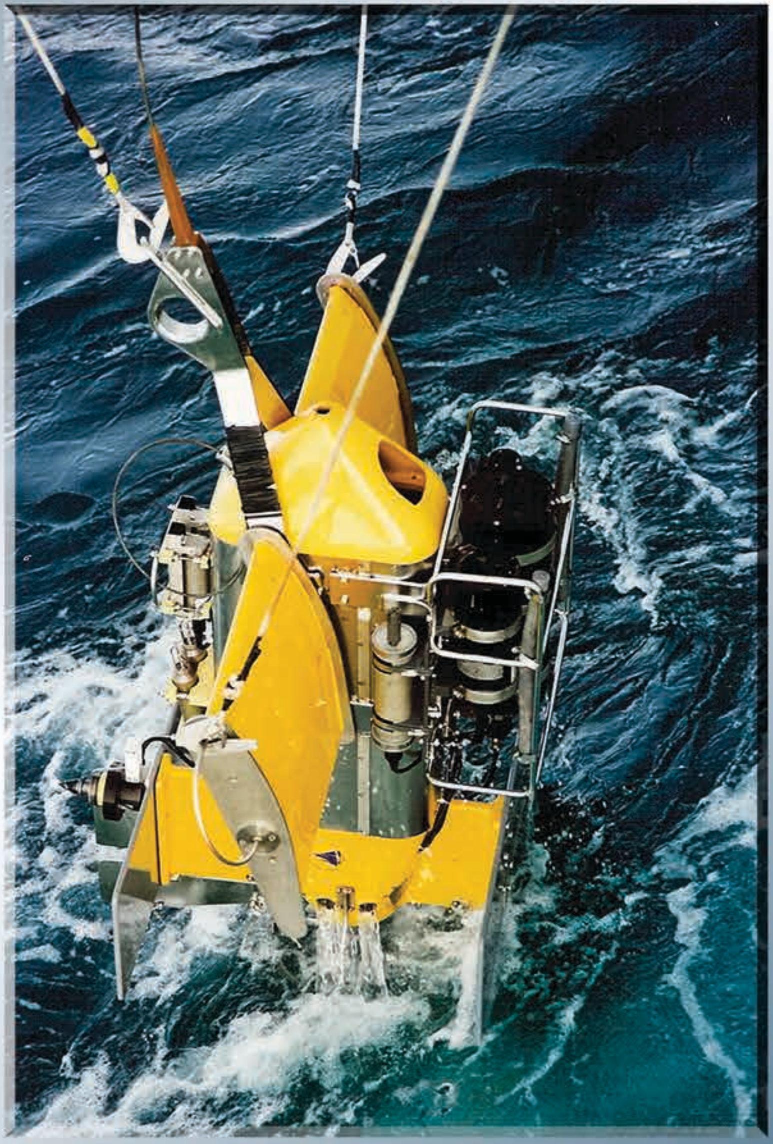
AGU Chapman Conference on Organic Matter Fluorescence



University of Birmingham, Edgbaston, Birmingham, UK
20–23 October 2008

UNIVERSITY OF BIRMINGHAM

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Conference Park

48 Edgbaston Park Road Edgbaston
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We Are Here

1 = Peter Scott House
2 = Lucas House
3 = Garth House
4 = Hornton Grange

●● = Walk from University Station

There are a number of buses from the city centre. The No.46 stops directly outside Conference Park.

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AGU Chapman Conference on Organic Matter Fluorescence

University of Birmingham, Edgbaston, Birmingham, U.K.
20–23 October 2008

Conveners

- **Andy Baker**, School of Geography, University of Birmingham, Edgbaston, Birmingham, U.K.
- **Paula Coble**, College of Marine Science, University of Florida, St. Petersburg, FL, USA

Program Committee

- **George Aiken**, U.S. Geological Survey, Boulder, CO, USA
- **Brian Bergamaschi**, U.S. Geological Survey, California State University, Sacramento, CA, USA
- **Jennifer Boehme**, The Smithsonian Environmental Research Center, Edgewater, MD, USA
- **Robyn Conmy**, College of Marine Science, University of South Florida, St. Petersburg, FL, USA
- **Diane McKnight**, Institute of Arctic and Alpine Research, Boulder, CO, USA
- **Darren Reynolds**, Environmental and Interdisciplinary Sciences, University of the West of England, Bristol, U.K.
- **Rob Spencer**, Department of Land, Air and Water Resources, University of California, Davis, CA, USA
- **Colin Stedmon**, Department of Marine Ecology, National Environmental Research Institute, Frederiksborgvej, DK

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Cover caption: Seasoar profiler with instrumentation to measure conductivity, temperature, depth, (CTD) chlorophyll a *and CDOM being deployed in the Arabian Sea. Photo credit: P. Coble, University of South Florida, St. Petersburg, Florida.*

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MEETING AT A GLANCE

Sunday, 19 October

1700h – 1800h	Registration
1800h – 1930h	Welcome Reception

Monday, 20 October

0730h – 0830h	Breakfast
0800h – 0845h	Registration
0900h – 1010h	Oral Discussions
1010h – 1030h	Coffee Break
1030h – 1200h	Oral Discussions
1200h – 1400h	Lunch and Poster Viewings
1400h – 1530h	Oral Discussions
1530h – 1545h	Coffee Break
1545h – 1700h	Oral Discussions
1900h – 2000h	Dinner

Tuesday, 21 October

0730h – 0830h	Breakfast
0800h – 0845h	Registration
0900h – 1030h	Oral Discussions
1030h – 1100h	Coffee Break
1100h – 1200h	Oral Discussions
1200h – 1400h	Lunch and Poster Viewings
1400h – 1530h	Oral Discussions
1530h – 1545h	Coffee Break
1545h – 1700h	Oral Discussions
1900h – 2000h	Dinner

Wednesday, 22 October

0730h – 0830h	Breakfast
0800h – 0845h	Registration
0900h – 1030h	Oral Discussions
1030h – 1045h	Coffee Break
1045h – 1200h	Oral Discussions
1200h – 1400h	Lunch and Instrument Demonstrations (Exhibits)
1400h – 1530h	Instrument Demonstrations (Exhibits)
1530h – 1545h	Coffee Break
1545h – 1700h	Breakout Group Discussions
1700h – 1800h	Hands-on PARAFAC Tutorial
1900h – 2100h	Conference Banquet

Thursday, 23 October

0730h – 0830h	Breakfast
0800h – 0845h	Registration
0900h – 1015h	Oral Discussions
1015h – 1045h	Coffee Break
1045h – 1145h	Oral Discussions
1145h – 1330h	Lunch
1330h – 1530h	Oral Discussions
1900h – 2000h	Dinner

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SCIENTIFIC PROGRAM

Note: Oral Discussions will be held in the Edgbaston Room of the Lucas House. Poster Viewings and Instrument Demonstrations (Exhibits) will take place in the Harborne Room and Edgbaston Room of the Lucas House.

SUNDAY, 19 OCTOBER 2008

1700h – 1800h: Registration, Foyer, Peter Scott House
1800h – 1930h: Welcome Reception, Foyer, Peter Scott House

MONDAY, 20 OCTOBER 2008

0730h – 0830h: Breakfast, Lucas Dining Room, Lucas House
0800h – 0845h: Registration, Foyer, Lucas House

LEARNING FROM DIFFERENT DISCIPLINES: INTERCALIBRATION, STANDARDS AND SAMPLE HANDLING

SESSION CHAIRS: GEORGE AIKEN, JENNIFER BOEHME

0900h – 0940h: The Results of an Interlaboratory Study Designed to Improve Intercalibration and Data Comparability for Fluorescence Analyses of Natural Organic Matter
George Aiken (U. S. Geological Survey, Boulder, Colorado, USA) and Kate Murphy (Centre for Water and Waste Technology, School of Civil and Environmental Engineering, The University of New South Wales, Sydney NSW, Australia)

0940h – 1010h: Fluorescence Data Correction: Methods and Materials for Optimal Wavelength and Intensity Characterization of Dissolved Organic Matter
Jennifer Boehme (Smithsonian Environmental Research Center, Edgewater, MD, USA)

1010h – 1030h BREAK Lucas Coffee Area, Lucas House

1030h – 1115h: Data Correction Methods for in situ Fluorometers
Robyn Conmy (College of Marine Science, University of South Florida, St. Petersburg, FL, USA)

1115h – 1200h noon: Sample Collection and Preparation for Absorbance and Fluorescence Analyses of Dissolved Organic Matter
Robert Spencer (University of California, Davis, CA, USA)

1200h noon – 1400h: LUNCH (Lucas Dining Room, Lucas House) AND POSTER VIEWINGS (Harborne and Edgbaston Rooms, Lucas House)

1400h – 1530h: Breakout Group Discussion on Intercalibration Results and Next Steps

1530h – 1545h **BREAK** **Lucas Coffee Area, Lucas House**

1545h – 1700h: Breakout Group Discussion on Intercalibration Results and Next Steps

1900h – 2000h: Dinner, Hornton Grange Dining Room, Hornton Grange House

TUESDAY, 21 OCTOBER 2008

0730h – 0830h: Breakfast, Lucas Dining Room, Lucas House
0800h – 0845h: Registration, Foyer, Lucas House

ENVIRONMENTAL EFFECTS

SESSION CHAIRS: ANDY BAKER, ROBERT SPENCER

0900h – 0930h: Introduction: Environmental Effects on OM Fluorescence
Robert Spencer (University of California, Davis, USA)

0930h – 1000h: Inner-Filtering Corrections for Fluorescence Measurements of Dissolved Organic Matter
Caroline Eliot-Laize (Centre for Ecology and Hydrology, Crowmarsh Gifford, Wallingford, U.K.)

1000h – 1030h: Natural Organic Macromolecules and Metal Speciation in Natural Waters
Jamie Lead (University of Birmingham, U.K.)

1030h – 1100h **BREAK** **Lucas Coffee Area, Lucas House**

1100h – 1130h: The Effects of Salinity on the Fluorescence and Photoreactivity of Dissolved Organic Matter in Coastal Environments
Chris Osburn (North Carolina State University, Raleigh, USA)

1130h – 1200h noon: Photochemical and Biochemical Cycling of Dissolved Organic Matter in Lake Superior: Clues from Organic Matter Fluorescence
Rose Cory (Los Alamos National Laboratory, New Mexico, USA)

1200h noon – 1400h: LUNCH (Lucas Dining Room, Lucas House) AND POSTER VIEWINGS (Harborne and Edgbaston Rooms, Lucas House)

1400h – 1530h: Breakout Group Discussion on Environmental Effects: Results and Next Steps

1530h – 1545h **BREAK** **Lucas Coffee Area, Lucas House**

1545h – 1700h: Breakout Group Discussion on Environmental Effects: Results and Next Steps

1900h – 2000h: Dinner, Hornton Grange Dining Room, Hornton Grange House

WEDNESDAY, 22 OCTOBER 2008

0730h – 0830h: Breakfast, Lucas Dining Room, Lucas House
0800h – 0845h: Registration, Foyer, Lucas House

CHARACTERISING AND INTERPRETING ORGANIC MATTER FLUORESCENCE

SESSION-LEAD: COLIN A. STEDMON

0900h – 0930h: CDOM EEM Analyses Using Conventional Spectral and Peak-picking Techniques OR Human Visualization Analysis
Paula Coble (College of Marine Science, University of South Florida, St. Petersburg, USA)

0930h – 1000h: Application of Principal Component Analysis to Evaluate Changes in Dissolved Organic Matter Fluorescence
Jennifer Boehme (Smithsonian Environmental Research Center, Edgewater, MD, USA)

1000h: – 1030h: Parallel Factor Analysis of Fluorescence Spectra
Kate Murphy (Centre for Water and Waste Technology, School of Civil and Environmental Engineering, The University of New South Wales, Sydney, NSW, Australia)

1030h – 1045h BREAK Lucas Coffee Area, Lucas House

1045h: – 1115h: Characterizing and Classifying Time Resolved Excitation Emission Matrices (TREEM) Using a Combined PARAFAC and SIMCA Approach
Greg Hall (Department of Science, U. S. Coast Guard Academy, New London, Conn., USA)

1115h – 1145h: N-PLS Analysis of EEM Fluorescence Spectra of Raw and Partially Treated Water as a Basis for the Determination of Organic Matter Removal Efficiency at Water Treatment Works
Magdalena Bieroza (School of Geography, Earth and Environmental Sciences, University of Birmingham, U.K.)

1200h - 1400h: **LUNCH (Lucas Dining Room, Lucas House) AND INSTRUMENT DEMONSTRATIONS (EXHIBITS) (Harborne Room, Lucas House)**

1400h - 1530h: Instrument Demonstrations (Exhibits)

1530h - 1545h BREAK Lucas Coffee Area, Lucas House

1545h - 1700h: Breakout group discussion on characterising and interpreting organic matter fluorescence

1700h - 1800h: Hands-on PARAFAC Tutorial* - Colin Stedmon

*Users are expected to have their own PC and copy of MATLAB. The rest will be provided (including data).

1900h – 2100h: Conference Banquet, Hornton Grange Dining Room, Hornton Grange House

THURSDAY, 23 OCTOBER 2008

0730h – 0830h: Breakfast, Lucas Dining Room, Lucas House
0800h – 0845h: Registration, Foyer, Lucas House

WHAT'S NEXT? FUTURE DIRECTIONS AND NOVEL APPLICATIONS

SESSION CHAIR: DARREN REYNOLDS

0900h – 0915h: Introduction to the Session *(Darren Reynolds)*

0915h – 0945h: The Technology – What's Next
Simon Fitzgerald (The SPEX® Fluorescence Division of Jobin Yvon)

0945h – 1015h: Rainwater Fluorescence and the World of Humic-Substances
Catherine Muller (University of Birmingham, U.K.)

1015h – 1045h BREAK Lucas Coffee Area, Lucas House

1045h – 1115h: High Resolution Measurements of Chromophoric Dissolved Organic Matter (CDOM) in Coastal Areas
Robert Chen (University of Massachusetts, Boston, USA)

1115h – 1145h: Visualisation of EEM-based Water Quality Assessment via Google Earth
Chris Brunsdon (Leicester University, U.K.)

1145h – 1330h: LUNCH (Lucas Dining Room, Lucas House)

1330h – 1530h: Wrap-up Discussions

1530h: CONFERENCE ADJOURNS

1900h – 2000h: Dinner, Hornton Grange Dining Room, Hornton Grange House

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POSTER SESSIONS

Posters will be on display in the Harborne and Edgbaston Rooms of the Lucas House. Posters are listed below in alphabetical order based on day of presentation.

MONDAY, 20 OCTOBER: METHODS AND FRESHWATER APPLICATIONS

Methods (Posters will be displayed in the Harborne Room)

A01 Al-Janabi, S., Bridgeman, J., Baker A., *Investigating the Mechanism of Chlorine Quenching Fluorescence of Natural Organic Matter*

B04 Butler, K., Aiken, G. R., Spencer, R., Murphy, K. R., *Design of an Interlaboratory Study to Determine the Precision of Excitation Emission Matrices of Dissolved Organic Matter*

C01 Cawley, K., McKnight, D., *Fluorescence Properties of Dissolved Organic Matter (DOM) Produced by a Mixotrophic Dinoflagellate Alexandrium Fundyense*

G01 Gonzales, A., Salinas, S., *Fluorescence of Selected Organic Matter: Effect of Concentration, Ionic Strength and pH*

H02 Hambly, A., Henderson, R. K., Murphy, K., Baker, A., Stuetz, R., Khan, S., *Exciting Effluent: Fluorescence as a Tool for Detection of Cross-Connections in Dual Reticulation Water Supply Systems*

H07 Hudson, N., A. Baker, *Changes in Organic Matter Fluorescence Intensity Associated with Freezing/Thawing and Dehydration/Rehydration: Implications for Sample Storage*

M02 Mendoza, W., Zika, R. G., *A Simple Thin-layer Water CDOM Sampling Strategy in Shallow Coastal Waters*

P01 Parlanti, E., Vacher, L., Huguet, A., Ibalot, F., *New Criteria for the Characterisation of Fluorescent Dissolved Organic Matter in Aquatic Environments*

P04 Pfeiffer, E., Baker, A., Reynolds, D., Tipping, E., Pavelescu, G., *Measuring the Temperature Influence on Organic Matter Fluorescence*

Freshwater Applications (Posters will be displayed in the Edgbaston Room)

A02 Avery, L.M., Vinten, A., *Stream Colloids and Their Interactions with Coliform Bacteria*

B01 Beggs, K., Scott Summers, R., McKnight, D. M., *Fluorescence and Disinfection Byproducts: Applications in the Drinking Water Field*

H03 Henderson, R. K., Hambly, A., Murphy, K., Baker, A., Stuetz, R., Khan, S., *Linking the Fluorescent Fingerprint of Recycled Water to Organic Matter Character*

L01 Lapworth, D. J., Gooddy, D. C., Allen, D., *Tracing Groundwater-Surface Water Processes in a Chalk Catchment Using Fluorescence Properties of Dissolved Organic Matter*

M01 Marius, M. S., Smallman, D. J., Stringfellow, A. M., Atkinson, T., *Characterisation of Landfill Leachate Age Using Fluorescence Excitation-Emission Spectra*

N01 Naden, P. S., Old, G. H., Eliot-Laize, C., Granger, S., Hawkins, J., Bol, R., Haygarth, P., *Issues in the Use of Fluorescence Spectroscopy to Trace and Quantify Agricultural Pollution From Both Diffuse and Point Sources*

N02 Needoba, J., Schoen, J., *Evaluation of Fluorescent Whitening Agents as indicators of Anthropogenic Wastewater Discharges in the Columbia River, USA*

P02 Parlanti, E., Al-Sid-Cheikh, M., Ibalot, F., Nicolau, R., Mounier, S., *Effect of River Floods on Marine Organic Matter Fluorescence*

P05 Pfeiffer, E., Baker, A., Boomer, I., Pavelescu, G., *Continuous Monitoring of Dissolved Organic Matter Fluorescence in an Urban River*

S01 Saeed, A. B., Marco, D., Amy, G. L., *Characterization of Natural Organic Matter in Drinking Water Treatment Processes and Trains Using Fluorescence and PARAFAC*

Y01 Yamashita, Y., Kloeppel, B., Knoepp, J., Jaffé, R., *Dissolved Organic Matter Composition and Dynamics in Headwater Streams of an Eastern Deciduous Biome Under Different Forest Management Regimes: Applications of EEM-PARAFAC*

TUESDAY, 21 OCTOBER: APPLICATIONS FOR CHEMISTRY AND CHEMICAL OCEANOGRAPHY

Chemistry (Posters will be displayed in the Harborne Room)

B02 Bergamaschi, B. A., Downing, B. D., Fleck, J. A., Pellerin, B. A., *Understanding Physical Forcing of Biogeochemical Processes Using in situ Optical Measurement Systems*

D01 Downing, B., Bergamaschi, B. A., Spencer, R., Hernes, P. J., *Applications for EEMs spectroscopy in DOM Investigations*

H01 Haase, S., *Freeze Fractionation of Fluorescent Dissolved Organic Matter During Sea Ice Formation*

H04 Hernes, P. J., Bergamaschi, B. A., Eckard, R. S., Spencer, R. G. M., *Fluorescence-Based Proxies for Lignin in Dissolved Organic Matter*

H06 Hudson, N., Baker, A., *Biological and Chemical Processing of River Organic Matter Observed Through Changes in Organic Matter Fluorescence and Water Chemistry*

P03 Parlanti, E., Relexans, S., Amouroux, D., Bridou, R., Bouchet, S., Etcheber, H., Abril, G., *Transformation Processes of Colloidal Organic Matter at Superficial Sediment Interfaces*

R01 Romera-Castillo, C., Nieto-Cid, M., Álvarez-Salgado, X. A., Repeta, D., Marrasé, C., *Optical Properties of Seawater High-Molecular-Weigh Ultrafiltered Dissolved Organic Matter*

R02 Rosario-Ortiz, F., Suffet, M., Snyder, S., *Use of Fluorescence to Understand the Reactivity of Organic Matter*

U02 Unciano, N., Bigol, U. G., Bigol, M. B., Cabacang, R. M., *Microbial Biofluorescence Expressed by Bacterial Isolates Exposed to Organic Sulfur*

Chemical Oceanography (Posters will be displayed in the Edgbaston Room)

B03 Brown, T., McKay, L., McCarthy, J., *Fluorescence Characterization of Carbonate Aquifers in East Tennessee*

G02 Guéguen, C., *Dissolved Organic Matter in the Arctic Ocean Modeled by PARAFAC*

H05 Huang, Q.H., Li, J. H., *Characterizing Dissolved Organic Matter in a Brackish Lake of the Yangtze River Delta by Using Fluorescence Technology*

J01 Jaffé, R., Yamashita, Y., Chen, M., *Characterizing the Dynamics of Dissolved Organic Matter in the Florida Coastal Everglades by Fluorescence Analysis*

J02 Jaffé, R., Yamashita, Y., Maie, N., Briceño, H., *Optical Characterization of Dissolved Organic Matter in Tropical Rivers of Venezuela*

M03 Miller, M., McKnight, D. M., *Reactive Transport Modeling of Dissolved Organic Matter in an Alpine Lake*

M04 Mladenov, N., Reche, I., Olmo-Reyes, F. J., Alados-Arboleas, L., *Making Connections Between Water Soluble Organic Compounds and Organic Aerosol Columnar Properties Using Fluorescence Spectroscopy*

O01 Ortiz, S., Corredor, J. E., Morell, J., *Fluorescence of Colored Dissolved Organic Matter at JOBANERR, Puerto Rico*

S02 Singh, S., D'Sa, E. J., *Fluorescence Spectral Properties of Chromophoric Dissolved Organic Matter Along a Transect in the Barataria Bay, Louisiana, USA*

T01 Tzortziou, M., Neale, P. J., Megonigal, J. P., *Fluorescence Properties of Dissolved Organic Matter (DOM) Exported from Tidal Marshes and Effects of Microbial and Photochemical Processes*

U01 Uher, G., Mann, P. J., Upstill-Goddard, R. C., Woodward, E. M. S., *Seasonal Variation of Dissolved Organic Matter Fluorescence in the Coastal North Sea*

W01 Walker, S., Amon, R. M. W., Stedmon, C. A., *Organic Matter Fluorescence as a Tool for Tracing Water Mass Origins and Circulation in the Arctic Ocean*

ABSTRACTS

Oral discussions: listed in order of daily presentation.

Monday, 20 October

Learning from Different Disciplines: Intercalibration, Standards and Sample Handling

Session Chairs: George Aiken, Jennifer Boehme

The Results of an Interlaboratory Study Designed to Improve Intercalibration and Data Comparability for Fluorescence Analyses of Natural Organic Matter

Murphy, K. R. (Centre for Water and Waste Technology, School of Civil and Environmental Engineering, The University of New South Wales, Sydney NSW 2052, Ph. +612 9385 5227, Fax: 612 9313 8624; E-mail: katem@civeng.unsw.edu.au) G R Aiken (U.S. Geological Survey, 3215 Marine Street, Boulder CO 80303; Ph. 303-541-3036; Fax: 303-541-3084; E-mail: graiken@usgs.gov)

Fluorescence has become a useful tool in a number of disciplines in the water sciences for studying and monitoring the concentration and nature of DOM in aquatic systems. On the surface, fluorescence is an attractive method because data collection is easy and straightforward, it provides information about both the concentration and composition of DOM, it can be readily employed in detector systems for a variety of process-based studies and separation techniques to study DOM composition, and it can be employed in situ, allowing for the collection of environmental data in real time. However, the ease of data collection and the potentially powerful applications of fluorescence spectroscopy to monitor compositional changes in DOM belie the inherent complexity of the method. The measurement and comparability of fluorescence signals are non-trivial due to a number of complicating factors including instrumental inefficiencies and variability, inner filter effects, and the dependency of measured data on environmental conditions of the samples, such as pH, temperature and metal ion content. In this paper, the results of a large scale interlaboratory study (24 labs) designed to address intercalibration and data comparability issues will be presented. The intercalibration experiment was designed to assess performance, including sample replication, using, in addition to well characterized fluorophores, a set of natural fluorophores that cover a range of DOM types likely to be encountered in the study of aquatic systems. It is anticipated that the results of this study will provide the basis for fruitful discussion of standard approaches and appropriate reference materials in order to improve data collection and comparison among the growing numbers of scientists and engineers who use fluorescence spectroscopy in the study of aquatic systems.

Fluorescence Data Correction: Methods and Materials for Optimal Wavelength and Intensity Characterization of Dissolved Organic Matter

Boehme, J. R. (Smithsonian Environmental Research Center, Edgewater, MD 21037; Ph. 443-482-2438; Fax: 443-482-2375; E-mail: boehmej@si.edu)

Fluorescence spectroscopy provides a sensitive and non-destructive means to examine natural dissolved organic matter (DOM) variability in marine and freshwater systems, under the assumption that DOM in aquatic systems behaves similarly to pure components in solution. Thus measured shifts in fluorescence efficiency, intensity, peak width and maxima can be interpreted based on variability in the provenance of terrestrial and marine chemical components, the effects of production and removal via biological activity and photobleaching, and the physical regime of the sample environment (pH, salinity, etc.).

The power of fluorescence analysis coupled with improvements in cost and in situ instrument design have yielded a significant increase in environmental DOM fluorescence spectroscopy. While fluorescence spectroscopy possesses advantages of

sensitivity, utility, and relative ease of use, great care must be taken in the selection of instrumentation and experimental design. Excitation and emission distortions from light sources and optical components will significantly affect fluorescence response, and the resulting instrument bias must be corrected to provide reproducible quantitative information on peak wavelength and intensity variability, and enable inter-laboratory comparison of fluorescence results. Such corrections are especially important to fluorescence studies of DOM, given that its optically active constituents are at present poorly characterized and its environmental concentration can vary widely. Moving forward, one goal for the DOM fluorescence community is to critically examine current data correction practices and provide recommendations for standardizing fluorescence data generated across environmental applications.

To provide a framework for community discussion, here is presented a review of correction procedures relevant to laboratory-based fluorescence analysis of natural DOM from environmental samples. Fluorescence data correction relies on the use of fluorescent standards, and a summary of standard reference materials and their usage, storage effects, and applicability to DOM characterization is included. Topics will cover component-related bias and fluorometer design, generation of excitation and emission wavelength corrections, and a comparison of CDOM wavelength and intensity standardization practices.

Data Correction Methods for in situ Fluorometers

Conmy, R. N. (140 7th Ave South, St Petersburg, FL, 33701, USA, Ph. 727-692-5333, Fax: 727-553-1189, rconmy@marine.usf.edu)

Advances in the field of spectroscopy have given rise to field sensors that have expanded the temporal and spatial resolution of fluorescence measurements. Widely used are fluorometers, both single channel and multi-spectral, for monitoring DOM in a range of aquatic environments from lakes to global oceans. The increased use of sensors for obtaining optical, chemical and environmental information warrants a detailed discussion regarding the accepted and published methods for data collection and calibration. This presentation will focus on examining the optical standards and calibration methods of in situ fluorometers. Special emphasis will be given to operational concerns such as the effect of particles, temperature, bubbles, bio-fouling and chemical contaminants on fluorescence signal. A review of commercially available sensors will also be given, with a comparison of design types, sensitivities, and manners of deployment. This overview will serve as a basis for understanding current practices and technologies as the community looks the future for new sensor development.

Sample Collection and Preparation for Absorbance and Fluorescence Analyses of Dissolved Organic Matter

Spencer, R. G. M (Department of Land, Air and Water Resources, University of California Davis, Davis, CA 95616, USA, Ph. 530-754-4327, Fax:. 530-752-5262, E-mail: rgspencer@ucdavis.edu); Andy Baker (School of Geography, Earth and Environmental Sciences, University of Birmingham, Edgbaston, Birmingham, B15 2TT, UK, Ph. 0121 4158133, Fax:. 0121 4145528, E-mail: a.baker.2@bham.ac.uk); and Paula G. Coble (College of Marine Science, University of South Florida, St. Petersburg, FL 33701, USA, Ph. 727-553-1631, Fax:. 727-553-1189, E-mail: pcoble@marine.usf.edu)

The number of studies utilizing fluorescence and absorbance analyses to examine dissolved organic carbon (DOC) concentration and dissolved organic matter (DOM) composition in recent years has proliferated. These analyses have become very attractive to investigators across a diverse range of studies in no small part due to the fact that they are relatively inexpensive to conduct and generate a lot of useful data in a short amount of time. However, as with all analyses investigating DOC/DOM care has to be taken during sample collection and preparation to avoid contamination and also to separate the dissolved and particulate phases.

Here we present an overview of sample collection protocols designed to minimize changes in sample concentration and composition resulting from contamination, sorption onto collection vessels and through biological and photochemical pathways as well as provide recommendations of materials for sample collection. Particulate material may interfere with analyses and can also contain organisms which produce or utilize DOM and thus filtration upon sample collection is recommended. Data showing the impact of filter pore size will be presented and also suggestions provided on appropriate filters and their preparation. Finally, the issues of sample storage and stability will be addressed and the main causes of sample instability discussed. Results will be shown to highlight the impact of acidification and freezing as storage protocols on samples and recommendations will be provided for analysis of samples with respect to storage of different water types.

Tuesday, 21 October

Environmental Effects

Session Chairs: Andy Baker, Robert Spencer

Inner-Filtering Corrections for Fluorescence Measurements of Dissolved Organic Matter

Eliot-Laize, C. (E-mail: carolineeliot@hotmail.com); P S Naden (Centre for Ecology and Hydrology, Crowmarsh Gifford, Wallingford, OX10 8BB, UK; Ph. +44 (0)1491 692365; Fax: +44 (0)1491 692424; E-mail: psn@ceh.ac.uk); G H Old (Centre for Ecology and Hydrology, Crowmarsh Gifford, Wallingford, OX10 8BB, UK; Ph. +44 (0)1491 692486; Fax: +44 (0)1491 692424; E-mail: gho@ceh.ac.uk)

Quantitative estimates of dissolved organic matter (DOM) using fluorescence spectroscopy can be hampered by factors, such as photobleaching, scattering, quenching and/or inner-filter effects (IFE), which cause deviations from linearity in the relationships between fluorescence intensities and fluorophore concentrations. IFE comprise both primary and secondary inner-filtering, which are due to the absorption of the exciting light before it reaches the interrogation zone and of the emitted fluorescent light between the interrogation zone and the exit plane, respectively. These effects can be caused by the fluorophore itself and/or other components of the sample.

Ways of addressing the issues relating to IFE found in the literature fall into three groups: (i) dilution of the sample to reduce the absorbance down to an acceptable level, (ii) empirical corrections based on extraction of the Raman scatter peak, and (iii) mathematical corrections based on optical density or absorbance such as those described by Parker and co-workers or Lakowicz. All the treatments for IFE compensation offer advantages as well as limitations, which will be discussed. Our review will then focus on the third group of IFE treatments, which encompasses absorbance-based mathematical corrections. These can be divided into two sub-groups depending on whether the absorbance values are obtained directly—using a separate spectrophotometer—or indirectly—using the same fluorescence spectrophotometer albeit with varying pathlengths.

Finally, examples of absorbance-based corrections for IFE are presented in the context of four commonly found components of DOM: tyrosine, tryptophan, fulvic acid, and humic acid. Standard solutions of these—singly and in mixtures—were designed to map the boundaries of linearity, specificity, addition, and discrimination in the raw and corrected excitation-emission matrices. This study thus provides a basis for quantitative estimation of these four fluorophores in natural water samples.

Natural Organic Macromolecules and Metal Speciation in Natural Waters

Lead, J. R. (School of Geography, Earth and Environmental Sciences, University of Birmingham, Edgbaston, Birmingham, B15 2TT, U.K; Ph. +121 414 8147; E-mail: J.R.Lead@bham.ac.uk)

Natural organic macromolecules (NOM) and colloids are significant in the binding of trace metals in natural freshwaters. This is usually hypothesised to be due to the increase in specific surface area with decreasing size, although surface site density and binding strength may change with size in a less predictable manner. In addition, the smallest, nanoparticulate fraction of colloidal material (< 10-25 nm) is likely to be of particular importance because of the quantum related effects, analogously to manufactured nanoparticles, in addition to surface area effects. However, the polydispersity and complexity of NOM has precluded isolation of these different mechanisms.

Bioavailability and the impact of speciation on bioavailability is organism dependent. For many organisms and many environmental conditions, mass transport and kinetic dissociation of metals is of particular importance, although currently standard speciation and toxicity models consider the solution phase to be at equilibrium. Given this, this nanoparticulate fraction of NOM may be quantitatively important in binding metals and also be a controlling influence on biouptake in many cases. This talk will consider new methods of characterisation of NOM and NOM-metal interactions within this framework.

The Effects of Salinity on the Fluorescence and Photoreactivity of Dissolved Organic Matter in Coastal Environments

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In coastal environments, fresh water and salt water mix, creating a gradient of salinity into which dissolved organic matter (DOM) is both transported and produced. The effect of salinity on DOM fluorescence and absorption is an important consideration for the utility of these optical properties as conservative tracers of DOM in coastal environments. Salinity can affect DOM fluorescence and photoreactivity by altering intramolecular reactions, such as conformational change and charge transfer, which mediate and produce the intensity of fluorescence excitation and emission. The result is an observed increase in photoreactivity. Hence salinity must contribute to the transformation of DOM in coastal waters. DOM origin, composition, and prior biological and photochemical processing all constrain the ultimate effects of salinity on its fluorescent properties and photoreactivity.

Photochemical and Biochemical Cycling of Dissolved Organic Matter in Lake Superior: Clues from Organic Matter Fluorescence

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Lake Superior, an ultra-oligotrophic lake, has the largest surface area of any lake in the world. Despite low dissolved organic carbon (DOC) concentrations of 1-2 mg C L^{-1}, Lake Superior contains a large pool of organic carbon (1.5 to 1.9 x 10^{13} g). A deep euphotic zone and short duration of stratification suggests that much of this DOC is susceptible to photodegradation. Photochemical transformations alter the bioavailability of dissolved organic matter (DOM), suggesting that photochemical and microbial cycling of DOM in Lake Superior may be tightly coupled. We employed UV-Vis absorbance and fluorescence spectroscopy to analyze transformations of the Lake Superior DOM as they occur in-situ in the lake as a function of distance offshore, depth and time (multiple seasons over three years) as well as light exposure or long-term bacterial incubation in the laboratory as a first step in the continuing goal of relating the in-situ shifts in the lake DOM to photochemical and biochemical processes.

The dominant fluorescing constituents of the Lake Superior DOM were resolved by parallel factor analysis (PARAFAC), and were found to be very similar in number and spectral shape to components identified by PARAFAC models of marine waters. Some of the significant modifications in the optical properties of the Lake Superior DOM due to light exposure or bacterial incubation were consistent with changes observed spatially and temporally in Lake Superior. For example, the observed shifts in the spectral slope, fluorescence index, and PARAFAC components with distance offshore for every season were consistent with an increased contribution of autochthonous material in the offshore DOM pool. Several PARAFAC components were strongly correlated to measures of photochemical and biochemical reactivity, such as the yield of singlet oxygen, a reactive oxygen species produced photochemically by DOM, or bacterial abundance, an indicator of the bioavailability of the organic matter.

Wednesday, 22 October

Characterising and Interpreting Organic Matter Fluorescence

Session-lead: Colin A. Stedmon

CDOM EEM Analyses Using Conventional Spectral and Peak-picking Techniques OR Human Visualization Analysis

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Colored dissolved organic matter (CDOM) is a complex mixture of compounds derived from biological materials and ubiquitous in surface waters and at all depths in the ocean. Excitation Emission Matrix Spectroscopy (EEMS) has provided one of the complete and convenient techniques for the study of CDOM composition with excellent sensitivity and without creating artifacts. EEMs from natural water samples show the presence of varying combinations of humic-like, protein-like, and pigment-like components, identified as fluorescence peaks within specific excitation and emission domains of the EEM.

Direct visualization of the EEM data provided the first evidence of the usefulness of hyperspectral analysis and also formed the background for error-checking and development of analytical procedures. Spectral analysis is also a powerful technique for identifying subtle changes in CDOM composition during environmental transformation. This paper will provide an historical perspective on use of the technique as well as examine its strengths and weaknesses.

Application of Principal Component Analysis to Evaluate Changes in Dissolved Organic Matter Fluorescence

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Changes in dissolved organic matter (DOM) fluorescence reflect the effects of physical and chemical processes that occur in the aquatic environment as well as variations in DOM chemical composition and concentration from different sources. Given that DOM can be considered a mixture of unknown components with potentially numerous fluorophores, three-dimensional fluorescence analysis via excitation emission matrix spectroscopy (EEMS) provides a significant advantage for characterizing DOM variability. EEMS research across varying geographic regions and seasons continues to expand, and thus the need exists for quantitative comparisons of fluorescence matrices within large data sets. Principal component analyses has been successfully applied to statistically differentiate changes in DOM fluorescence, and expands the evaluation of large data sets beyond basic monitoring of wavelength and intensity changes at local fluorescence maxima. Variability in fluorescence peak wavelengths and changes in spectral bandwidth are expressed by each of the components generated by PCA, and the scores and loadings associated with sequential principal components allow DOM variation to be assessed based on an entire data matrix. This presentation will provide a basic summary of principal component analysis as it pertains to DOM fluorescence data sets and discuss its pertinence to various environmental applications.

Parallel Factor Analysis of Fluorescence Spectra

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The past 15 years has seen a rapid expansion in the use of Excitation-Emission Matrix Spectroscopy (EEMS) for mapping the fluorescence of dissolved organic matter as a function of excitation and emission wavelengths. A major drawback to this approach has been that EEMs are data-intensive and difficult to parameterize.

Hence, research has tended to focus upon a handful of visually distinguishable peaks characterized in terms of their positions, heights and ratios. Since the locations of individual peaks vary between environments, and may be obscured by overlapping spectra, some subjectivity in data interpretation using this approach has been unavoidable. Multivariate analysis tools have generated great interest in recent years because of their utility for distinguishing between variable and conservative regions of EEMs, enabling wavelength selections to be optimized. Parallel factor analysis (PARAFAC) in particular is an increasingly popular tool for reducing complexity in fluorescence EEMs, via their decomposition into the least squares sum of several mathematically independent components parameterized by concentrations (loadings) and excitation and emission spectra. Since PARAFAC can isolate spectra from overlapping components, it can potentially expose patterns within a dataset that are visually obscure and overlooked by traditional interpretive methods. In this presentation, an overview of the PARAFAC method will be provided, and the application of PARAFAC to identifying sources of ships' ballast water will be discussed.

Characterizing and Classifying Time Resolved Excitation Emission Matrices (TREEM) Using a Combined PARAFAC and SIMCA Approach

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Multi-way data, such as multidimensional fluorescence, is ideal for analysis by methods such as Parallel Factor Analysis (PARAFAC). When the dimensionality of this data is three-way or larger, the solution of a PARAFAC model is unique. Therefore, such methods allow for the characterization of the number and identity of fluorescent components, as well as the relative contribution of each to the overall intensity without standards. These relative amounts, or scores, can be utilized in classification models such as Soft Independent Model of Class Analogy (SIMCA) models.

SIMCA models of PARAFAC scores from the Time-Resolved Excitation Emission Matrices (TREEM) of water from three different U.S. ports (Boston, Baltimore, and Sturgeon Bay) were used to classify new samples from these ports with great specificity. TREEMs are of particular interest since a TREEM of a single sample has enough dimensionality to produce a unique result by itself. These results were compared with similar models utilizing subsets of the TREEM such as EEM and Wavelength Time Matrices (WTM). The ability of such tools to elucidate longitudinal and temporal trends without reliance on pure standards allows for great promise in oceanographic studies.

N-PLS Analysis of EEM Fluorescence Spectra of Raw and Partially Treated Water as a Basis for the Determination of Organic Matter Removal Efficiency at Water Treatment Works

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Fluorescence spectroscopy has been successfully utilized in environmental studies, providing robust, holistic and non-destructive source of information on organic matter function and structure in a variety of environments. In the current study, fluorescence spectroscopy has been used for determination of organic matter at 16 water treatment works (WTWs) across the Midlands region of U.K. The work has concentrated on characterising organic matter removal across different stages of municipal water treatment and providing qualitative information on organic matter properties relevant to treatment processes efficiency, and in particular for the formation of carcinogenic disinfection by-products.

Standard techniques for EEM analysis include identification of particular fluorophores independently, by assessment of the position of the fluorescence peak and intensity (“peak-picking”), and spectra subtraction for the evaluation of the relative changes in the fluorescence indicative of changes in organic matter quantity and quality (e.g., organic matter removal during the treatment processes). Therefore, to handle a large amount of fluorescence data, a more comprehensive approach is warranted, which both preserves the important topological and metric relationships of the fluorescence data and establishes the valid correlations between various process parameters. The most common techniques include different multivariate analysis tools from chemometric analysis (multi-way analysis: Principal Components Analysis (PCA), Partial Least Squares Analysis

(PLS), Parallel Factor Analysis (PARAFAC); Multiple Linear Regression (MLR), Multivariate Curve Resolution (MCR)) and other computation and modelling techniques such as Artificial Neural Networks (ANNs) and Fuzzy Logic.

In the current study the multi-way analysis method, N-PLS, was used to calibrate the fluorescence data characterizing water treatment works performance. TOC removal across the clarification stage (indicating organics removal efficiency) was derived from measured raw and clarified water TOC concentrations at each site, and then compared to change in fluorescence properties (EEMs of raw and clarified waters). N-PLS is the extensions of partial least squares method to multi-way data, in which the two-block model with both set of independent (fluorescence data) and dependent data (TOC removal) being decomposed simultaneously. The method was used to calibrate raw and clarified water fluorescence data with TOC removal. Additionally, a combined PARAFAC-N-PLS model was developed, in which the scores of the three PARAFAC components for raw and clarified water, were used to pre-process the original fluorescence data.

Thursday, 23 October

What's Next? Future Directions and Novel Applications

Session Chair: Darren Reynolds

The Technology – What's Next

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Continued innovation in fluorescence instrumentation provides new detection capabilities for a wide range of sample types. Some of the latest developments are summarised and their application to specific analyses are discussed. Examples from various research fields will be shown. (1) Array based visible and near infra-red spectrofluorimeters allowing fast excitation-emission matrix (EEM) acquisition are revolutionising the analysis of new materials such as carbon nanotubes. (2) New techniques for time resolved fluorescence analysis allows complete measurements to be made on the millisecond timescale, enabling such analyses to be harnessed for the study of reaction kinetics. (3) Combining fluorescence spectroscopy with confocal microscopy provides information with high spatial resolution (1 µm). Hybrid microscopic techniques such as combined Raman-TCSPC fluorescence offer even more detailed information about molecular and electronic structure.

Rainwater Fluorescence and the World of Humic-Substances

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Global rainwater dissolved organic carbon (DOC) flux has been estimated as 430 x 10^{12} g C yr^{-1}, yet little is known about the wide range of chemical compounds present, their sources, temporal patterns of variation, and the subsequent impact on climate and the environment. This presentation will (a) provide a summary of studies carried out in the field of atmospheric HUmic-LIke Substances (HULIS), rainwater DOC and fluorescence; and (b) provide an overview of results from a study carried out in Birmingham, U.K. between April 2005 and May 2007, whereby rainwater samples were collected and DOC compounds were analysed using fluorescence spectrophotometry. HULIS, TYrosine-LIke Substances (TYLIS) and TRYptophan-LIke Substances (TRYLIS) were identified. Peak fluorescence intensities and locations for each fluorephore were examined, and their relationship with various meteorological parameters were investigated. Results demonstrated that fluorescence spectrophotometry is a powerful means of fingerprinting rainfall DOC compounds in real time for small sample volumes.

High Resolution Measurements of Chromophoric Dissolved Organic Matter (CDOM) in Coastal Areas

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Chromophoric or Colored Dissolved Organic Matter (CDOM) has been used as a tracer for studying the sources, distributions, and transformations of dissolved organic matter in estuaries and coastal waters worldwide. CDOM fluorescence is an easily measured property of DOM that can be measured in the high temporal and spatial resolution necessary to observe coastal, estuarine, and watershed processes such as tides, tidal creek inputs, rain events, and sewage effluents. Over the last ten years, towed-vehicles combined with discrete sampling, moorings, and incubations have been used to study the distribution and characteristics of CDOM in a variety of United States Estuaries including the Mississippi River Plume, Atchafalaya Estuary, Chesapeake Bay, Delaware Bay, San Francisco Bay, San Diego Bay, Hudson Estuary, Boston Harbor, Neponset Estuary, and Plum Island Sound. CDOM has a variety of relationships with dissolved organic carbon (DOC), salinity, turbidity, and chlorophyll fluorescence in a variety of estuaries. In general, it has been found that: 1) freshwater CDOM endmembers vary with season, land use, and rainfall, 2) mixing of terrestrial CDOM with seawater is mostly conservative, 3) relationships between CDOM and salinity vary with season and between estuaries, and 4) significant inputs from coastal wetlands and sewage effluents affect CDOM distributions.

Overall, four-dimensional, high-resolution CDOM measurements have proven useful in illustrating several important processes controlling dissolved organic matter in estuaries. Through our studies, we have investigated the significance of coastal wetlands in DOM cycling, the impact of sewage in coastal environments, and the relationship between coastal watershed properties and coastal ocean optical properties. This presentation will highlight similarities and differences of CDOM distribution and behavior in a variety of estuaries.

Visualisation of EEM-based Water Quality Assessment via Google Earth

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The public domain Google Earth package provides a powerful, free software tool allowing users to view sections of the earth’s surface to a high degree of accuracy. The package provides access to aerial and satellite images, which can be viewed at continuously varying scales, and terrain may be viewed three-dimensionally. A key feature of the software is its ability to incorporate further geographically referenced data, using the Keyhole Markup Language (KML). This provides a flexible means of describing spatially referenced objects; for example, arbitrary images, sounds, or URLs can be linked to geographical locations, and may be retrieved via the Google Earth interface. This can be used as an intuitive tool for exploring spatial pattern in a wide variety of entities.

Here it will be demonstrated that Google Earth provides a useful tool for exploring Excitation-Emission Matrix (EEM) data resulting from fluorescence spectroscopy analysis of geographically-referenced water samples. Fluorescence spectroscopy is a technique allowing the chemical content of water to be determined. EEMs can be regarded broadly as a chemical 'signature' of a sample—different patterns of intensity corresponding to the presence of different chemicals in the sample. Intense areas in this diagram correspond to certain responses to excitation at certain wavelengths, and ultimately to the presence of certain chemical compounds in the water.

This suggests that combining EEM information with Google Earth is a useful approach—the aerial and satellite imagery provides contextual information about the paths of rivers—as well as the surrounding terrain, which will be useful in implementing the above approach. In addition to this, it provides a backdrop on which other kinds of related information may be added - for example, locations of factories or geological data. In this talk, issues relating to the visualisation of EEMs in a geographical context will be discussed, and a number of example applications will be shown.

ABSTRACTS

Poster Sessions: listed in alphabetical order by last name of First Author.

Investigating the Mechanism of Chlorine Quenching Fluorescence of Natural Organic Matter

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The presence of natural organic matter (NOM) in water can serve as precursor for disinfection by products (DBPs) formation in water treatment works (WTW) and water distribution systems. Because of its effect on public health, the control of NOM has been widely studied by many researchers. UV_{254} absorbance is routinely analysed within the water industry as an OM surrogate. In particular, the specific UV absorbance, SUVA, (defined as UV_{254} absorbance per milligram of organic carbon) has been also used as a surrogate for DBP precursors in potable water. Although commonly used, UV_{254} the use of a single wavelength can induce a potential random error. Furthermore, this method is incapable of explaining the complexity of NOM properties, the mechanisms of chlorination of NOM, the reaction pathways and many of the end products in potable water. In view of these limitations, some workers have successfully used advanced optical techniques such as fluorescence spectroscopy which provides more detailed information regarding the presence, characteristics and reaction of NOM in various types of water (e.g. river water, waste water, groundwater). More recently, this technique has been used in WTW to detect and predict DBPs production. One of the major concerns in using this technique, is that the intensity of fluorescence can be affected by a wide variety of chemical and environmental parameters such as changes in pH, temperature and the presence of chemicals such as metal ions.

The main goal of this study is to investigate the affects of chlorine on the intensity of NOM fluorescence in potable water. Known doses of chlorine (0.5, 1.0, 1.3, 1.7 and 2.1 mg/l) were added to partially-treated (pre-disinfected) water samples collected from geographically disperse WTW in different seasons. The chlorine concentrations and fluorescence intensities were measured simultaneously at specific time intervals until the chlorine residual in water depleted to below detection limits. Fluorescence was measured using a Varian Cary Eclipse fluorescence spectrometer; chlorine concentration was measured using Hach Pocket Colorimeters.

Results showed that for all chlorine concentrations, maximum quenching of fluorescence intensity of NOM is between 10-50% of the initial value, occurs instantaneously. As chlorine is allowed to deplete over several days, quenching decreases proportionally to chlorine concentration and for low initial chlorine concentration fluorescence intensity approaches the initial raw value. The data measured in this process provides a base of knowledge on the affect of chlorine quenching fluorescence of NOM in potable water and can be used as a valuable indicator of total organic halogens (TOX) formation resulting from chlorination.

Stream Colloids and Their Interactions with Coliform Bacteria

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Faecal bacteria derived from farmland are transported in large quantities during storm events. The rapid increase of in-stream coliform concentrations during high flow conditions is a key factor in determining marine bathing water quality. Colloidal particles, with a large surface area facilitating bacterial binding, may influence transport and viability, but factors influencing binding and release of bacteria from stream colloids are poorly characterized. We hypothesize that dilution of electrolyte and increasing shear forces during storm flows leads to separation of bacteria from colloidal particles, rendering them more readily transportable and less predisposed to sedimentation.

Novel flow cytometric approaches combined with fluorescent staining to differentiate between free and particle-bound bacteria were applied to mixtures of a laboratory strain of E. coli and colloidal suspensions of the two clays—a Montmorillonite and a Kaolinite. In flow cytometric analyses, the percentage of the fluorescent population (stained bacteria) representing small, simple structures increased from <10% (at different NaCl concentrations) up to 86%. This corroborates centrifugation based experiments which demonstrated that bacteria were binding to colloid particles and demonstrates the potential of this novel approach for quantitative study of bacteria-colloid interactions. Effects of changing electrolyte (NaCl) concentrations and shear forces are discussed.

Fluorescence and Disinfection Byproducts: Applications in the Drinking Water Field

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Dissolved organic matter (DOM) has been identified as the primary carbon precursor in DBP formation. Though much work has been done in relating TOC to DBP formation, the reactive fraction of the TOC responsible for DBP formation is not yet well understood. Five coagulated and filtered waters with varying water quality were used in a bench scale study to test DBP formation under common disinfection schemes; chlorination, booster chlorination, chlorine dioxide/chlorination and chlorination/chloramination. Samples were taken at a number of times after chlorination to investigate formation kinetics, and were analyzed for chlorine residual, THM and HAA concentrations and fluorescence intensity. The coagulated and filtered waters had higher fluorescence indices than the raw water indicating that the larger, more aromatic, "terrestrial" DOM is removed during these treatment processes. The fluorescence intensity of chlorinated waters decreased over time as fluorescing components within the DOM react with chlorine through oxidation, addition and substitution reactions. Parallel factor analysis (PARAFAC) was used to examine changes on the component level using the model developed by Cory and McKnight (2005). PARAFAC results showed that while all components showed a decrease in loading, the contribution of individual components changed over the chlorination period. The redox index (Miller, 2007) was also investigated and showed an increase in oxidation state of the chlorinated water through the change in the redox state of identified quinone components.

Understanding Physical Forcing of Biogeochemical Processes Using in situ Optical Measurement Systems

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Physical hydrodynamics such as tides, and currents, as well as variations in other physical forcings such as temperature, irradiation, wind speed and wind direction are important drivers for biogeochemical processes that shape the aquatic environment. But our understanding of the interactions between these forcings and biogeochemical processes is limited because of the difficulties in sampling—samples must be collected at sufficiently high temporal resolution to permit adequate analysis, and the duration of such samplings must be sufficient to cover the full range of environmental variation.
In situ optical instrumentation permits the explicit examination of such processes because they allow high frequency analysis of samples in situ over long deployment periods. In many cases, it is possible to relate the optical properties measured in situ to specific biogeochemical properties of interest. This linkage allows us to examine how physical, chemical, and biological processes interact directly in the environment, providing new insights into the temporal and spatial scales of environmental processes.

We have deployed a wide variety of in situ optical measurement devices in riverine, estuarine, wetland, and lacustrine environments, and found heretofore unreported variability in DOM concentration, composition, source, and turnover. The observed temporal and spatial variability is often related to physical forcing, but it may also be unrelated, or the relationship confounded. We will present data from a variety of our recent deployments to demonstrate the temporal and spatial scales of change in DOM composition, to provide examples of how these instruments may be useful in biogeochemical studies, and to stimulate discussion of difficult-to-understand data.

Fluorescence Characterization of Carbonate Aquifers in East Tennessee

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We conducted a preliminary spectroscopic characterization of fluorescent dissolved organic matter (FDOM) in carbonate aquifers of the southern Appalachians. Karst and fractured rock aquifers are primary community drinking water supply sources, and are inherently susceptible to contamination due to rapid recharge rates and preferential flow paths. This study investigated the utility of monitoring natural FDOM as a tool for managing and protecting sensitive groundwater basins.

Data was collected on the optical properties of 23 community water supply sources in East Tennessee. Wells and springs were relatively equally distributed between sites with high contamination potential versus those at relatively lower risk, as determined by topography, geology, hydrochemistry and land use. Seasonal, geographic, and diurnal variations in the intensity and excitation/emission wavelengths of FDOM were measured and correlated with precipitation, latitude, elevation, vegetation and soils. The fluorescent properties of some springs were observed to change over short intervals, while others exhibited little fluctuation regardless of time frame. The study was conducted under severe drought conditions, providing a reference for FDOM behavior at base flow. In general, fulvic acid-like spectral signatures prevailed in winter and spring months, while short wavelength, protein-like signatures dominated most groundwater sources during the warm season. Results indicate that comparative fluorescence measurements can reveal important information about the influence of vegetation, climate and other external factors on high-risk wells and springs, as well as on some low-risk sources.

Design of an Interlaboratory Study to Determine the Precision of Excitation Emission Matrices of Dissolved Organic Matter

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Three-D fluorescence measurement using Excitation Emission Matrices (EEMs) has become a useful tool for characterizing dissolved organic matter (DOM) in aquatic systems. The community of interdisciplinary scientists utilizing these data is increasingly concerned about data comparability due to differences in instruments, sample preparations, acquisition of data and data correction techniques. To address these concerns, an interlaboratory study was designed to determine comparability of fluorescence data obtained for a diverse set of samples. Participants in this study are representative of a diverse group of aquatic scientists with different applications for fluorescence analyses.

Solutions of seven samples, representing a range of types of DOM and having different salinities and carbon compositions, were sent to participating laboratories in duplicate to determine inter- and intralaboratory precision. Each laboratory (N = 20) analyzed the samples for UV absorbance, dissolved organic carbon concentration, and 3-D fluorescence using specified sample handling and data collection procedures. The raw blind data were forwarded, along with instrument correction factors, to a central

data manager. Analyses of quinine sulfate and Starna Fluorescence Reference cells with different excitation and emission ranges (#3 p-Terphenyl, #4 Tetraphenylbutadiene, #5 Compound 610, and #6 Rhodamine B) were also included in the reported data. To determine the degree to which instrument parameters and data correction factors influence comparability, participants were instructed to also analyze the samples using their own instrument parameters and to correct the resulting EEMs using their own correction techniques.

Fluorescence Properties of Dissolved Organic Matter (DOM) Produced by a Mixotrophic Dinoflagellate Alexandrium Fundyense

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Algae have been shown to release DOM during growth. Further, DOM from algal sources has been shown to have distinct chemical properties when analyzed with spectral techniques. At the same time some algal species, including harmful algal bloom (HAB) forming species, can be mixotrophs, i.e. they may be able to use DOM as a carbon source. We applied fluorescence spectroscopy to study DOM excretion and uptake by algae in surface waters. To elucidate the fluorescent properties of DOM produced by an HAB forming species we grew Alexandrium fundyense in laboratory culture and collected fluorescence excitation-emission spectra from samples of the culture medium. DOC concentration, total dissolved nitrogen, and cell density were also measured. Spectra were modeled using the Cory and McKnight (2005) PARAFAC model. An increasing DOC concentration, UV-vis absorbance, and fluorescence index value with increasing cell density indicate an increase in the amount and algal character of the DOM in the culture medium. Additionally, PARAFAC modeling showed an increase in the fluorescence loadings of several components associated with microbial DOM sources, including quinone-like components and a tryptophan-like component. These results show that fluorescence spectroscopy is an effective technique for tracking the composition of the DOM pool as it changes with algal inputs.

Applications for EEMs Spectroscopy in DOM Investigations

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EEMs spectroscopy has been a powerful tool for elucidating changes in DOM composition, source and insight into critical biogeochemical processes. Ongoing development of methods involving EEMs decomposition using various multivariate techniques (factor analysis, partial least squares, principal components analysis) to rapidly, reliably, and inexpensively characterize DOM in public drinking water sources are a boon to both investigators and water management agencies. Here we present the results of various multivariate analyses involving EEMs measurements to identify and quantify biogeochemical parameters and their variation. For instance, initial analysis of EEMs from a study in the Santa Ana Basin, California, USA indicated that there was a substantial amount of discriminatory, source-related information available. Deconvolution of the EEMs using a simple linear mixing model provided reasonable identification of DOM from different sources in the study. In another drinking water study based in the Sacramento–San Joaquin Delta, California, USA, investigation of disinfection byproduct formation potentials (DBP) due to chlorination, variation in EEMs were found to relate directly to the DBP formation potential as well as the chlorine demand for disinfection. Finally, we present results from the same study involving lignin phenols. Lignin phenols are powerful biomarkers with laboratory analyses that are complex, time consuming and costly.

Here we present a series of cross-validated Partial Least Squares models that use EEMs properties to explain up to 94% of lignin compositional and concentration variability in samples collected seasonally over two years in the study area. With adequate cross validation and calibration, similar models could be used to significantly expand our ability to study sources and processing of DOM in many surface water systems.

Fluorescence of Selected Organic Matter: Effect of Concentration, Ionic Strength and pH

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Initially used for the qualitative characterization of organic matter and monitoring of changes in ecosystems, currently fluorescence spectroscopy is also becoming a tool for the quantitative characterization. For the latter, sample handling procedures, standards, calibration and analysis techniques are being studied with the aim to develop a reliable methodology. The results presented in this poster show the effect of concentration, ionic strength and pH on the outcome of fluorescence tests performed with selected organic matter (OM): Albumin, SRFA (Suwannee River Fulvic Acid), SRHA (Suwannee River Humic Acid), Tryptophan and DSR–Florida strait (Deep Seawater Reference material, 700 m depth). It is observed that these parameters exert significant changes in the intensity of the results, which becomes important when quantification of the OM is desired (e.g. using Parallel Factor Analysis). The results of this research will contribute to the selection of standards, the construction of calibration curves and the formulation of a quantification method.

Dissolved Organic Matter in the Arctic Ocean Modeled by PARAFAC

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Dissolved organic matter (DOM) is a complex mixture of compounds derived from the decomposition of dead organisms, phytoplankton activity and inputs from rivers, and can come from both terrestrial and marine sources. Although the Arctic Ocean only comprises ~1% of the global ocean volume, it receives about 10% of the global river discharge. Therefore, a greater influence of terrigenous organic matter from the river discharge is expected in the Arctic Ocean than in other ocean basins.The ability to differentiate and quantify the source of DOM is hence critical to understanding the carbon cycle in the Arctic Ocean. In this study, the nature and origin of DOM in the Arctic Ocean was investigated using parallel factor analysis (PARAFAC) of excitation-emission matrix. Detailed spectral analysis revealed significant variation in DOM composition with depth. The spatial distribution of the main components of DOM will be discussed in relation with water masses.

Freeze Fractionation of Fluorescent Dissolved Organic Matter During Sea Ice Formation

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Sea ice plays an important role in heat flux mechanisms of the oceans such as air-ocean interaction, thermohaline mixing and albedo feedback. In addition, the brine channels of sea ice serve as a habitat for various organisms. A main factor controlling the biology of sea ice, but also optical properties, is dissolved organic matter (DOM) which is strongly influenced by the initial freezing process. Therefore, the behavior of DOM during the ice formation needs to be described in detail to allow predictions about the character and concentration of DOM in sea ice.

This study about the freeze fractionation of DOM from the Gulf of Finland used 450 liter tanks to grow sea ice at -5°C. The initial conditions were compared to the ice and under-ice water by measuring the absorption coefficient of chromophoric DOM, fluorescent DOM and the size distribution of DOM. Excitation-Emission Matrices (EEMs) of DOM fluorescence were used for parallel factor analysis (PARAFAC).

In order to investigate the behavior of DOM relative to salts, an enrichment factor was calculated for CDOM and FDOM for the initial water samples and one week after ice formation. The mean enrichment factor was found to be 1.4 in ice whereas 1 in under-ice water which means that enrichment only took place within the ice. The size exclusion chromatography shows a shift in size distribution towards higher molecular size in ice. This change is less obvious for young ice and hence depends on physical processes during the ice formation and growth. The components identified by PARAFAC behave differently during the freeze fractionation, but were always enriched in the ice relative to salts. The tank experiment leads to the assumption that the freeze fractionation of DOM depends on molecular size, composition of DOM and physical processes such as diffusion and convection.

Exciting Effluent: Fluorescence as a Tool for Detection of Cross-Connections in Dual Reticulation Water Supply Systems

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The increasing demand for recycled water supply to urban areas has led to the increasing implementation of dual reticulation systems for the delivery of non-potable recycled water in Australia. These schemes, where recycled water is delivered via a piping system separate to potable water, have been observed to have inherent risks associated with their construction and maintenance. The risk of cross-connecting potable and non-potable water sources has been recognized as an on-going problem requiring improved management. Cross-connection events risk serious health implications and undermine public confidence in such recycled water schemes.

Fluorescence excitation-emission matrix (FEEM) spectroscopy shows great potential as a tool for detecting cross-connection events, as the sensitivities are far greater than the various alternative techniques that are currently widely available. The aim of this ongoing work is to develop FEEM spectroscopy into a fast, reliable technique, able to detect small amounts of recycled water within potable water supplies.

A 12-week sampling regime was undertaken at a dual-reticulation scheme in western Sydney, and analysed using FEEM spectroscopy along with other water quality parameters such as UV absorbance, pH, conductivity, turbidity, chlorine residual and total organic carbon (TOC). FEEM spectra were obtained using a Varian Cary Eclipse Fluorescence spectrometer, with excitation wavelengths of 200-400nm and emission wavelengths of 280-500nm. Peak-picking, peak ratios and multivariate data analysis methods are being compared for their utility to distinguish between sample types and stages of treatment processing. The technique was also used to detect low concentrations of recycled water within potable water samples in a laboratory environment. Currently, more sampling schemes are being undertaken at dual reticulation schemes across Australia to further investigate its capabilities as a rapid, reliable method of cross-connection detection.

Linking the Fluorescent Fingerprint of Recycled Water to Organic Matter Character

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The reuse of treated municipal effluents (recycled water) is an increasingly important strategy in many urban centers as water scarcity and rising populations drive sustainable practices. Treated effluents are being applied to applications with variable degrees of intended and unintended human contact including irrigation, toilet flushing and the recharge of potable supplies. These applications carry variable risks in terms of potential contamination of potable water supplies with sewage-derived dissolved organic matter (DOM). A sensitive technique is thus required to trace and characterize sewage-derived DOM in potable water sources. Fluorescence excitation-emission matrix (FEEM) spectroscopy has shown promise in this regard. The aim of this research was to compare the information acquired from rapidly obtained FEEM spectra and more laborious organic matter characterization techniques that are undertaken to determine process performance and aid optimisation.

Advanced-treated effluent was examined using FEEM spectroscopy, XAD resin fractionation to obtain hydrophobic and hydrophilic portions, and size fractionation by both ultrafiltration and size exclusion chromatography. It was observed that peak intensities at approximately $\lambda_{ex/em}$=325/425 nm and $\lambda_{ex/em}$=290/350 nm were reduced in lower size fractions. In contrast, peaks observed at excitation wavelengths of 225 nm were unaffected. Accordingly, it was determined that analysing such peak ratios from FEEM spectroscopy allows a rapid assessment of organic matter size distribution. The majority of fluorescent matter was contained within the hydrophobic portion of the DOM and no proteinaceous-like fluorescence was observed in hydrophilic acid or neutral fractions. Importantly, the FEEM of hydrophobic neutral and acidic fractions was very different. For example, tryptophan-like fluorescence was almost exclusively present in the hydrophobic neutral fraction.

In conclusion, examination of FEEM fingerprints of residual organic matter can provide rapid, valuable insights into DOM character from an operational perspective. With further studies and increased characterization, it is expected that this tool may prove to be a robust surrogate measure for use in place of traditional labour-intensive characterization experiments.

Fluorescence-Based Proxies for Lignin in Dissolved Organic Matter

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Lignin phenols have proven to be powerful biomarkers in environmental studies, however, the complexity of the lignin analysis limits the number of samples and thus spatial and temporal resolution in any given study. In contrast, spectrophotometric characterization of dissolved organic matter (DOM) is rapid, non-invasive, relatively inexpensive, requires small sample volumes and can even be measured in-situ to capture finescale temporal and spatial detail of DOM cycling. Here we present a series of cross-validated Partial Least Squares models that use fluorescence properties of DOM to explain up to 94% of lignin compositional and concentration variability in samples collected seasonally over two years in the Sacramento River/San Joaquin River Delta in California. These models were subsequently used to predict lignin composition and concentration from fluorescence measurements collected during a diurnal study in the San Joaquin River. While modeled lignin composition remained largely unchanged over the diurnal cycle, changes in lignin concentration were much greater than expected and indicate that lignin cycling in rivers may be much more dynamic than previously thought. With adequate calibration, similar models could be used to significantly expand our ability to study sources and processing of DOM in complex surface water systems.

Characterizing Dissolved Organic Matter in a Brackish Lake of the Yangtze River Delta by Using Fluorescence Technology

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Natural organic matter (NOM) is an important chemical component in rivers and lakes. NOM from the Yangtze River can enter an estuarine brackish lake (Beihu Lake) through the floodgates and undergoes poorly understood complex reactions. Dissolved organic matter (DOM) in Beihu Lake in the Yangtze River Delta was characterized by using fluorescence technology. The results showed that the concentrations, sources and composition of DOM varied seasonally, and were influenced by water scheduling. The concentrations of DOM in the Beihu Lake in summer were higher than those in spring, and higher than those in autumn and winter. Due to the input of terrestrial freshwater in summer, sudden increase of DOM in the lake caused strong fluorescence signal of humic-like fraction, which was found to be weakened in autumn. Such removal behavior could be attributed to the photochemical degradation and/or microbial decomposition, which would release nutrient and promote primary production.

However, a significant protein-like fluorophore in spring algal blooms could be derived from the metabolism of algal. In general, DOM in the lake water showed an additive behavior in spring and a removal behavior in summer. The characteristics of DOM behavior would be beneficial to understand the algal dynamics in this brackish lake.

Biological and Chemical Processing of River Organic Matter Observed Through Changes in Organic Matter Fluorescence and Water Chemistry

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Organic matter is known to be processed within rivers, from source to sea, through a combination of microbial and (photo-) chemical processes. Analysis of changes in water chemistry and the fluorescence intensities of 4 common fluorophores, derived from excitation-emission-matrices (EEMs), are expected to indicate trends in organic matter alteration.

We report results from 5 river waters from central England which were filtered to obtain i) unfiltered, ii) the colloidal/ dissolved, and iii) filter sterilized fractions and were stored under a range of conditions (4°C dark, 11°C light/dark, 11°C dark, and 20°C dark) to reflect natural environmental conditions. Over a period of 26 days organic matter was routinely characterised by fluorescence analyses and organic matter concentration was measured by TOC. Dissolved oxygen, pH, conductivity and counts of colony forming units, on plated samples stored under identical conditions, were also recorded.

Fluorescence analyses demonstrates that waters undergo significant variations in response to light and temperature and that organic matter may be highly influenced by source, size fraction, and storage condition, suggesting a complex range of organic matter characteristics. Bacterial abundance is not influenced by environmental conditions to the same degree and a poor relationship exists with tryptophan-like fluorescence, suggesting an alternative source of this fluorophore. This work illustrates the dynamic character of river organic matter which impacts upon our understanding of carbon cycling in the environment and sample storage stability prior to laboratory analysis.

Changes in Organic Matter Fluorescence Intensity Associated with Freezing/Thawing and Dehydration/ Rehydration: Implications for Sample Storage

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Freezing is sometimes used as a method of sample preservation, particularly when sample sites are remote from laboratories as it is believed that the freezing process does not substantially affect the fluorescence of the organic matter present. This work investigates changes in fluorescence intensity in natural waters as a result of one or multiple cycles of freezing and thawing. Data is also presented for single and multiple cycles of dehydration and rehydration (although this is not a common method of sample storage for liquid samples).

Samples analysed included 13 river waters from Central England and laboratory water. The samples were decanted, with no pre-treatment, into bottles for freezing and Petri dishes for dehydration and were subjected to 5 cycles of freezing/ thawing and dehydration/ rehydration. After each cycle the frozen samples were thawed and analysed by fluorescence analysis, dehydrated samples were rehydrated with 18M? deionised water before fluorescence analysis. The fluorescence intensities of four common peaks (tryptophan-like T1 and T2 and humic-like A and C) derived from fluorescence excitation-emission-matrices (EEMs) were recorded.

Fluorescence intensity in samples which have been frozen and thawed (either once or over a number of cycles) is found to demonstrate a common reduction in fluorescence intensity for all peaks, although the extent of change is not consistent. This suggests that organic matter is substantially altered by freezing and that, for this reason, freezing is not a suitable method of sample preservation for fluorescence analysis. In addition, dehydration and rehydration are found to affect the fluorescence intensity of the 4 common peaks. In all cases the degree of change in fluorescence intensity is not associated with, and cannot be predicted by, the original chemical character of the water.

Characterizing the Dynamics of Dissolved Organic Matter in the Florida Coastal Everglades by Fluorescence Analysis

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In this study, an extensive sampling and analysis of DOM quantity (TOC) and quality (EEM-PARAFAC) was applied in the Florida coastal Everglades, in an attempt to better understand the dynamics of DOM in this landscape. DOM in surface and groundwater, dominant vegetation and soil leachates were characterized using EEM-

PARAFAC and potential degradation processes were assessed through bio-and photo-degradation studies. Field studies revealed spatial and temporal variations of DOM quantity and quality in this system. Compositional changes in DOM along a North-to-South transect throughout the entire Everglades ecosystem were observed, suggesting higher soil derived DOM contributions at the most Northern, agriculturally impacted areas and a switch to more biomass derived DOM towards the less impacted Southern Everglades. Increased microbial source loadings in estuarine areas of Florida Bay were observed during the peak summer months, and are believed to be associated with peak primary productivity of seagrass communities. In contrast, the highest relative abundance for humic components was observed during late summer to fall, suggesting a hydrologic control for this parameter. Photo- and bio-degradation of plant leachates readily showed that the combination of both processes was most effective in promoting DOM compositions similar to those in natural surface water of the Florida Coastal Everglades, while groundwater in the region showed a different composition.

While the data generated in this study make a significant contribution to our better understanding of the environmental dynamics of DOM in this ecosystem, the data presented here also highlight the applicability of EEM-PARAFAC and other fluorescence determinations in DOM biogeochemical studies.

Optical Characterization of Dissolved Organic Matter in Tropical Rivers of Venezuela

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Fluorescence spectroscopy, particularly EEM-PARAFAC, has shown an enormous potential to not only characterize the composition of DOM but also to assess complex environmental dynamics of this important carbon pool in the greater context of carbon cycling. In this particular study, optical measurements including EEM-PARAFAC were applied to surface water samples from three tropical rainforest river watersheds, expected to be mainly controlled by soil and higher plant derived DOM. The fluorescence index values clearly reflect a primarily terrestrial, humic signal for the DOM, with some very low values (1.0-1.2) which may represent highly diagenetically reworked OM sources. In agreement with this observation, EEM-PARAFAC analyses revealed the presence of five fluorescent components in the DOM of these water samples, tentative assignments to humic type materials with only one component representing proteins.

However, even with such strong allochtonous sources, and in quite similar tropical rainforest environments, principle components analyses of the PARAFAC data statistically set the riverine DOM apart in composition as controlled by source, lithology, geomorphology and degree of degradation.

Tracing Groundwater-Surface Water Processes in a Chalk Catchment Using Fluorescence Properties of Dissolved Organic Matter

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Understanding the nutrient movement within catchments is important for effective environmental management of river and wetland ecosystems. The fluorescence properties of groundwater and surface water (including a waste-water outlet) samples were examined in a Chalk catchment to investigate the use of dissolved organic matter (DOM) as a natural tracer of groundwater-surface water interactions and to 'fingerprint' sources of DOM within the groundwater and surface water system. Fluorescence centres were observed in fulvic acid-like and aromatic protein-like regions of the emission-excitation matrix in both groundwater and surface water samples. A decrease in the fluorescence intensities of the fulvic acid-like material was observed with depth (down to 25m) in the Chalk interfluve and adjacent to the river highlighting the role of the soil zone as an important source of DOM. Groundwater from gravels adjacent to the river show a signature that is a mixture of both members, i.e. deep groundwater and the surface water. Samples from sand deposits adjacent to the river show less of a river signature (i.e., less connectivity) than the gravel aquifers. There appears to be little evidence to suggest that there is a significant source of DOM in the shallow groundwater system (from animal waste sources) emanating from a cattle barn adjacent to the river, and that the sewage outlet is the main source of DOM within the river system down stream. These findings corroborate the conceptual model of groundwater movement and demonstrate the potential of intrinsic fluorescence as a natural tracer for investigating groundwater-surface water interactions.

Characterisation of Landfill Leachate Age Using Fluorescence Excitation-Emission Spectra

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Leachate is formed primarily by the percolation of rainwater though waste material in a landfill. The biogeochemical composition of leachate is transient, as it is fundamentally dependant on the composition of waste, its age, and its relative stage of decomposition. Dissolved organic matter (DOM) is a ubiquitous substance in leachate and is commonly used to characterize leachate composition and age. The fluorescent properties DOM are currently being utilized in aquatic environments as a quick and non destructive method of identifying fluorescent groups as discrete novel fingerprints using the presence of specific or unique fluorescent centres (fluorophores) to identify and differentiate point and non-point sources of DOM, particularly in estuarine coastal waters. Existing literature shows that little has been documented by way of leachate fluorescence. This research therefore seeks to use fluorescence spectroscopy to characterize the age of the leachate by the relative occurrence and intensity of different fluorescent centres.

A selection of eleven municipal solid waste (MSW) leachates of varying origin and age were obtained from landfill sites across the UK. Leachate quality was investigated using water quality parameters of pH, COD, TC, IC and TOC. 3-dimensional excitation-emission spectra (EEM) scans of the leachates were also produced to identify and characterise the fluorophores. Excitation wavelengths were incremented at 10nm intervals from 190nm-800nm, and emission wavelengths detected from 200-800nm in 2nm increments. The 3D EEM spectra compiled for the leachate samples showed between 0 and 6 main centres of fluorescence, depending on the sample. These peaks were located in regions defined by excitation/emission wavelengths: (region 1) 217-225/290-300, (region 2) 225-245/335-370, (region 3) 215-250/435-455, (region 4) 275-305/315-375, (region 5) 315-355/415-450 and (region 6) 475-505/510-520nm.

From the compilation of experimental results it was observed that carbon concentration was positively correlated with fluorescence intensity which indicates that fluorescence is directly related to organic abundance. The two leachates (H and K) that yielded the lowest COD and concentrations of carbon demonstrated discrete fluorophore locations covering regions 1 to 6 and the lowest levels of fluorescence intensity. This may indicate the presence of high molecular mass humic acids which are less fluorescent. Thus leachates H and K may be described as aged leachates as the high molecular mass humic acids increases as the amount of degradable material decreases progressively with age.

The highest levels of COD and TOC (generally in excess of 1000mg/L and 460mg/L carbon, respectively) were observed in leachates A to C. The location of fluorophores within these leachates extended over the regions 2-5. The fluorophores yielded the highest intensities (up to 190 activity units) in regions 3 and 5 which are generally associated with humic acid-like and fulvic acid-like substances.

The occurrence of discrete well defined fluorophores in regions 1 and 4, with varying intensity, were visible in the remaining six leachates. These fluorophores are generally associated with protein-like materials such as tryptophan and tyrosine. These are products of further degradation of the initial humic and fulvic like products. This therefore suggests that these leachates are older than leachates A to C which primarily show humic and fulvic-like fluorescence, but younger than leachates H and K.

In conclusion, fluorescence spectroscopy in combination with other common laboratory tests appears to generate information which can be used to characterize the age of the leachates. Further work is required to provide more data on the nature of the relation of total organic carbon to fluorophore location and its associated DOM constituents.

A Simple Thin-layer Water CDOM Sampling Strategy in Shallow Coastal Waters

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A new simple method of sampling was devised to collect thin-layer water aboard a medium size research vessel. The purpose of this study is to determine how CDOM concentration in thin-layer surface water varies with sampling location in the research vessel and with bottom depth. A thin-layer (chromophoric dissolved organic matter) CDOM bottle sampler (TLCBS) was used to collect water in the bow and stern sides of the vessel in the upper ~ 2.4 cm of the surface water during the South Florida Quarterly Hydrographic Survey. This sampler can collect an average of 68 ml/s of thin-layer surface seawater. CDOM concentration of the water collected using this method was compared to existing method (i.e. Niskin). Results showed no significant difference exist between the NISKIN sampled CDOM concentration from the stern and bow collected water using the TLCBS at depths >10 m. CDOM signals were significantly diffferent at depths <5 m between sampling means (NISKIN vs. TLCBS) and between ship sampling locations (bow vs. stern). Although, CDOM concentration has been observed to decrease with increasing salinity, bottom depth appears to influence the CDOM variability in the immediate thin-layer surface and lower surface (< 1 m) water. This observation could have an implication in the actual CDOM concentration in shallow coastal water where bottom sediment containing high CDOM gets easily disturbed from boat propellers and wave action. Using TCLBS, it appears to minimize external sources to the natural CDOM signal in shallow water sampling sites.

Reactive Transport Modeling of Dissolved Organic Matter in an Alpine Lake

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In alpine lake and stream ecosystems, the source and chemical character of dissolved organic matter (DOM) changes rapidly during the spring and summer. During snowmelt there is a large terrestrial source of recalcitrant, aromatic, humic DOM to lake ecosystems; whereas later in the summer season, when phytoplankton growth is greatest, there is a greater contribution of non-humic microbially derived DOM. Loss of DOM from the lake can be from heterotrophic uptake by bacteria and degradation by UV light. On the other hand, both non-humic and humic DOM can be produced within the lake through direct microbial release and decay of organisms from higher trophic levels.

This study characterized the source and chemical character of DOM during the summer growing season in an alpine lake using fluorescence spectroscopy and PARAFAC modeling. Moreover, a new approach was developed to separate the DOM into three pools based on source and reactivity. A reactive transport model for the lake was developed to investigate temporal changes in the relative contribution of the three DOM pools over the course of the season. Results indicate that production of non-humic DOM is strongly dependent on the concentration of chlorophyll a in this low productivity system. Model simulations suggest that the decay of aromatic terrestrially derived humic DOM is strongly dependent on photochemistry. Conversely, decay of the non-humic and the less conjugated algal derived humic DOM fractions is influenced by heterotrophic degradation. The chemical quality of the algal derived humic fraction also appeared to influence degradation, when the algal derived humic fraction was highly oxidized the degradation appeared to decrease, suggesting a lesser availability to microorganisms as an energy source.

Making Connections Between Water Soluble Organic Compounds and Organic Aerosol Columnar Properties Using Fluorescence Spectroscopy

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Understanding the chemical composition of organic matter in the atmosphere is of great interest because of its role in the radiative balance of the atmosphere as well as the influence of organic aerosol deposition on the quality of oligotrophic lakes. Water soluble organic compounds (WSOC) in aerosol deposition have been found to exhibit fluorescence and absorbance properties similar to humic substances. Here, we present a novel view on the fluorescence of WSOC using recent advances in fluorescence characterization with PARAFAC modeling. With this approach, we examined seasonal changes in the distribution and redox state of fluorophores of WSOC from active (high volume air sampler) and passive (wet and dry deposition) aerosol samplers in the Sierra Nevada mountains (Spain) and in a contrasting urban setting, Granada (Spain). We further explored the relationships between fluorescence properties of aerosol WSOC and aerosol columnar properties, such as aerosol optical thickness, particle size distribution, and albedo, to determine whether the methods of one discipline can be used to inform another. Our results indicate that reduced quinone-like fluorescence is more dominant during Saharan dust deposition periods while protein-like fluorescence increases with the increased occurrence of marine air masses. Furthermore, significant relationships between both quinone-like and protein-like fluorescence and aerosol optical depth showed that columnar measurements and fluorescent properties can be used together to provide insight into the sources of organic aerosols.

Issues in the Use of Fluorescence Spectroscopy to Trace and Quantify Agricultural Pollution From Both Diffuse and Point Sources

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Animal wastes such as slurry and manure show characteristic fluorescence signals which are high in “tyrosine-like” and “tryptophan-like” fluorescence. It is, therefore, hypothesised that agricultural losses following the application of animal slurry to land can be traced and potentially quantified using fluorescence spectroscopy. Experimental work was carried out at the Rowden site at North Wyke Research, Devon, U.K. Here, we were able to sample the drainage waters during storm events from both undrained and drained 1-Hectare grassland plots following slurry spreading. Samples were filtered in the laboratory and both fluorescence and absorbance were measured within 24-48 hours of sample collection. Decay of the fluorescence signal of the applied slurry was also monitored week-by-week. Instrument and inner-filtering (based on absorbance measurement) corrections were applied to the fluorescence data before fitting a PARAFAC model.

The results are assessed in terms of both their ability to trace slurry-derived material and prospects for quantification. Finally, the work is put into the context of a small headwater catchment and direct agricultural losses from a hard-standing area.

Evaluation of Fluorescent Whitening Agents as indicators of Anthropogenic Wastewater Discharges in the Columbia River, USA

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Fluorescent whitening agents (FWAs) are industrial fluorophores that are designed to absorb UV radiation and emit visible blue light. They are used in commercial laundry detergents to improve the appearance of clothes and in manufacturing to enhance the whiteness of paper products. Since FWAs are introduced into the environment via wastewater, they are potentially excellent indicators of sewage or industrial discharges to aquatic environments. In order to determine the potential for FWAs to be indicators of wastewater in the lower Columbia River, we first measured the rates of photo-degradation, as this is the primary removal process of the fluorescence signal. Laboratory measurements showed that photo-degradation significantly lowered the fluorescent signal of commercially available FWAs, however their excitation and emission wavelengths were not altered and therefore the fluorescence fingerprint remained intact. In addition, changes in salinity did not alter the rates of photo-degradation compared to freshwater samples. Subsequently, we conducted field sampling over a 150 km transect from the Columbia River Estuary to Portland, Oregon. Samples were collected upstream and downstream of urban and industrial regions. The results from excitation/emission scans showed that variations in fluorophore activity at some sites (downstream versus upstream) were indicative of the addition of fluorescent compounds that could be distinguished from common CDOM components and indicative of FWAs. This study suggests that monitoring for FWAs by fluorescence spectroscopy has the potential to be an effective method of wastewater detection in large rivers.

Fluorescence of Colored Dissolved Organic Matter at JOBANERR, Puerto Rico

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We report characterization of fluorescence components at Jobos Bay National Estuarine Research Reserve, a mangrove-lined embayment, using the Excitation Emission Matrix technique. Five components are identified in this area. The principal peak, component A, exhibits excitation at 350 nm and emission at 442-446 suggesting the presence of terrigenous humic material. Component B: (320-325) Ex / (436-439) Em is associated with anthropogenic humic matter. Component C: 315 Ex / (395-437) Em is also related to anthropogenic humic matter but is present only in enclosed mangrove areas. Component D: (290-305) Ex / (399-446) Em may be produced by microbial decomposition and is present with high fluorescence intensity in enclosed mangrove areas as well. This component is also present in offshore waters but exhibits lower fluorescence intensity. Component E: (265-275) Ex / (304-455) Em is also related to humic matter. Fluorescence intensity of components A, B and E decrease towards offshore waters. The components present in the bay are principally photolabile matter as they appear to undergo photodegradation during transit through the bay.

New Criteria for the Characterisation of Fluorescent Dissolved Organic Matter in Aquatic Environments

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The aim of this work was to apply fluorescence spectroscopy for the study of different aquatic environments in order to investigate the evolution of coloured dissolved organic matter (DOM) properties during estuarine mixing. Samples from various environments (aquatic ecosystems such as freshwaters, seawaters and estuaries) were studied. The humification index (HIX), introduced by Zsolnay et al. (1999) in order to estimate the maturation of DOM in soils, was applied to aquatic environments. Referring to this index, we built another parameter BIX to characterise the recent autochthonous production of fluorescent DOM in aquatic environment. A number of samples from various aquatic ecosystems were studied. Spatial and temporal variations of DOM spectroscopic properties were investigated. Fluorescent DOM exhibited specific trends in the studied estuaries (especially Gironde, Loire and Seine estuaries in France) depending on environmental conditions (salinity, maximum turbidity zone (MTZ), seasons) and in marine waters (especially in Atlantic Ocean). Seasonal variations of fluorescent DOM were observed. This work showed that the HIX and BIX indices were particularly well adapted to the characterisation and classification of fluorescent DOM in marine and coastal environments. The number of samples studied from different environments (freshwaters to pure marine waters, under various conditions) allowed us to draw up a scale of values for each index. These new criteria for the characterisation of fluorescent DOM in aquatic environments can be proposed as an easy way to define and classify DOM characteristics in such ecosystems.

Effect of River Floods on Marine Organic Matter Fluorescence

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The goal of this study was to characterize the organic matter inputs from a small river (Eygoutier River) into the Mediterranean Sea (Toulon Bay). We studied the organic matter inputs during the lowest water levels of the river and its floods for two years (2004 and 2005). This work showed that the fluorescence intensity ratios as well as the HIX and BIX indices were particularly well adapted to the characterization and classification of colored dissolved organic matter (CDOM) in marine and coastal environments. The increase of terrestrial CDOM inputs in seawater was very well correlated with the increase of the river flow. Samples were collected every hour from the very beginning of the first rain for each flood. The influence of floods on Mediterranean coastal water CDOM was mainly detected on surface water samples. Major modifications of the quality and quantity of CDOM were observed. CDOM was notably characterized by higher HIX values. This index appeared to be a good indicator of the impact of the floods in seawater. Even if the effects were less significant for the deep water samples, we could observe some modifications of CDOM due to the flood inputs. The terrestrial inputs did not reach however the most remote sites studied.

Transformation Processes of Colloidal Organic Matter at Superficial Sediment Interfaces

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The maximum turbidity zone (MTZ) of an estuary is especially characterized by intense cycles of settling and resuspension of anoxic mud fluid. Moreover dissolved organic matter (DOM) accumulates in the MTZ where it has a longer residence time and is then submitted to flocculation and sedimentation processes that modify the size distribution of the macromolecules during the transit of organic material to the marine medium. Due to intense diurnal, tidal and seasonal cycles as well as to high organic matter amounts, superficial sediments are submitted to a lot of redox oscillations and show a great reactivity. The role played by the colloidal fractions is of great interest to understand the variability of sediment reactivity during these oxic/anoxic cycles. The aim of this study was to simulate in vitro series of oxic/anoxic cycles in coastal and estuarine superficial sediments. The forcing parameters studied in the experiments were mainly aerobic and anaerobic conditions. Gas allowed moving suspended sediment from oxic to anoxic conditions, and vice versa. Continuous measures were possible in both gaseous and dissolved phases. Fine superficial sediments from the Arcachon Bay and from the Adour Estuary (South western France) were collected as marine and estuarine samples respectively.

A detailed study of DOM fluorescence behaviour during oscillating oxic/anoxic conditions is reported here. As DOM is a mixture of organic macromolecules with a broad range of molecular size and weight it was fractionated according to molecular size by using tangential-flow ultrafiltration. Each isolated fraction (filtrate and retentate) was then characterized using EEM spectroscopy. This study showed significant modifications of DOM during oxic/anoxic oscillations.

Measuring the Temperature Influence on Organic Matter Fluorescence

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The fluorescence signal of water samples is known to be highly influenced by internal and external factors, especially storage and measuring temperature. This study focuses on the effects of temperature on fluorescence intensity (called thermal quenching), specifically the protein-like (peak T) and humic-like (peak C and A) fluorescence, for samples collected from different sources (urban and rural rivers), and at one rural site at monthly intervals to assess seasonal variations. The effect of temperature has also been investigated at temperatures below 10°C for the first time. All samples have been measured in triplicate, and both filtered and unfiltered. Previously published work on thermal quenching is also reviewed. Fluorescence intensity increase with approximately 20% has been noticed for all fluorophores when sample temperature decreased from 20°C to 0°C, similar to previously published work. Tryptophan-like fluorescence tends to have different temperature sensitivity than the humic substances. Seasonal variations in humic-like thermal quenching were observed, suggesting that thermal quenching can provide useful information on changes in organic matter character through time. No difference in temperature sensitivity was observed when temperatures approached 0°C.

Continuous Monitoring of Dissolved Organic Matter Fluorescence in an Urban River

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It has been proven that the concentration of dissolved organic matter in rivers can vary annually and seasonally. Recent work brings us into attention the fact that dissolved organic matter may also have a diurnal variability. Continuous monitoring of DOM character and concentration at hourly resolution are rare, despite the importance of analysing organic matter variability at high temporal resolution in order to evaluate the river carbon budgeting, river water health by detecting episodic pollution, and to determine short term variations in chemical and ecological function. We report a two week experiment performed on riverine DOM sampled from Bournbrook, Birmingham, U.K., an urban river for which spectrophotometric (fluorescence, absorbance), physiochemical (dissolved organic carbon, electrical conductivity, pH) and isotopic (D/H) have been measured at hourly frequency. Our results show that the river had sub-daily variations in both organic matter concentration and characteristics. After rain and snow events, organic carbon concentration increased, with an associated increase in intensity of both humic-like and tryptophan-like fluorescence. D/H isotopic ratio demonstrates different hydrological responses to different rainfall events, and organic matter character reflects this difference.

Optical Properties of Seawater High-Molecular-Weigh Ultrafiltered Dissolved Organic Matter

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Absorption spectra (250–700 nm) and fluorescence excitation–emission matrices (EEm) of high-molecular-weight dissolved organic matter (HMW-DOM) concentrated from riverine, coastal, and open ocean water samples have been composed. HMW-DOM was obtained by cross-flow ultrafiltration and represents the size fraction of DOM between 1 kDa and 0.2 μm. These materials were concentrated from the Delaware River, Chesapeake Bay, Vineyard Sound, West Neck Bay, the Pacific subtropical gyre at Hawaii (surface and 600 m) and the Black Sea (surface, 90 m and 750 m).

C-specific absorption coefficients at 340 nm, log-linearised absorbance spectrum slopes, C-specific fluorescence intensities for different humic- and protein-like fluorophores, and apparent quantum yield of fluorescence (fluorescence-to-absorption ratio) for each HMW-DOM sample are obtained and the differences observed are discussed. HMW-DOM of diverse origins displays contrasting optical properties, which are the reflection of different complex mixtures of chromophores and fluorophores. The intensity of humification and/or photodegradation processes experienced by each water mass amends the optical properties of HMW-DOM.)

Use of Fluorescence to Understand the Reactivity of Organic Matter

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The use of fluorescence spectroscopy has been used to characterize natural organic matter in the environment. Both steady state emission and three-dimensional fluorescence have been used to identify chemical signatures of different groups and the relative contributions of these groups. The ability to identify and quantify these groups also offers the advantage of understand the reactivity of organic matter towards physicochemical processes, including oxidation. As part of ongoing investigations with regards to the treatability of organic matter during water treatment, we have used fluorescence (specifically the fluorescence index) to correlate the second order reaction rate constants for the reaction between hydroxyl radical (OH) and organic matter. A positive correlation indicated that as the fluorescence index increased, the reaction between OH and organic matter became faster. This application is of importance during the study of the effect of organic matter on the use of advanced oxidation technologies for water and wastewater treatment.

Characterization of Natural Organic Matter in Drinking Water Treatment Processes and Trains Using Fluorescence and PARAFAC

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Natural organic matter (NOM) causes adverse aesthetic qualities in drinking water such as colour, taste and odour; it produces undesirable disinfection by-products; it impedes the performance of water treatment processes such as granular activated carbon filtration, oxidation processes, and membrane filtration; and it leads to increased bio-film growth in water distribution pipes. A thorough understanding of the physical and chemical properties of the various components of NOM would contribute greatly towards optimisation of the design and operation of drinking water treatment processes. However, because of its complex and heterogeneous nature, it is currently impossible to fully describe the chemical structure for each molecular component of NOM in the natural environment. Nevertheless, an improved picture of NOM can be achieved by analysing its operationally defined organic fractions. The aim of this study is to identify and quantify the different NOM fractions in drinking water from different treatment processses and trains as well as to identify those that may influence biostability in the distribution network.

This should provide a basis for the development of models to predict the removal of problematic NOM fractions and to optimise the design and operation of drinking water treatment processes and trains. Novel NOM analytical tools which are employed include: size exclusion chromatography (SEC) with multiple detectors such as online dissolved organic carbon (DOC), dissolved organic nitrogen (DON), fluorescence and variable UV-VIS; fluorescence excitation–emission matrices (EEMs); and PARAFAC multiway analysis for decomposing fluorescence EEMs into constituent components.

Fluorescence Spectral Properties of Chromophoric Dissolved Organic Matter Along a Transect in the Barataria Bay, Louisiana, USA

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Fluorescence measurements of Chromophoric Dissolved Organic Matter (CDOM) were made along a transect extending from the mouth of Barataria Bay, located between Bayou Lafourche to the west and the Mississippi River delta to the east, to the northwest end of the bay. The present study was done for the water samples collected on March 20, 2008. Samples were brought back to the laboratory and filtered immediately with 0.2 micron nucleopore membrane filters. Further the data were acquired on spectrofluorometer (Horiba Jobin Yvon Fluoromax-4) and the analyses were done using Fluorescence Toolbox (FL Toolbox 1.91-MATLAB).

We have observed CDOM fluorescence increase from the mouth of the bay (station 1) to farther into the bay (station 36). Fluorescence decreased with increase in salinity, low values of CDOM fluorescence near the mouth (high salinity) and higher values in the interior of the bay (low salinity). In general, CDOM fluorescence increases with the increase in temperature along the transect. From the EEM (excitation-emission matrix) plots, the T peak (tryptophan-like, protein-like) was evident only at the first station of the mouth of the bay. Peak A (humic-like) was sharper at one station near the end of the transect (station 33) whereas Peak C (humic-like) and Peak M (humic-like) are mostly prominent at all the stations along the transect. The results of the peak fluorescence intensities (A, C, T, and M peaks) with the absorption values have been plotted and found to similar as reported in previous literatures in bay regions.

Fluorescence Properties of Dissolved Organic Matter (DOM) Exported from Tidal Marshes and Effects of Microbial and Photochemical Processes

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Estuarine and coastal margin ecosystems are hot spots of DOM cycling because of intense physical and biological activity. Fluorescence spectroscopy is a useful tool that can be applied for tracing the sources and transformation pathways of colored DOM (CDOM) in these systems. Synchronous fluorescence spectroscopy and fluorescence excitation-emission-matrix scans were used to examine the quality of CDOM exported from freshwater and brackish tidal marshes in the optically complex and biologically productive Chesapeake Bay estuary. Photobleaching experiments were performed to examine the effects of the spectral quality of solar exposure on the fluorescence properties of marsh-exported CDOM. Preliminary results of a novel application of the bioreactor approach are also presented, showing the changes in the bioavailability of DOM tidally exchanged in these marsh systems, and effects on fluorescence spectral characteristics.

Seasonal Variation of Dissolved Organic Matter Fluorescence in the Coastal North Sea

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We present the results of a seasonal study of dissolved organic matter (DOM) fluorescence properties at the Dove Marine Time Series site located ~5.5 nautical miles off Northeast England in the North Sea (55° 07'N, 01° 20'W). Depth profiles (0-50 m) were collected from 20th February 2007 to 6th May 2008 at approximately monthly intervals, and complemented by surface seawater samples collected on 9 transects extending from Blyth Harbour, NE England, offshore. Fluorescence excitation-emission matrices (Ex: 200-400, Em: 280-600) were recorded on a total of 102 discrete samples. Samples were also analysed for spectral dissolved organic matter absorbance, DOC, DON, inorganic nutrients, chlorophyll a, and ancillary parameters (salinity, temperature and turbidity). We used a multidimensional decomposition technique (PARAFAC) to decompose excitation-emission matrices into independent spectral components, in order to study the effects of allochthonous (terrestrial) versus autochthonous (marine-derived) sources on the seasonal variation of DOM in the coastal North Sea.

We will discuss relationships of PARAFAC fluorescence components with spectral DOM absorbance and bulk DOM composition in the context of changes in freshwater inputs and coastal hydrography in the study region.

Microbial Biofluorescence Expressed by Bacterial Isolates Exposed to Organic Sulfur

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The occurrence of environmental organic pollutants such as the organic sulfur thiophene, dibenzothiophene (DBT) could lead to conditions suited for microbial growth with select specialized metabolism for utilizing such compounds. These factors in one way or another may lead to formation of fluorescence, which could be byproducts of these organic pollutants or may become cellular as in the formation of sulfur globules in sulfur acquiring microorganisms. Microbial bioindicators have unique machinery for procurement of toxicants and may offer visual display of these processes for routine assessment.

Using soil microcosm and petroleum diesel enrichment in flask cultures, we have recently isolated several strains with colony fluorescence and showed visible fluorescence at the mid UV range. These strains showed a bright white blue and blue fluorescence. We have characterized them for growth on several organic compounds (ethanol, yeast extract, casamino acids) and performed UV VIS scanning spectrophotometry of culture fractions taken from these isolates to reveal any indication of peak activities in the range (230 to 350 nm) for soluble organic matter. The associated visual fluorescence spectra of these strains may correlate with absorption peaks at the UV region and varies according to strain. These isolates showed a major peak at 289 to 290 nm, which appears protein related. In addition major peaks were detected in the range of 230 to 274 nm. The bright white blue fluorescence correlates with peaks at 232 and 234.6 nm (for MGDI 42f1 isolate); at 232 and 234.7 nm (for MGDI 42e1 isolate); and 232 and 273.5 nm (for MGDI 42f2 isolate). Initial results showed that this bright fluorescence is "quenched" in the aqueous culture media, lending to the idea that environmental culture milieu affects this fluorescence phenotype. Environmental factors, stresses could affect formation of fluorescence of organic matter and detritus, which could be associated with microbial action as observed with waste treatment effluent (Saadi et al. 2006).

Strains expressing the bright fluorescence showed low concentration growth dependence, which was distinct with the MGDI 42f2 isolate in the range from 0.25 nanomole to 0.25 picomole of DBT and these colonies appeared fluorescent. Recent results with chemical data from certain environments in hydrothermal vents indicates that organic sulfur activities are at the low range from 10^{-7} to $10^{-14.6}$ for methanethiol and from $10^{-7.6}$ to $10^{-11.5}$ for dimethylsulfide (Schulte and Rogers 2008).

The blue fluorescence correlates with peaks at 242.6 and 286.3 nm (for MGDI 3Jn); at 231 and 234.9 nm (for MGDI 14Mob1 isolate); 232 nm (for MGDI 14Mob2 isolate); and 232, 235 nm (for MGDI 142L). Fluorescent colonies were also observed with the MGDI 3Jn isolate, which could persist for several days of culture.

Saadi, I., et al. (2006) *Chemosphere* **63**, 530-539.
Schulte, M. and Rogers, K. L. *Abstracts of Papers*, Goldschmidt Conference, University of British Columbia Vancouver, Canada; Cambridge Publications: Cambridge, UK, 2008; Abstract A841.

Organic Matter Fluorescence as a Tool for Tracing Water Mass Origins and Circulation in the Arctic Ocean

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The Arctic Ocean is a unique environment to study the fluorescence of dissolved organic matter because it is a semi-enclosed basin that contains an abundance of fluorescence components from a variety sources. Large river runoff and high productivity in certain areas allows one to trace both marine and terrestrial components throughout the basin as well as components that result from the degradation of organic matter. Samples were collected during a unique Arctic transect in 2005 from Barrow Alaska to Svalbard via the North Pole. There have been two other trans-Arctic cruises but this cruise is unique because it is the first time EEM data has been obtained from all the basins in the Arctic. Using a combination of excitation emission matrix spectroscopy and parallel factor analysis, organic matter fluorescence in the Arctic Ocean was broken down into seven components. These components were compared to different hydrographic parameters to investigate the various sources contributing to the fluorescence signal.

For example, one component is strongly correlated to lignin phenol concentrations and is found in elevated concentrations throughout the halocline layer. The halocline layer isolates the surface waters from the warm Atlantic Ocean and plays an important role for the heat budget of the Arctic Ocean. Despite its importance the formation and maintenance of the halocline is not fully understood. The full potential of the PARAFAC components will be realized when data from other groups are related to the fluorescence data. This study illustrates how fluorescence paired with PARAFAC can be used to describe the nature of DOM and shows promising results helping us to describe the ventilation of the upper Arctic Ocean.

Dissolved Organic Matter Composition and Dynamics in Headwater Streams of an Eastern Deciduous Biome Under Different Forest Management Regimes: Applications of EEM-PARAFAC

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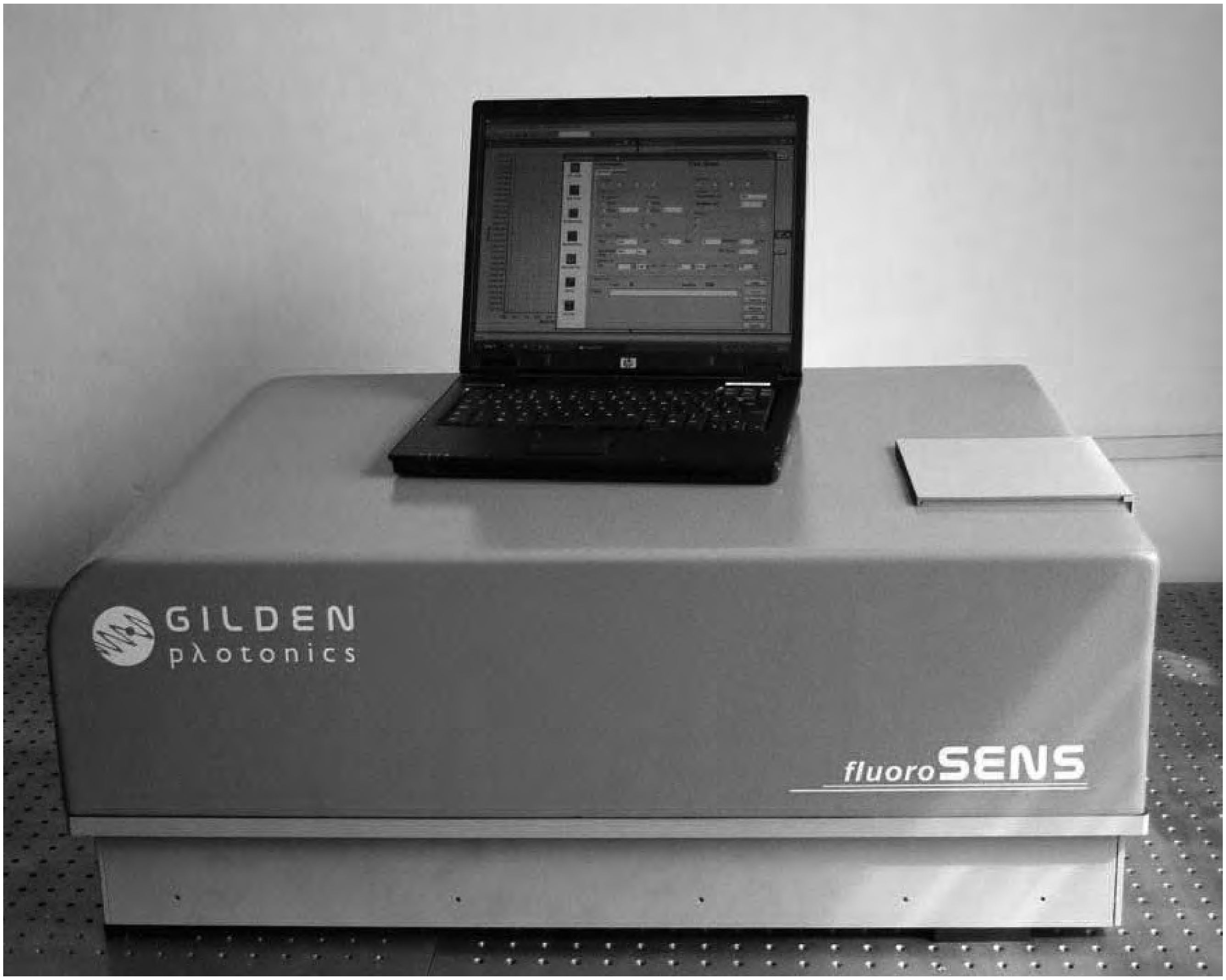
Monthly monitoring of DOM optical properties was applied to stream waters from an Eastern deciduous biome (COWEETA Hydrological Station, North Carolina) for one year with the aim of evaluating seasonal changes in and effects of past forest management on DOM quality and quantity. Since its establishment in 1934 various forest management strategies have been implemented on a watershed scale at COWEETA. EEM-PARAFAC results showed differences in seasonal variations among fluorescent components.

For the period between July and January, levels of terrestrial and microbial humic-like components reached maximum concentrations during November at the reference watershed (untreated, WS2) and the watershed that was clear-cut in 1977 (7), but not at the site converted from hardwoods to white pine in 1957. Differences among watersheds are likely the result of greater leaf litter inputs during the fall in native deciduous watersheds (WS2 and 7) compared to the pine dominated watershed (WS1). On the other hand, the tyrosine-like fluorescent component showed high levels from September to October in all three watersheds, suggesting that it has different sources than humic-like components and might be derived within the stream and/or the riparian zone. PCA analyses show differences in the overall DOM composition between the undisturbed and the managed watersheds, where the latter seemed to contain higher abundances of microbial components compared to the former.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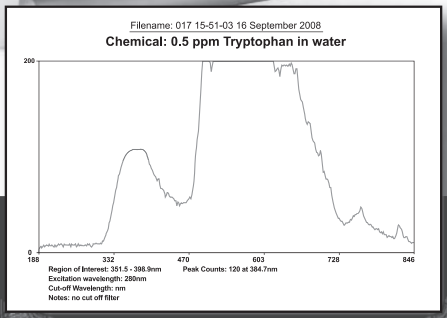

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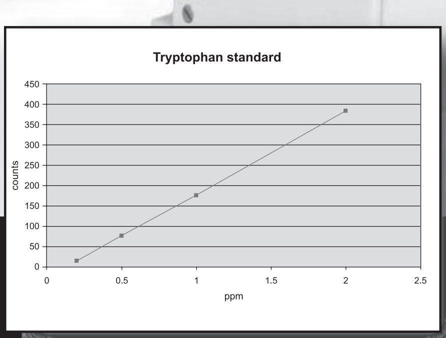

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