

RAPID PORTABLE CROSS-CONNECTION DETECTION BY SENSITIVE FLUORESCENCE SPECTROSCOPY

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ABSTRACT

The implementation of dual reticulation systems for returning recycled water to the home for non-potable use is now common in new Australian housing developments. Managing the associated public health risk requires consideration of the potential for cross-connections between recycled and potable water pipes. While current protocols for detection exist, they are time consuming and cross-connections have occurred despite their implementation. Cross-connections may occur anywhere from a network to single property scale and hence a highly sensitive, rapid and portable device is required for the detection of contaminated potable water. Fluorescence intensities at $\lambda_{\text{ex/em}}=300/350$ nm have been previously shown to distinguish recycled water from potable water grab samples with a high degree of sensitivity and reliability using lab-scale equipment. To this end, this paper investigates two potential portable fluorescence systems, describing and discussing the results of *in-situ* fluorescence analysis programs undertaken at an Australian dual distribution system from the perspective of cross-connection detection.

INTRODUCTION

Population increases and changing weather patterns have caused urban water management in Australia to increase its focus on the sustainability of water resources. As such, water recycling and reuse now play an essential role.

New housing developments are increasingly incorporating dual distribution or third pipe systems, in which wastewater is treated offsite and redistributed back to households as recycled water for non-potable uses such as irrigation and toilet flushing. Within dual distribution systems the potential for cross-connections between recycled and potable water exists (Storey *et al.* 2007). Cross-connection incidences may damage public confidence in dual reticulation schemes and even present a possible health risk to users, particularly if treatment failure or underperformance occurs. Incidences of cross-connection between potable and recycled water have been documented at Rouse Hill (de Rooy

and Engelbrecht 2003; Sydney Water 2004), Newington (Sydney Water 2005) and Pimpama-Coomera (ABC News 2009), and though adverse health effects are yet to be officially attributed to cross-connection incidences in Australia (Storey *et al.* 2010), the inherent risk remains. In order to minimise this risk a rapid, highly sensitive method of detection is therefore needed to ensure proper management of these networks.

Within the water quality sciences, fluorescence spectroscopy has been investigated in natural, waste and polluted waters (Hudson *et al.* 2007) and has been utilised to characterise polluted river waters (Baker *et al.* 2003), to detect tissue-mill effluent in rivers (Baker 2002), determine organic matter removal efficiency within water treatment systems (Bieroza *et al.* 2010) and as a surrogate for biochemical oxygen demand (BOD) measurements (Reynolds and Ahmad 1997; Hudson *et al.* 2008). The use of fluorescence spectroscopy has also been highlighted as having great potential as a monitoring tool in dual reticulation systems (Henderson *et al.* 2009) and has been supported by recent investigations into the fluorescence of static grab samples from within an Australian dual reticulation network (Hambly *et al.* 2010b). This study evaluated a number of water quality parameters for their ability to distinguish recycled water from potable water such as conductivity and dissolved organic carbon, and found fluorescence to have the greatest potential with a typical 10 times distinction. The ability for bench-scale fluorescence analysis to distinguish between recycled and potable water samples has been verified by further studies at a number of other dual reticulation systems across Australia which yielded similar results (Hambly *et al.* 2010a).

Partial cross-connections may potentially occur within properties, where only limited intrusion of recycled water into potable water supplies occurs. This mixture of recycled and potable water may also vary over time depending on relative water supply pressures and so a high level of sensitivity is paramount in detecting cross-connections with a high confidence level. Monte-Carlo analysis of grab sample fluorescence using strict criteria required a greater than 45% intrusion of recycled water in

potable water, whereas conductivity required a minimum of 70% intrusion to achieve the same confidence level (Hambly *et al.* 2010b). Static mixing of recycled and potable water samples show a linear fluorescence response, making it possible to identify very low levels of recycled water in potable water.

Hence, the current challenge is to investigate the potential for converting this highly sensitive analytical tool from a bench scale research tool to a portable, engineering tool that is capable of capturing real-time, in-situ data.

METHODS

Two *in-situ* trials were conducted between August and October 2010 at an Australian Water Recycling Plant, evaluating two portable fluorimeters: the SMF2 and the SMF4 (STS, UK) (Figure 1). SMF2 fluorescence data was recorded via a Datalogger D80 datalogger and downloaded using Delogger 5 software (v. 4.0.3.4), whilst SMF4 fluorescence data was recorded internally and downloaded using Terminal software (v. 1.9b).

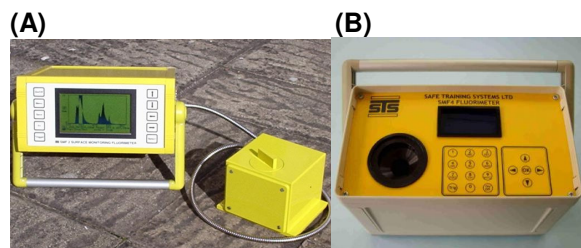


Figure 1. (A) SMF2 and (B) SMF4 portable fluorimeters.

SMF2 fluorimeters were employed between 20/08/2010 and 16/09/2010 to record a number of fluorescence emission regions between 190 and 450 nm. The fluorimeters utilise a xenon flash lamp with a broad excitation wavelength band between 280 and 300 nm, powered by a 9 V lead-acid battery. The optimal ratio for distinction between the potable and recycled water sources was then observed to be at emission wavelengths of 300 nm / 390 nm. SMF4 fluorimeters were employed between 20/09/2010 and 15/10/2010 and utilised a 280 (± 3) nm L.E.D. excitation source to record fluorescence at a single emission wavelength of 360 (± 3) nm. Both portable fluorimeters were connected to a 240 V mains power supply during the *in-situ* trials, however their internal power supplies typically allow for 8 hours of operating time before recharging is required.

Two identical fluorimeters and 3 mL flow through cuvettes (Lightpath Optical, UK) were employed within each trial – one connected to a recycled water flow-through system and the other

connected to a potable water flow-through system. Each system consisted of a fluorescence measurement, followed by conductivity and temperature measurements (HACH HQ40d) to account for any anomalies (Figure 2). Individual components of the flow-through system were connected by flexible 5 mm diameter black polypropylene tubing, from which no significant fluorescent leaching was measured. Flow rates were dependent on the pressure of the water distribution systems and were observed to vary between 20 mL.min⁻¹ and 150 mL.min⁻¹.

Portable fluorimeter baselines were established using a sealed cuvette of MilliQ water (Varian, Australia) and SMF2 and SMF4 fluorimeter data were obtained at 5 minute intervals.

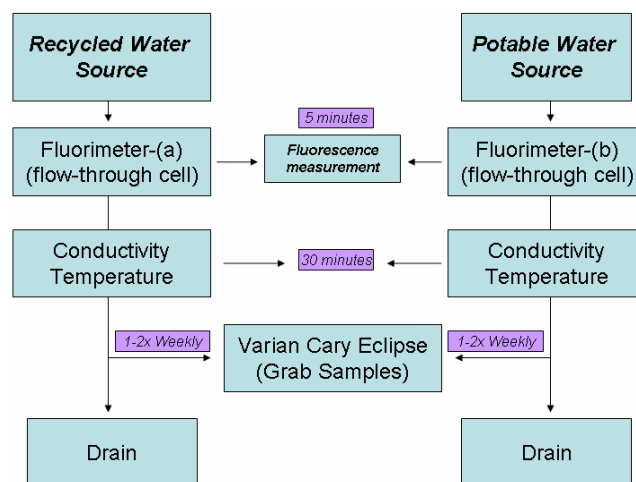


Figure 2. Flow diagram of experimental setup.

Grab samples of potable water and the final product of recycled water were also obtained on 13 occasions during the total study period, each from which an excitation-emission matrix (EEM) was obtained to compare recycled and potable water quality with grab samples from previous research at the same site. No sample preparation was undertaken prior to running EEM analysis. Raw EEM spectra were obtained in 4 mL quartz cuvettes (Starna, Australia) using a Cary Eclipse Fluorescence Spectrophotometer (Varian, Australia). EEMs were measured from 200 to 400 nm (excitation) and 280 to 500 nm at 5 nm intervals (emission) with excitation and emission slit widths of 5 nm, at a photomultiplier tube (PMT) voltage of 800 V and a scan speed of 9600 nm.min⁻¹. The Raman intensity of water in a sealed cell (Varian, Australia) was measured at $\lambda_{\text{ex}} = 348$ nm before each grab sample analysis to ensure instrument stability and was constant at 20 ± 1 arbitrary fluorescence units (afu) over the course of the study.

EEMs were blank subtracted using a sealed cuvette of MilliQ water (Varian, Australia), and locally generated emission and excitation correction factors were applied. All EEM data

correction was carried out using Matlab software (Mathworks).

RESULTS AND DISCUSSION

Grab samples: Cary Eclipse Spectrophotometer

The raw EEM spectra illustrated clear differences between the fluorescence character of recycled water and potable water samples (Figure 3). Recycled water samples exhibited high fluorescence in the humic-like (emissions centred around $\lambda_{ex/em} = 325/425$ nm and $\lambda_{ex/em} = 230/425$) and protein-like (centred around $\lambda_{ex/em} = 300/350$ nm and $\lambda_{ex/em} = 230/350$ nm) regions. Potable water was typically observed to have much lower fluorescence intensities across the entire EEM, particularly within the protein-like region. The grab samples taken within this study agree with previous research which found clear distinctions of typically 10 times between recycled and potable water samples when analysed at $\lambda_{ex/em} = 300/350$ nm on a benchtop fluorescence spectrophotometer (Hambly *et al.* 2010b).

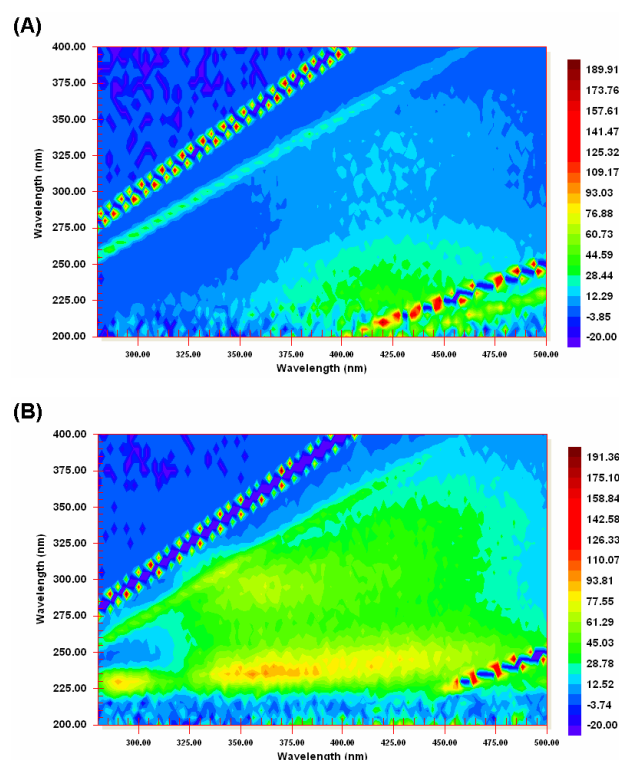


Figure 3. Typical raw EEMs of (A) potable; and (B) recycled water throughout the experimental period.

Fluorescence intensities at $\lambda_{ex/em} = 300/350$ nm were also similar to previous sample studies, varying between 100 and 175 afu for recycled water, while potable water varied between 13 and 22 afu (Table 1). Fluorescence intensities within the range of the SMF4 spectrometer ($\lambda_{ex/em} = 280/360$ nm) were typically lower than at $\lambda_{ex/em} = 300/350$ nm, ranging from 79 to 150 afu and potable water varied from 15 to 22 afu. The

fluorescence ratio of recycled water / potable water was also typically observed to be slightly lower at $\lambda_{ex/em} = 280/360$ nm (4.9 to 8.6) than at $\lambda_{ex/em} = 300/350$ nm (5.6 to 10.5) (Tables 1 and 2).

Table 1. Fluorescence intensities at $\lambda_{ex/em} = 300/350$ nm from grab samples over the experimental period.

| $\lambda_{ex/em} = 300/350$ nm | | | |
|--------------------------------|---------------|----------------|--------------------|
| Date | Potable (afu) | Recycled (afu) | Recycled / Potable |
| 20/08 | 18.8 | 105.8 | 5.6 |
| 23/08 | 19.2 | 123.5 | 6.4 |
| 26/08 | 17.3 | 157.3 | 9.1 |
| 30/08 | 18.8 | 138.7 | 7.4 |
| 03/09 | 13.7 | 144.5 | 10.5 |
| 06/09 | 18.4 | 172.1 | 9.4 |
| 10/09 | 16.2 | 124.1 | 7.7 |
| 13/09 | 20.5 | 151.3 | 7.4 |
| 20/09 | 22.2 | 153.9 | 6.9 |
| 23/09 | 16.0 | 100.0 | 6.25 |
| 30/09 | 16.3 | 160.1 | 9.8 |
| 05/10 | 18.7 | 167.0 | 8.9 |
| 08/10 | 14.9 | 140.8 | 9.5 |

Table 2. Fluorescence intensities at $\lambda_{ex/em} = 280/360$ nm from grab samples over the experimental period.

| $\lambda_{ex/em} = 280/360$ nm | | | |
|--------------------------------|---------------|----------------|--------------------|
| Date | Potable (afu) | Recycled (afu) | Recycled / Potable |
| 20/08 | 16.2 | 79.4 | 4.9 |
| 23/08 | 16.1 | 106.1 | 6.6 |
| 26/08 | 17.9 | 128.6 | 7.2 |
| 30/08 | 16.3 | 106.1 | 6.5 |
| 03/09 | 16.4 | 120.5 | 7.3 |
| 06/09 | 21.4 | 132.7 | 6.2 |
| 10/09 | 15.1 | 108.6 | 7.2 |
| 13/09 | 17.5 | 150.3 | 8.6 |
| 20/09 | 14.9 | 125.4 | 8.4 |
| 23/09 | 20.0 | 77.9 | 3.9 |
| 30/09 | 22.2 | 125.7 | 5.7 |
| 05/10 | 22.4 | 124.3 | 5.5 |
| 08/10 | 22.0 | 111.8 | 5.1 |

Data obtained from the grab samples are in agreement with earlier work (Hambly *et al.* 2010b), indicating that a significant distinction between recycled and potable water should still be possible by fluorescence analysis.

In-situ trial 1: SMF2 Fluorimeter

Conductivity was observed to vary between 236 and 251 $\mu\text{S}\cdot\text{cm}^{-1}$ for potable water and between 226 and 1049 $\mu\text{S}\cdot\text{cm}^{-1}$ for recycled water. Although the conductivity range of recycled water was quite different from earlier grab sample analysis (where conductivity was found to typically vary between 867 and 1045

$\mu\text{S}\cdot\text{cm}^{-1}$ for recycled water) it was typically between 900 and 1050 $\mu\text{S}\cdot\text{cm}^{-1}$, but decreased markedly on a number of occasions (Figure 4).

Potable water was observed to have a temperature range between 17 and 20 degrees Celsius, whereas recycled water was observed to vary between 10 and 24 degrees Celsius. Both water sources displayed diurnal variation in accordance with local environmental temperature and is most likely indicative of plumbing network differences between the two water sources. For both conductivity and temperature, the recycled water source was much more variable than the potable water source (Figure 4).

In contrast to conductivity and temperature data, fluorescence was always able to discern between the recycled and potable water sources. The calculated fluorescence ratio of 300/390 nm typically gave a 2 times distinction between recycled and potable water (Figure 5). Recurring power failures to the SMF2 fluorimeter monitoring recycled water began occurring approximately 12 days into the study and were unable to be completely resolved before the study came to an end (Figure 5).

Though fluorescence is temperature dependent and has been identified as an important matrix effect to consider in fluorescence water quality monitoring (Hudson *et al.* 2007; Spencer *et al.* 2007; Henderson *et al.* 2009), the data shows the effect on sensitivity is likely to be minimal when daily variation is taken into account.

***In-situ* trial 2: SMF4 Fluorimeter**

The conductivity of recycled water displayed much less variability than during trials with the SMF2 fluorimeter. It was typically observed between 980 and 1050 $\mu\text{S}\cdot\text{cm}^{-1}$ though just as during the SMF2 trials it decreased noticeably on a number of occasions. Potable water displayed good stability and ranged from 230 to 260 $\mu\text{S}\cdot\text{cm}^{-1}$ (Figure 6).

Diurnal temperature variation was again present in recycled water and to a much lesser extent potable water. Similar temperature ranges were observed for recycled water (9 to 24 degrees Celsius) and potable water (18 to 21 degrees Celsius) as to during the SMF2 trials.

Fluorescence data from the SMF4 fluorimeter was much more convergent to the promising results previously obtained from bench-scale fluorescence analysis. Recycled water ranged from 1500 to 2300 afu, whereas potable water ranged from 390 to 600 afu, which gave a typical 4 to 5 times distinction between recycled and potable water (Figure 7).

Fluorescence data within this study further accentuate the promise of fluorescence spectroscopy for detection cross-connections between recycled and potable water systems. As optical technology continues to advance, the future could see cheap, reliable, fast, portable and sensitive fluorescence cross-connection detection systems become available.

CONCLUSIONS

Two portable fluorimeters have been assessed for their ability to discern between recycled and potable water at an Australian Water Recycling Plant. The results of this study highlight the advancement in portable fluorescence technology for water quality analysis, particularly within the context of cross-connection detection.

Previous studies from weekly grab samples have calculated fluorescence to detect down to 45% intrusion of recycled water into potable water. This could be greatly improved by increasing the dataset and hence acquiring a more reliable baseline for recycled and potable water fluorescence. *In-situ* monitoring of data such as within this study is an example as to how this can be made possible.

Fluorescence intensities at Peak T_1 ($\lambda_{\text{ex/em}}=300/350$ nm) were previously shown to be able to distinguish recycled water samples from potable water samples with a high degree of sensitivity and reliability. Monitoring the fluorescence at peak T_1 was found to be the most appropriate parameter for this distinction, where the intensities were determined to be typically 10 times that of potable water. This study has shown that by monitoring at a similar excitation and emission wavelengths with a portable fluorimeter ($\lambda_{\text{ex/em}}=280/360$), recycled water is typically able to be distinguished from potable water by a factor of 4 to 5. Accordingly, fluorescence spectroscopy is a promising technique for highly sensitive detection of cross-connections between recycled water and potable water distribution systems. As portable fluorescence technology continues to improve, the instrumentation is expected to evolve to provide highly sensitive portable capabilities.

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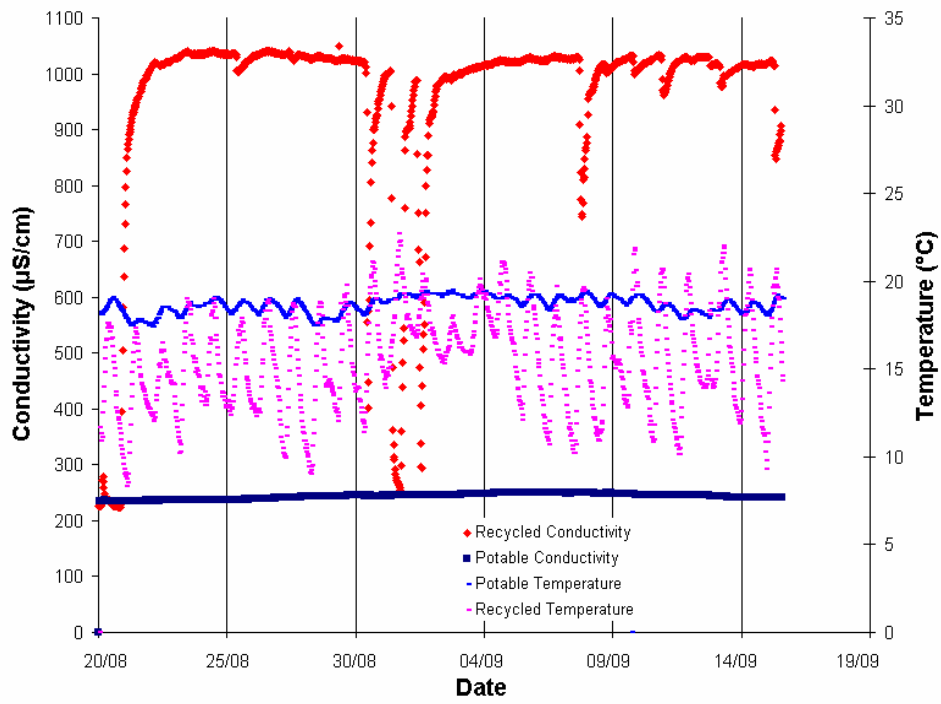


Figure 4. Conductivity and temperature of recycled and potable water during in-situ trial 1.

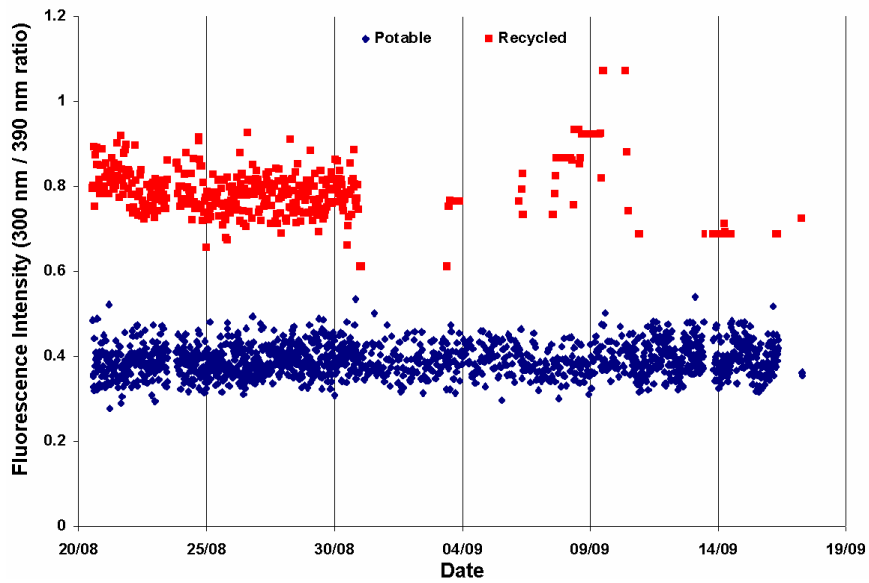


Figure 5. SMF2 fluorescence ratio (emission 300/390 nm) of recycled and potable water during in-situ trial 1.

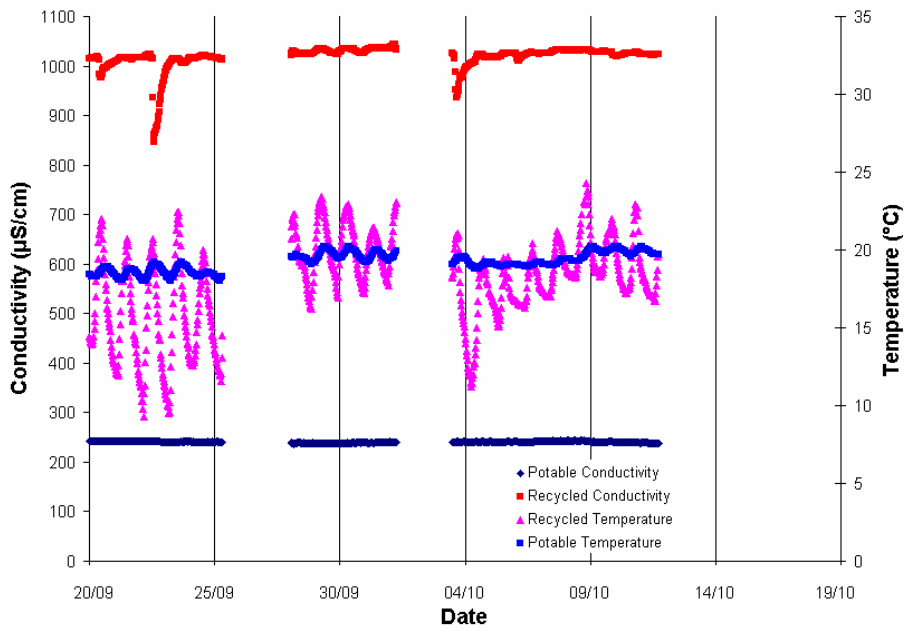


Figure 6. Temperature and conductivity of recycled and potable water during in-situ trial 2.

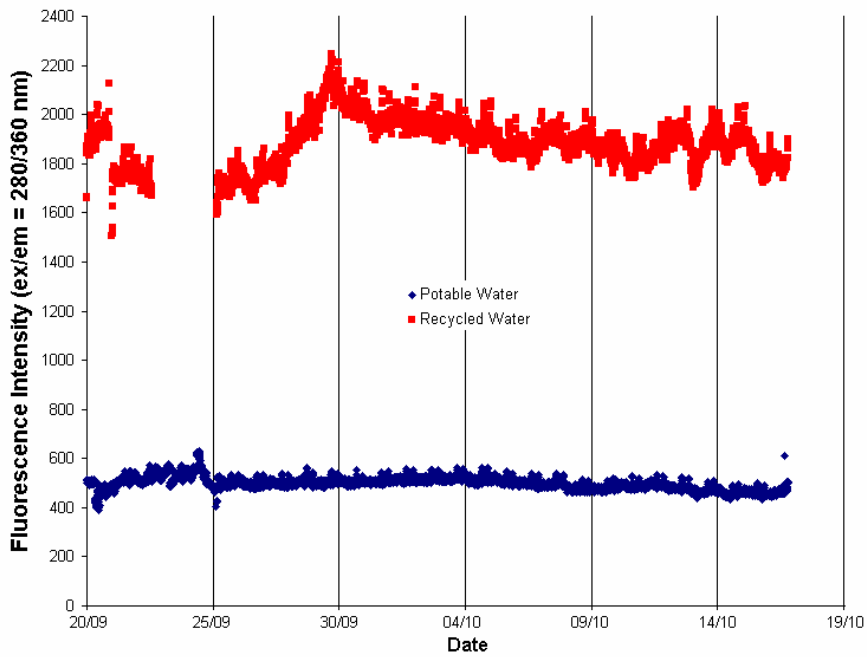


Figure 7. SMF4 fluorescence (in afu) at $\lambda_{ex/em} = 280/360$ nm for recycled and potable water during in-situ trial 2.