Characterising water treatment works performance using fluorescence spectroscopy

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Summary

Dissolved organic matter arising in river water has distinctive fluorescence properties, and recent research has utilised these properties in combination with new technology to quantify dissolved organic substances in both ground waters and geological materials, and to determine both quality and quantity in rivers and lakes.

These findings have great significance for integrated river basin management and improving water quality in line with the demands of the Water Framework Directive. This project extends the use of fluorescence techniques from raw water quality monitoring to the monitoring of water treatment works intakes and the assessment of water treatment works performance by assessing the removal of dissolved organic matter (DOM) through the unit process stages of various water treatment works treating different raw waters.

The project involves undertaking a combination of desktop, field and laboratory studies to investigate the potential for using fluorescence spectroscopy as a site based method of determining the characteristics (e.g. concentration and source of organic matter) of raw and partially treated water.

In particular the work encompasses the development of an understanding of the ability of fluorescence spectroscopy to characterise intake water quality at water treatment works and so identify the presence of pollutants, the development of an understanding of the ability of fluorescence spectroscopy to characterise unit process performance at water treatment works, and the development of techniques for the use of fluorescence as a tool to determine the formation and prevalence of disinfection byproducts in water treatment works. The project is partially funded by Severn Trent Water.

Methodology

Fluorescence spectroscopy measurements and total organic carbon (TOC) analyses were carried out on samples of raw and clarified water from 16 surface WTWs, collected monthly between August 2006 and February 2008. The treatment works are located in the Midlands region, central UK and are owned and operated by Severn Trent Water Ltd. They treat a range of raw waters from upland sources with natural organic matter of high TOC concentrations to lowland sources reflecting anthropogenically-impacted microbial organic matter character.

In summary, fluorescence excitation-emission matrices (EEMs) were collected using a Cary Eclipse Fluorescence Spectrophotometer (Varian, Surrey, UK) equipped with a Peltier temperature controller. For each unfiltered water sample, the fluorescence was measured in duplicate by scanning the excitation wavelengths from 200 to 400 nm in 5 nm steps, and detecting the emission intensity in 2 nm steps between 280 and 500 nm. Excitation and emission slit widths were 5 nm. Each measurement was carried out in standard quartz 4 cm3 capacity cuvette (1.0 cm path length) and was completed within 2 minutes.

To maintain the consistency of measurements and standardise the fluorescence data, all fluorescence intensities were corrected to Raman peak intensity of 20 units measured for deionised water at 348 nm excitation and 396 nm emission wavelengths.

In fluorescence EEM technique fluorescence intensity of water sample is scanned over the range of excitation and emission wavelengths to produce three-dimensional matrix (Figure 1). Fluorescent OM exhibits discrete intensity peaks located at different excitation-emission wavelengths.

Therefore, the presence and relative concentration of particular fluorophores (fluorescent organic matter fractions) can be derived from EEM. For all water samples in the study, the presence of three main fluorescence peak regions was observed: fulvic-like fluorescence (peak C, fluorescence excited between 300 and 340 nm, and emitted between 400 and 460 nm), humic-like fluorescence (peak A, fluorescence excited between 220 and 250 nm, and emitted between 400 and 460 nm), and tryptophan-like fluorescence (peak T, fluorescence excited between 270 and 280 nm and emitted between 330 and 370 nm)

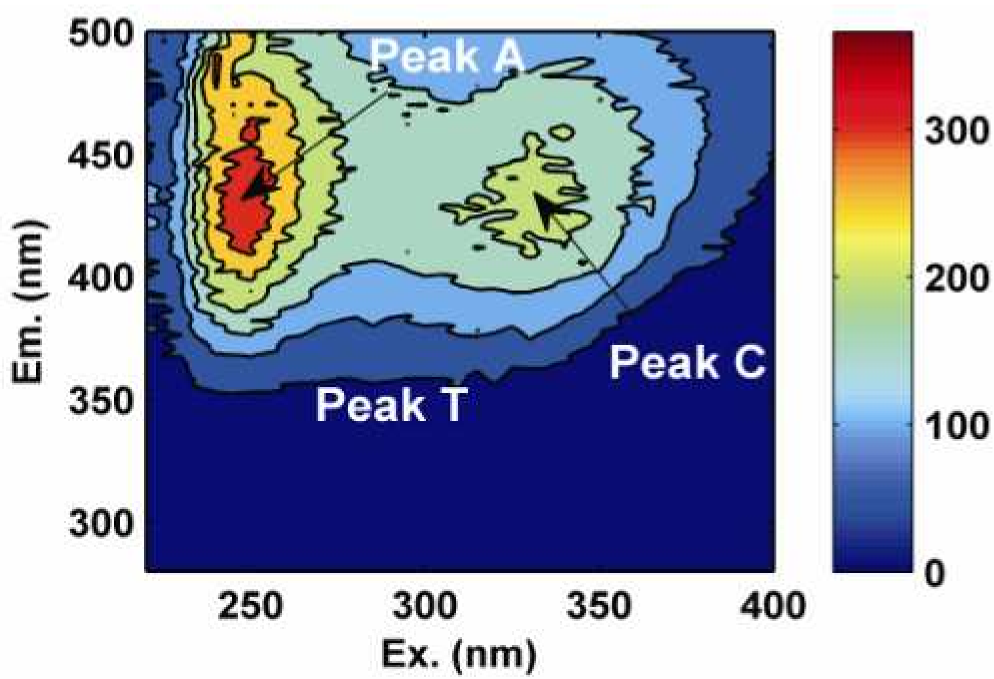

Figure 1. Fluorescence EEM of raw water.
Fluorescence regions: fulvic-like fluorescence (Peak C),
humic-like fluorescence (Peak A), tryptophan-like fluorescence (Peak T).

Results

Previously, a TOC removal prediction model was calculated for whole fluorescence dataset (all 16 WTWs, August 2006 – February 2008) containing fluorescence properties of raw water. A stepwise regression approach was employed to determine the statistically significant subset of fluorescence variables and their order of importance in predicting TOC removal efficiency (based on actual TOC concentrations of raw and clarified water).

It was found that the most important fluorescence-derived predictors of TOC removal are tryptophan-like fluorescence intensity, peak C emission wavelength and intensity, with the variance explained by the raw water model of R2 = 55%.

A similar approach was adopted to examine the relationship between TOC removal and fluorescence properties of both raw and clarified water. Tryptophan-like fluorescence intensity of clarified water, peak C emission wavelength of raw water (surrogate for the degree of hydrophobicity that indicates the amount of easier to remove OM fraction), and peak C intensities of raw and clarified water (surrogate for TOC concentration) were selected in the model.

The most important fluorescence predictor, tryptophan-like fluorescence intensity of clarified water can be attributed to the amount of microbially-derived, hydrophilic and low-molecular weight fraction of organic matter recalcitrant to removal by coagulation.

This residual organic matter content determines the effectiveness of organic matter removal, and following water treatment processes (disinfectant demand, GAC performance, biofilm growth in distribution system). A higher correlation coefficient of combined raw and clarified water model ($R2 = 0.91$) suggested better organic matter removal prediction when compared with the TOC removal based solely on raw water fluorescence properties.

The effectiveness of both models was tested with the independent fluorescence data for selected WTWs. In all cases, the raw and clarified water model significantly outperformed the raw water model.

The results obtained to date indicate that fluorescence spectroscopy can be effectively utilized at WTWs for characterisation of both OM properties and its removal efficiency. Fluorescence technique enables quantification of the different OM fractions, including those of key importance to the TOC removal efficiency: easier to remove aromatic, high-molecular weight compounds of humic acids (denoted by a high peak C emission wavelength), and more difficult to remove low-molecular weight, hydrophilic acids emitting light at lower wavelengths (tryptophan-like region, blue-shifted peak C region).

The regression model incorporating fluorescence properties of raw and clarified water provided a good prediction of TOC removal for baseline conditions (all sites) and for the optimised coagulation at Campion Hills. Thus, fluorescence analysis provides an efficient framework for comprehensive characterisation of organic matter removal.