

Understanding and modelling fluorescent dissolved organic matter probe readings for improved coagulation performance in water treatment plants

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Abstract: Removing dissolved organic matter (DOM) from the source water is critical for the drinking water treatment process; the low molecular weight hydrophilic fraction of DOM is generally recalcitrant to removal by coagulation, and the DOM bypassing the coagulation/filtration stages of treatment will likely react with the disinfecting agent in the end of the treatment process, leading to the formation of potentially carcinogenic disinfection by products (DBPs) such as trihalomethanes (THMs). Each specific fraction of DOM reacts with a particular disinfecting agent to form different DBPs, some with higher toxicity and carcinogenicity than others and varying on health guidelines values. Understanding the DBPs formation pathways, however, is a difficult task since humic substances present in the source water are likely to be highly degraded compounds that differ from each other, forming a mixture of diverse molecules which is extremely challenging to individually characterize. Hence there is a need for monitoring certain fractions of DOM, tracking down DOM character and its concentration in source waters.

DOM characterization techniques can be divided into three groups. The first group investigates the abundance and nature of structural units, providing detailed structural information. The second looks into the chemical behaviour of DOM, its molecular weight, molecular size, distribution, hydrophobicity-hydrophilicity, focusing on its polymeric nature and providing good molecular separation. The third measures the fluorescence signal of DOM in situ, without directly scrutinizing chemical identities of functional groups or molecules. However, the methods of the first two groups are not simple and time-intensive, hence not suitable for online monitoring of DOM characteristics; in contrast, the currently available fluorescence probes are a simple, sensitive, rapid, non-invasive way of providing an in-situ estimation of the fluorescent DOM (fDOM). Despite the potential beneficial applications of this relatively new technology, field fDOM measurements are subject to interferences caused by changes in temperature, turbidity, pH, salinity and inner filter effect (IFE). This often makes probe readings untrustworthy, and as a result they are rarely used by the water treatment plant operators. Thus accurate, reliable compensation models should be designed and applied.

In this study, we firstly conducted a number of field sampling and laboratory experiments to investigate the effects of temperature, turbidity and IFE on fDOM sensor measurements. We collected the required data and developed compensation models, in order to understand what the actual amount of fDOM is, compared to what the probe reads. The methodology adopted for each of these investigations was perfected from previous studies, albeit using unusual equipment deployed in particular water bodies (i.e. instrument-specific temperature compensation, site-specific and instrument-specific turbidity compensation, instrument-specific secondary IFE compensation). Threshold autoregressive models were explored as an attempt to best describe nonlinearities of light scattering and light absorption due to suspended particles on fDOM readings. In the second stage of this project, we will conduct further experiments to determine the character and molecular weight of the DOM contained in our samples, collected in a South-East Queensland reservoir; finally, data-driven models will be developed to link compensated fDOM readings with DOM character and other commonly measured quantities (e.g. SUVA and UV₂₅₄). The benefit of a better understanding and modelling of the actual fraction of DOM measured by the fDOM sensor is the possibility to build a more precise, real-time tool for the estimation of the ideal pH during coagulation, amount and type of coagulants to be dosed, in order to maximize DOM removal and avoid the formation of DBPs in the distribution systems.

Keywords: *Dissolved organic matter, drinking water treatment, fluorescence, remote sensing*

1. INTRODUCTION

A set of physical and chemical processes are undertaken in drinking water treatment plants (DWTPs) aiming to maximize pathogenic and pollutant removal. However, in certain circumstances, the combination of raw water characteristics, low treatment efficiency and type of chemicals used in final disinfection ends up producing drinking water which potentially contains carcinogenic substances known as DBPs (Tubić *et al.*, 2013). In particular, DBPs may also be formed in the water distribution systems in post-treatment reactions, such as of chlorine with DOM residual (Aslam *et al.*, 2013). Interestingly, each DBP is potentially formed by the reaction of specific fractions of the DOM present in the water with the disinfectant (Tubić *et al.*, 2013). For example, it is known that low molecular weight DOM (<1 Ka) is the main precursor for THM formation when chlorine is used as disinfecting agent (Yang *et al.*, 2016). Therefore, the monitoring and removal of certain fractions of DOM is of paramount importance in order to avoid formation of DBPs in drinking water.

In drinking water reservoirs, the source of DOM can be aquatic or terrestrial, with its composition varying seasonally but predominantly consisting of dissolved organic carbon (DOC) and dissolved organic nitrogen (DON). In laboratorial analysis, DOC is quantified usually with high temperature combustion followed by the detection of carbonic dioxide, whereas DON is measured by deducting dissolved inorganic nitrogen from total dissolved nitrogen. Investigations on the abundance and nature of structural units in the DOM molecules have been conducted over the last few decades through several distinct advanced instrumental analytical techniques, namely infrared spectroscopy, nuclear magnetic resonance spectroscopy, microscale sealed vessel pyrolysis gas chromatography mass spectrometry, Fourier-transform ion cyclotron mass spectrometry. Other techniques look into the chemical behaviour of DOM, its molecular weight, size, distribution, hydrophobicity-hydrophilicity, focusing on its polymeric nature, e.g. tangential flow ultrafiltration or reverse osmosis followed by high performance size exclusion chromatography. Importantly, analyses like fluorescence spectroscopy with excitation emission matrix and parallel factor analysis, ultraviolet-visible absorbance, i.e. UV absorbance at 254nm (UV₂₅₄), and specific UV absorbance (SUVA) represent a range of techniques measuring a fluorescence signal of DOM, often in situ, but not directly scrutinizing chemical identities of functional groups or molecules (Minor *et al.*, 2014; Sandron *et al.*, 2015).

Most of the analytical methods described above for extraction and characterization of DOM are non-trivial and time-consuming, thus limiting their ability to be deployed in water reservoirs for real-time water quality monitoring and management (Brown *et al.*, 2016). Alternatively, a number of currently available fluorescence probes can provide an in situ estimation of fDOM through a non-invasive, rapid measuring approach (Zamyadi *et al.*, 2016). Specifically, they emit a beam of UV light at a certain wavelength to excite determined organic molecules in a given sample matrix, and detect the UV signal at lower energy emitted by the excited molecules. A fDOM probe that has an excitation/emission pair of $365 \pm 5\text{nm}/480 \pm 40\text{nm}$, for example, is exciting molecules on the peak-C-like region of the spectra, which substances are interpreted to be related primarily to terrestrial vascular plant sources having highly aromatic, conjugated, and mainly high molecular mass components (Jiang *et al.*, 2017). However, field fDOM measurements are subject to interferences caused by changes in temperature, turbidity, pH, salinity, metal ions and IFE, and for these they should be adjusted or corrected (Carstea, 2012). Despite pH can affect fluorescence intensity to some extent, the usual pH range in natural waters, between pH 5-9, seems to have minor impact on fluorescence analysis, so it is not of major concern (Spencer *et al.*, 2007). Similarly, metal ions can cause fluorescence quenching or enhancement in certain regions of the spectra, however, since it is outweighed by more important environmental factors controlling DOM fluorescence, quenching effects of metals do not cause great concern (Hudson *et al.*, 2007). Through charge transfer and conformational change, salinity alters intramolecular reaction and interferes with fDOM readings. It is suggested that high salinity leads to changes in chromophoric DOM, and the likely trend is, at 350nm excitation wavelength, there is a shift of the position of the emission maxima to shorter wavelengths (Del Castillo *et al.*, 1999).

This study is focused on modelling environmental interferences on a fDOM probe for its calibration, and subsequently linking the calibrated readings to the prevalence of specific DOM fractions. A better understanding of the fraction of DOM measured by the fDOM probe would lead to the development of more accurate coagulant dosing models, as well as THM formation potential prediction models, predominately based on real-time fDOM data, to allow for a more proactive water treatment management.

2. MATERIALS AND PROCEDURES

The study location was Lake Tingalpa and the connected Capalaba DWTP, in South-East Queensland (Australia). A sampling program was designed and implemented in order to obtain data regarding fDOM probe readings and its correlations with temperature, turbidity, inner filter effect, UV₂₅₄, DOC and SUVA. From 07 March 2017 to 08 June 2017, raw water samples were collected on a weekly basis from the Tingalpa

reservoir, at the sampling point number CAP-SP120, located at Capalaba DWTP. The DWTP and the dam are operated by Seqwater, which is the industry partner of this study. The sampling followed Seqwater’s protocols, ensuring safety measures were adopted and sample contamination avoided. As several laboratory analyses were conducted, there was a need for high-volume samples, therefore 10 litres samples were collected each time. Sampling following large storm events (e.g. ex tropical cyclone Debbie) was useful to acquire representative data-set of the range of fDOM, turbidity and colour found in this particular catchment.

The fDOM was measured using an EXO fDOM Smart Sensor (YSI, USA) and reported as quinine sulfate units (QSU) and relative fluorescence units (RFU). This fDOM probe has an excitation/emission pair of $365 \pm 5\text{nm}/480 \pm 40\text{nm}$. A two-point calibration was performed, where the first standard was ultrapure water (0QSU or 0RFU) and the second standard a 300 $\mu\text{g/L}$ quinine sulfate solution (Sigma-Aldrich, USA), equivalent to 300QSU or 100RFU. Turbidity measurements were conducted on an EXO Turbidity Smart Sensor (YSI, USA) with output expressed in units of formazin nephelometric units (FNU). This turbidity sensor employs a near-infrared light source at $860 \pm 15\text{nm}$ and detects scattering at 90 degrees of the incident light beam, which is considered to be the least sensitive to variations in particle size. Calibration of the turbidity probe was undertaken using two points, where ultrapure water was the 0 FNU standard and 6073G Turbidity Standard (YSI, USA) the 124 FNU standard. Temperature was measured in $^{\circ}\text{C}$ units by the EXO Conductivity & Temperature Smart Sensor (YSI, USA), which uses a highly stable and aged thermistor with extremely low-drift characteristics. According to EXO User Manual, no calibration of the temperature sensor is required. The fDOM and turbidity sensors’ faces were wiped prior to each measurement using EXO2 Central Wiper (YSI, USA) to remove any bubbles and avoid sensor fouling. All the probes were connected with the EXO2 Multiparameter Sonde (YSI, USA), and thus all the readings were taken at the same instant. All the fDOM, turbidity and temperature readings were taken from samples inside the EXO2 Calibration and Storage Cup (YSI, USA), being this 500mL container pre-rinsed prior to each analysis.

UV absorbance at 254nm, 365nm and 480nm were measured following filtration, using a 1cm (for UV₂₅₄ and UV₃₆₅) and 4cm quartz cell (for UV₄₈₀), on an UV-1800 UV-Visible Spectrophotometer (Shimadzu Corporation, Japan), with results given in cm^{-1} . All cuvettes used for UV absorbance analysis were pre-rinsed with a small volume of filtered sample prior to analysis. DOC was determined following filtration using a high-temperature catalytic oxidation TOC-L CPH Total Organic Carbon Analyser (Shimadzu Corporation, Japan) with non-dispersive infrared gas detector, where results were expressed in mg/L, and carrying 20% of uncertainty. 40mL DOC vials were preserved with sulfuric acid for a few days before analysis. Ultrapure water was produced by a Milli-Q Integral Water Purification System (Merck Millipore, USA) unit utilizing Quantum cartridges to remove the remaining ionic and organic contaminants below trace levels. Filtration was undertaken through 33mm diameter sterile Millex-HP Syringe Filter units (Merck Millipore, USA) of 0.45 μm pore size hydrophilic polyethersulfone membrane. In order to saturate any site that may adsorb DOC, filters were pre-rinsed with 25mL of sample that was thrown away prior to analysis (Karanfil *et al.*, 2003).

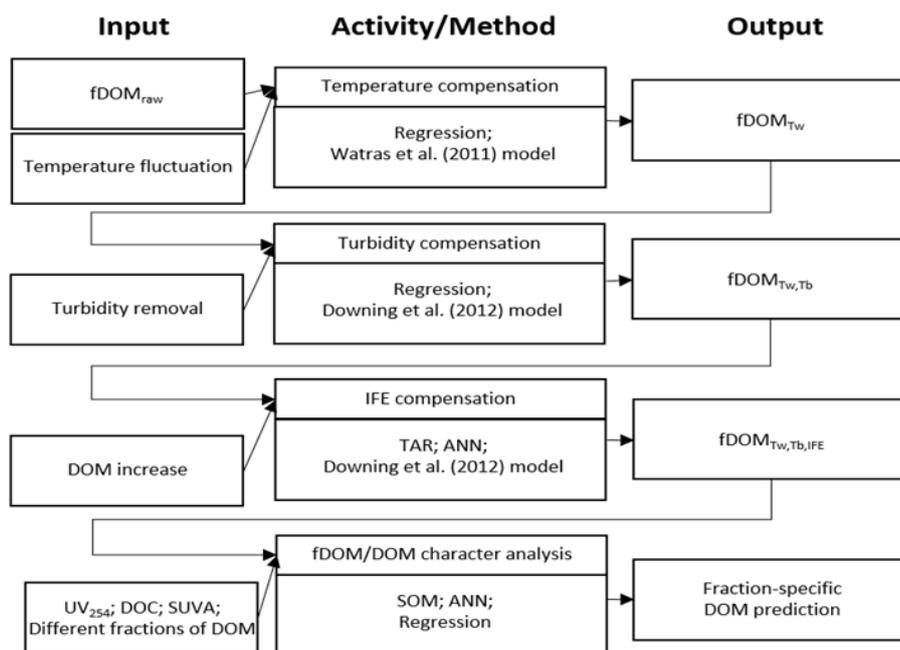


Figure 1. Data analysis and sequential modelling methodology

All the data collected from the multiparametre sonde was downloaded through the KOR-EXO software and exported onto MS Excel prior to data analysis. Data from UV₂₅₄, UV₃₆₅, UV₄₈₀ and DOC tests was also inserted onto MS Excel. The collected dataset was pre-processed and checked for outliers and missing data. Data analysis consisted essentially of general statistics, linearity tests, and scatter plots. Based on data analysis, linear/nonlinear prediction models were developed to separately account for each interference; however, both a sequential modelling approach (i.e. apply separately each model one after each other) and multivariate models (i.e. account for all interferences at once with one single model) have been explored and assessed. Sequential compensation of interferences on fDOM is in accordance with fundamental optical theory (Lakowicz, 2006) and seems to incur in a minor error, as for these experiments, parameters could be isolated or kept constant for investigation and modelling. Figure 1 outlines our modelling approach.

2.1. Evaluation and modelling of temperature effects

The sample was filtered into the storage cup to remove suspended particles and reach low levels of turbidity (~0FNU). The storage cup was placed in a bucket with hot water, as a means to warm up the sample to around 40°C. The multiparametre sonde containing the fDOM, turbidity and temperature sensors was immersed in the storage cup to achieve equilibrium with sample temperature. Once in equilibrium, the storage cup was removed from the bucket and left to cool down to room temperature (~22°C); the sonde was set to take readings every 90 seconds on the accelerated averaging data filtering mode. When the sample reached room temperature, the storage cup was put in a bucket containing ice, where it was left until the sample was as cool as 5°C. This way, the sample was chilled over a 3 hours period which allowed the collection of approximately 120 readings over a temperature range of 40°C to 5°C. Similar methodology was applied by Watras *et al.* (2011) to correct fDOM measurements for temperature effects on two commercial chromophoric dissolved organic matter fluorimeters. In our case, a site-specific, instrument-specific temperature compensation model was developed using data collected in April and tested on data collected in March. Based on the statistical features of the data, a linear regression model was developed for this purpose.

2.2. Evaluation and modelling of turbidity effects

In order to increase the concentration of suspended particles, natural turbidity powder from Lake Tingalpa was prepared by sampling raw water after a big storm event in 03 April 2017 (i.e. ex cyclone Debbie), waiting a few hours for the solids to settle down, removing the bulk water from the surface, placing the mixture from the bottom of the container in a tray, air-drying the mixture until only the solids were present, scraping it from the tray, putting it into a vial and keeping it refrigerated at 4°C for 20 days. Approximately 4.4g of this powder was added into 1L of raw water collected in 27 April 2017, manually stirred and shaken vigorously for 30 minutes up to a point where most of the soluble NOM and damaged algal cells had dissolved, precluding the release of additional DOM during the experimental measurements. 500mL of this highly turbid mixture were filtered to decrease turbidity (~2FNU) and placed in the storage cup for analysis. The sonde with the fDOM, turbidity and temperature sensors was immersed in the storage cup; sensors were wiped by the central wiper and first three readings taken. DOC and UV₂₅₄ analyses of this filtered mixture were undertaken. The turbid mixture was gradually added into the storage cup, this way increasing turbidity from ~2FNU up to ~483FNU. Three readings were taken every time the turbid mixture was added, and after the sensors were wiped. DOC and UV₂₅₄ analyses of the filtered mixture with highest turbidity (~483FNU) were also undertaken. The DOC and UV₂₅₄ analyses were important to check whether there were any changes on the character and concentration of DOM during the experiments, due to the addition of turbid mixture. Previous works have either used environmental standard reference soil (Elliott Soil) obtained from the International Humic Substances Society to determine absorption and scattering effects due to suspended particles on fDOM measurements (Downing *et al.*, 2012), or soils collected from the study watershed (i.e. Bukmoongol Watershed) to prepare artificial turbid stream water (Lee *et al.*, 2015). In this work, a site-specific and instrument-specific turbidity compensation model was developed using natural turbidity from the study site based on data collected in April and tested to fDOM data collected in May. Given the higher complexity of the collected data, several modelling linear and nonlinear options were considered for this specific modelling task.

2.3. Evaluation and modelling of inner filter effects

According to the EXO User Manual, on serial dilution of a colorless solution of quinine sulfate, the EXO fDOM sensor shows virtually perfect linearity ($R^2=1.0000$), albeit some underlinearity is observed on serial dilution of stained water field samples. Therefore, this study focused only on the investigation and modelling of the secondary inner filter effect. Approximately 216µg of quinine sulfate powder was dissolved in 1L of

ultrapure water to prepare a solution of ~216QSU. The solution was poured into the storage cup, and the fDOM, turbidity and temperature sensors connected to the multiparametre sonde immersed into it to take the first three readings. Small volumes (approx. 50 μ L) of Fluorescent Water Tracer Red 25 - Rhodamine WT (Kingscote Chemicals, USA) were slowly added into the solution, thus progressively increasing its colour and absorbance at 480nm (i.e. target for secondary IFE). Sensor readings were taken at each step of this colour-increasing procedure, together with UV₂₅₄, UV₃₆₅ and UV₄₈₀ analyses. Similarly to the turbidity model, due to the higher level of nonlinearity and complexity of the data for this particular modelling task, different modelling approaches were experimented.

3. RESULTS AND DISCUSSION

3.1. Temperature effects on fDOM measurements

Thermal quenching interferes in the fluorophores properties, but the fluorescent intensity variation caused by temperature should be reversible in most cases. Importantly, reduced fluorescence emission intensity is caused by an increase in temperature, which increases the probability of an excited electron to go back to its ground state by radiationless decay. Therefore, temperature is expected to have an inverse relationship with fDOM of roughly 1% per °C (Downing *et al.*, 2012; Henderson *et al.*, 2009; Watras *et al.*, 2011). As concluded by Watras *et al.* (2011), a single DOC concentration should suffice for determination of temperature effect on fDOM measurements. Therefore, in this work the investigation of temperature interference on fDOM readings was performed only using natural raw water collected in April 2017 from Lake Tingalpa at DOC concentration of 13mg/L. The linear regression compensation model for temperature over the range 5 to 40°C showed below (Figure 2) resulted in a near-perfect fit ($R^2 > 0.99$), meaning that the fDOM reading can be accurately adjusted to account for temperature values moving away from the reference value.

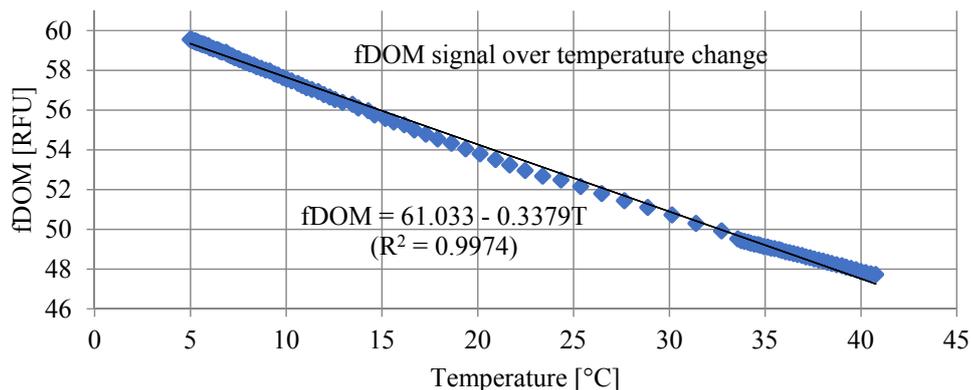


Figure 2. Linear regression of fDOM against temperature

Adapting from Watras *et al.* (2011): $fDOM_r = fDOM_m / [1 + \rho(T_m - T_r)]$, where T is temperature (°C), ρ is the temperature coefficient (°C⁻¹), and the subscripts r and m stand for the reference and measured values; $\Delta fDOM$ and $\Delta Temperature$ were normalized at the fDOM reading corresponding to the temperature of reference (~22.5°C), as this was the temperature during fDOM calibration with quinine sulfate solution, resulting in the following equation (1):

$$fDOM_r = fDOM_m / [-0.0064 (T_m - T_r) + 1.009] \quad (1)$$

Where T is temperature (°C) and the subscripts r and m stand for the reference and measured values, respectively. In order to test this model, Equation 1 was applied to the data collected in March 2017, resulting in a root mean square error (RMSE) of 0.49.

3.2. Turbidity effects on fDOM measurements

Suspended particles can affect optical measurements through light scattering and light absorption. Because changes in the concentration of suspended sediments, its particle size distribution, chemical composition, and shape are believed to determine the degree of fDOM signal bias, the assessment of fDOM-turbidity relationship is site-specific (Saraceno *et al.*, 2017). As turbidity increases in the water, more and more of the

excitation lights emitted by the fDOM sensor scatter, which means there is less light available in the sampling volume to excite fDOM. The result is that the fDOM signal becomes nonlinear over a certain turbidity level (Downing *et al.*, 2012). Figure 3 shows the relationship between turbidity and fDOM values based on the data collected through such experiments. By plotting fDOM against turbidity, it was evident that the fluorescence behavior was linear at the lower end of the turbidity range, and nonlinear after a certain threshold (~40FNU). UV₂₅₄ remained relatively constant throughout the experiment, with absorbance values varying from 0.508 to 0.533cm⁻¹, and DOC was held steady at 14mg/L. Consequently, in these experiments, after normalization of fDOM the data was fitted with a threshold autoregressive model (Tong, 2012) containing linear and logarithmic terms, based on the systems of equations 2 and 3:

$$\{fDOM_r = fDOM_m / [-0.0079 T_b + 1.0023]; T_b \leq 40 \quad (2)$$

$$\{fDOM_r = fDOM_m / [-0.254 \ln T_b + 1.622]; T_b > 40 \quad (3)$$

Where T_b is turbidity in FNU, and the subscripts r and m stand for the reference and measured values, respectively. To evaluate turbidity correction performance of the TAR model, data acquired in May was tested and resulted in RMSE = 0.21. Future work could include evaluation of a larger number of storms, as characteristics of suspended particles (algae, sand, silt, clay etc.) should vary with time, altering fDOM signal bias.

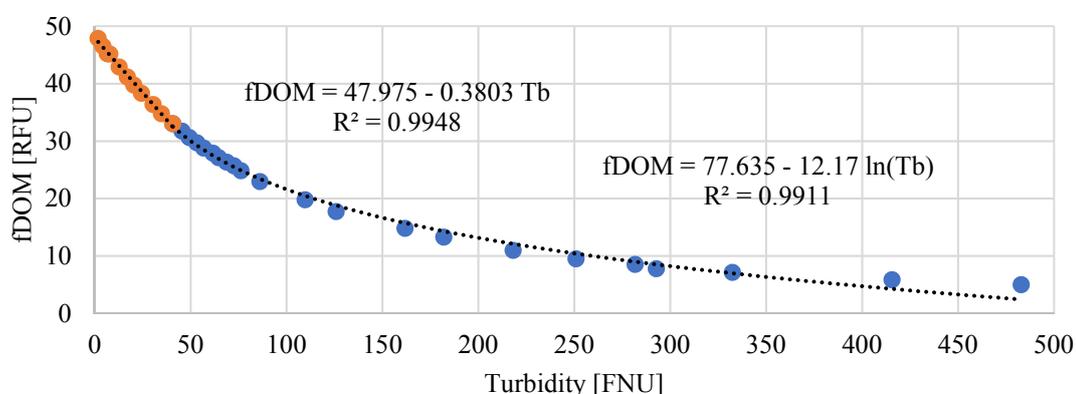


Figure 3. Behaviour of fluorescence intensity across the turbidity range

3.3. Secondary inner filter effect on fDOM measurements

When the fluorophore concentration is high, there seems to be a self-quenching phenomenon of distortion of band shape and/or a decrease in emission quantum yield, also known as IFE, possibly caused by the absorption of excited and emitted radiation by the sample matrix (Henderson *et al.*, 2009). Our investigation of secondary IFE on fDOM measurements is still in progress. Data collected indicate that fluorescence intensity decreases logarithmically as UV absorbance at 480nm increases in the water. Our IFE correction model is under development, and data-set for performance test will be collected in the near future. Future work on IFE should include the use of Fluorescent Liquid Tracer Yellow/Green Dye (Fluorescein) (Cole-Parmer, USA), besides Fluorescent Water Tracer Red 25 (Rhodamine). Fluorescein has its maximum absorbance peak at 490nm, whilst Rhodamine peaks at 550nm. As the chosen fDOM probe detects emissions at 480 ± 40 nm; it is expected that fluorescein will produce better results.

4. CONCLUSIONS AND RECOMMENDATIONS

A sequential compensation model to account for in-situ interferences (i.e. temperature, turbidity, color) on measurements of a fDOM probe has been developed, based on raw water sampled from a South-East Queensland reservoir and data carefully collected during laboratory experiments. Temperature had a linear, inverse relationship with fDOM, whereas turbidity effect on fDOM was best described by threshold autoregressive models, as it was linear at the lower end of the turbidity range, and nonlinear after a certain level (~40FNU). Current work is focusing on collecting further data for building and validating the IFE component. Based on the current model components, the sequential model has a higher accuracy than a developed multivariate regression model; however, when more data are available, we will compare the final sequential compensation model against more complex data-driven models such as artificial neural networks. Future work will focus also on conducting more experiments to determine how the fDOM readings are affected by the DOM character, and in turn whether the fDOM probe can provide insights on the character of

the measured DOM. The final objective will be to use such information to develop more accurate, real-time coagulation prediction models to enhance DOM removal and/or to better control DBPs formation in the water distribution system.

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