Fluorescence monitoring at a recycled water treatment plant and associated dual distribution system – Implications for cross-connection detection

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ABSTRACT

Dual distribution systems are becoming increasingly common in greenfield housing developments in Australia for the redistribution of recycled water to households for non-potable use. Within such schemes there exists the potential for cross-connections between recycled and drinking water systems. Due to the high level of recycled water treatment, these events are unlikely to lead to outbreaks of illness in the community. Nonetheless, they do represent a breach of the recycled water risk management strategy and therefore an elevated level of risk to consumers. Furthermore, cross-connection events have the potential to undermine public confidence in these types of water recycling. A rapid, highly sensitive method of cross-connection detection may therefore provide an additional level of confidence in these schemes. The aim of this research was to determine the potential for using fluorescence spectroscopy as a monitoring tool in water treatment plants and dual distribution systems. Samples from both the water recycling plant and dual distribution system were collected on a weekly basis over 12 weeks. Fluorescence excitation–emission matrix (EEM) spectra and water quality parameters including dissolved organic carbon, UV_{254}, pH, conductivity, free chlorine and turbidity were obtained for each sample. The fluorescence EEM spectra of recycled and drinking water were distinctly different and exhibited low variability throughout the course of the sampling program, indicating a degree of stability of the fluorescent components within the organic matter. A ten-fold difference in mean fluorescence intensity was observed for recycled water compared to drinking water, which was greater than the difference observed for the other measured water quality parameters. Probabilistic analysis was used to determine the reliable detection limit of recycled water contamination of drinking water. Accounting for the inherent variability of both recycled water and drinking water, a 45% contamination of recycled water in drinking water could be detected with a signal-to-noise ratio greater than 3 for more than 95% of individual random sample pairs. Greater sensitivity can be assured by averaging numerous samples. In comparison, a 70% contamination of recycled water in drinking water was required for the same detection using conductivity.

1. Introduction

Municipal water recycling is gaining increasing popularity in urban water management systems across the world, and has been used in many parts of Australia over the last decade. This development has taken place as a response to unpredictable rainfall patterns, rapid population growth and increasingly stringent environmental regulations. In some cases, recycled water (as highly treated municipal effluent) is distributed back to domestic properties via a dedicated recycled water distribution system and then used for applications including toilet flushing and irrigation (Cooper, 2003). Such recycling schemes are commonly known as 'dual distribution systems' and established examples exist within Australia at Rouse Hill (north-west Sydney) (Storey et al., 2007), Sydney Olympic Park (Listowski et al., 2009) and Pimpama-Coomera (South East Queensland) (Willis et al., 2009). Similar schemes exist elsewhere such as in Utrecht (Netherlands), Irvine and Colorado Springs (USA) and the pioneering scheme in Tucson (USA) which has been in operation for over 20 years. Dual distribution systems have some specific inherent risks associated with their construction and maintenance, which must be carefully managed to protect consumer safety. Among these is the possibility of incorrectly cross-connecting drinking and non-potable water sources such as recycled water (Korfali and Jurdi, 2007; Lee et al., 2003; Oesterholt et al., 2007). In Australia, for example, fifty potential cross-connections were discovered at Rouse Hill prior to commissioning in 2001 and at least four cross-connection events attributed to contractor plumbing error have been documented since that time (de Rooy and Engelbrecht, 2003). Similar events have also occurred at Sydney Olympic Park (Sydney Water, 2005) and Pimpama-Coomera (The Australian, 2008). Such events may have public health implications (Mena et al., 2008; Propato and Uber, 2004) and risk undermining public confidence in recycled water schemes (Storey et al., 2007).

Current testing procedures for the presence of a cross-connection typically require shutting off water pressure and testing for water flow (Sydney Water, 2005), which is time-consuming and often only undertaken in the event of a customer complaint. Various control measures have been implemented in dual distribution systems including the multiple treatment barrier approach, to ensure that the recycled water quality will pose a low risk to human health should a cross-connection occur, as well as backflow prevention devices (Storey et al., 2007). These devices however prevent the reversal of normal flow direction (Pontius and Evans, 2008) and hence the backflow and back siphonage of recycled water into the drinking water distribution system, rather than an accidental cross-connection of recycled and drinking water pipes. To facilitate the proper management of such recycled water systems, a rapid, highly sensitive method of detection to monitor both recycled and drinking water quality is required.

In order to distinguish recycled water from drinking water and detect contamination of drinking water with low proportions of recycled water, a parameter that consistently differentiates between the two water types must be identified. Only a limited number of studies have been undertaken in this area, and these typically investigate water quality parameters including electrical conductivity, total organic carbon (TOC) measurement, turbidity and UV–visible (UV–vis) light absorption among others (Toifl and O'Halloran, 2008). The use of TOC concentration for cross-connection detection has met with limited success as recycled water generally has TOC concentration approaching that of drinking water (Drewes et al., 2003; Urbansky, 2001). TOC in drinking water however is derived from a different source to that of recycled water and therefore has a very different organic character (Drewes and Fox, 2000). For example in drinking water, organic carbon is derived mainly from natural organic matter present in the source water, while in wastewater systems, TOC is derived from the biomass contributed from the sewage and also from the biological processes used to treat the sewage. Dissolved organic carbon may be characterised using methods such as size exclusion chromatography (SEC) (Allpike et al., 2005; Drewes et al., 2006), XAD resins to determine hydrophobicity (Sharp et al., 2006), or UV absorption, in particular specific UV absorption (SUVA) (UV_{254}:DOC). An alternative approach of steadily increasing interest is the use of fluorescence-based techniques (Ahmad and Reynolds, 1999; Baker, 2001; Hudson et al., 2007).

Three-dimensional fluorescence excitation–emission matrices (EEMs) are gaining interest in water quality applications. The main analytical advantages of fluorescence EEMs are the acquisition time required is as little as one minute, the process is non-destructive, requires no sample preparation for relatively clean water samples and the technique is one to three orders of magnitude more sensitive than UV–vis spectroscopy (Webster, 1999). Fluorescence EEMs have been used in the characterisation of marine dissolved organic matter (DOM) (Coble, 1996), recently in freshwater applications including tracking sewage-derived outfall in rivers and estuaries (Baker, 2001; Baker et al., 2003) and the sensitivity of fluorescence has been highlighted more recently by its use with in-situ spectrometers (Baker, 2004; Spencer et al., 2007; Downing et al., 2009). Several studies have recently been undertaken to investigate the fluorescence of drinking water to detect fouling events (Peiris et al., 2010a,b) and organic matter removal efficiency (Bieroza et al., 2009a,b; Bieroza et al., in press; Bieroza et al., 2010) and a recent article reviewed fluorescence literature to determine the potential for using fluorescence spectroscopy to detect contamination with recycled water (Henderson et al., 2009). It was determined that by measuring "protein-like" ($\lambda_{ex/em} = 225-275/309-340$ nm) and "humic-like" ($\lambda_{ex/em} = 300-390/410-480$ nm) fluorescence peaks there may be potential to detect contamination of drinking water with treated wastewater — a situation analogous to cross-connections in dual distribution systems. This review also highlighted knowledge gaps in how individual treatment processes affect the fluorescence of recycled water.

The aim of this research was to investigate the impact of different treatment processes on fluorescent material in recycled water at an Australian water recycling plant that is connected to a dual distribution network that delivers both recycled water and drinking water to a community. The potential for utilising fluorescence spectroscopy as a monitoring tool within dual distribution systems, particularly for the detection of cross-connections, is assessed by employing
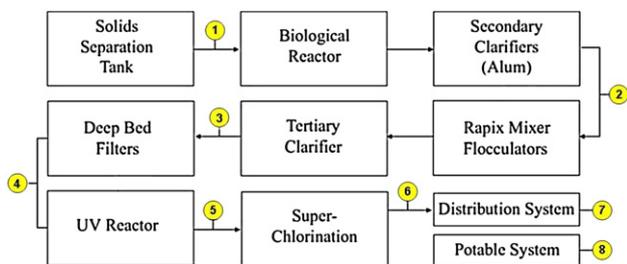
Fig. 1 – Simplified schematic of treatment process chain at Rouse Hill Recycled Water Plant with eight weekly sampling points indicated.

probabilistic techniques including distribution function fitting and Monte Carlo simulation.

2. Materials and methods

2.1. Samples

A 12-week sampling program was undertaken at Rouse Hill Recycled Water Plant and associated dual distribution system. The recycled water plant is located approximately 50 km northwest of Sydney. The site has been in operation since 2001 and is responsible for distributing over 1.9 billion litres of non-potable recycled water per year to over 17,500 homes within the greater Rouse Hill area (Sydney Water, 2009). The recycled water plant uses processes such as deep bed sand filtration, ultraviolet (UV) disinfection and super-chlorination to achieve its final recycled water product. Grab samples were acquired weekly between March and June 2008, after six treatment processes: (1) primary settlement; (2) secondary clarification; (3) tertiary clarification; (4) deep bed filtration; (5) UV disinfection; and (6) chlorination (Fig. 1 and Table 1). Finished recycled water and drinking water grab samples were taken simultaneously from a domestic property within the distribution network. All samples were collected in 500 mL polyethylene terephthalate (PET) bottles and transported in cold storage to UNSW for analysis, where they were each transferred in triplicate to 50 mL, gamma-sterilised polypropylene bottles. A leachate study was undertaken which determined there were no fluorescent leachates from the PET containers within the sample transport period.

2.2. Sample analysis

No sample preparation was undertaken prior to fluorescence EEM analysis. Fluorescence EEM spectra were obtained using a Cary Eclipse Fluorescence Spectrophotometer (Varian, Australia) in a 4 mL quartz cuvette (Starna, Australia) and temperature was controlled at 25 °C. Fluorescence EEMs were measured for excitation wavelengths of $\lambda_{ex} = 200–400$ nm at 5 nm increments and $\lambda_{em} = 280–500$ nm, with excitation and emission slit widths of 5 nm, at a photomultiplier tube (PMT) voltage of 800 V using a scan speed of 9600 nm min^{-1}. The Raman intensity of water in a sealed cell (Varian, Australia) was measured $\lambda_{ex} = 348$ nm on a daily basis to ensure instrument stability and was constant at 20 ± 1 arbitrary fluorescence units (afu) over the course of the study.

Other water quality parameters were analysed to determine their suitability as cross-connection detectors as well as to determine matrix effects on fluorescence. UV absorption spectra were obtained using a Cary 50 Bio UV–vis Absorption Spectrophotometer (Varian, Australia). Spectra were acquired from samples in 4 mL quartz cuvettes (Starna, Australia), from $\lambda_{abs} = 200–600$ nm at a scan speed of 9600 nm min^{-1}. Conductivity and pH were measured with a HACH HQ14d portable meter (HACH, Australia) and DOC was measured with a TOC-5000A Analyser (Shimadzu, Australia) using the non-purgeable organic carbon method. Turbidity was measured using a HACH 2100N Turbidimeter. Data provided by Sydney Water indicated that free chlorine concentrations in the outlet of the chlorine contact tank were between 5.6 and 6.1 mg/L. However, at the time of sample analysis at UNSW free chlorine concentrations were consistently less than 1.0 mg/L, indicating that any significant fluorescence quenching due to chlorine had already occurred. Free chlorine was measured by n,n-diethyl-p-phenylene-diamine (DPD) method on a HACH HQ40d digital meter (HACH, Australia). All analyses were carried out within 48 h of sample collection.

2.3. Post processing and EEM interpretation

Data correction is routinely carried out on fluorescence spectral data to account for intra- and/or inter-laboratory

Table 1 – Detail of the treatment process chain undertaken at Rouse Hill Recycled Water Plant.			
Sample type	Processes involved	Chemicals added	Process flow rate (L/s)
1. Primary settled	Screens Grit Solids separation	–	180
2. Secondary clarified	Biological reactor Secondary clarification	FeCl$_3$ NaOH (alkalinity)	180
3. Tertiary clarified	Rapid mixing Flocculation Tertiary clarification	Alum Cationic polymer	180
4. Deep bed filtered	Deep bed filtration	–	180
5. UV disinfected	UV photolysis (254 nm)	–	180
6. Chlorinated	Super-chlorination	NaOCl	153
7. Finished recycled water	(Distribution system)		153

Table 2 − Mean water quality data (±1 s.d) for each sample type over the 12-week sampling period.

Sample type	UV$_{254}$ cm^{-1}	DOC (mg L^{-1})	Conductivity (μS cm^{-1})	pH	Turbidity (NTU)
1. Primary settled	0.96 (±0.27)	28.6 (±5.9)	1240 (±100)	7.1 (±0.2)	20 (±16)
2. Secondary clarified	0.26 (±0.05)	16.2 (±4.4)	930 (±30)	7.1 (±0.2)	0.8 (±0.3)
3. Tertiary clarified	0.16 (±0.04)	9.9 (±0.5)	970 (±30)	6.6 (±0.3)	0.3 (±0.1)
4. Deep bed filtered	0.17 (±0.04)	10.1 (±0.5)	980 (±30)	6.9 (±0.3)	0.3 (±0.1)
5. UV disinfected	0.14 (±0.05)	10.2 (±0.6)	990 (±40)	7.0 (±0.2)	0.2 (±0.1)
6. Chlorinated	0.13 (±0.04)	10.8 (±0.9)	1020 (±30)	7.3 (±0.2)	0.3 (±0.1)
7. Finished recycled water	0.10 (±0.04)	8.9 (±1.3)	970 (±140)	7.6 (±0.4)	0.2 (±0.2)
8. Drinking water	0.07 (±0.04)	5.2 (±0.3)	250 (±10)	7.4 (±0.2)	0.2 (±0.1)

variances such as daily fluctuations in spectrometer lamp intensity. For this study, fluorescence EEMs were blank subtracted using a sealed cuvette of milliQ water (Varian, Australia), and locally generated emission and excitation correction factors were applied. All data correction and excitation/emission pair extraction was carried out using Matlab software (Mathworks).

A number of single wavelength pair intensities were extracted from EEMs and analysed as: peak A ($\lambda_{ex/em}$ = 235/426 nm), peak C$_1$ ($\lambda_{ex/em}$ = 325/426 nm), peak T$_1$ ($\lambda_{ex/em}$ = 300/350 nm) and peak T$_2$ ($\lambda_{ex/em}$ = 225/350 nm) for both drinking water and recycled water samples. Comparable wavelength peaks were first identified by Coble (1996) and have since been regularly observed in natural systems (Baker, 2001). Protein-like (peak T$_1$) and humic-like (peak C) peaks were also

analysed as ratios (T:C) to highlight some of the more distinct changes in fluorescence EEM character.

2.4.   Cross-connection detection (probabilistic analysis)

Mixtures of varying proportions of recycled and drinking water were also analysed to determine the sensitivity of the method for detecting low levels of recycled water in drinking water and to ensure that the fluorescence response was only dependent on concentration. These mixtures were prepared using triplicate samples of drinking and finished recycled water from a single week, which were collected after the conclusion of the initial 12-week sampling period. In order to determine the limits of detection, each of the triplicate drinking and recycled water samples from within the 12 week
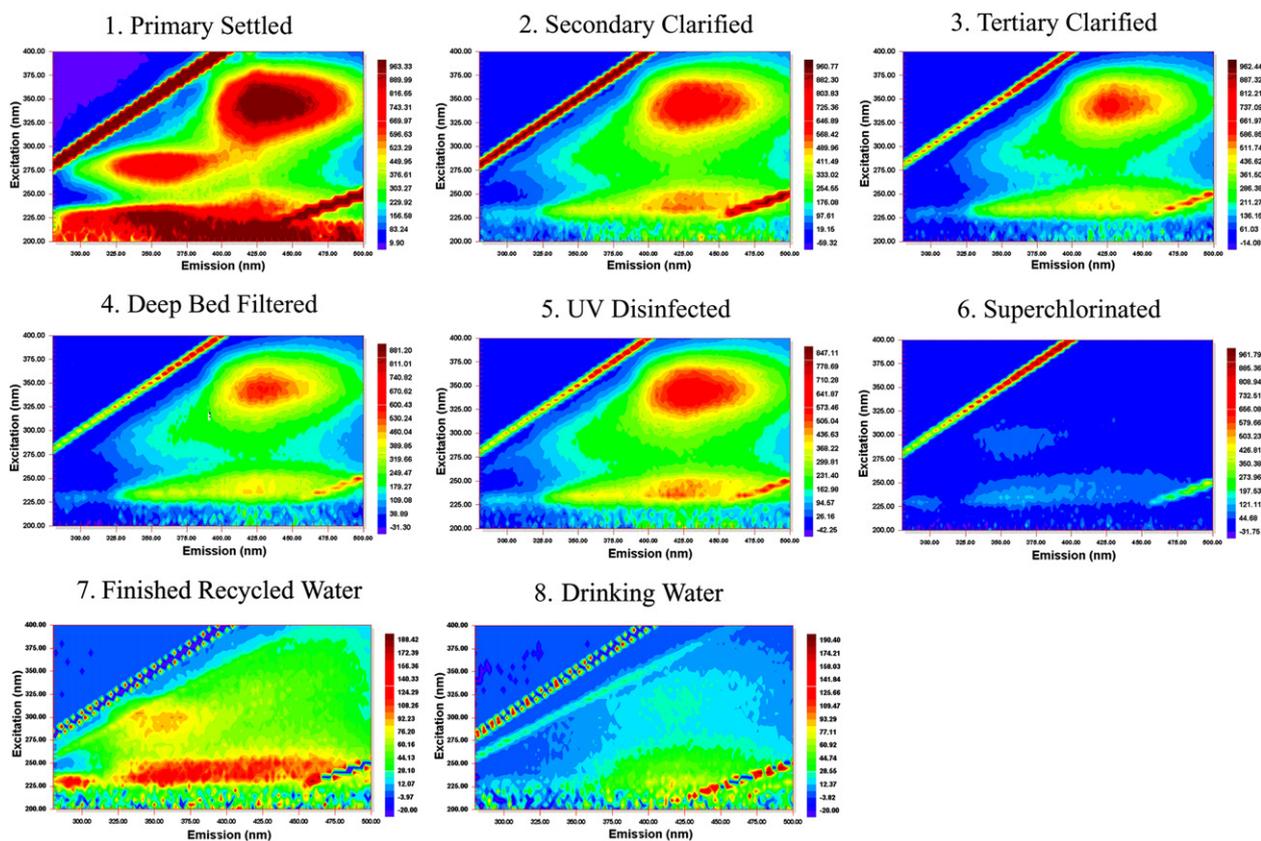
Fig. 2 − Typical fluorescence excitation−emission matrices (EEM) for recycled and drinking water samples over the 12-week sampling period. Note that finished recycled water and drinking water EEMs are shown on a lower scale (maximum intensity of 200 afu).

Table 3 – Mean fluorescence intensity (±s.d) for each sample type over the 12-week sampling period. Values above each bar indicate the peak T:C ratio.

Post-treatment type	Peak T_1 (afu) $(\lambda_{ex/em} = 300/350$ nm$)$	Peak T_2 (afu) $(\lambda_{ex/em} = 225/350$ nm$)$	Peak C_1 (afu) $(\lambda_{ex/em} = 325/426$ nm$)$	Peak A (afu) $(\lambda_{ex/em} = 235/426$ nm$)$
1. Primary settled	866 (±45)	2065 (±102)	1491 (±99)	1369 (±62)
2. Secondary clarified	524 (±23)	545 (±26)	1043 (±49)	1101 (±66)
3. Tertiary clarified	488 (±21)	466 (±21)	834 (±63)	913 (±57)
4. Deep bed filtered	482 (±23)	460 (±19)	834 (±56)	877 (±54)
5. UV disinfected	371 (±86)	351 (±81)	624 (±178)	692 (±173)
6. Chlorination	196 (±13)	176 (±12)	88 (±9)	176 (±14)
7. Finished recycled water	198 (±21)	175 (±20)	87 (±8)	187 (± 15)
8. Drinking water	22 (±3)	22 (±4)	51 (± 9)	139 (±19)

study were analysed and the resulting 36 data points for peak T_1 were fitted to a log-normal probability distribution function (PDF) using @Risk software (Palisade Corporation). PDF's were derived by fitting to a cumulative log-normal distribution using the experimental data points and corresponding fractile plotting positions as described in detail elsewhere (Khan, 2010). This PDF-fitting was undertaken in preparation for a Monte Carlo simulation to assess various mixing scenarios of recycled water in drinking water. The Monte Carlo simulation was also performed using @Risk software with Latin Hypercube sampling over 10,000 iterations.

3. Results and discussion

3.1. Impact of treatment processes on water quality

3.1.1. Water quality data
Mean data is presented for the UV_{254}, DOC, conductivity, pH and turbidity of finished recycled and drinking water over the entire sampling programme (Table 2). The largest decrease in turbidity was observed after secondary clarification from 20 NTU to 0.8 NTU, after which tertiary clarification reduced it to 0.3 NTU. The turbidity of the drinking water was equal to that of finished recycled water and the pH remained consistent between each of the water samples. UV_{254} decreased by

73% on secondary clarification, and then decreased gradually with each successive treatment stage, giving a final absorbance of 0.1 cm^{-1} for finished recycled water, which was not significantly different from that observed for drinking water. Conductivity was not significantly decreased by the treatment processes used at the plant, and thus had a value of 970 ± 140 $\mu S\ cm^{-1}$ in finished recycled water, which was nearly four times greater than that of drinking water. DOC was decreased by nearly 70% by the treatment process train; however, the resultant DOC of 8.9 ± 1.3 $mg\ L^{-1}$ was still greater (1.7 times) than that of drinking water.

3.1.2. Fluorescence EEMs
Typical fluorescence EEMs observed during the 12 week study at each sample location are shown in Fig. 2. Each EEM includes fluorescence peaks C_1, A, T_1 and T_2 as identified by Coble (1996). Visual comparison suggests that these four peaks dominate over other areas of the EEM. Furthermore, it can be seen that peaks A and T_2 are less sensitive areas of the EEM due to increased noise generated at lower excitation wavelengths and therefore discussion will focus on peaks T_1 and C_1.

Mean fluorescence data for peak T_1, T_2, C_1 and A are shown in Table 3. Secondary clarification and chlorination generated the most evident changes in fluorescence intensities. The ratio of protein-like (T_1) to humic-like (C_1) fluorescence (T:C) remained between 0.70 and 0.51 from primary settled samples
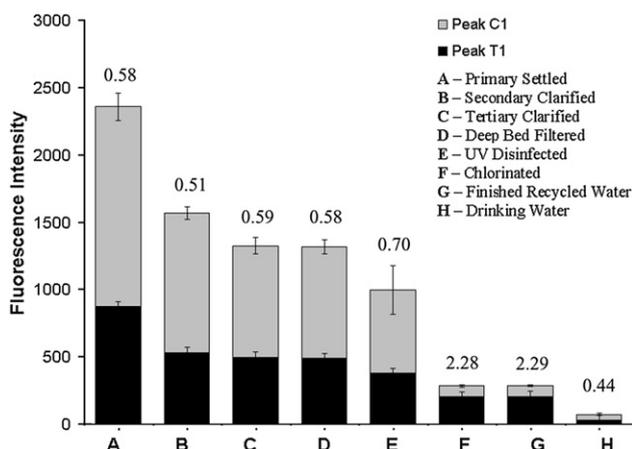
Fig. 3 – Mean corrected fluorescence intensities at peak T1 $(\lambda_{ex/em} = 300/350$ nm$)$ and peak C1 $(\lambda_{ex/em} = 325/425$ nm$)$ for each sample location.
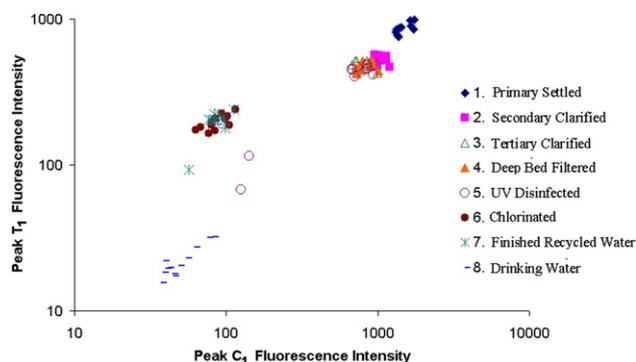
Fig. 4 – Corrected fluorescence intensities at peak T1 $(\lambda_{ex/em} = 300/350$ nm$)$ and peak C1 $(\lambda_{ex/em} = 325/425$ nm$)$ for water samples throughout the treatment process over the sampling period.

Table 4 — Average percentage decreases in peak C and peak T fluorescence intensities for each treatment process. Percentages which appear in brackets are what the percentage decreases would be if 3 weeks of anomalous post-UV data were excluded from the dataset.

Treatment type	Average peak T percentage decrease	Average peak C percentage decrease
1. Primary settlement	n/a	n/a
2. Secondary clarification	39	30
3. Tertiary clarification	6	20
4. Deep bed filtration	1	1
5. UV disinfection	23 (5)	25 (4)
6. Chlorination	47 (57)	85 (89)
7. Finished recycled water	−1	1

Fig. 6 — Mean corrected fluorescence intensities at peak T1 ($\lambda_{ex/em}$ = 300/350 nm) as a function of conductivity for finished recycled water and drinking water throughout the sampling period.

through to UV disinfected samples despite decreases in overall fluorescence (Fig. 3). However the ratio was significantly altered by chlorination, where the most significant fluorescence reduction is observed. The chlorination process reduced humic-like fluorescent organic matter to a greater extent than protein-like fluorescent organic matter, which can be seen by the T:C ratio increasing from 0.70 to 2.28. The effect of chlorination processes on water and wastewater is largely unknown with limited studies undertaken (Beggs et al., in press) and the results of this work suggest its impact on the fluorescence of water and wastewater is substantial. Residual free chlorine has also been indicated as causing fluorescence quenching (Henderson et al., 2009) and further work is therefore required in this area.

Unlike chlorination, UV disinfection did not have a significant impact on the presence of fluorescent organic matter (Fig. 3). The large standard deviation in post-UV samples is due to anomalous data from three weeks (weeks 5, 6 and 9) where the fluorescence was observed to decrease to around one third of typical values (around half the value of finished recycled water) (Table 3). This may be due to sampling or equipment error and if these anomalous data points were to be treated as outliers, the mean fluorescence for UV disinfected samples would not be significantly different to secondary clarified, tertiary clarified and deep bed filtered samples.

With the exception of the anomalies for UV disinfected samples, variations in fluorescence intensity for other samples locations were low throughout the study with an average standard deviation of 3% for all recycled water samples and 16% for drinking water samples. The only exception was week 11 samples of recycled product water, where the fluorescence intensity at peak T_1 decreased from an average of 198 afu to 92 afu (54% reduction). This was confirmed to be caused by a partial process shutdown, causing the recycled distribution system to be 'topped up' with drinking water to meet demand according to the Rouse Hill site operating protocol. This event accounts for the low fluorescence intensities of that sampling week as replacement of recycled water through the system with drinking water resulted in a dilution of the fluorescent organic matter. The prominence of this event within the data gives strong indication of the high level of stability in the fluorescence of recycled water at this site, and therefore the potential for robust online fluorescence monitoring.

By assessing protein-like (peak C_1) and humic-like (peak T_1) fluorescence, drinking and treated water samples can be
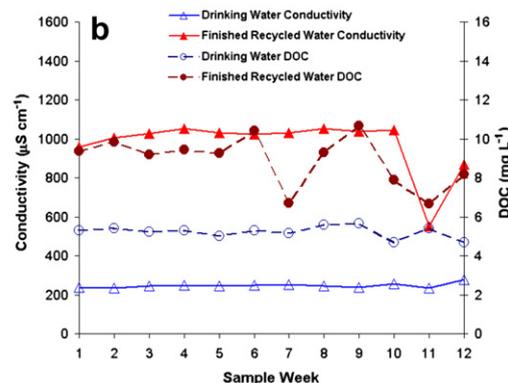
Fig. 5 — (a) Peak T1 fluorescence intensity; and (b) mean dissolved organic carbon (DOC) and conductivity; for finished recycled water and drinking water samples over the 12-week sampling period.
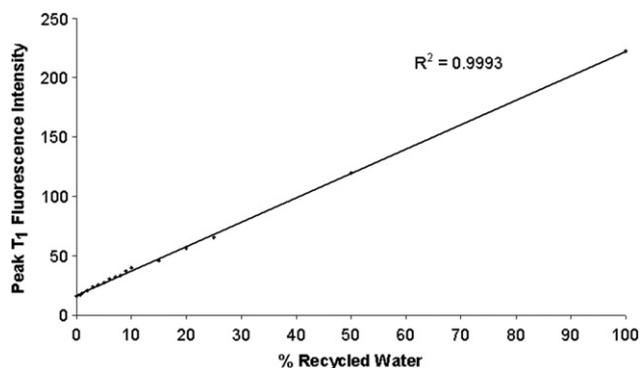
Fig. 7 — Mean (±s.d) fluorescence intensities at peak T1 ($\lambda_{ex/em}$ = 300/350 nm) of drinking water mixed with finished recycled water.

classified into four main groups as follows: (A) primary settled; (B) secondary clarified, tertiary clarified, deep bed filtered and UV disinfected; (C) chlorinated and finished recycled; and (D) drinking water (Fig. 4). Overall, peak T_1 was found to give a better separation between drinking and finished recycled water samples, whereas peak C_1 was found to have a more significant role in distinguishing between recycled water from different treatment processes, such as between deep bed filtered and chlorinated samples (Fig. 4). Peak T_1 was thus further investigated for use in cross-connection detection.

3.2. Cross-connection identification

Drinking water samples during this study typically exhibited low but quantifiable fluorescence with a T:C ratio between 0.38 and 0.56. In contrast to this, finished recycled water samples are typically higher in both humic-like fluorescence and (particularly) protein-like fluorescence and the T:C ratio is between 1.6 and 2.7. These results are comparable to a recent study where the fluorescence of natural water systems affected by intermittent sewage overflow was investigated (Baker et al., 2003). This study found the T:C ratio to vary from 0.52 to 1.64 during sewage pollution events, otherwise being

between 0.44 and 0.75, indicating strong potential of protein-like fluorescence as a detector of recycled water within drinking water supplies. The protein-like fluorescence region has previously been linked to the presence of microbially-derived organic matter, either living or dead and either cellular or extracellular material or exudates (Hudson et al., 2008). Hence, the high peak T_1 fluorescence of recycled water may be attributed to the presence of such material, probably exudates within recycled water originating from wastewater and the associated biological processes (Table 4).

The peak T_1 fluorescence intensities of drinking water varied between 15 afu and 32 afu while for finished recycled water the peaks varied between 180 afu and 240 afu (Fig. 5a). The exception was the week 11 decrease caused by drinking water top up of the recycled water distribution system. It was also determined that DOC and conductivity both enabled differentiation between recycled and drinking water; however UV_{254} absorbance, pH and turbidity were similar for finished recycled and drinking water samples (Table 2). Fig. 5b illustrates the variation in DOC and conductivity over the 12 week period. Finished recycled water varied from 6.7 mg L^{-1} to 10.7 mg L^{-1} and 553 μS cm^{-1} to 1055 μS cm^{-1}, respectively, while the DOC concentration and conductivity of drinking water varied from 4.7 mg L^{-1} to 5.6 mg L^{-1}, and 234 μS cm^{-1} to 279 μS cm^{-1}, respectively. The conductivity results for week 11 supported those of the fluorescence, however while the DOC decreased for this week, it was not significant when the weekly variation was taken into account. Overall, the two parameters which significantly identified recycled water from drinking water were peak T_1 fluorescence, which typically showed a ten-fold difference, and conductivity which was typically 5-fold in difference.

Multi-parameter monitoring has been shown to protect water distribution systems against health and security threats by providing robust early warning systems (Kroll, 2009). The use of multiple parameter (for example conductivity and fluorescence intensity) or multiple wavelength (for example peak T_1 and peak C_1 fluorescence intensity) systems may also distinguish between recycled and drinking water at some dual distribution schemes, and furthermore limit the number of false alarms. In order to achieve this, single wavelength pair
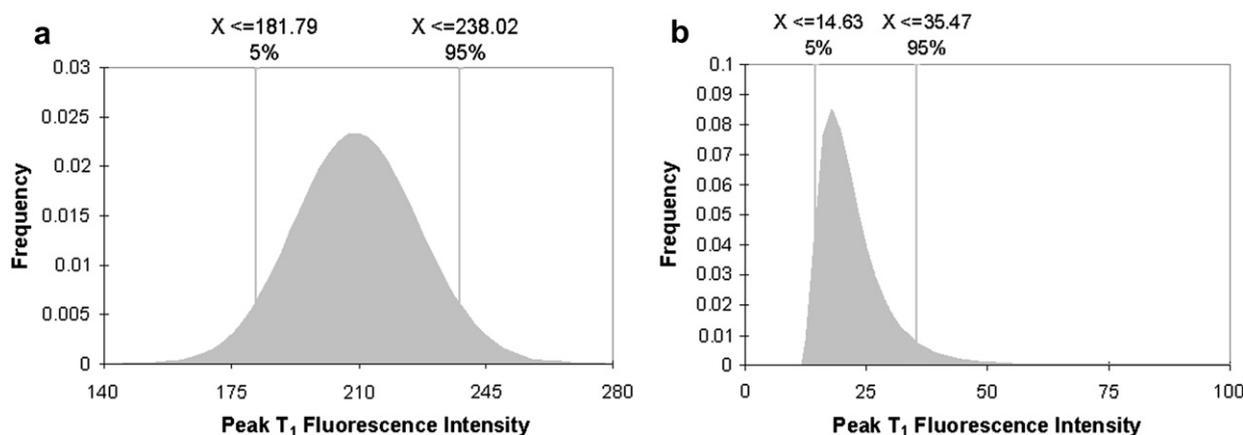
Fig. 8 — Fitted PDFs for peak T1 fluorescence (afu) of: (a) finished recycled water; and (b) drinking water; showing 5th and 95th percentile values.
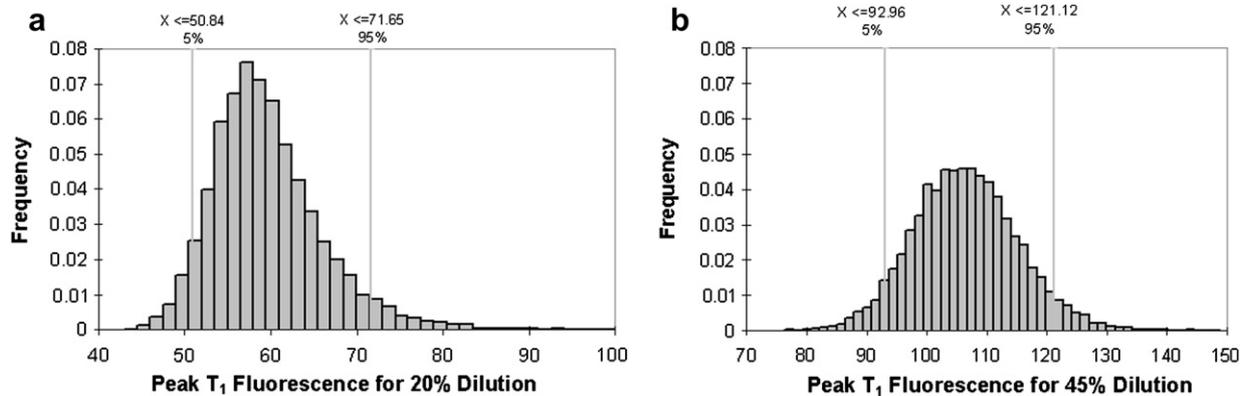
Fig. 9 – Derived PDFs of: (a) blend of 20% finished recycled water and 80% drinking water; and (b) blend of 45% finished recycled water and 55% drinking water.

fluorescence may be coupled with another analytical technique such as conductivity to act as a dual sensor system. By using these two parameters, improved detection reliability may be obtained as illustrated in Fig. 6. In this case, the combination of conductivity and peak T_1 fluorescence intensity clearly detect the presence of drinking water within the recycled water distribution system (week 11), which may be considered analogous to detecting the cross-connection of recycled and drinking water systems.

3.3. Probabilistic analysis to determine detection limits

Cross-connections may not always result in a complete displacement of drinking water with recycled water. A mixing study was therefore undertaken to determine the detection limits of recycled water within drinking water supplies and to ensure that the fluorescence response was only dependent on concentration. Mixtures of a single sample of finished recycled water and a single sample of drinking water were prepared, and fluorescence intensities at peak T_1 were analysed in triplicate (Fig. 7). The relationship between the fluorescence intensity at peak T_1 and the percentage of recycled water present returned a linear response with a correlation coefficient of 0.999. This means that there are no significant dilution effects on the fluorescence matrix of finished recycled water and thus dilution of finished recycled water with drinking water returns a linear response.

In order to determine the limits of detection of finished recycled water in drinking water, probabilistic analysis using Monte Carlo simulations were carried out. PDFs were first fitted for peak T_1 in drinking water and finished recycled water (Fig. 8). Delimiters are included in Fig. 8 to indicate the 5th and 95th percentile values of peak T_1 fluorescence in both water types. From this it is observed that the 95th percentile of the drinking water T_1 intensity is much less than the 5th percentile of recycled product T_1 intensity and thus the two types of water should be clearly distinguishable by this peak under representative circumstances. It follows that a highly concentrated (near 100%) contamination of finished recycled water in a drinking water system should be directly observable by the measurement of peak T_1 intensity. However for lower concentrations of recycled water contamination in drinking water, it will become increasingly difficult to confidently distinguish any rise in T_1 intensity that may be due to recycled water contamination from the underlying natural variability of T_1 intensity in drinking water.
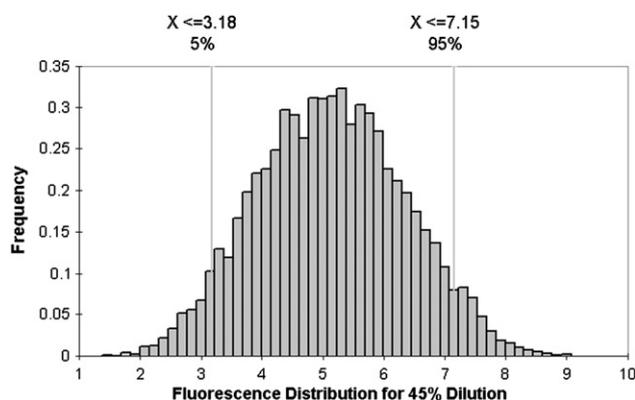
Fig. 10 – Simulated PDF for peak T1 fluorescence ratios of drinking water contaminated with 45% finished recycled water.
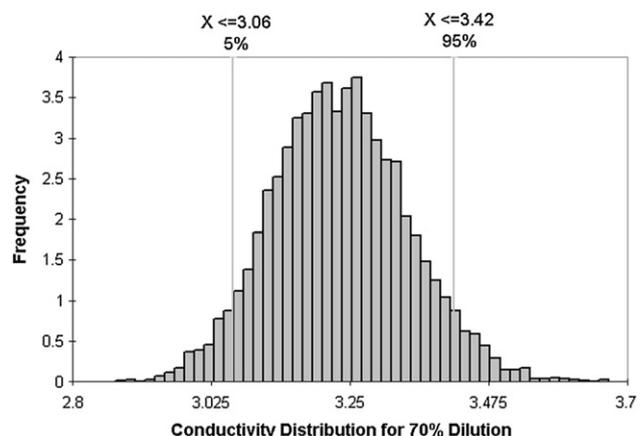
Fig. 11 – Simulated PDF for conductivity ratios of drinking water contaminated with 70% finished recycled water.

It is established practice in analytical sciences for a limit of detection (LOD) to be defined as the concentration at which the 'signal-to-noise' ratio (S/N) is equal to three (S/N = 3). Concentrations above this level are assumed to be readily distinguishable from the underlying variability in background noise. This definition for LOD was adopted by assuming that the 'signal' is defined by the peak T_1 reading in any drinking water sample contaminated by finished recycled water and the 'noise' is defined by the inherent variability in peak T_1 for non-contaminated drinking water. Accordingly, a concentration of recycled water in drinking water would be detectable if it was sufficient to consistently raise the peak T_1 intensity to a value of at least three times the inherent variability in peak T_1 intensity of uncontaminated drinking water. The LOD was therefore defined as the concentration at which the intensity of peak T_1 in contaminated water sample readings would be at least three times as great as the intensity in non-contaminated drinking water readings for at least 95% of readings (ie. at the 5th percentile).

The mixing study described above confirmed a linear relationship between the mixing ratio and peak T_1 intensity (Fig. 7) and indicates that concentration effects (such as reabsorption) could be discounted and a simple theoretical analysis could be used to determine the mixing ratio required to give S/N = 3. A Monte Carlo simulation was used for this purpose since the ratio to be determined was that of two PDFs rather than single point values. Using the established PDFs for peak T_1 in finished recycled and drinking water, a series of theoretical PDFs were derived to describe the expected variability of peak T_1 in theoretical mixtures of finished recycled and drinking water. A range of mixtures were evaluated in order to determine the LOD by this method, and the derived PDFs for two moderate contaminations of drinking water with finished recycled water (20% and 45%) are presented in Fig. 9.

The simulated distribution of peak T_1 ratios in the theoretical 45% solution of recycled water in drinking water compared to uncontaminated drinking water samples is presented in Fig. 10. It can be observed that for this situation, the S/N ratio at the 5th percentile is 3.18, indicating that the S/N is greater than or equal to 3.18 for at least 95% of the PDF. This indicates that a 45% solution of recycled water could be reliably identified in drinking water by a single sample reading with an estimated 95% reliability against false negatives. Increased sensitivity can easily be obtained by averaging multiple samples and thus effectively dampening the variability. When the same simulation was performed on conductivity data, a S/N ratio at the 5th percentile of above 3 (S/N > 3) was only obtained with a mixture comprising at least 70% recycled water (Fig. 11).

4. Conclusions

- Fluorescence intensities at Peak T_1 ($\lambda_{ex/em} = 300/350$ nm) and C_1 ($\lambda_{ex/em} = 325/426$ nm) were able to clearly show decreases in dissolved fluorescent organic matter throughout a number of wastewater treatment processes. Fluorescence intensities at peak C_1 and peak T_1 were able to separate treated water samples into four main groups. (A) Primary settlement; (B) secondary clarification, tertiary clarification,

deep bed filters and UV treatment; (C) chlorination and final recycled water; and (D) drinking water.
- Monitoring the fluorescence at peak T_1 ($\lambda_{ex/em} = 300/350$ nm) was found to be the most appropriate for distinguishing recycled water from drinking water, where the intensity was found to be approximately 10 times that of drinking water and much more sensitive than common water quality parameters such as conductivity and DOC.
- By applying a detection limit defined by a S/N ratio of 3, it was determined that a 45% solution of recycled water in drinking water should could be confidently identified by a single sample reading with 95% reliability. This was much more sensitive than conductivity which required a minimum of 70% recycled water in drinking water to read above this detection limit. Increased fluorescence sensitivity can be obtained by averaging multiple readings, which highlights the sensitivity of this technique and is an important factor in validating its use in an online detection system.
- Fluorescence spectroscopy is a promising technique for highly sensitive detection of cross-connections between recycled water and drinking water distribution systems.
- Future research will focus on further increasing the distinctions between recycled and drinking water using multivariate data analytical techniques and transferring this technique from bench to portable equipment to enable in-situ measurements. It is anticipated that this work will lead to the development of an in-situ monitoring tool.

REFERENCES

Ahmad, S.R., Reynolds, D.M., 1999. Monitoring of water quality using fluorescence technique: prospect of on-line process control. Water Research 33 (9), 2069–2074.

Allpike, B.P., Heitz, A., Joll, C.A., Kagi, R.I., Abbt-Braun, G., Frimmel, F.H., Brinkmann, T., Her, N., Amy, G., 2005. Size exclusion chromatography to characterize DOC removal in drinking water treatment. Environmental Science and Technology 39 (7), 2334–2342.

Baker, A., 2001. Fluorescence excitation–emission matrix characterisation of some sewage impacted rivers. Environmental Science and Technology 35, 948–953.

Baker, A., Inverarity, R., Charlton, M., Richmond, S., 2003. Detecting river pollution using fluorescence spectrophotometry: case studies from the Ouseburn, NE England. Environmental Pollution 124 (1), 57–70.

Baker, A., Ward, D., Lieten, S.H., Periera, R., Simpson, E.C., Slater, M., 2004. Measurement of protein-like fluorescence in river and waste water using a handheld spectrophotometer. Water Research 38, 2934–2938.

Beggs, K.M., Goetz, S.J., Dubayah, R.O., Henebry, G.M., Hunsaker, C.T., Imhoff, M.L., Nelson, R.F., Parker, G.G., Radeloff, V.C., 2009. Characterizing chlorine oxidation of dissolved organic matter and disinfection by-product formation with fluorescence spectroscopy and parallel factor analysis. Journal of Geophysical Research, 114, G04001, doi:10.1029/2009JG001009.

Bieroza, M., Baker, A., Bridgeman, J., 2009a. Relating freshwater organic matter fluorescence to organic carbon removal efficiency in drinking water treatment. Science of the Total Environment 407, 1765–1774.

Bieroza, M., Baker, A., Bridgeman, J., 2009b. Exploratory analysis of excitation–emission matrix fluorescence spectra with self-organizing maps as a basis for determination of organic matter removal efficiency at water treatment works. Journal of Geophysical Research 114, G00F07. doi:10.1029/2009JG000940.

Bieroza, M., Baker, A., Bridgeman, J. Classification and calibration of organic matter fluorescence data with multi-way analysis methods and artificial neural networks: an operational tool for improved drinking water treatment. Environmetrics, in press.

Bieroza, M., Baker, A., Bridgeman, J., 2010. Fluorescence spectroscopy as a tool for determination of organic matter removal efficiency at water treatment works. Drinking Water Engineering Science 3, 63–70.

Coble, P.G., 1996. Characterization of marine and terrestrial DOM in seawater using excitation–emission matrix spectroscopy. Marine Chemistry 51 (4), 325–346.

Cooper, E., 2003. Rouse Hill and Picton reuse schemes: innovative approaches to large-scale reuse. Water Science and Technology: Water Supply 3 (3), 49–55.

de Rooy, E., Engelbrecht, E., 2003. Experience with residential recycling at Rouse Hill. In: Water Recycling Australia 2nd National Conference, Brisbane, 1–2 September 2003, Brisbane, Australia. Australian Water Association.

Downing, B.D., Boss, E., Bergamaschi, B.A., Fleck, J.A., Lionberger, M.A., Ganju, N.K., Schoellhamer, D.H., Fujii, R., 2009. Quantifying fluxes and characterizing compositional changes of dissolved organic matter in aquatic systems in situ using combined acoustic and optical measurements. Limnology and Oceanography-Methods 7, 119–131.

Drewes, J.E., Fox, P., 2000. Effect of drinking water sources on reclaimed water quality in water reuse systems. Water Environment Research 72 (3), 353–362.

Drewes, J.E., Reinhard, M., Fox, P., 2003. Comparing microfiltration–reverse osmosis and soil-aquifer treatment for indirect potable reuse of water. Water Research 37 (15), 3612–3621.

Drewes, J.E., Quanrud, D.M., Amy, G.L., Westerhoff, P.K., 2006. Character of organic matter in soil-aquifer treatment systems. Journal of Environmental Engineering 132 (11), 1447–1458.

Henderson, R.K., Baker, A., Murphy, K.R., Hambly, A., Stuetz, R.M., Khan, S.J., 2009. Fluorescence as a potential monitoring tool for recycled water systems: a review. Water Research 43 (4), 863–881.

Hudson, N.J., Baker, A., Reynolds, D., 2007. Fluorescence analysis of dissolved organic matter in natural, waste and polluted waters – a review. River Research and Applications 23, 631–649.

Hudson, N.J., Baker, A., W, D., Brunsdon, C., Reynolds, D., Carliell-Marquet, C., Browning, S., 2008. Fluorescence spectrometry as a surrogate for the BOD5 test in water quality assessment: an example from South West England. Science of the Total Environment 391, 149–158.

Khan, S.J., 2010. Quantative Chemical Exposure Assessment for Water Recycling Schemes. In: Waterlines Report Series No. 27 Canberra, ACT.

Korfali, S.I., Jurdi, M., 2007. Assessment of domestic water quality: case study, Beirut, Lebanon. Environmental Monitoring and Assessment 135 (1–3), 241–251.

Kroll, D., 2009. Water security: the importance of designing dual use into solutions. In: Optics and Photonics in Global Homeland Security V and Biometric Technology for Human Identification VI, Proceedings of SPIE. The International Society for Optical Engineering, Orlando, FL, USA.

Lee, J.J., Schwartz, P., Sylvester, P., Crane, L., Haw, J., Chang, H., Kwon, H.J., 2003. Impacts of Cross-connections in North American Water Supplies. IWA Publishing, London.

Listowski, A., Ngo, H.H., Guo, W.S., Vigneswaran, S., Palmer, C.G., 2009. Concepts towards a novel integrated assessment methodology of urban water reuse. Desalination and Water Treatment 11, 81–92.

Mena, K.D., Mota, L.C., Meckes, M.C., Green, C.F., Hurd, W.W., Gibbs, S.G., 2008. Quantitative microbial risk assessment of a drinking water–wastewater cross-connection simulation. Journal of Engineering Science 7, 525–530.

Oesterholt, F., Martijnse, G., Medema, G., Van Der Kooij, D., 2007. Health risk assessment of non-potable domestic water supplies in the Netherlands. Journal of Water Supply: Research and Technology – AQUA 56 (3), 171–179.

Peiris, R.H., Budman, H., Moresoli, C., Legge, R.L., 2010a. Understanding fouling behaviour of ultrafiltration membrane processes and natural water using principal component analysis of fluorescence excitation–emission matrices. Journal of Membrane Science 357, 62–72.

Peiris, R.H., Halle, C., Budman, H., Moresoli, C., Peldszus, S., Huck, P.M., Legge, R.L., 2010b. Identifying fouling events in a membrane-based drinking water treatment process using principal component analysis of fluorescence excitation–emission matrices. Water Research 44, 185–194.

Pontius, F.W., Evans, W.B., 2008. An analysis of potential costs for small community cross-connection control. Journal of the American Water Works Association 100 (7), 66–80.

Propato, M., Uber, J.G., 2004. Vulnerability of water distribution systems to pathogen intrusion: how effective is a disinfectant residual? Environmental Science and Technology 38 (13), 3713–3722.

Sharp, E.L., Jarvis, P., Parsons, S.A., Jefferson, B., 2006. Impact of fractional character on the coagulation of NOM. Colloids and Surfaces A: Physicochemical and Engineering Aspects 286 (1–3), 104–111.

Spencer, R.G.M., Pellerin, B.A., Bergamaschi, B.A., Downing, B.D., Kraus, T.E.C., Smart, D.R., Dahlgren, R.A., Hernes, P.J., 2007. Diurnal variability in riverine dissolved organic matter composition determined by in situ optical measurement in the San Joaquin River (California, USA). Hydrological Processes 21 (23), 3181–3189.

Storey, M.V., Deere, D., Davison, A., Tam, T., Lovell, A.J., 2007. Risk management and cross-connection detection of a dual reticulation system. In: 3rd Australian Water Association Water Reuse and Recycling Conference (REUSE07). UNSW Publishing and Printing Services, Sydney, Australia.

Sydney Water, 2005. Media Release – Recycled Water Cross-connection at Newington. http://www.sydneywater.com.au/WhoWeAre/MediaCentre/MediaView.cfm?ID=295.

Sydney Water, 2009. Rouse Hill Recycled Water Scheme. http://www.sydneywater.com.au/SavingWater/RecyclingandReuse/RecyclingAndReuseInAction/RouseHill.cfm.

The Australian, 2008. Recycled Sewage as a Last Resort. http://www.theaustralian.news.com.au/story/0,24897,24626801-601,00.html.

Toifl, M., O'Halloran, R.O., 2008. Detecting cross connections in dual reticulation water systems. In: 2nd Australian Young Water Professionals Conference. University of Queensland, Brisbane, Australia.

Urbansky, E.T., 2001. Total organic carbon analyzers as tools for measuring carbonaceous matter in natural waters. Journal of Environmental Monitoring 3 (1), 102–112.

Webster, J.G., 1999. The Measurement Instrumentation and Sensors Handbook. CRC Press.

Willis, R.M., Stewart, R.A., Emmonds, S.C., 2009. Pimpama–Coomera dual reticulation end use study: baseline situational context and post-commission end use prediction. 7th IWA World Congress on Water Reclamation and Reuse (REUSE09), Brisbane, Australia.