Fluorescence Sensors for Early Detection of Nitrification in Drinking Water Distribution Systems – Interference Corrections

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AWWA Water Quality Technology Conference, November 12-16, 2017, Portland, OR

UNIVERSITY OF ARKANSAS
College of Engineering

MOTIVATION, APPROACH, AND OVERVIEW

Early detection of nitrification events in chloraminated drinking water distribution systems remains an ongoing challenge for many drinking water utilities, including Dallas Water Utilities (DWU) and the City of Houston (CoH). Each year, these utilities experience nitrification events that necessitate extensive flushing, resulting in the loss of billions of gallons of finished water. Biological techniques used to quantify the activity of nitrifying bacteria are impractical for real-time monitoring because they require significant laboratory efforts and/or lengthy incubation times. At present, DWU and CoH regularly rely on physicochemical parameters including total chlorine and monochloramine residual, and free ammonia, nitrite, and nitrate as indicators of nitrification, but these metrics lack specificity to nitrifying bacteria.

To improve detection of nitrification in chloraminated drinking water distribution systems, we seek to develop a real-time fluorescence-based sensor system to detect the early onset of nitrification events by measuring the fluorescence of soluble microbial products (SMPs) specific to nitrifying bacteria. Preliminary data indicates that fluorescence-based metrics have the sensitivity to detect these SMPs in the early stages of nitrification, but several remaining challenges will be explored in this poster. We will focus on results from a benchtop fluorometer and tryptophan sensor from ongoing batch and biofilm annular reactor experiments designed to (1) identify fluorescence wavelength pairs and data processing techniques suitable for measurement of SMPs from nitrification and (2) assess and correct potential interferences, such as those from monochloramine, pH, iron, nitrite, nitrate and humic substances.

This work will serve as the basis for developing fluorescence sensor packages for full-scale testing and validation in the DWU and CoH systems. Findings from this research could be leveraged to identify nitrification events in their early stages, facilitating proactive interventions and decreasing the severity and frequency of nitrification episodes and water loss due to flushing.

METHODS AND POTENTIAL INTERFERENCES

Fluorescence-interference testing consisted of three rounds designed to assess the impact of:

1. Monochloramine as a function of NOM concentration (Fig. 3). Ohio River NOM extracts were reconstituted at high pH, filtered, and kept in fridge before use. NOM samples were amended with 10 mM KCl and 10 mM $NaHCO_3$, titrated to pH 9, stabilized overnight before being dosed with freshly-made preformed monochloramine. The experimental matrix including NOM concentrations of 1 and 5 mg/L as C dosed with monochloramine at 4 and 8 mg/L as Cl_2, respectively.
2. NOM and pH on tryptophan fluorescence. The experimental matrix included reconstituted Ohio River NOM at 0.5, 2.5, and 5 mg/L as C, pH 7, 8, and 9, and spiked tryptophan concentrations of 0, 20, and 100 µg/L.
3. Nitrite, nitrate, and pH on the tryptophan sensor reading. Nitrate and nitrite ranged from 0 to 1 mg/L-N and pH was set at 7.0, 8.0, 8.5, and 9.0.

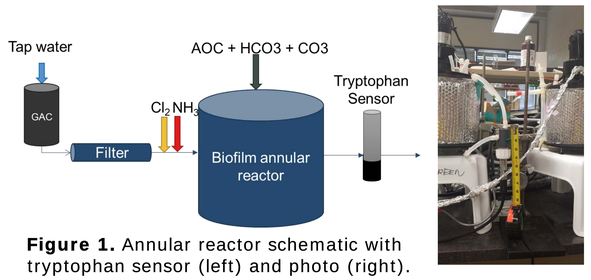

Figure 1. Annular reactor schematic with tryptophan sensor (left) and photo (right).

Two biofilm annular reactors were used to stimulate nitrification events and assess nitrification arrest, all while monitoring fluorescence signals and potential interferences. Tap water from Fayetteville, AR was pre-treated with GAC to reduce chlorite (ClO_2^-) to <0.01 mg/L-ClO_2^- before feeding it to the reactor. Organic cocktail and phosphate were added to the reactor to support biofilm growth. Reactors were operated at a 7-hour hydraulic retention time and spun at 50 rpm in a 28 ºC water jackets to simulate flow in a distribution system.

Identifying fluorescence wavelength pairs suitable for measurement of nitrification at different stages. The tryptophan peak – Ex/Em=285/350 nm – was detected during the early stages of nitrification (Fig. 2b) and nitrification arrest (Fig. 2d).

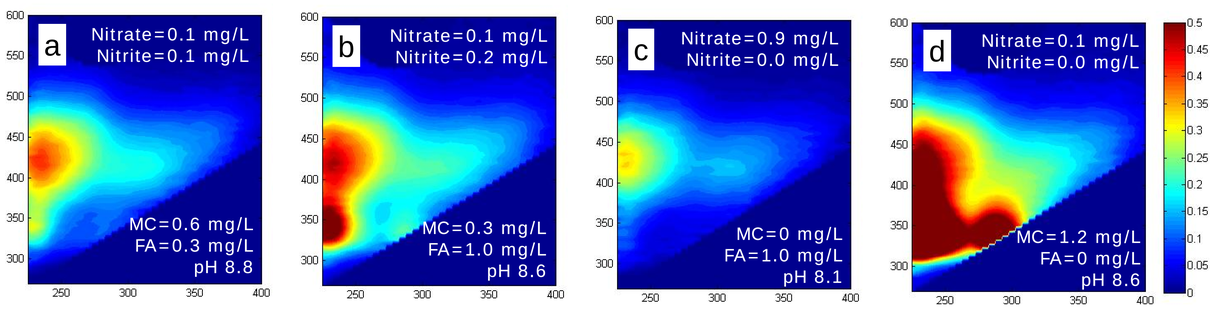

Figure 2. Fluorescence excitation-emission matrices (EEMs) of biofilm annular reactor effluents at (a) no nitrification, (b) early stages of nitrification, (c) complete nitrification, and (d) during nitrification arrest. MC = monochloramine residual; FA = free ammonia added.

The variable monochloramine, nitrite, nitrate, and pH through the nitrification process and its arrest makes interference testing necessary. It is anticipated that each of these parameters will impact the fluorescence intensity differently based on the excitation-emission wavelengths.

INTERFERENCE TESTING: RESULTS & CORRECTIONS

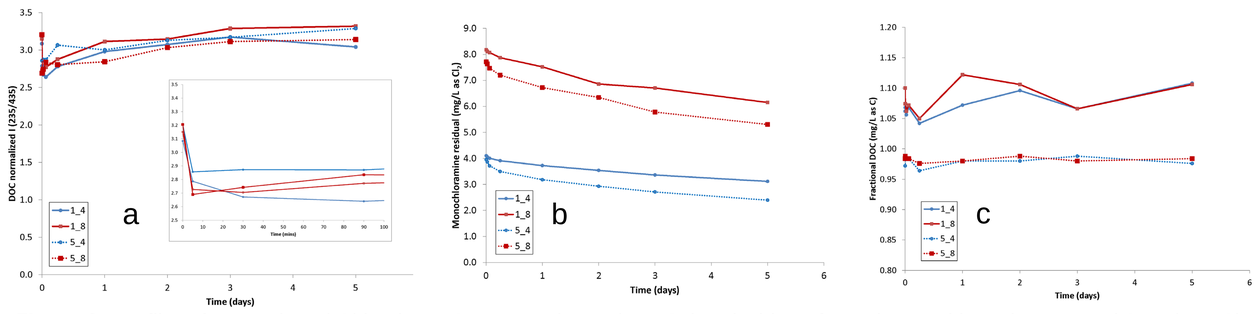

Figure 3. Profiles of reconstituted Ohio River NOM at 1 and 5 mg/L as C dosed with preformed monochloramine at 4 and 8 mg/L as Cl_2 at pH 9 for (a) Fluorescence Intensity Ex/Em at 235/425 nm, (b) monochloramine residuals, and (c) dissolved organic carbon. Profiles at 5 mg/L in Panels (a) and (c) were normalized by a value of 5 mg/L as C, which is the corresponding dilution factor.

- $I_{235/425}$ in Fig. 3a:
  - Decreased ~15% within first 5 mins of reaction with monochloramine
  - Increased ~15% through Day 5
- Comparison of Fig. 3a to 3b:
  - Increasing $I_{235/425}$ may be due to decreasing monochloramine
  - Could be interference or oxidation
- Fractional DOC (Fig. 3c) was stable over 5 days, indicating incomplete DOC oxidation by monochloramine

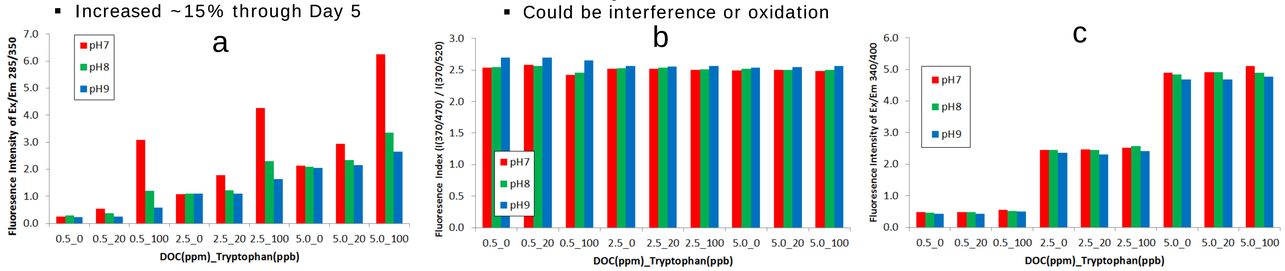

Figure 4. Fluorescence Intensity of reconstituted Ohio River NOM at 0.5, 2.5, and 5 mg/L as C spiked with 0, 20, and 100 µg/L of L-tryptophan at pH 7, 8, and 9 for (a) Ex/Em 285/350, (b) Fluorescence Index, and (c) Ex/Em 340/400

- Tryptophan fluorescence (Fig. 4a) was lower at higher pH for all DOC levels tested
- Fluorescence Index (Fig. 4b) indicated no interferences at an excitation of 370 nm
- Fluorescence at Ex/Em 340/400 (Fig. 4C) indicated no interferences at an excitation of 340 nm

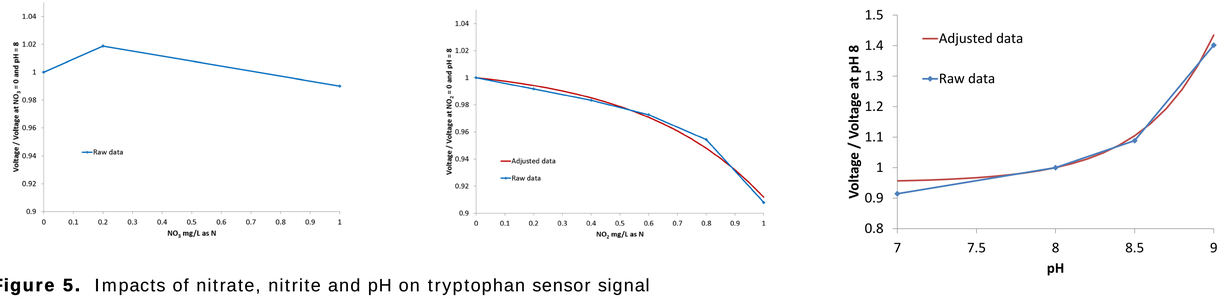

Figure 5. Impacts of nitrate, nitrite and pH on tryptophan sensor signal

- Monochloramine could consume fluorescence active groups; partially oxidized organic matter may have higher fluorescence signal
- Alternatively, monochloramine could be suppressing the fluorescence signals at low excitation (235 nm)
- Fluorescence interferences from NOM and pH were observed low excitation wavelengths (<285 nm) only
- Inference corrections for the tryptophan sensor should be considered (Fig 5) for nitrite and pH (not nitrate); monochloramine corrections likely not feasible

REFERENCES AND FUNDING ACKNOWLEDGMENTS

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