

Session M3: Evaluation of New In-situ Sensors

Room A106
10:00 – 11:30 am

0215
M3-1

Recommendations for Improving *In situ* Dissolved Organic Carbon Fluorescence Sensors Based on Analysis of Nationwide Excitation Emission Matrix (EEM) Data

Kenna Butler¹, Brian Bergamaschi², Tamara Kraus², Bryan Downing², Travis VonDessonneck² and George Aiken¹

¹US Geological Survey Branch of Regional Research, Central Region, National Research Project, Boulder, Colo., USA, ²US Geological Survey California Water Science Center, Sacramento, Calif., USA

In situ single-wavelength fluorometers are increasingly used to estimate dissolved organic carbon (DOC) concentrations in aquatic systems. For historic reasons, these instruments measure fluorescence at an excitation center wavelength near 370 nm and an emission center wavelength near 460 nm, with varying bandpass filters. This excitation-emission pair has been shown to be an excellent proxy for DOC concentration in many settings. However, developing robust correlations with DOC and making comparisons among instruments across space and time is difficult because this region of the EEM spectrum is on the sloping edge of a commonly identified fluorophore (peak C), which makes it particularly sensitive to small differences in excitation and emission bandpasses among instruments. Moreover, natural shifts in the position of the peak occur due to differences in DOC source (waste water, algal, soil, urban) as well as due to changes in pH, salinity, and metal concentrations. We examined several thousand EEMs collected from a variety of fresh, estuarine, and marine settings to identify regions within the fluorescent spectrum where *in situ* measurements may be less susceptible to these interferences and confounding factors. We identified the most stable regions of the EEM landscape that are strongly related to DOC concentration. Our results demonstrate that changing the center wavelength pair of *in situ* DOC fluorescence sensors will improve the stability and comparability of these measurements across instrument types and aquatic systems. We also identified cases where water receiving different sources of DOC, such as wastewater and urban runoff, may require measurement of additional wavelength pairs to adequately determine DOC concentration.

0166
M3-2

Real-Time Monitoring of Dissolved Organic Matter Amount, Composition, Source and Reactivity Using Fluorescence Sensors: Applications for Drinking Water Quality

Tamara Kraus¹, JohnFranco Saraceno¹, Jami Goldman², Kurt Carpenter², Gordon McGhee³, Bryan Downing¹ and Brian Bergamaschi¹

¹US Geological Survey, California Water Science, Sacramento, Calif., USA, ²US Geological Survey, Oregon Water Science Center, Portland, Oreg., USA, ³Clackamas River Water Utility, Clackamas, Oreg., USA

There is growing interest in the use of *in situ*, continuous fluorescence spectroscopy as a proxy for dissolved organic carbon (DOC) concentration. To date, *in situ* fluorometers designed to estimate DOC concentration are single wavelength sensors centered near the excitation/emission (ex/em) pair 370/460 nm. Additional information about dissolved organic matter (DOM) composition has only been obtainable from benchtop fluorometers that provide multi-spectral data. Changes in DOM composition are important as they provide insight into DOM source (*e.g.*, terrestrial, algal, wastewater) and reactivity. Recent advances in sensor technology make it possible to build *in situ* instruments for measuring multiple fluorescence ex/em pairs, including pairs with excitations in the lower “deep UV” region (*e.g.*, 270/340 nm) associated with fresher, more labile DOM pools as well as wastewater. The deployment of multi-spectral sensors will provide real-time continuous data showing not only changes in DOM concentration, but also changes in composition. This information is particularly relevant to drinking water utilities because a fraction of DOM reacts upon disinfection (*e.g.*, chlorination and ozonation) to form toxic disinfection byproducts (DBPs) which are regulated by the EPA. To test this application, we designed a multi-wavelength sensor package that measures three ex/em pairs (370/470, 370/520 and 270/340 nm) for deployment near a drinking water intake on the Clackamas River in Oregon. Comparison of the continuous data with discrete sample data indicates these tools can track both quantitative and qualitative changes in the DOM pool. The availability of this type of continuous data in real time could enable utilities to minimize the formation of DBPs by instantaneously optimizing treatment plant operations in response to changes in source water quality. In addition, collection of high-frequency data will improve understanding of watershed DOM dynamics and help identify sources of DOM and DBP precursors, thereby informing long-term management of drinking water resources.

0547
M3-3

A Microfluidic Chemical-Spectrophotometry (MCS) System for *In situ* Monitoring of Heavy Metals

Justus Ndukaife and George Nnanna

Purdue Univ. Calumet, Hammond, Ind., USA

This work presents the fabrication and calibration of a Microfluidic Chemical-Spectrophotometry (MCS) system for in situ monitoring of heavy metals (Hexavalent-Chromium, Mercury (II) and Vanadium (V)) in aqueous environment. The MCS system consists of valves, micro flow cell, light source, optical fiber cables, quartz glass transparent window fixed on two opposite ends of the flow cell, and spectrometer. The micro-flow cell is fabricated from a Teflon (PTFE) material, which has good chemical resistance properties. Dispensing of sensing reagents into the cell is gravity-driven, and the volumetric flow-rate has been estimated using Bernoulli and Conservation of Mass equations. Contaminant detection is carried out by propelling contaminated water into the cell, followed by actuation of a valve to introduce the gravity-driven sensing reagent for target contaminant. After chemical reaction, an aqueous solution with distinct optical properties from the reactants is formed. Using the fiber as a waveguide, light is transmitted into the solution within the cell via the transparent quartz glass window. The optical absorbance spectrum is acquired by the spectrometer and correlated with concentration of the target contaminant. Subsequently, an exit valve is actuated to discharge the waste solution, and another valve is actuated to dispense deionized water for cleaning the cell. The process is repeated for detection of other contaminants of interest. Actuation of the solenoid valves is carried out using a solid state relay data acquisition module, which was programmed using LabVIEW.

The prototype MCS system is capable of continuous monitoring of multiple contaminants sequentially, and can be controlled remotely over the internet by running the LabVIEW control programs using remote desktop control software. Thus the system can be installed on a site and be remotely controlled by an operator many miles away. In this study, hexavalent chromium was detected using a diphenylcarbazide based reagent, while vanadium and mercury (II) were tested with 2-(5-Bromo-2-pyridylazo)-5-(diethylamino)phenol and dithizone-based reagents respectively. Several reagents selective to target contaminants can also be utilized. The MCS system is robust and integration with existing wireless sensor network technology would enhance water quality monitoring and water security by allowing in situ, continuous, and on-line monitoring of hazardous water-borne chemical contaminants.

0530
M3-4

The Effects of Iron on the Optical Properties of Dissolved Organic Matter

Brett Poulin and George Aiken

US Geological Survey, Boulder, Colo., USA

The effects of dissolved iron on dissolved organic matter (DOM) optical properties have long been observed as a source of potential spectroscopic interference. Ferric (Fe(+3)) iron is known to increase the ultraviolet (UV) absorbance of DOM and to reduce or quench the fluorescence intensity. Measurements of UV absorbance at 254 nm and dissolved organic carbon (DOC) concentration are used in the calculation of specific UV absorbance ($SUVA_{254}$) which has been linked to DOM aromaticity. In addition, *in situ* measurements of spectral slope (S_R) parameters are utilized as proxies for average DOM molecular weight and DOC concentration. Fluorescence excitation-emission matrix spectroscopy and measurements of fluorescence indices (FI) are also widely used to characterize and quantify changes in DOM, and *in situ* DOM optical sensors are based on organic matter fluorescence. Despite the growing popularity of these optical approaches for studying DOM, the confounding effects of iron on DOM optical properties are poorly defined and have been largely ignored. Here we present results of a study designed to better define the effects of Fe(+3) and Fe(+2) on the UV absorbance and fluorescence of DOM. In our analyses, we studied these effects on DOM isolates and whole water samples from a wide variety of environments differing in DOM origin. We observed a positive, additive effect of Fe(+3) on the absorbance ($\lambda = 254$ nm) of both DOM isolates and whole water samples. In contrast, the presence of Fe(+3) was observed to decrease S_R ratios. No effect on UV absorbance was observed in the presence of Fe(+2). The addition of both Fe(+2) and Fe(+3) resulted in significant fluorescence quenching for all the whole water samples and DOM isolates, yet the sensitivity between samples varied. Quenching efficiencies of Fe(+3) and Fe(+2) were observed to be greater in regions of the fluorescence spectrum associated with more conjugated molecules. In turn, the addition of Fe(+3) and Fe(+2) resulted in an increase in the FI. In conclusion, our results demonstrate the importance of accounting for iron and its speciation in natural water samples. Further investigation into fluorescence quenching phenomena will be critical for the proper interpretation of DOM spectral properties.