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Cross-connection detection in Australian dual reticulation systems by monitoring inherent fluorescent organic matter

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New housing developments are now commonly incorporating dual reticulation water systems for the redistribution of recycled water back to households for non-potable use. Within such distribution systems is the potential for cross-connections between recycled and drinking water pipelines, and a number of such events have been documented both in Australia and internationally. While many cross-connections are unlikely to present a source of health concern given the high level of recycled water treatment, they do have the potential to negatively impact public confidence in dual reticulation systems. A rapid and highly sensitive method of cross-connection detection is required to increase consumer confidence in the construction and maintenance of such recycled water distribution systems. This paper reviews a number of current and potential cross-connection detection methods, highlighting the use of fluorescence spectroscopy as a highly promising analytical tool for portable cross-connection detection.

Keywords: fluorescence; cross-connection; monitoring; dual reticulation; recycling

Introduction

The depletion of limited freshwater resources is being brought closer to the attention of the public and the scientific community as changing rainfall patterns, significant population growth and stringent environmental regulations become increasingly prevalent. This is particularly the case in some parts of Australia, where extended droughts are common which, when coupled with expanding city populations, have placed increasing stress on urban water supplies. One response to improve the management of water supply networks is the implementation of stormwater and wastewater recycling in order to preserve or redirect the use of our natural water resources. As such, municipal water recycling has gained increased importance as component of urban water management systems in many parts of Australia over the last decade. Throughout the late twentieth century, municipal wastewaters have typically been treated to a primary, secondary or tertiary level and discharged into the environment. However, the trend towards recycling represents an opportunity to treat this wastewater as a resource to be further utilized, rather than as waste requiring disposal. Recycled or reclaimed water has been used worldwide for many different purposes, ranging from a variety of agricultural purposes to use in the augmentation of potable water supplies [1–4]. With recycled water industries growing at a rapid rate on a national and international level, increasing emphasis is being placed on health risk

and treatment-related research into recycled water and its distribution. This emphasis is embodied in the Australian Guidelines for Water Recycling [5,6] and a sensitive, rapid technique to detect cross-connections is urgently required. This paper reviews a number of existing water quality monitoring techniques for their applicability to monitoring recycled water dual reticulation systems, particularly highlighting fluorescence methods for their strong potential to detect cross-connection events.

Dual reticulation systems and their potential for cross-connections

Despite the potentially high treatment levels applied to recycled water, much of the public perception (particularly in Australia) has caused opposition to its use for potable purposes [7,8]. Public perception plays an integral role in the successful implementation of water recycling and, as such, water reuse applications have typically favoured the use of recycled water for non-potable purposes. Separating potable and non-potable water supply systems may help to minimize the negative impact of public perception issues regarding the acceptance of recycled water as an important component of water management. Although the production of recycled water is typically more expensive than that of potable water [9] due to factors such as the extra construction and further treatment processes involved, the

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environmental benefits [10] and its ability to be supplied independently from climate conditions [11] may outweigh the economic differences. The increased costs may also be minimized by treating the water on a 'fit for purpose' basis, as well as by implementing the systems during the initial construction of housing estates [12].

In many cases, recycled water is subsequently distributed back to domestic properties as highly treated municipal effluent via a separate, dedicated distribution system. The recycled water can then be used exclusively for non-potable applications including car washing, washing machines, hard surface cleaning, toilet flushing and irrigation [13]. Such recycled water distribution systems are commonly known as 'dual reticulation systems', 'dual distribution systems' or 'third pipe systems', and a rapidly growing number of examples exist within Australia and internationally [12,14–16].

Notable dual reticulation schemes

Many of the pioneering schemes for dual reticulation water recycling can be found in the USA. The first large-scale urban dual reticulation system in the United States began in 1969, supplying recycled water for residential, commercial and industrial purposes across St. Petersburg, Florida [12]. Another notable dual reticulation system exists in Alamoonte Springs, Florida, which has distributed recycled water to residents since 1989 [17]. Comparable water recycling distribution schemes also exist in cities such as Colorado Springs, Colorado, and Tucson, Arizona, as well as in San Diego, San Jose and Irvine, California, and have been operating successfully for up to 40 years [18–20].

Similar dual reticulation systems are in existence, such as in Japan, Germany, France, and the UK. Fukuoka and Tokyo in Japan have utilized dual reticulation water recycling since 1980 and 1984, respectively [16], with their main uses being for toilet flushing in high-rise buildings, where dual reticulation systems are now mandated. As early as 1990, over 800 buildings in Japan were already recognized as utilizing recycled water through a dual reticulation system [17]. Until recently, Europe was generally viewed as having a plentiful supply of fresh water sources; however, changing conditions have led to municipal water reuse being more commonly considered for implementation. Some examples of this include those in Vauban, Germany, and Annecy, France, where in both cases greywater is treated and used to supply recycled water to dual reticulated residencies. A number of multi-source dual reticulation systems have also been successfully implemented in the UK, such as at the Millennium Dome in London and a housing estate in Blackburn [15]. Dual distribution schemes also are in existence throughout the Middle Eastern and North African region, such as in Palestine, at Bir Zeit University, and in two mosques in Mecca and Medina, Saudi Arabia, where treated wastewater is used for toilet flushing [21].

Over the last 20 years the management of Australia's water resources has shifted and the prevalence of water recycling and dual reticulation water recycling systems across Australia has risen significantly, particularly within new housing developments. Rouse Hill's (north-west Sydney) sewage treatment plant and dual reticulation system was commissioned in 1994, and is recognized as being Australia's first full-scale application of domestic non-potable reuse [22]. The system now supplies over 20,000 homes, and that number is expected to increase to around 36,000 properties [23]. Another dual reticulation system within the western Sydney suburb of Newington has grown to service over 2000 homes since it was originally operated as the official athlete's village for the Sydney 2000 Olympic and Paralympic Games [24]. A number of dual reticulation systems exist in South Australia, such as New Haven Village, which has been receiving treated domestic wastewater on a smaller scale for 65 residential properties within its dual reticulation system since 1995 for uses including toilet flushing and garden watering [25]. Mawson Lakes in South Australia also incorporates a dual reticulation system which supplies recycled water to 4000 homes [26]. More recently commissioned dual reticulation systems include Pimpama-Coomera (south east Queensland), which is a large-scale dual reticulation system and is expected to supply over 35,000 homes [14,27], Aurora Estate and Highlands Estate (Victoria), which currently comprises 2000 domestic properties and is anticipated to supply up to 8500 properties [28], as well as Inkerman Oasis (Victoria) which currently redistributes treated greywater to over 200 apartments [29]. More developing dual reticulation schemes in Australia include Hoxton Park (New South Wales) which is expected to service up to 7000 homes [30], Ropes Crossing (New South Wales), which will supply 1550 homes upon completion [31] and Vermont (Pitt Town, New South Wales), which is expected to supply recycled water to over 900 domestic properties upon completion [32].

Reported cross-connection events

The construction and maintenance of dual reticulation water recycling systems must be carefully managed to minimize associated risks and protect the safety of consumers. The inadvertent cross-connection between drinking water pipes and recycled water pipes [33–35] is one such risk which can be associated with these systems. A number of cross-connection events have occurred both in Australia and internationally: for example, more than 50 cross-connections were discovered at Rouse Hill before commissioning in 2001, and at least four events attributed to plumbing error have been documented since that time [36]. This includes one single event which was reported to have affected 82 properties [37], and comparable events have also occurred at Sydney Olympic Park [38] and at Pimpama-Coomera [39,40]. In March 2007, recycled water was supplied inadvertently for 19 days to a kitchen at

Melbourne Water's Eastern Treatment Plant, which was reported to have led to a number of staff illnesses [39,41].

On an international level, there have been a number of documented cases of cross-connections of potable water with varying levels of recycled water – some of which have been reported to have had serious health implications. In the Netherlands, for example, a number of cross-connections have been reported [33]. One particular case resulted in an outbreak of waterborne gastroenteritis as a result of a cross-connection between the drinking-water distribution system and a greywater distribution system in a new residential area [42]. Based on these occurrences, recycled water use in domestic properties was discouraged by the Dutch government and the distribution schemes in question are no longer in operation. In Nokia, Finland, pipes between potable water and treated sewage were found to have been cross-connected from November to December 2007 and were reported to have resulted in over 6500 illnesses [43,44]. Despite the significant presence of dual reticulation systems across the USA, very limited research into cross-connection events and cross-connection detection has been published.

Understandably, cross-connection events between potable and finished recycled water may also have potential public health implications [45,46]. The use of highly treated recycled water for direct or indirect consumption is already faced with a low level of community support within Australia, with up to 77% of residents in one study displaying concerns over recycled water quality [47]. Cross-connection events risk a similar negative attitude towards non-potable water recycling, and risk undermining public confidence in the further implementation of dual reticulation systems [48].

In certain cases, observed public health impacts have been incorrectly attributed to cross-connection events. For example, in 2010, media sources hastily attributed an outbreak of gastroenteritis at a Gold Coast childcare centre to contamination of drinking water by recycled water [49]. A subsequent investigation found no problems with the drinking water quality, and that the centre was not even connected to the recycled water dual reticulation network. The incident came soon after a number of publicized cross-connection incidents within the nearby Pimpama-Coomera dual reticulation network [50,51] and highlights the significant effect which these events have on public confidence in and acceptance of dual reticulation systems.

Typical procedures for cross-connection testing require the shutting off of each water source individually and testing for appropriate water flow [38], which may be considered a disruptive and time-consuming process and is usually only carried out as a result of a consumer complaint. These flow-based checks are also unable to detect cross-connections beyond an individual property level, which is important given that events impacting multiple households have occurred a number of times within these systems [37,51]. New homes connected to dual reticulation systems in Australia require a number of plumbing inspections prior

to occupancy approval, and various control measures have been implemented in dual distribution systems which aim to minimize the potential for cross-connection or contamination events. These include the use of purple piping to distinguish recycled water pipes from potable water pipes, a multiple treatment barrier approach to ensure that the recycled water quality will pose a low risk to human health should a cross-connection occur, and the installation of backflow prevention devices [48]. Backflow prevention devices prevent the reversal of normal water flow direction [52] and hence the backflow of recycled water into the drinking water distribution system. They are unable to protect against the cross-connection of recycled and drinking water pipes as the resulting contamination occurs with normal flow direction, and so the prevention and detection of cross-connections remain major issues which must be resolved.

Potential monitoring techniques

To reliably differentiate recycled water from potable water and hence detect cross-connections, a parameter that consistently distinguishes between the two water types must be identified. Very few studies have been undertaken in this area despite cross-connections having been documented as an issue since the introduction of dual reticulation systems. The limited studies which have been carried out have typically investigated differentiation by water quality parameters such as electrical conductivity (EC), total organic carbon (TOC), turbidity and UV-visible (UV-vis) absorption [53], as well as the introduction of anti-ingestant chemicals and colourants to the finished recycled water [48]. One study has assessed potential indicators for the detection of drinking water contamination by evaluating how a range of water quality parameters responded to radiological, chemical and biological exposure [54]. Wastewater was one of the contaminants to which drinking water was exposed, and this situation may be considered as being analogous to a cross-connection between potable water and recycled water. A range of common water quality parameters were studied, including pH, free chlorine, oxidation reduction potential (ORP), dissolved oxygen (DO), specific conductance, turbidity, TOC, chloride, ammonia, and nitrate. The parameters which showed greatest response to wastewater injection were chloride, ORP, specific conductance, turbidity, free chlorine, and TOC.

A number of studies have evaluated some less common analytical methods for the detection of various wastewaters. These have used, to varying success, genetic and enzyme markers such as *Bacterioides* species [55,56] and β -D-galactosidase [57], as well as a number of chemical markers including 1-aminopropanone [58], polycyclic aromatic hydrocarbons (PAHs), caffeine [59], and a number of fragrance materials and steroids [60]. These compounds have shown promise as markers to detect up to secondary-treated wastewater in marine water, surface

water and drinking water sources; however, it remains to be seen whether the same success would be possible with finished recycled water in the form of advanced treated wastewater or greywater. The techniques employed include both normal and quantitative PCR, liquid chromatography, gas chromatography and mass spectroscopy, all of which are particularly complex, time consuming and expensive, and require highly trained staff to operate.

A recent review [61] has included the evaluation of a number of more typical water quality monitoring parameters for their potential in monitoring water recycling systems (including dual distribution systems), such as TOC, EC, free chlorine, pH and turbidity (Table 1). Turbidity was found to be similar between the two water sources, ranging from 0.1–0.3 NTU for potable water and from 0.09–0.3 NTU for recycled water, as was pH, which ranged from 7.3–8.6 for potable water and from 7.0–7.7 for recycled water. Free chlorine levels were also found to have similar ranges between potable (0–0.98 mg/L) and recycled (0.05–0.50 mg/L) water. Hence, it was concluded that turbidity, pH and chlorine would be of limited value for cross-connection detection. The use of TOC and the EC showed more promise, as in some instances values of potable and recycled water were able to be differentiated; however, there were still significant overlaps between each water source, and therefore use of these parameters independently cannot be seen to provide a solution to cross-connection monitoring. It is therefore understandable that the use of methods such as TOC concentration for cross-connection detection has met with limited success [62,63].

Alternative, novel methods have therefore been sought to improve cross-connection monitoring. An emerging alternative approach to monitoring, characterizing and tracking aquatic DOC is by way of a number of fluorescence-based techniques [64–68]. Fluorescence analysis of organic matter has been continually evolving over the last 20 years of water science research, and is currently showing great promise for detailed characterization of many different water sources.

Fluorescence spectrophotometry

Fluorescence spectrophotometry is a highly useful analytical characterization technique, and has the potential to

Table 1. Commonly reported water quality parameters for a variety of recycled and potable waters, from Henderson et al. [61].

Water Quality Parameter	Reported Potable Water Values	Reported Recycled Water Values
TOC (mg/L)	0.4–6.4	0.1–6.7
Conductivity (EC) ($\mu\text{S}/\text{cm}$)	13–570	65–1240
Free Chlorine (mg/L)	0–0.98	0.05–0.5
pH	7.3–8.6	7.0–7.7
Turbidity (NTU)	0.1–0.3	0.09–0.3

provide a monitoring tool to overcome the limitations of the existing water quality monitoring techniques described above.

Fluorescence theory

Fluorescence is a form of photoluminescence and a phenomenon which occurs at a molecular level. When an electron is subjected to an energy source (such as light) and absorbs a photon, this will cause it to move above the ground state to a higher energy level, or excited state. When the energy source is removed, the excited state electron relaxes back to its ground state by moving through vibrational energy levels of the molecule, emitting some of the excess light and relaxing back to its initial ground state (Figure 1). The fluorescence can be measured as the intensity of the excess light emitted. As some energy is always lost through heat or vibration, the emitted light is always of a lower energy (and hence longer wavelength) than the excitation light [69].

Fluorescence spectroscopy is considered as being up to 1000 times more sensitive than other optical methods such as UV absorption spectrometry [69]. For absorption measurements, the sample transmittance is compared with a blank, which both give high signals at low concentrations; however, in fluorescence spectrometry, the solvent blank has a low output so that the background is much less [70].

Due to the tremendously sensitive emission profiles, spatial resolution, and high specificity of fluorescence spectroscopy, the technique is rapidly becoming an important scientific tool within the water sciences. Fluorescence spectroscopy has evolved from its initial use within purely chemical studies, and has now become commonplace within many medical and microbiological studies, and is an important research tool in biochemistry and biophysics [69,71]. Such uses include fluorescence microscopy to observe cell function [72]. Many new fluorescent dyes have become available to interact with and identify specific biological targets [73], and fluorescent-activated cell sorters can be used to separate white blood cells from other cells found in

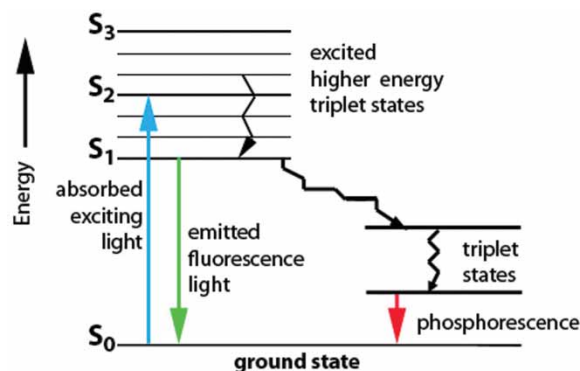


Figure 1. A simplified Jablonski energy diagram showing the excitation of an electron and the subsequent emission of a photon (fluorescence).

blood. The high potential sensitivity and specificity of fluorescence spectroscopy techniques is clearly indicated by the ability to detect and monitor single molecules [74] even under physiological conditions [75].

Fluorescent tracer monitoring

One potential method for using fluorescence to track and monitor water sources is by the addition of a fluorescent tracer compound and subsequent monitoring by fluorescence spectroscopy. Fluorescent dyes are commonly employed as tracer material to label marine and ground water and elucidate the dispersion rates and directions of water flow or contaminants, where some have been used since the end of the nineteenth century [76]. Dyes such as fluorescein and rhodamine and their derivatives are widely regarded as the most sensitive and widely applicable technique available for water tracing. Detection of distances up to 1300 km have been reported and persisted even after several weeks [77], and as such are used in tracking dispersion rates for ocean outfalls such as desalination concentrate [78].

By applying the same logic, a fluorescent tracer dye may be useful in detecting cross-connections within dual reticulation water recycling systems. In order to successfully achieve this aim, the added fluorescent tracer must satisfy a number of criteria. Primarily it must be non-toxic to guarantee the safety of consumers in case of accidental ingestion. It must also be non-reactive in order to survive within the water matrix for long retention times throughout the water distribution system. Another main criterion is that the tracer compound must be highly fluorescent and highly water soluble, even at very low concentrations.

Despite the high sensitivity of fluorescence spectroscopy, the necessity of these main criteria amongst others makes finding potential candidate compounds difficult and highlights a number of disadvantages to the tracer process. The addition of a chemical into the water source would require a trade-off between its non-reactive nature and potential chemical build-up within the system. The addition process also creates a potential for dosing problems at the water treatment plant. The effect of salinity, pH and chemical composition is known to hinder the fluorescence analysis of many fluorescent tracer compounds [79], and the susceptibility of chemicals to chlorine and chloramine disinfection processes would be likely significant. For example, sodium-fluorescein (or uranine) is readily broken down by strong oxidizing agents such as ozone, chlorine and chlorine dioxide—chemicals which are commonly used in water disinfection processes [80]. The susceptibility of potential tracers may lead to an increase in the disinfectant demand within the system, and as such would also require thorough investigation. Many dual reticulation systems also provide recycled water for laundry purposes in addition to other non-potable uses, and contact with optical brighteners and other chemicals within laundry powders

could create potential reaction pathways and thus cause the recycled water source to become unfit for laundry or other purposes.

A number of compounds have been investigated in one study as potential recycled water markers (as anti-ingestants and colourants) [48]; some of which are incidentally highly fluorescent, such as caffeine and quinine. In this case, the compounds were not selected for or evaluated by their ability to be detected by fluorescence spectroscopy, but rather to be detected by colour or taste, and subsequent evaluation including low working concentration and ultimately estimated cost. Caffeine and quinine were not concluded to be good candidates by these criteria. This research concluded that the continual use of anti-ingestants and colourants was likely impractical due to their instability in chlorine, disinfection demand and potential to stain laundry as well as other hard surfaces.

Fluorescence of inherent organic matter

An emerging trend in monitoring water source fluorescence is by way of the inherent dissolved natural organic matter within the system. Dissolved organic matter (DOM) is a ubiquitous component of natural and engineered aquatic systems [81] and has more traditionally been monitored by methods such as total/dissolved organic carbon, UV₂₅₄ absorption and specific ultraviolet adsorption (SUVA). A significant proportion of the organic carbon in drinking water, however, is derived from a different source to that of recycled water and therefore has a different organic character [82,83]. For example in drinking water, organic carbon is derived mainly from natural organic matter present in the source water, while in wastewater systems the organic carbon is derived from the biomass contributed from the sewage and also from the biological processes used to treat the sewage, and this may be reflected by differences in fluorescence profiles. The use of fluorescence-based techniques to observe, detect and quantify the different fluorescent portions of DOM within these systems has met with success and has been continually evolving [84–86].

Traditional fluorescence measurements have been acquired in a linear fashion as two-dimensional (2-D) emission spectra at the maximum (fixed) absorption wavelength. This has been particularly useful in the characterization of single chemicals or to measure kinetic changes of chemical reactions. This has developed further to synchronous fluorescence scanning, which is the measurement of emission spectra at an offset of the emission wavelength minus the excitation wavelength [87,88]. This has commonly proven to be a more useful analytical tool than fluorescence at a fixed excitation wavelength, particularly when a mixture of compounds is present in a solution, as it is able to reveal a larger range of a sample's fluorescent character. More recently, 3-dimensional (3-D) excitation–emission matrices (EEMs) have received particular attention amongst water science researchers. These matrices are produced when a

sample's emission spectrum is recorded for a number of consecutive excitation wavelengths and combined to form a three-dimensional 'fingerprint' of water fluorescence character (Figure 2). Fluorescence analysis also has a number of other analytical advantages including high sensitivity (being up to three orders of magnitude more sensitive than UV-visible spectroscopy [89]), a short acquisition time (as little as one minute), a non-destructive nature and requiring no sample preparation for relatively clean water samples where inner-filtering effects are insignificant [61].

A number of features are inherent within aquatic fluorescence EEMs, such as the Rayleigh scatter and Raman scatter, as well as their second-order derivatives (Figure 3). Within these scatter lines, a number of broad fluorescence peaks have been commonly observed in freshwater and marine aquatic samples: Peak B, Peak T₁, Peak T₂, Peak A and Peak C which has been further divided into Peak C₁ and Peak C₂ in some studies [65,90]. Their classification

has been developed based on Coble [92] and they are now commonly defined as listed in Table 2.

Some characteristic differences between the fluorescence of natural and artificial water sources have been previously reported in a number of studies. Fluorescence EEMs have been used in the observation and characterization of marine DOM [85,91–93], where predominantly humic- and fulvic-like fluorescence is exhibited. They have also been used in the characterization of DOM in marine and estuarine waters for the purpose of confirming ship ballast water exchange [94,95].

Fluorescence EEM spectroscopy has been successfully utilized to monitor natural organic matter in a number of freshwater applications, such as for the characterization and classification of spatially separated rivers and other surface waters [96,97], identification of DOM variability in estuaries [98], and the monitoring of organic fluxes through groundwater [99,100] amongst others.

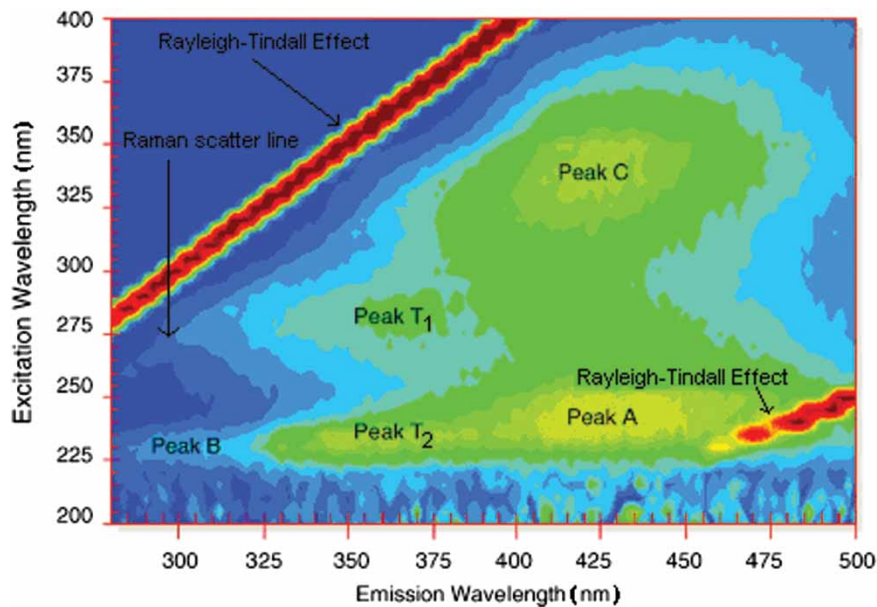


Figure 2. An example of a fluorescence excitation–emission matrix EEM for an impacted river water sample with labelling for five commonly observed peaks.

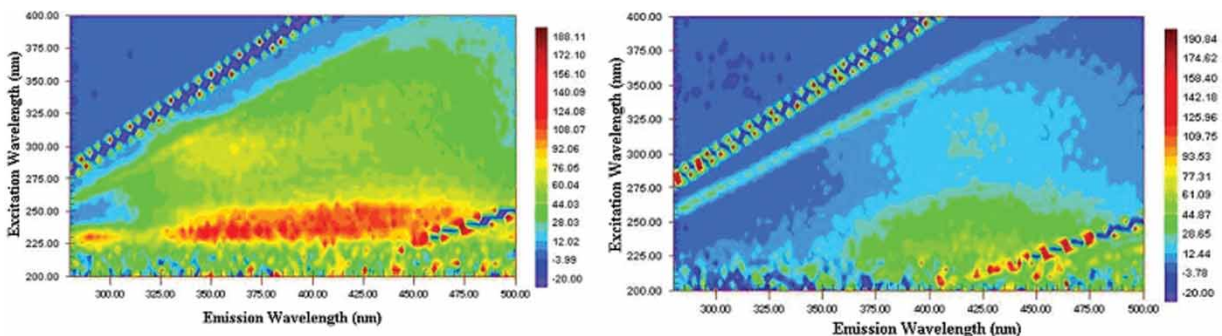


Figure 3. Typical recycled water and potable water fluorescence excitation–emission matrix 'fingerprints' (from Hambly et al. [118]).

Table 2. Typical nomenclature for commonly observed fluorescence peaks within natural and artificial water EEMs.

Peak		λ_{ex} (nm)		λ_{em} (nm)	
B	Tyrosine-like	225–235 275		310–320	
T ₁	Tryptophan-like	275–300		340–360	
T ₂	Tryptophan-like	225–235		340–380	
C	C ₁ Fulvic-like	300–370	320–340	400–500	410–430
	C ₂ Humic-like		370–390		460–480
A	Humic-like	235–260		400–500	

Identification of contamination using fluorescence fingerprinting

Over the last decade, the use of EEM spectroscopy has proliferated and EEMs have also been used to identify and quantify many types of contamination of natural water sources (Table 3). This has included the detection of tissue mill effluent in river water [101], differentiating between biodegradable and non-biodegradable DOM in wastewaters [102], and to discriminate between different landfill leachate sources in groundwater [103] and surface waters [104]. Tracking sewage-derived outfall in rivers, lakes and estuaries has also been achieved [65,105–108], as sewage-derived DOM typically exhibits significantly higher intensities in the tryptophan-like (Peaks T₁ and T₂) fluorescence regions. This is in contrast to pristine lake and river samples where humic- and fulvic-like (Peaks C and A) are much more prominent [66], and can be explained by taking into account the source of the DOM for each type of water. In non-impacted river waters, DOM is predominantly derived from plant material, whereas sewage-derived DOM has been linked to having microbial origins [108].

The research applications of aquatic fluorescence tracking have also been extended to include drinking water sources [68]. Several fluorescence studies have recently been undertaken to investigate the performance of drinking water treatment processes and have been able to successfully detect membrane fouling events [109,110] as well as to quantify organic matter removal and efficiency [111–114]. This area has also seen the early development of a deep-UV LED and laser-induced fluorescence system for fluorescence detection of water-dissolved organic species, looking toward the real-time fluorescence monitoring of drinking water [115]. Recent studies have also shown the potential for differentiating between grab samples of finished recycled water and potable water [116–118]. In these studies, grab samples were analysed by EEM fluorescence and it was observed that the fluorescence EEM fingerprint of finished recycled water was variable but observably different to that of potable water, particularly in the tryptophan-like area of the matrix (Figure 3). This is in keeping with data in Table 3 where contaminants have been commonly identified within the Peak T or Peak B areas, and is strong

evidence of the potential ability of these regions to identify cross-connection events.

Recent advances in optical technology have also allowed fluorescence analysis as a water quality tool to become much more portable and accessible. LED-based sensors are becoming increasingly available in lighter and smaller dimensions, at lower costs, higher efficiencies and at increasingly lower wavelengths to target previously inaccessible spectral areas [119]. Such developments have allowed the high sensitivity and specificity of fluorescence spectroscopy within water sciences to be demonstrated, and this has been highlighted more recently by its use with *in situ* spectrometers [67,120,121] for uses such as detecting river pollution by monitoring protein-like fluorescence and to monitor diurnal variability in river water DOM.

While the analysis of tryptophan-like fluorescence may ultimately provide simple and rapid indicators for cross-connection detection, greater sensitivity and robustness may be expected by exploiting the characteristics of multiple regions of EEMs. Multivariate data analysis has been

Table 3. Summary of notable publications in which fluorescence has been used to detect water contamination events.

Water Source	Contaminants	Fluorescence Peaks (approximated)
River	Tissue mill effluent [101]	T
	Diesel fuel [152]	T ₂
	Sewage [65,105,106,153]	B, T
	Landfill leachates [104]	T ₂
	Oil [154]	B, T
Lake	Petroleum distillates [155]	T, C
	Coal [156]	A
Marine	Petroleum [157]	T
	Landfill leachate [103]	T
Groundwater	Wastewater [158]	T/C (ratio)
	PAHs [159]	B, T, A
	Recycled water [116–118]	T ₁

widely applied within psychometrics [122] and chemometrics [123,124], where techniques such as principal component analysis (PCA), partial least-squares (PLS), Tucker decomposition and more specifically parallel factor (PARAFAC) analysis have become increasingly popular for their ability to decompose large and complicated datasets and extract relevant information.

These multivariate approaches have been applied to fluorescence-based water research to detect the presence and quantify the underlying fluorescence characteristics of complex mixtures of DOM [98,125]. A number of studies have been carried out on fluorescent DOM with multivariate analysis techniques in marine water [126], estuarine water [96,127,128], fresh water [86,129] glacial systems [130,131] and, more recently, in drinking water [114, 132] and sewage treatment [133], including process performance [134] as well as to elucidate changes in fluorescence throughout the treatment trains of a number of water recycling plants [135]. Another approach to the interpretation of EEM data is by fluorescence regional integration (FRI) – a method where the EEM is divided into separate regions as appropriate and the intensity area of each region is integrated for comparison [136]. While this technique may be considered as simpler than the multivariate techniques listed, it may also be limited in that information on specific peak locations is not retained. Such statistical analyses and comparisons between data from different studies can only be conducted with confidence if the spectra have been corrected to account for appropriate instrument-specific wavelength responses resulting from differences between excitation light sources, monochromators and emission detectors [85]. A number of other potential challenges exist to implementing and maximizing the sensitivity of fluorescence for cross-connection detection, and compensation for these possible quenching effects must also be investigated and performed before statistical analyses can be carried out with confidence.

Challenges to cross-connection detection by fluorescence

A variety of sample matrix factors may affect fluorescence, where the intensities and the position of excitation and emission spectra can be heavily influenced by a number of variables. Henderson et al. [61] identified a number of potential matrix effects which may interfere with fluorescence signals and hence the ability of fluorescence to monitor recycled water systems, including inner filtering effects and fluorescence quenching by temperature, pH, metal ions and oxidants. Within the context of cross-connection detection (finished recycled water and potable water) these may become key challenges to the successful implementation of fluorescence monitoring.

Inner filtering effects are of concern for accurate fluorescence analysis at high fluorophore concentration and UV_{254} absorption [137]; however, the UV_{254} absorption

and DOC levels typically observed within both finished recycled water and potable water are typically low. For example, one study observed the UV_{254} absorption of finished recycled water to be 0.1 cm^{-1} and not significantly different from that of potable water [118]. The average DOC concentrations of recycled and potable water were also low (8.9 and 5.2 mg.L^{-1} , respectively), and is further evidence that any significant effects caused by inner filtering can typically be discounted.

Studies have been carried out on how pH changes affect fluorescence of freshwater samples [138]; however, within the context of recycled and potable water, no studies have yet been carried out. The pH of finished recycled water and potable water may have overlapping ranges [117], but within these ranges significant pH effects are unlikely. As pH is essentially constant within pipework, it is also unlikely for pH effects to impact fluorescence signals as it should have a low variability within the distribution system.

While there is significant evidence for metal-ion quenching of natural DOM [139–142], the extent of fluorescence quenching in environments relevant to finished recycled water and potable water is also largely unknown. An investigation on the effect of metal ions on wastewater fluorescence demonstrated that for samples of final effluent, iron, aluminium and nickel metal ions appeared to have no significant impact on fluorescence intensity [143], and this suggests that metal quenching effects of advanced treated recycled water would also be minimal.

Fluorescence intensity has long been known to be highly dependent on temperature [144], and all fluorophores are subject to intensity variations as a function of temperature. As the effect of temperature on fluorescence quenching is linear [145], thermal quenching effects may be overcome in single samples or multiple compositionally identical samples by applying simple correction factors. However, chemical composition is notably different between sewage-impacted and potable water, as well as being seasonally and even daily variable. This may lead to each source having significantly varying temperature dependencies and hence complicate any mathematically based correction. Temperature effects on the fluorescence of DOM in river waters have been shown [146], where a large reduction in fluorescence has been observed when sample temperature is increased from 10°C to 45°C (Figure 4). Fulvic-like fluorescence was found to decrease by 22–24% for river waters, and between 19–26% for sewage-impacted samples, whereas tryptophan-like fluorescence intensity was found to decrease by between 24–25% for river waters, and between 30–37% for sewage-impacted waters. Recycled water has been successfully differentiated from potable water using fluorescence EEM spectroscopy; however, these analyses were all conducted on grab samples at 25°C in the laboratory [116–118]. The effect of temperature on the fluorescence of finished recycled water and potable water have not yet been reported within the literature, and diurnal temperature ranges have been found to

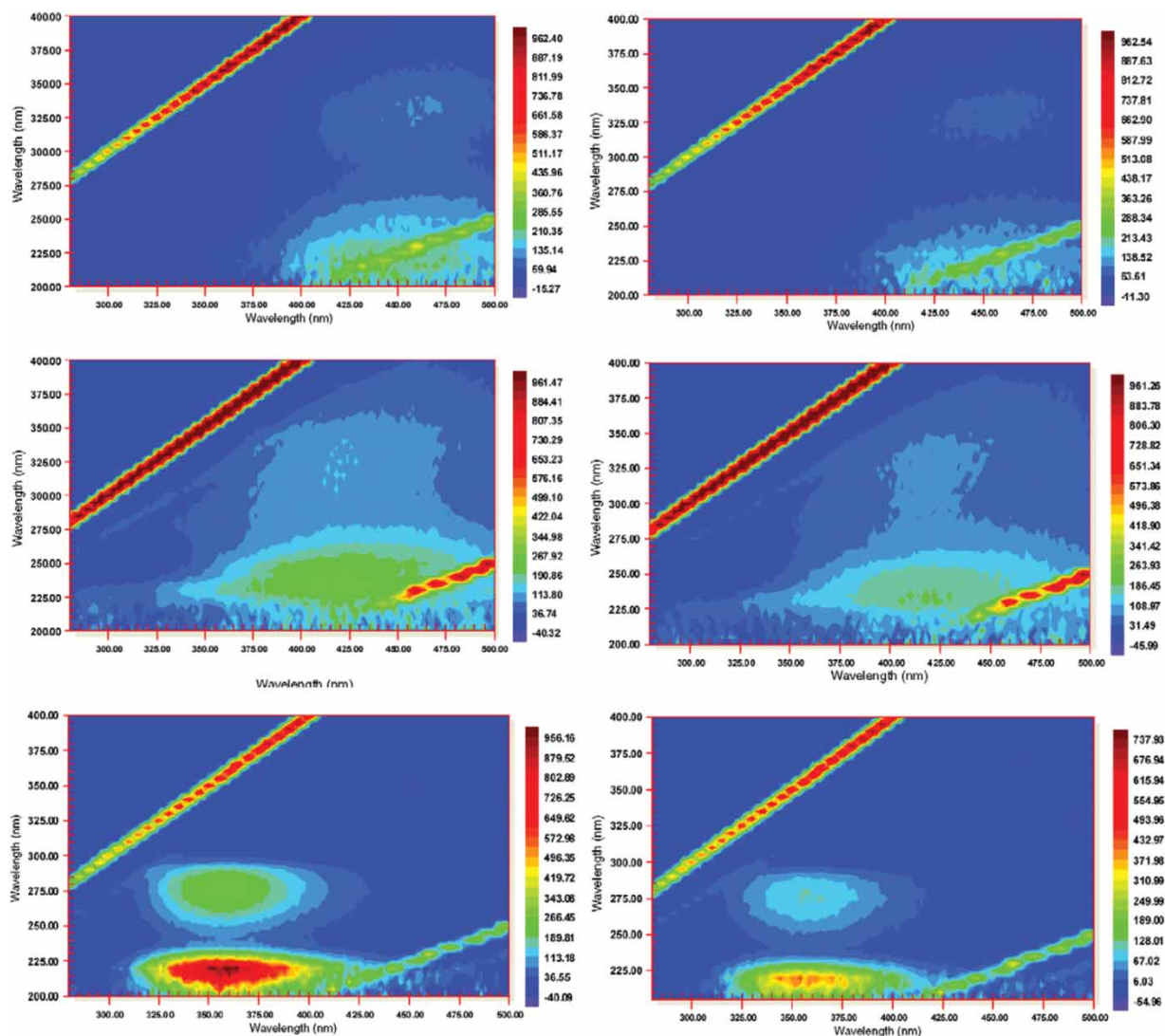


Figure 4. Fluorescence excitation–emission matrices at 10°C (left) and 45°C (right). Top: Nordic Fulvic Acid. Middle: Urban River (Bourn Brook). Bottom: 100ppb tryptophan standard (from Baker [146]).

vary in an Australian Water Recycling Plant by more than 25°C during summer [147], which may result in a diurnal variation of up to 30–35% in protein-like fluorescence. Analyses carried out in the field with portable fluorimeters are likely to be exposed to such temperature ranges, and so the effects of temperature on the fluorescence of finished recycled water and potable water remain key areas which require investigation.

Chlorination is by far the most common method of wastewater disinfection and is used worldwide for the disinfection of pathogens before discharge into receiving streams, rivers or oceans [5,148,149]. Chlorination is also used as a vital disinfection process within the water recycling treatment train, with a free chlorine residual limit of 0.5 mg/L at the point of use being currently employed within Australia [5]. Literature studies clearly show significant impacts of chlorination on the fluorescence

intensity of organic matter [150,151], where in all cases fluorescence is decreased in proportional to chlorine dose. However, a very limited number of studies have been published to date which show impacts of residual free chlorine levels on fluorescence intensity, particularly for recycled water. This will require investigation to ascertain its effect on fluorescence detection of cross-connections.

The above assessments have all been made under the assumption that the recycled water and potable water networks have not been compromised. For example, broken pipework may lead to increased turbidities and the fluorescence signals may be potentially affected by light scattering, or pH dosing malfunction at the treatment plant may lead to significant quenching of fluorescence signals. However, assuming appropriately controlled treatment plants and distribution systems are in place, the key areas which require investigation are temperature and free chlorine

for their potential to affect the successful monitoring of cross-connections by fluorescence.

Conclusions and research recommendations

As the incorporation of dual reticulation systems has become commonplace within new housing developments, there is a clear need for a sensitive, fast and reliable technique to be developed for the detection of cross-connections between drinking water and recycled water pipes. This is an area where traditional water quality parameters have proven to be ineffective, and fluorescence spectroscopy shows great potential to provide this important tool for portable cross-connection detection, due to its high sensitivity and specificity. Contamination detection by fluorescence spectroscopy has typically been most successful within the tryptophan-like regions of the fluorescence matrix in a variety of water sources and, importantly, in recycled water and potable water, and therefore this region has been indicated as the most promising for successful portable cross-connection detection.

Variable sample parameters such as temperature, pH, free chlorine concentration, turbidity and inner filtering have been demonstrated as having the ability to cause significant interference with fluorescence measurements and, accordingly, fluorescence analysis should be undertaken with careful consideration of these parameters. Although these effects have been highlighted, the differentiation between finished recycled water and potable water has still been successful, albeit at identical sample temperatures. The effects of residual free chlorine concentrations and temperature variations are considered to be most relevant in their ability to affect fluorescence monitoring; however, within the context of advanced treated recycled water and drinking water, their overall consequences on the technique's effectiveness may be insignificant or overcome by the use of correction factors. These parameters should, however, be further investigated in order to maximize the sensitivity and confidence of fluorescence spectroscopy and see its successful application as a sensitive tool for portable cross-connection detection.

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