# Simultaneous absorbance and fluorescence excitation-emission maps reveal effects of ozone and microfiltration in wastewater recycling

## Adam .M. Gilmore<sup>1</sup>, G.L. Oelker<sup>2</sup>, <u>I. A.S.Carvalho<sup>3\*</sup></u>

<sup>1</sup>HORIBA Instruments Inc., 3880 Park Ave. Edison, NJ 08820, adam.gilmore @horiba.com
<sup>2</sup> United Water, 1935 S Hughes Way. El Segundo, CA 90245, gregg.oelker@unitedwater.com
<sup>3</sup>HORIBA Instr. do Brasil. Av. Presítero Plínio Alvez de Souza,645, Jundiaí SP 13212-181, <u>igor.carvalho@horiba.com</u>

Keywords: Ozone Pre-destruction; Microfiltration; Fluorescence Excitation-Emission Mapping

#### Introduction

The Edward C Little Water Recycling Facility treats wastewater from a nearby plant which exhibits wide concentration variability of dissolved organic components. Historically the plant encountered irreversible organic fouling of its microfiltration (MF) membranes and therefore installed an ozone process upstream of the MF units. The new ozone process however exhibited control issues and did not effectively abate the MF-fouling problem. An intensive study was undertaken to assess the ozone using instrument capable control an of simultaneously measuring the complete UV-NIR absorbance spectra and fluorescence excitationemission matrix (EEM). The EEM method provided qualitative and quantitative information on the organic component composition including the suspected organic MF foulants. The EEM data were evaluated using Parallel Factor Analysis (PARAFAC), indicating 4 main organic components which were independently compared to the various steps through the ozone and MF process. Concomitantly the complete UV-NIR spectral absorbance data were also evaluated. This paper explains how the absorbance and EEM data revealed both the main suspected foulant and source of the control issues associated with the ozone process.

# **Results & Discussion**

The main result centred on identification of 4 main organic fluorescent components which were present in varying concentrations in all samples of the study. Figure 1A shows the dominant deep UV excitationemission component (C1), a second UV component consistent with tryptophan -like fluorescence (C2) and two longer wavelength components consistent with fulvic and humic acid components, (C3) and (C4), respectively. The model was split-half validated with over 99% matching efficiency. Figure 1B shows that following ozone treatment over the period of 10 months revealed wide variation in all components, especially C1. To study the nature of the component variation and to help identify the key fouling suspect components an intensive 1 dav studv was

undertaken to sample the key raw water, locations in the 2 ozone basins and the MF influent, filtrate and backwash steps, all compared the online and Aqualog A254 data. Figure 1C shows a) high concentrations of all components in the raw water, b) ozone treatment decreased all components by around (25-40%) and c) MF further reduced C2-C4 by around (7%) with the largest removal of C1 (22%). The MF backwash was most enriched in C1 indicating it had the highest MF membrane affinity and thus suspected as a membrane foulant. Figure 1 D shows both the online (UV Filtered) and Aqualog A254 nm data did not correlate with C1-C4 component variation in the ozone treatments. There was incidentally a higher correlation between all the components with Aqualog absorbance around 230 nm (data not shown).



**Figure 1.** Panel (a) shows the excitation (bold) and emission loadings for the 4 PARAFAC components,(b) shows component score variation in ozone treated samples over 10 months,(c) shows mean component scores as a function of process for 1 day and D shows A254 and component scores at various ozone sites over 1 day.

## Conclusões

It was concluded the lack of sensitivity for the A254 online monitors correlated with poor control of the ozonation process correlating with continued MF fouling.

Obs: It is such an innovative work, so no reference concerning the technique was used up to date