provided by the latest on-line monitors and best practices the field has to offer to improve the capability of a utility in contaminant detection and water security management. The aim of this paper is therefore to describe existing and emerging technologies, water utility experiences and approaches to water security management. This review is by no means exhaustive, though is aimed at identifying current global trends as well as future needs and considerations for the urban water industry. Furthermore this review is not intended to evaluate specific technologies, nor imply endorsement to their use. For many of the emerging technologies the data simply is not available yet to allow a sound and statistically significant appraisal of these systems. However, to allow some comparison and critique of the technologies reviewed, some of the available advantages and limitations of each system are outlined in Table 1. Finally, it should be stressed that some online monitors may be more useful than others to particular water quality managers depending on location and/or the different and changing guidelines present in a given country. Indeed in some instances a combination of monitors may be most beneficial. Thus it is necessary and appropriate that each on-line monitor is assessed in the context of an individual water management body.

2. Existing technologies

Many commercially-available technologies used for the detection of routine water quality parameters continue to provide the most reliable means of detecting anomalies within water systems. Whilst there exists a need for more robust instrumentation for the measurement of ammonia and fluoride, many solid state instruments including those for pH, chlorine, total organic carbon (TOC), conductivity and temperature continue to provide the most reliable means by which changes in drinking water quality can be measured in real time. More recently technologies have been developed including the J-Mar Biosentry™, a laser-based technology that is designed for the continuous on-line measurement of particles in water, and the submersible UV−VIS s::can spectro::lyser™, which is designed to measure multiple water

quality parameters including turbidity, TOC equivalent, biochemical oxygen demand (BOD), nitrate, nitrite and aromatic compounds. Other multiparametric instruments, including Hach Event Monitor™, YSI Sonde™, Censar™ and s::can Water Quality Monitoring Station™ technologies have been deployed at various water utilities throughout Europe and the United States for the real-time on-line analysis of water quality and contamination events.

Furthermore, instrumentation including gas chromatography-mass spectrometry (GC-MS), an automated system that can be used to detect volatile trace organic micropollutants, liquid chromatography-MS (LC-MS) and high performance liquid chromatography (HPLC), have also been used in an on-line capacity by water utilities and can provide reliable information on micropollutants, particularly in water intake monitoring, in near to real time. In addition to changes in water quality, a number of monitors have been deployed by water utilities within source and treated waters in recent years to detect contamination events in real time (Hall et al., 2007, 2009). Biological monitors such as bacterial bioluminescence and fish monitors have been in use for many decades, however significant advances have been made in this field in recent years over a range of tropic levels including those for bacterial bioluminescence, Daphnia (water flea), algal cell and fish monitoring. TOXcontrol™ (microLAN) is a realtime biological toxicity monitor used to measure toxicity in environmental samples and is based on the ability of Vibrio fischeri, a luminescent bacterium, to produce light as a byproduct of its cellular respiration (Meighen, 1991). Bacteria react rapidly to toxins changing their metabolism and therefore emitted amount of light.

In more recent years this device has been coupled with the s::can spectro::lyser™ to increase the sensitivity in the detection of chemical contaminants in water at low concentrations. The combination of two instruments further allows for the verification of alarm signals from one instrument with the signal of the other, thereby reducing false alarm rates. Other devices such as the Algae Toximeter (BBE) continuously measure the photosynthetic activity of algae to detect the presence of toxic substances. The presence of toxins reduces the activity of the algae, decreasing the amount of natural (auto) fluorescence. Herbicides are the most important class of toxins detected by this type of on-line monitor. The analogue of this instrument used for the detection of pesticides is the Daphnia Toximeter™ (BBE). The Daphnia Toximeter™ is based on the sensitivity of the water fleas Daphnia magna to changes in water quality and observes Daphnia behaviour (speed, movement, swimming height and growth rate) under the influence of constantly running sample water. The live images obtained using a CCD-camera are evaluated on-line using digital image analysis with an integrated PC to analyse changes in the behaviour of the Daphnia. As with most biological assays this test is not yet suitable for finished (chlorinated) water, since D. magna is sensitive to chlorine (OECD 2004). One of the limitations (and findings of this review) is that there are no chlorine-resistant bioassays that could be proposed in this case. However, some emerging alternatives to D. magna include the cladoceran Simocephalus mixtus. S. mixtus, which has been used as a test organism in acute and chronic toxicity assays of untreated waste waters and sediments, was found to be a more

sensitive test organism than *D. magna* in this application (Martínez-Jerónimo et al., 2008). A photobacterium bioassay has also been successfully used in the testing of wastewater chlorination disinfection processes (Wang et al., 2007).

Though they have been in use in water utilites worldwide for many decades, significant advances have been made in fish monitoring in recent years. Fish, often local indigenous species such as the Australian Rainbow trout, are generally placed in chambers through which water continually flows. In the event of erratic behaviour in one or more, the presence of toxins in the water is assumed. The ToxProtect™ (BBE) fish monitor is used to detect toxins in water by analysing the swimming activity of up to 20 fish across an array of 80 photoelectric light diode barriers in real time. Other fish monitors analyse electrical signals generated by the movements of fish muscles, as well as ventilation rate and depth, gill purge frequency and whole body movement.

Research being conducted through the Agency for Science and Technology Research (A-Star) in Singapore has combined complex video surveillance algorithms and CCTV (closedcircuit television) in its Fish Activity Monitoring System (FAMS) for use in the Singapore water distribution system. As with each of the other biological monitors, the major limitation of this technique is that fish are generally sensitive to chlorine, and that the test is neither selective nor specific. The Singapore water utility (PUB) is circumventing this by dechlorinating the water, though this has its own limitations by altering the properties of the source water. In many instances, while behavioural tests are the current benchmark in terms of rigorously tested bioassays, cell based bioassays (including microbial and human) are beginning to emerge as important tests particularly in the assessment of the effects of combinations of toxins/contaminants in a system (Pomati et al., 2008). These authors have shown that both the bacterium Escherichia coli and human cells (embryonic and tumor) were valid and highly reproducible models for testing the effects of a range of micropollutants found in waterways, as well as their antagonistic-synergistic interactions.

Water utilities throughout Europe and the United States have deployed many of the technologies described in this section. The focus in Europe has been for the most part on the protection of source waters, largely river intake monitoring, whilst in the United States a greater emphasis has been placed on distribution system protection in regard to homeland security in recent years. The efficacy of many of these commerciallyavailable technologies and their response to changes in water quality through simulated contamination events has been evaluated in a number of programs, most notably in Europe during the EU Techneau Programme, and by the USEPA, Office of Ground Water and Drinking Water, Water Security Division (http://water.epa.gov/infrastructure/watersecurity/lawsregs/ initiative.cfm). The latter was performed by the National Homeland Security Research Center, a research center within the U.S. EPA's Office of Research and Development.

3. Emerging technologies

In addition to many commercially-available technologies used for the detection of contaminants in drinking water systems, there are a number of emerging sensor technologies in various stages of research and development that could find future applications in the urban water industry. Many emerging biological sensors rely on the detection of specific biomolecules including adenosine triphosphate (ATP), enzymes and other proteins, as well as immunoassay and polymerase chain reaction (PCR) techniques (e.g. Pomati et al., 2004; Hawkins et al., 2005). The major limitation of these and many other biological systems lies in their sensitivity and their ability to detect low concentrations of microorganisms, which unlike chemicals, are not uniformly distributed in aqueous environments. Other biological sensors rely on the optical properties of water and analytes and include those based on evaporative light scattering detection, refractive index measurement, fluorescence detection, and Raman spectroscopy.

Fluorescence is a technique that uses emitted light to measure the excitation spectra of specific compounds such as chlorophyll, aromatic compounds, pesticides and humic acids, and can be used to identify compounds using the combination of the wavelength of the emitted light and the wavelength of the irradiated light. The application of fluorescence as a monitoring tool for the detection of cross-connection in dual reticulation systems, where recycled water had been inadvertently introduced into a drinking water system, has been recently explored (Henderson et al., 2009). As there is a potential for accidental (or deliberate) cross-connection from recycled water to a potable water distribution system, there is a need for monitoring to ensure water safety and to maintain public confidence (Storey et al., 2007). There have been several incidents of non-potable to potable cross-connections leading to disease outbreaks including a large incident in the Netherlands and several reports from the United States (Liang et al., 2006).

Raman spectroscopy has been further developed into two technologies for microbial detection, surface enhanced Raman spectroscopy (SERS) and laser tweezer Raman spectroscopy (LTRS). SERS is the identification of microorganisms from the spectra produced at the surface of the organism which has reacted with antibodies. The LTRS technique produces an optical "tweezer" to 'catch' a microorganism and then laser light is used to produce a unique Raman spectrum that can be used to discriminate between different strains of bacteria or bacterial spores. From this spectrum the dynamic changes in biological molecules such as proteins, nucleic acids, lipids, and carbohydrates can be monitored (Marshall et al., 2007).

Other sensor-based technologies that rely on the optical properties of water and contaminants include infra-red (IR) spectroscopy which relies on the ability of various organic functional groups including proteins, carbohydrates, lipids and nucleic acids to absorb infra-red light at specific wavelengths. Sensors based on surface acoustic wave (SAW) devices include the electronic nose and tongue and $\mu\text{ChemLab}$. In SAW devices an acoustic wave is generated which produces a mechanical wave that travels through the surface of the device (Groves et al., 2006). The surface changes due to analytes that are bounded on the surface and changes in frequency provide information about the concentration of the compound. The electronic nose or tongue consists of a number of non-specific biological or chemical sensors whose responses are analysed with pattern recognition routines or artificial neuronal

networks (Krantz-Ruckler et al., 2001). Other sensors used in the electronic nose or tongue include optical chemical detectors, quartz microbalance devices, conducting polymers, mass spectroscopy and electrochemical devices. µChemLab monitors consist of gas and liquid-phase types that are able to detect biotoxins and other inorganic and high molecular weight chemical compounds. The gas phase type consists of GC channels and SAW sensors, while the liquid type combines various chip-based techniques with fluorescence detectors. Further developments are being made in this technology to detect viruses and bacteria, and the ultimate goal is to develop a low-cost, fast deployable and real-time sensor for on-line water quality measurements.

Other emerging sensor technologies are based on electrochemical detection techniques and include ion selective electrodes, photoionisation/mass spectrometry and amperometric sensors. Amperometric sensors are widely used to detect free chlorine and comprise a flow-through cell and electrode layer that is able to conduct amperometric measurements due to changes in analyte concentrations. Amperometric sensors can be used for on-line measurements and their integration into on-chip optics is currently under development.

4. Sensor placement, data handling, and communications

Significant advances have been made in recent years in tools for the optimal placement of on-line monitoring stations and the real-time management of data and communications. Sensor placement optimization tools including optiMQ-S and TEVA-SPOT (Berry et al., 2008), in combination with event detection software CANARY have been developed and may improve operations and assist in the detection of contamination events within water systems. Software such as optiMQ-S was developed to determine the optimal location of monitoring stations aimed at detecting deliberate external terrorist hazard intrusions into a water distribution system (Ostfeld and Salomon, 2005). The algorithm takes into consideration hydraulic demands and water quality conditions, as well as contaminant transport and points of contaminant introduction. The main difference between the two tools is that TEVA-SPOT is an open source software tool available for free on the web. The TEVA-SPOT software contains multiple optimizers (heuristic, lagrangian, and integer programming) while optiMQ-S uses genetic algorithms to optimize sensor placement.

Recent collaboration of USEPA, SANDIA National Laboratories, and Argonne National Laboratory has seen the development and application of Threat Ensemble Vulnerability Assessment (TEVA) Sensor Placement Optimization Tool (TEVA-SPOT). As its name implies TEVA-SPOT can be used in the design of contamination warning systems for improving the security of drinking water distribution systems (Hart et al., 2008; Murray et al., 2010a), and amongst other benefits can be used to

- (i) recommend optimal sensor placement
- (ii) assess the consequences of contamination events and
- (iii) improve water distribution system network models.

TEVA-SPOT relies on a number of input parameters including the required detection (and response) time, and as part of the tool calculates the health impacts. Both optiMQ-S and TEVA-SPOT require utility-specific input (e.g. a water distribution system network model such as EPANET), and through the application of this software, improvements can be made to distribution system models, which can in turn benefit the water utility's understanding and management of the distribution system.

A range of software has been developed to assist in the detection of water quality anomalies or events within water systems and the handling of large volumes of water quality data. Event monitors such as Hach Event Monitor™ and s::can Water Quality Monitoring Station™ are generally supported by proprietary event detection software, while others such as CANARY was developed by the EPA's National Homeland Security Research Center, though not specifically for the WSi (Murray et al., 2010b). CANARY software uses a range of detection algorithms to evaluate standard water quality parameters such as free chlorine, pH and total organic carbon, and uses mathematical and statistical techniques to identify the onset of anomalous water quality incidents (Hart et al., 2009). Event detection software such as CANARY can utilize ongoing operational data or training data acquired to determine the natural variation of these water quality parameters, and assist utility personnel to understand the expected false alarm rates. In addition to anomalous conditions or potential contamination events, CANARY can detect unexpected "normal" events, such as a sensor malfunction or a pipe break.

Recent advances in automated metering and wireless technology has presented a platform on which improved data handling and management can be made. In addition to providing a communications platform that can feed back information in real time, automated meter reading (AMR) has an added benefit of being dual purpose, where it can be used in other network operations such as billing and leak detection. Research currently being undertaken through the University of Cincinnati in collaboration with the USEPA is using AMR technology to build a real-time network model that can be used to improve existing hydraulic models and estimate contaminant transport.

5. Water security initiative

Previously termed the "Water Sentinel" project, the Water Security Initiative (WSI) is a program of the USEPA, Office of Ground Water and Drinking Water, Water Security Division aimed at addressing the risk of intentional contamination of drinking water distribution systems (USEPA 2005b, USEPA 2008). Five major water utilities (in Cincinnati, San Francisco, New York, Philadelphia, and Dallas) were recruited for the WSI, which involves the deployment of real-time monitors and early warning systems to detect possible contamination in drinking water distribution systems. Water quality monitoring stations and analytes (pH, turbidity, temperature, conductivity, TOC and chlorine) were chosen on the basis of their sustainability for long-term operation and to provide

"dual-use" benefits to drinking water utilities, such as improved water quality management.

The WSI consists of 5 components including:

- (i) on-line water quality monitoring stations located throughout the distribution system, combined with
- (ii) public health surveillance such as over the counter pharmaceutical sales, hospital admission reports and infectious disease surveillance
- (iii) field and laboratory analysis of distribution system samples
- (iv) enhanced security monitoring and
- (v) customer complaint data in real time.

The WSI also uses TEVA-SPOT and CANARY software packages for the optimal placement of sensors and analysis of data. TEVA-SPOT has been used to design the monitoring network for all five WSi pilots, and CANARY is used for real-time monitoring at one of the five WSi pilots, and is under evaluation at three WSi pilots.

6. Conclusions

Despite recent advances in biological monitors and microsensor technologies, there is no universal monitor for water quality monitoring and contaminant detection. Whilst technologies are emerging from the microsensor and nanotechnology sector, they are not at a stage where they can be readily deployed within existing operations. Technology therefore needs to co-evolve and become less expensive and more reliable. Although operations and technology go hand-inhand, it is likely that technology in terms of monitoring will need to evolve to meet the many operational constraints. Ultimately it will be a balance between cost and ease of implementation. In the meantime though, water utilities should focus on addressing existing operational needs such as nitrification control and cross-connection detection using available technologies, improved data handling and interpretation, as well as improved communications. In this way a platform can be laid for the future deployment of an early warning system. To ensure their survival in network operations, early warning systems must furthermore demonstrate operational benefits (such as better water quality, decreased operating costs or reduced customer complaints). A focus on water security alone does not provide sufficient grounds for its survival in operations, given the maintenance, technical expertise and cost required, and the number of false alarms often associated with them.

Utilities should also focus their efforts on the real-time management of large amounts of data. One way to validate any technology (either existing or emerging) is for water companies to make data available for research, and there is thus a need to build an information platform that could be provided by automated meter reading (AMR) and wireless technologies. AMR has an added benefit in that it is dual purpose, given its intended use in billing and potential use in leak detection. Solid-state instrumentation that measures traditional water quality parameters including pH, chlorine, temperature, flow and turbidity continues to provide the most

reliable information and should form the focus of water utility attention. There is a need for predictive models that better describe distribution system dynamics and contaminant transport within a distribution system. Furthermore, there is a need for improved incident management strategies to restore operations and public confidence in the event of contamination of source waters and distribution systems.

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