

International Training Workshop on Organic Matter Characterization Using Spectroscopic Techniques
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Poster Presentations

THURSDAY, 20 MAY 2010

AUTHORS	TITLE AND ABSTRACT
Samantha Bateman, Professor David Sear and Professor Paul Carling	<p>SOURCING AND QUANTIFYING ORGANIC MATERIAL AND SEDIMENT OXYGEN DEMAND OF INFILTRATED SEDIMENT WITHIN SALMONID REDDS.</p> <p>Sedimentation of rivers is a global environmental problem, particularly affecting the habitat of spawning salmonids. Southern English chalk streams are acknowledged to be particularly impacted by the accumulation of fine sediment and high organic content. Fine sediment accumulation in redds affects the rate and amount of dissolved oxygen available to incubating salmonid embryos. In particular, organic fine sediment is little quantified and identified within redd sediments and the research attempts to address this by exploring the identity, oxygen consumption and origin of organic material which can accumulate within the redd environment. Using an intensive field survey methodology, the spatial and temporal variation in the quality of spawning habitat was observed over the incubation period throughout the catchment. Long term sediment oxygen demand rates calculated from sediments at hatch (range 0.16 – 2.07 mg O₂ g⁻¹ day⁻¹) across the catchment differed to those at emergence (range 3.09 – 8.47 mg O₂ g⁻¹ day⁻¹). Correlations were not apparent between total organic content established by loss on ignition experiments and sediment oxygen demand in preliminary results. An attempt to establish the associated fine organic sediment inputs that drive the sediment oxygen demand were made using fluorescence and UV-vis absorbance spectroscopy techniques displayed by EEM's. Organic sediments could then be sourced from redd to catchment using the sediment fingerprinting theory. The results of this study will be useful in calibrating habitat models such as SIDO-UK for improving approaches to the management of salmonid populations. Key words: salmonid, sediment oxygen demand, organic sediment, River Itchen and fluorescence and UV-vis absorbance spectroscopy.</p>
Kathleen M. Brannen(1), Annette Summers Engel(1), Justin E. Birdwell(2); 1) Department of Geology & Geophysics, Louisiana State University, Baton Rouge, LA 70803 USA; 2) Central Energy Resources Science Center, U. S. Geological Survey, USA	<p>CREATING HUMIC MATTER INDICES FOR THE INTERPRETATION OF ECOSYSTEM ENERGETICS</p> <p>Cave and karst ecosystem energetics is an important factor in understanding microbial processes in aquifers. Determining the flux of dissolved organic matter (DOM) from the surface into the subsurface is one way of tracking the ecosystem energetics. The relative contributions of different sources of DOM can be evaluated using excitation-emission matrix (EEM) fluorescence spectroscopy because there is no photodegradation of OM in cave and karst waters. This method can characterize DOM at natural, low abundance levels, and can differentiate recalcitrant DOM (e.g., humic substances) from more biologically labile material (e.g., proteins, peptides, and amino acids). Consequently, in karst environments, the influence of surface derived (allochthonous) DOM can be distinguished from autochthonous DOM produced by microbial chemolithoautotrophy. However, many karst environments are heavily influenced by surface water recharge and allochthonous DOM. Autochthonous humic matter (smaller proteins) is often overshadowed by the allochthonous matter</p>

AUTHORS	TITLE AND ABSTRACT
	<p>(larger humic complexes), meaning allochthonous humic matter fluoresces brighter than autochthonous matter. It is important to differentiate allochthonous from autochthonous humic matter for the interpretation of cave and karst ecosystem energetics. In this study, our aim was to create an index of humic/fulvic acids and protein (tryptone) mixtures to help differentiate the overshadowing effects of the brighter humic substances by using difference mg/L concentrations of tryptone, Suwannee River Fulvic Acid (SRFA), and Pony Lake Fulvic Acid (PLFA), and different mixtures of tryptone and SRFA and tryptone and PLFA. In a previous study from several different sulfidic cave waters, fluorescence signatures were dominated by fluorescent amino acids tyrosine and tryptophan. In some cases, humic-like fluorescence was observed, but was significantly blue-shifted from what is typically found for soil and surface water derived humic substances. The indices that we create should be able to help decipher these signals with blue-shifted humic substances. Although the SRFA and PLFA standards mixed in different ratios with the protein tryptone will be a less complex (humic matter) version of cave waters, we will be able to see if there is any substantial fluorescence overshadowing of tryptone by SRFA and PLFA.</p>
<p>Elisabet Ejarque, Eusebi Vázquez, Andrea Butturini; Department of Ecology, University of Barcelona.</p>	<p>DEALING WITH EEM HETEROGENEITY: A COMPARISON OF TWO DECOMPOSITION METHODS A set of 68 Excitation-Emission Matrices (EEM) were analysed with the aim of evaluating the influence of hydrology in Fluorescent Dissolved Organic Carbon (FDOC) properties along a riverine longitudinal gradient. The interpretation of the EEMs was not straightforward, as there was high variability in the location of the intensity peaks. In order to overcome this difficulty, a statistical criterion to discriminate the different fluorescent components was needed. With that purpose, two decomposition methods were assessed: PARAFAC and PCA. By means of PARAFAC, a 2 bimodal component model was split-half validated. However, the examination of the residuals gave evidences that the model was not correctly representing the original samples. On the other hand, PCA identified 4 coordinates in the EEM which were hosting peaks of fluorescence variability among samples. These coordinates coincided with those of the components validated by PARAFAC, indicating that the information of FDOC variability among samples lies indeed in these points. However, due to the apparent contradiction between PARAFAC validation criteria, the exact number of fluorescence compounds could not be reliably determined. Moreover, even if a well numerous number of matrices have been included in the analysis, PARAFAC does not seem to entirely cope with the overall heterogeneity. In this sense, it is set forth whether PCA might be an alternative to PARAFAC in highly heterogeneous sample sets.</p>
<p>Laura Forsström, University of Helsinki and University of Jyväskylä, Kirsten Christoffersen, University of Copenhagen, Matteo Cazzanelli, University of Copenhagen, Milla Rautio, Université du Québec à Chicoutimi and University of Jyväskylä</p>	<p>DOM CHARACTERISTIC IN SMALL LAKES OF ZACKENBERG, NE GREENLAND Absorbance and fluorescence of DOM was analysed in seven small, shallow lakes located in NE Greenland (74°30'N, 21°00'W), in the zone of continuous permafrost. CDOM absorption was measured every 1 nm over the wavelength (λ) range 250-850 nm using a 10 cm quartz cuvette in a Cary 300 UV-Vis spectrophotometer in dual-beam mode. Spectral slope, S, was calculated using non-linear regression for ranges of 300-650 nm, 275-295 nm and 350-400 nm. Synchronous fluorescence spectrum was measured with a Cary Eclipse fluorescence spectrophotometer with wavelength difference between excitation and emission beams of 14 nm. Lakes had a very wide range of DOC concentration (7-130 mg l⁻¹), but even the lakes with highest DOC were clear water lakes, with CDOM absorption at 440 nm < 2 m⁻¹. DOC-specific absorption was very low, 0.01-0.26 m² g⁻¹ C. High DOC is not fully explained by salinity, since conductivity of these lakes varied between 21 and 132 μS cm⁻¹ and the lake with highest DOC had lowest conductivity. $S_{300-650}$ varied between 9-17</p>

THURSDAY, 20 MAY 2010

AUTHORS	TITLE AND ABSTRACT
	<p>μm^{-1}, S₂₇₅₋₂₉₅ between 15 and 20 μm^{-1} and S₃₅₀₋₄₀₀ between 10 and 18 μm^{-1}. Specific UV absorbance (SUVA) at 254 nm varied between 0.03 and 1.13. Synchronous fluorescence spectra indicated a dominance of autochthonous DOM in most of the lakes, while allochthonous DOM had a significant contribution in a couple of lakes. Compared to other high-arctic areas, our study lakes have much higher DOC but very low CDOM. The variation in DOC concentration and DOM characteristic was high despite the fact that all lakes are located in a relatively small area. Similar DOC levels have been found from lakes in SW Greenland, but with much higher conductivity.</p>
Rachel Gabor, Nina Russell, Rachel McLoughlin, Diane McKnight (Institute of Arctic and Alpine Research, University of Colorado-Boulder, Boulder, Colorado, USA)	<p>THE USE OF FLUORESCENCE SPECTROSCOPY TO ANALYZE THE SOLUBLE ORGANIC MATTER OF SOIL EXTRACTS AND COMPARE IT TO DISSOLVED ORGANIC MATTER FROM THE SAME WATERSHED</p> <p>As worldwide trends of increasing DOM concentrations continue to be reported, and their source investigated, it is becoming more important to elucidate the link between soluble organic matter in a catchment and dissolved organic matter in the corresponding aquatic system. Within the Boulder Creek Critical Zone Observatory, soil samples were collected along transects and from several deep pits on both south- and north-facing slopes in the Boulder Creek Watershed, Colorado. The extractable DOM from each sample was leached with 0.5 M potassium sulfate and both whole water and fulvic acid fractions were analyzed with UV-VIS and fluorescence spectroscopy. Parallel factor analysis (PARAFAC) was then used to model the fluorescence excitation-emission matrices to characterize the chemical properties of the DOM. While available soluble organic matter was significantly higher at the surface and tended to steadily decrease with depth, amount and chemical character did vary with soil horizon. Organic matter from the surface was much more similar to the stream DOM than matter near bedrock. In addition, soil samples showed a shift in fluorescence index with depth, with an increase in microbial signal near bedrock, along with a corresponding increase in protein content and oxidized character, potentially indicating microbial use of DOM as an electron acceptor in bedrock weathering processes. These results were also compared to the chemical signature of the DOM from the stream the catchment feeds.</p>
Matías Mudarra(1), A. Baker(2) and B. Andreo(1). (1)Centre of Hydrogeology of University of Malaga (CEHIUMA), Malaga, Spain. (2)Connected Waters Initiative, University of New South Wales, 110 King St, Manly Vale, NSW2093, Australia and the National Centre for Groundwater Research and Training	<p>RELATIONSHIP BETWEEN HYDROCHEMICAL VARIABLES AND NATURAL FLUORESCENCE FROM DISSOLVED ORGANIC MATTER IN KARST SPRING WATERS</p> <p>Spectrofluorometry is one of the most important methodologies currently used for characterizing dissolved organic matter (DOM) in water in the natural medium. This technique is fast, economical and non-destructive, and has been utilized in many studies for determining the nature and properties of the natural fluorescence emitted by DOM in marine and continental waters. This method has enabled researchers to determine the relationship between natural fluorescence and certain hydrogeochemical and environmental variables in these aquatic media. However, spectrofluorescence has not been applied as a potential tool for characterizing and quantifying the DOM in the water from springs draining karst aquifers; neither has any analysis been made of the results between natural fluorescence and the principal hydrochemical variables of the water in these aquifers. This is a fundamental question, in view of the particular hydrogeological characteristics presented by these types of medium. Karst spring waters often show variable contents of organic carbon (OC), which may be present as particulate (POC) or dissolved organic carbon (DOC); the sum of both is the total organic carbon (TOC). In natural waters, DOC often makes up about 90% of the TOC, so the analytical determination of the TOC corresponds, almost in its entirety, to DOC. From April 2008 until March 2009, a study was carried out to characterize</p>

AUTHORS	TITLE AND ABSTRACT
	<p>DOM, using spectrofluorescence (excitation-emission matrix, EEM) and the analysis of Total Organic Carbon (TOC), together with a hydrochemical analysis of the water at several springs in the province of Malaga (southern Spain). The aim of this study was to determine the relationship between natural fluorescence and some of the most significant hydrochemical parameters for the water from these springs. Therefore, we applied, as well as the hydrochemical and natural fluorescence data, an index derived by identifying and quantifying the fluorophores recognized in the EEM (Peak C/Peak A) together with another indicator ratio for the TOC and the Peak A value (Peak A/TOC). The data were then processed by principal component analysis (PCA), which revealed that Axis 1 includes the main hydrochemical variables considered to be tracers of karst mineralization (E.C., T, Alc, Ca+2, Mg+2, SO4-2, Na+, K+, Cl-, F-, rMg/Ca) together with pH, while Axis 2 is characterized by the different variables related to organic materials (TOC, Peak A, Peak C, rPeak C/Peak A) and NO₃⁻ which, for the most part, are related to the natural tracers of infiltration into karst aquifers. Finally, Axis 3 is characterized exclusively by the Peak A/TOC index. There was found to be a direct relation between the variable NO₃⁻ and the Peak C/Peak A index, which was probably the result of the simultaneous enrichment of nitrogenated compounds and DOM in the soil overlying the karst, especially during the spring and summer months. The results obtained demonstrate the usefulness of characterizing the organic matter dissolved in the water of karstic aquifers, using spectrofluorometry, and the use of certain indexes derived from the latter information for the detailed characterization of infiltration processes within the karstic medium.</p>
<p>Mar Nieto-Cid, M.J. Pazó, V. Vieitez, M. Barreiro, X.A. Álvarez-Salgado (Instituto de Investigaciones Marinas (CSIC))</p>	<p>ABSORBANCE AND INDUCED FLUORESCENCE OF RAIN WATER IN A TEMPERATE COASTAL EMBAYMENT (RÍA DE VIGO, NW SPAIN).</p> <p>The dynamics of the Ría de Vigo, a large embayment in the NW Iberian coast, is primarily controlled by remote winds and secondarily by continental runoff. It is characterised by a 2-layered residual circulation pattern, positive under upwelling-favourable northerly winds and negative under downwelling-favourable southerly winds. The spring and autumn phytoplankton blooms occur during the seasonal transitions from downwelling to upwelling conditions and vice versa, respectively. Copious rainfall during those transitional periods could be a significant source of organic and inorganic nutrients to the surface layer of the ría.</p> <p>The chemical composition of rain water (total deposition) in contrasting rural, urban and marine environments of the Ría de Vigo was monitored on a daily basis during 2 years. Dissolved organic carbon (DOC), absorbance, and induced fluorescence spectra are used to quantify and characterise the organic loads of rain water.</p> <p>The concentration of dissolved organic carbon (DOC) correlated inversely ($R^2 > 0.42$; $p < 0.001$) with the daily precipitation rate (P) following the equation $DOC = a \cdot P^b$, where a is the DOC concentration at $P = 1$ mm/d and b is the dilution factor. The coefficient a was around 1050 ± 200 $\mu\text{mol/L}$ in the rural and urban stations but it was significantly lower ($p < 0.05$), 650 ± 100 $\mu\text{mol/L}$, in the marine station. The coefficient b was -0.8 ± 0.1 at the three sites. Linear regressions through the origin ($R^2 > 0.90$, $p < 0.001$) were obtained between DOC and the absorption coefficient at 254 nm, $a(254)$, but with different slopes: the absorptivity at 254 nm, $a^*(254)$, was significantly higher ($p < 0.005$) at the marine station (29.2 ± 0.8 $\text{m}^2/\text{mol C}$) than at the rural (23.6 ± 0.6 $\text{m}^2/\text{mol C}$) and urban (22.3 ± 0.5 $\text{m}^2/\text{mol C}$) sites. Rain water at the marine station</p>

AUTHORS	TITLE AND ABSTRACT
Julien Para(1), Paula G. Coble(2), Bruno Charrière(1), Marc Tedetti(1), Clément Fontana(3) and Richard Sempéré(1); (1) Laboratoire de Microbiologie Géochimie et Ecologie Marines, Centre d'Océanologie de Marseille, Université de la Méditerranée, (2) College of Marine Science, University of South Florida, USA (3) Laboratoire d'Océanographie Physique et Biogéochimique, Université de la Méditerranée, Marseille, France	<p>also presented significantly lower ($p < 0.001$) values of the $a(254)/a(365)$ ratio, 9.0 compared to >13.2, and the fluorescence quantum yield at 340 nm, $\Phi(340)$, 1.6% compared to 2.7%. Conversely, the ratio of the induced fluorescence at peak-T ($Ex/Em = 280nm/350nm$) and peak-A ($Ex/Em = 250/450$), characteristic of protein- versus humic-like fluorophores, was significantly higher ($p < 0.001$) at the marine (11.3) than at the urban and rural sites (<7.6).</p> <p>Concomitant collection of wet deposition samples at the urban site yielded that $a = 95 \pm 10 \mu\text{mol/L}$, $b = -0.57 \pm 0.05$, $a^*(254) = 30.6 \pm 0.9 \text{ m}^2/\text{mol C}$, $a(254)/a(365) = 13.5$, $\Phi(340) = 1.4\%$, and $\text{peak-T}/\text{peak-A} = 11.8$.</p> <p>These optical indices suggest that: (i) 100% of the DOC in rainwater is coloured; (ii) the aromaticity of rain water in the marine site is significantly higher than in the urban and rural sites; and (iii) aromatic amino acids are proportionally more abundant than aromatic humic substances in the marine site.</p> <hr/> <p>FLUORESCENCE AND ABSORPTION PROPERTIES OF CHROMOPHORIC DISSOLVED ORGANIC MATTER (CDOM) IN COASTAL SURFACE WATERS OF THE NORTHWESTERN MEDITERRANEAN SEA (BAY OF MARSEILLES, FRANCE)</p> <p>Seawater samples were collected in surface waters (2 and 5 m depths) of the Bay of Marseilles (northwestern Mediterranean Sea; $5^{\circ}17'30''\text{E}$, $43^{\circ}14'30''\text{N}$) during one year from November 2007 to December 2008 and studied for total organic carbon (TOC) as well as chromophoric dissolved organic matter (CDOM) optical properties (absorbance and fluorescence). The annual mean value of surface CDOM absorption coefficient at 350 nm [$a\text{CDOM}(350)$] was very low ($0.10 \pm 0.02 \text{ m}^{-1}$) with regard to CDOM absorption values usually found in coastal waters, and no significant seasonal trend in $a\text{CDOM}(350)$ could be determined. By contrast, the spectral slope of CDOM (SCDOM) was significantly higher ($0.023 \pm 0.003 \text{ nm}^{-1}$) in summer than in fall and winter periods ($0.017 \pm 0.002 \text{ nm}^{-1}$), reflecting either CDOM photobleaching or production in surface waters during stratification sunny periods. The CDOM fluorescence, assessed through excitation emission matrices (EEMs), was dominated by protein-like component (peak T) and marine humic-like component (peak M), while terrestrial humic-like fluorescence (peak C) remained very low. This reflected a dominance of relatively fresh material from biological origin within the CDOM fluorescent pool. At the end of summer, surface CDOM fluorescence was very low and strongly blue shifted, reinforcing the hypothesis of CDOM photobleaching. During our study period, we clearly observed, from SeaWiFS satellite data, the sporadic presence of a buoyant Rhône River plume extent in the Bay of Marseilles. Interestingly, these buoyant Rhône River plume extents enhanced autochthonous biological CDOM content (peaks M and T) without adding terrestrial fluorescence signatures (peak C). Besides Rhône River plumes, upwelling events of deep waters containing older, more humic CDOM appeared also as an important source of CDOM in surface waters of the Bay of Marseilles. Therefore, the assessment of CDOM optical properties, within the hydrological context, pointed out several biotic (in situ biological production, biological production within Rhône River plumes) and abiotic (photobleaching, stratification, mixing) factors controlling CDOM transport, production and removal in this highly urbanized coastal area. Key words: chromophoric dissolved organic matter, CDOM absorption, CDOM fluorescence, photobleaching, biological production, Rhône River plume, Bay of Marseilles, Northwestern Mediterranean Sea.</p>

THURSDAY, 20 MAY 2010

AUTHORS	TITLE AND ABSTRACT
Ignacio P. Mazuecos, Eva Ortega-Retuerta, Javier Arístegui, Josep María Gasol, Antonio Fernández-Barbero, Isabel Reche	<p>MEASURING MICROGELS IN AQUATIC ECOSYSTEMS USING FLUORESCENCE SPECTROSCOPY</p> <p>Microgels are polymeric structures formed by the assemblage of colloidal organic matter which undergo gel properties (Verdugo et al. 2004). These gel properties include: 1) autofluorescence emission (400- 480 nm) when excited with UV (365 nm), 2) fluorescence in the green (525 nm) after stain with chlortetracycline (CTC) when excited with UV (365 nm), 3) phase transitions induced by pH changes, and 4) polymer dispersion after calcium chelating by EDTA (Orellana et al. 2007). In this study, we provide an easy and reliable technique to determine the concentration of microgels and the percentage of organic matter that is selfassembled as microgels in both fresh and marine waters. Concentration gradients of alginic acid and xanthan gum as sources of algal derived-organic carbon, and humic and tannic acids as sources of terrestrial derived-organic carbon were tested as model substrates.</p>
Cristina Romera-Castillo, Xosé Antón Álvarez-Salgado, Mar Nieto-Cid and Cèlia Marrasé	<p>OPTICAL PROPERTIES OF THE DOM AS TRACER OF BIOGEOCHEMICAL PROCESSES</p> <p>CDOM distribution in a coastal upwelling system is mainly affected by i) physical conditions, i.e. water mass mixing; and ii) biogeochemical processes, i.e. photodegradation and biodegradation. It is not an easy task to determine which of the biogeochemical processes dominate in an aquatic system. However, spectroscopic techniques, such as absorbance and fluorescence, are useful tools to elucidate this question. This work proposes the use of both techniques to quantify the dominant biogeochemical processes occurring in the Ría de Vigo (NW Spain) when it is affected by two differentiate phenomenon, downwelling and upwelling events. During the upwelling event the optical properties of DOM were more dependent on water mass mixing than during the downwelling period. Regarding to the biogeochemical processes, photodegradation was the dominant process during the downwelling episode, with a relative contribution of 86% against the 14% due to biotic processes. On the other hand biodegradation prevailed during the upwelling event with a relative contribution of 77%.</p>
Teresa S. Catala., Isabel Reche	<p>DISTINCTIVE CHROMOPHORIC DISSOLVED ORGANIC MATTER IN MEDITERRANEAN INLAND WATERS</p> <p>Chromophoric dissolved organic matter (CDOM) in Mediterranean inland waters has been poorly studied in comparison to Northern temperate and boreal lakes. Those systems are submitted to an intense and frequent solar radiation, scarce rainfall and are located in watersheds with poorly developed soils. These factors lead to limited watershed exports, intense evaporation, and consequently, long water residence time producing distinctive CDOM properties. We analyzed CDOM properties (absorption coefficients, molar absorption, spectral slopes) in twenty inland waters ranging two orders of magnitude in dissolved organic carbon (DOC) concentration from 37 to 3795 μM and in absorption coefficients at 440 nm (a_{440}) from 0.13 to 11.8 m^{-1}. The results revealed a significantly lower absorption at 440 nm per organic carbon unit in Mediterranean inland waters in comparison with boreal or temperate lakes, likely related to intense photobleaching rates. We also found a significant and positive relationship between bacterial abundance (BA) and a_{440} and a negative relationship between BA and the ratio (SR) of the spectral slopes $S_{275-295}$ and $S_{350-400}$ underlining the key role of bacteria determining CDOM properties in these systems.</p>
Gemma Vila-Reixach and Montserrat Vidal	<p>SEASONAL DYNAMICS OF DISSOLVED ORGANIC MATTER ON THE CATALAN COAST USING SPECTROSCOPY TECHNIC</p> <p>Dissolved organic matter (DOM) is a key component of oceanic carbon fluxes. Besides, in coastal ecosystems DOM provides a source of nutrients and energy. Moreover, the chromophoric (or colored) DOM (CDOM) can influence the</p>

THURSDAY, 20 MAY 2010

AUTHORS

TITLE AND ABSTRACT

aquatic light field and the penetration depth of radiation potentially harmful to organisms. In this study, measurements of dissolved organic carbon (DOC), dissolved organic nitrogen (DON), dissolved organic phosphorus (DOP), absorption spectra, fixed wavelength fluorescence and synchronous fluorescence were performed in an effort to characterize temporal and spatial variability in concentration and source of dissolved organic matter in surface and deep waters. Samples were taken monthly at a fixed station and seasonally, through a vertical land-offshore section of the coast of Blanes (Girona). The absorption coefficients ranged from 0.01 m⁻¹ to 0.36 m⁻¹, and were modelled with an exponentially decreasing function. The spectral dependence of the CDOM absorption coefficients yields a slope from 0.004 to 0.02 nm⁻¹. The fluorescence of marine and terrestrial dissolved humics was of 0.1-6.6 ppb equivalent quinine sulphate (ppb eq Q) and 0.4-5.8 ppb eq Q, respectively, while that of dissolved aromatic amino acids was 0.1-16 ppb equivalent tryptophan. DOC, DON and DOP concentrations were 60-200 µM, 5-9 µM and 0.03-0.07 µM, respectively. These data are discussed in relation to the factors controlling the temporal and spatial variability of DOM and CDOM.

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CHARACTERISING DISSOLVED ORGANIC MATTER FLUX IN UK FRESHWATERS: SOURCES, TRANSPORT AND DELIVERY

The flux of nutrients to water bodies is increasing world wide as a function of climatic warming, the intensification of agriculture, car use and fossil fuel combustion in both developing and developed countries. Such nutrient enrichment (particularly Carbon and Nitrogen) is leading to devastating ecological responses resulting in excessive growth of seaweed and filamentous algae and an increased production of blue green algae leading to the development of hypoxia and associated fish kills in coastal areas. If these changes are to be brought under control a detailed understanding of the nature of nutrient delivery to waters from their catchments is required. Despite recent research indicating that dissolved organic nutrient fractions are important secondary and sometimes dominant constituents of the total nutrient load delivered to both natural and anthropogenically enriched systems, current policy, development and research has focussed only on inorganic nutrient concentrations. As part of a major research initiative by the University of Reading this project aims to characterise the chemical signature of dissolved organic nutrient fractions in a range of freshwater environments, as at present the question of what dissolved organic matter is and whether temporal variations of dissolved organic nutrients are directly comparable between basins has not been addressed.

AUTHORS	TITLE AND ABSTRACT
Shahad al Janabi; John Bridgeman; Andy Baker	<p data-bbox="569 337 1938 365">USING FLUORESCENCE SPECTROSCOPY TO CHARACTERISE DRINKING WATER QUALITY IN DISTRIBUTION SYSTEMS</p> <p data-bbox="569 370 1938 1144">The presence of natural organic matter (NOM) in water can serve as a precursor for disinfection by products (DBPs) formation in water treatment works (WTW) and water distribution systems. Because of the perceived effects of DBPs on public health, the control of NOM has been widely studied by many researchers. UV₂₅₄ absorbance is routinely analysed within the water industry as an OM surrogate. In particular, the specific UV absorbance, SUVA, (UV₂₅₄ absorbance per milligram of organic carbon) has been also used as a surrogate for DBP precursors in potable water. Although UV₂₅₄ is commonly used, 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 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 deplete to below detection limits. Fluorescence was measured using a Varian Cary Eclipse fluorescence spectrometer; chlorine concentration was measured using Hach Pocket Colorimeters. Results show that for all chlorine concentrations, maximum quenching of fluorescence intensity of NOM is between 10-50% of the initial value and 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 provide a base of knowledge on the effect 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.</p>
Katherine Beggs, R. Scott Summers	<p data-bbox="569 1149 1938 1209">WATERSHED SPECIFIC PARAFAC MODELS FOR ASSESSING COAGULATION AND FORMATION OF DISINFECTION BYPRODUCT FORMATION</p> <p data-bbox="569 1214 1938 1401">Dissolved organic matter (DOM) has been identified as the primary carbon precursor in disinfection byproduct (DBP) formation. Though much work has been done in relating the quantity of organic matter, dissolved organic carbon (DOC) concentration to DBP formation, the reactive fraction of DOM responsible for DBP formation is not yet well understood. To investigate the reactive fraction, watershed samples including surface waters and pine leachates were collected from a northern Colorado watershed over an 8-month period. Samples were filtered and/or coagulated, measured for DOC and chlorinated on the bench scale under uniform formation conditions. All samples were measured for ultraviolet absorbance</p>

AUTHORS	TITLE AND ABSTRACT
	<p>(UVA) and fluorescence before and after chlorination. PARAFAC models were developed using excitation and emission matrices (EEMs) from filtered, coagulated and chlorinated samples. Three models were developed, one for the watershed samples only, one for pine leachates only and one including both watershed and pine leachate samples. From the resulting models, humic-like components were well correlated to both total trihalomethane (TTHM) and haloacetic acid (HAA5) concentrations. Protein-like and tannin-like components were not well correlated to either TTHM or HAA5. DOC was not well removed by coagulation for the pine leachate samples which correlated with the behavior of a tannin-like component from the pine leachate only model. This non-removable fraction may cause a challenge for mountain utilities which must meet DOC removal regulations.</p>
Núria Catalán	<p>SPATIAL AND TEMPORAL SPECTROSCOPIC CHARACTERISATION OF DISSOLVED ORGANIC MATTER IN A MEDITERRANEAN COASTAL LAGOON.</p> <p>The patterns of dissolved organic matter (DOM) spectroscopic properties were examined in a Mediterranean coastal lagoon (s'Albufera des Grau, Menorca) and its 7 basin streams over a 2 years study. Measures of chromophoric dissolved organic matter (CDOM) concentration (a_{440}), spectral slope ($S_{350-500}$), aromaticity by means of Specific Absorbance at 254 nm ($SUVA_{254}$), fluorescence index (the ratio of the emission intensity at a wavelength of 450nm to that at 500nm at an excitation wavelength of 370nm) were determined. The correlation between CDOM and the vertical light attenuation coefficient (K_d) confirms the importance of CDOM in the underwater light regime in the studied lagoon. The observed values for a_{440} (between 1.9 and 6.1 m^{-1}) and for $SUVA_{254}$ (between 1.54 $Lmg^{-1}m^{-1}$ and 4.68 $Lmg^{-1}m^{-1}$), suggested colored and highly aromatic DOM regarding values found for another lagoons. Qualitative changes in DOM were studied using fluorescence excitation-emission spectroscopy and Parallel Factor Analysis (PARAFAC). Two terrestrial-like humic components were identified for the lagoon and for the 7 streams, corresponding to peaks A and C previously found in literature. Significant temporal but not spatial variations were found for fluorescence intensity maximum, describing a spatially uniform basin in terms of DOM. The reduction of the ratio between the fluorescence maximum of both components and an increasing of SUVA along the raining station can be related to an allochthonous material arrival, showing the importance of first annual torrential events.</p>
Clare Dalton, Anne Stringfellow, David Smallman	<p>CHARACTERISATION OF DISSOLVED ORGANIC CARBON IN LANDFILL LEACHATE USING FLUORESCENCE EXCITATION EMISSION MATRIX AND ULTRA VIOLET SPECTROSCOPY METHODS.</p> <p>Moisture in landfilled waste produces leachate, the quality of which is determined by the type and age of the waste deposited. The leachate is often highly contaminated and has a complex chemical composition which varies throughout the lifetime of the landfill. Compounds in leachate can sorb to solid materials in the waste or in mineral landfill liners resulting in the attenuation of contaminants. Dissolved organic carbon (DOC) present in the leachate is known to affect the sorption of hydrophobic organic contaminants, either inhibiting or promoting sorption to the solid phase. This effect on attenuation capacity of the soil or sediment has been linked to the composition of the organic matter, not just the amount present. Excitation-emission matrix (EEM) fluorescence analysis of samples can be used to identify the different types of dissolved organic matter present in the leachate sample and gauge the proportion of protein-like, humic-like and fulvic-like DOC as well as identification of known contaminants or spiked substances (e.g. fluorescein). Although UV</p>

AUTHORS	TITLE AND ABSTRACT
Adam M. Gilmore, HORIBA Scientific ; Rose M. Cory, University of North Carolina Chapel Hill, USA	<p>spectroscopy is generally used for the identification of concentration specific compounds, the UV absorbance spectra for a constant TOC value has been shown to vary in shape due to differences in the type of organic matter present. Therefore this method can also be used in the characterisation of types of DOC in leachates. The evolution of leachate DOC produced by three types of landfilled waste (municipal solid waste (MSW), incinerator ash from municipal solid waste (MSWI) and mechanical-biological pre-treated waste (MBP)) in a saturated anaerobic environment was investigated using fluorescence and UV spectrophotometry to characterise the DOC present.</p> <p>ENHANCED MEASUREMENTS OF CHROMOPHORIC DISSOLVED ORGANIC MATTER (CDOM) FOR WATER QUALITY ANALYSIS USING A NEW SIMULTANEOUS ABSORBANCE AND FLUORESCENCE INSTRUMENT</p> <p>Water quality, with respect to suspended particles and dissolved organic and inorganic compounds, is now recognized as one of the top global environmental concerns. Contemporary research indicates fluorescence spectral analyses coupled with UV-VIS absorbance assays have the potential, especially when combined and coordinated, to facilitate rapid, robust quantification of a wide range of compounds, including interactions among them. Fluorescence excitation-emission matrices (EEMs) collected over the UV-VIS region provide a wealth of information on chromophoric dissolved organic matter (CDOM). CDOM includes humic and fulvic acid, chlorophyll, petroleum, protein, amino acid, quinone, fertilizer, pesticide, sewage and numerous other compound classes. Analysis of the EEMs using conventional and multivariate techniques, including primarily parallel factor analysis (PARAFAC), provides information about many types of CDOM relevant to carbon cycling and pollution of fresh, marine and drinking water sources. Of critical concern also are the CDOM interactions with, and optical activities of, dissolved inorganic compounds. Many of the inorganic compounds and oxygen demand parameters can be analyzed with a wide range of UV-VIS absorbance assays. The instrument is designed and optimized for high UV throughput and low stray light performance. The sampling optics are optimized for both fluorescence and absorbance detection with the same sample. Both EEM and absorbance measurements implement NIST traceable instrument correction and calibration routines. The fluorescence detection utilizes a high dynamic range CCD coupled to a high-resolution spectrograph while absorbance utilizes diode based detection with a high dynamic range and extremely low-stray light specifications. The CDOM analysis is facilitated by a transfer of the data and model information with the PARAFAC routine. The EEM analysis software package facilitates coordinated correction of and correlation with the absorbance spectral data to quantify fluorescence reabsorption in the sample. The absorbance software also facilitates a wide range of UV-VIS assays with standard water quality kits as well as providing information on turbidity. This instrument performs the novel tasks of optimized, coordinated EEM and absorbance acquisition and analysis to facilitate a comprehensive optical evaluation of water quality samples. In conclusion, the instrument is generally applicable to both water quality research and analytical laboratories as well as a wide number of other applications utilizing EEM and or absorbance methodology.</p>
Jami Goldman, Joseph Needoba, Stewart Rounds	<p>EFFECTS OF FLUORESCENCE QUENCHING BY IRON AND ZINC ON THE COLORED DISSOLVED ORGANIC MATTER POOL IN AN URBAN WATERSHED</p> <p>Dissolved organic carbon (DOC) represents a significant carbon reservoir in all ecosystems, and recent advances in fluorescence spectroscopy can be used to quantify and characterize the colored dissolved organic matter (CDOM), a</p>

AUTHORS	TITLE AND ABSTRACT
Weidong Guo, Liyang Yang, Huasheng Hong, Fuli Wang, Jing Xu (State Key Laboratory of Marine Environmental Science, Xiamen University)	<p>subset of the DOC pool. Organic matter can interact with metal ions to form organometal complexes, which can have a quenching effect on the fluorescence signature, causing uncertainties in interpreting the complex three-dimensional excitation-emission matrices (EEMs). In the Portland, Oregon urban watershed zinc and iron are found in variable concentrations, 100nM to 5000nM, amongst the differing river basins due to groundwater and anthropogenic influences. This study identifies the impact of zinc and iron on the CDOM pool and its quenching capabilities on a range of samples with varying quantities and qualities of DOC. Quantification of changes in peak intensities and excitation/emission pairs, represented in the EEMs, demonstrates the quenching abilities of these metals on the natural organic matter.</p>
	<p>ASSESSING THE DYNAMICS OF CHROMOPHORIC DISSOLVED ORGANIC MATTER IN A SUBTROPICAL EUTROPHIC ESTUARY USING PARALLEL FACTOR ANALYSIS</p> <p>The spatial and temporal dynamics of chromophoric dissolved organic matter (CDOM) were studied using excitation emission matrix fluorescence spectroscopy (EEMs) and parallel factor analysis (PARAFAC) during five cruises in the subtropical, eutrophic Jiulong Estuary from August 2008 to June 2009. Two humic-like (C1 and C3), one aquatic (C2) and one tryptophan-like (C4) components were identified by PARAFAC and their behaviors from river-estuary interface to the coastal area were evaluated. The spatial distributions of the fluorescent components showed a remarkable loss in the upper estuary. The following significant addition in low salinity turbidity maximum zone suggested the contribution from sediment resuspension and the inputs from the surrounding mangrove ecosystem. The humic-like and aquatic components showed conservative behavior in middle and lower estuary indicated by the linear relationships between their fluorescence intensities and salinity, while protein-like component C4 was generally constant from the low to the middle salinity regions, indicating an addition from autochthonous production. Although humic-like components C1 and C3 showed no significant variation in estuary-coastal interface, components C2 and C4 decreased more rapidly beyond this interface, indicating the significant influence of coastal current to this estuarine environment. Protein-like component C4 had a most dramatic seasonal variation, with higher concentrations and higher relative contributions in the dry season. This was reverse to C1 and C3 which had relatively constant fluorescence intensities throughout the year and higher relative contributions in the wet season. Correlation analysis with DOC showed that components C2 were most suitable proxies for tracing DOC dynamics in the estuarine environment.</p>
Kristin K. Mueller, Claude Fortin and Peter G.C. Campbell	<p>EXPLORING LINKS BETWEEN FLUOROPHORES AND METAL BINDING BY NATURAL ORGANIC MATTER</p> <p>In aquatic systems, dissolved organic matter (DOM) plays a key role in metal ecotoxicology by complexing the free metal ion; the free metal ion species best predicts metal bioavailability and hence toxicity. However, the heterogeneous nature of DOM makes it difficult to predict the effect of DOM on the speciation of metals. The Windermere Humic Aqueous Model (WHAM) is a chemical equilibrium model that is widely used to predict the bioavailability of environmentally significant metals, such as Cd, Cu, Ni and Zn, to aquatic organisms in natural systems. When using WHAM the user must, however, choose what proportion of the measured DOM is actively involved in metal complexation, either based on laborious chemical separation techniques or on literature values for similar DOM. The ability to estimate this “percent active” DOM spectroscopically would be of great interest. We sampled the water column of 8 lakes on the Canadian Precambrian Shield chosen along spatial gradients in total dissolved metal concentrations, pH and dissolved organic</p>

AUTHORS**TITLE AND ABSTRACT**

carbon concentrations. Lake-to-lake variability in the spectroscopic quality of DOM, as determined by emission excitation matrix (EEM) fluorescence and parallel factor analysis (PARAFAC), was revealed by differences in the relative contributions of three fluorescence components, two representing humic fluorophores of terrestrial origin and one representing a fulvic acid fluorophore of both terrestrial and autochthonous origin. The relative contributions of the DOM fluorophores varied significantly among sampling regions indicating differences in DOM source. In parallel, we measured the free Cd²⁺, Cu²⁺, Ni²⁺ and Zn²⁺ concentrations in the lake samples and compared them to WHAM modeled concentrations. The proportions of free Cd²⁺ and Zn²⁺ fell within the range of values predicted by WHAM for 7 of the 8 lakes. However, the measured free Cu²⁺ concentration fell within the WHAM predicted range for only half of the lakes sampled, and for nickel WHAM systematically overestimated the proportion of Ni²⁺, i.e., underestimated Ni complexation. Moreover, the percent active DOM within the WHAM model could not be optimised to account for all the Cd, Ni and Zn complexation in the lakes sampled and revealed a weak relationship between this DOM activity and measured fluorescence quality of DOM. We conclude that the refinement of the WHAM model to incorporate variations in DOM quality must go beyond the simple adjustment of the “percent active DOM” and possibly include changes to DOM metal binding affinities, notably for Cu and Ni. We discuss the application of variations in DOM quality, as revealed by differences observed in the fluorescence spectra, to refine metal speciation predictions obtained with WHAM for environmentally significant trace metals in natural aquatic systems.

REVERSE OSMOSIS MEMBRANE PERFORMANCE USING FLUORESCENCE SPECTROSCOPY

Reverse osmosis (RO) membranes are a viable treatment method for reclamation of very high quality water from wastewater as they provide an effective barrier to the majority of undesirable contaminants. RO permeates are not completely devoid of contaminants with incomplete rejection, particularly of low molecular weight chemicals. Adequate monitoring, including membrane integrity monitoring, of such RO systems is essential to ensure process performance. Existing on-line chemical methods including conductivity and total organic carbon (TOC), for trace organic concentration, have limitations which impedes their effectiveness as an integrity monitoring tool. Fluorescence Excitation Emission Matrix (EEM) spectroscopy is a powerful analytical tool for water quality analysis. Fluorescent dissolved organic matter (fDOM) originating from both natural and anthropogenic sources can be found in various water supplies. The presence of these fluorescent markers are present in membrane treated recycled water and has the potential for monitoring membrane process performance and membrane integrity. This study investigates the changes to fDOM as it undergoes RO membrane treatment at an Australian pilot advanced water treatment plant (WTP). By monitoring fDOM through the RO membrane treatment system using fluorescence spectroscopy, we were able to characterise the organic matter present at each stage. Stage 2 permeates exhibited distinctly higher humic-like peak intensity (peak C₁) compared with stage 1 permeates. Tryptophan-like peak (T₁) was present at similar levels in both permeates. By relating peak C₁ and peak T₁ fluorescence, the two stages of RO permeates and RO feeds could be split into their respective process stages. Peak C₁ was found to be more important in distinguishing between the different stages of the RO process. Peak T₁ was only able to distinguish between the RO feed and the RO permeates. Peak C₁ was determined to be the most suitable for monitoring RO performance, as its concentration in the RO permeate was affected by changes to the feed quality. A

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AUTHORS	TITLE AND ABSTRACT
	<p>decrease in the fluorescent intensity difference between the respective RO feed and permeate would correspond to membrane underperformance or failure. This highly sensitive technique enables rapid determination of RO permeates quality and thus could be an invaluable tool for monitoring membrane performance and integrity. Furthermore, the technique can be converted to an on-line system, which will be the subject of future research.</p>
<p>Ester Torres (Institute of Environmental Assessment and Water Research, IDAEA-CSIC, Barcelona, Spain).</p>	<p>CHARACTERIZATION OF TWO WATER RESERVOIRS THAT RECEIVE ACID MINE DRAINAGE In order to predict the water quality of a future reservoir in the Odiel Basin (SW Spain) two existing reservoirs located in the same Basin are currently studied. Both of them receive acid mine drainage (AMD): one is slightly affected by AMD and his pH is neutral, whereas the other one is heavily affected by AMD and his pH is acidic. Sediments with 1 to 5% of organic carbon have been sampled in several points of the reservoir floor. The first results show that the reservoirs have a holomictic behavior. During most of the year a thermocline is stabilized and the lower mass of water is under reducing conditions. Turnover takes places during winter months, and oxidizing conditions are stabilized throughout the water column. This affects the solubility of some metals (like As, Fe, Mn, Al, etc) that are precipitated during oxidizing conditions and can be released during the reducing conditions. TOC and DOC concentrations are similar which means that practically all the organic carbon is dissolved. In both reservoirs the values during winter are lower than in summer and are practically constant through the water column ($\approx 10\text{mg/L}$). In summer the biologic productivity is higher (15mg/L to 20mg/L) with a maximum in the metalimnion. DOM, and particularly humic acids, are expected to play a significant role in the metal and sulfur cycles, whether adsorbed or as sulfide precipitation. Humic acids are wanted to be analyzed through their fluorescence index.</p>
<p>Yihua XIAO (Key Laboratory of Yangtze River Water Environment of Ministry of Education, Tongji University, Shanghai, China); Qinghui HUANG * (Key Laboratory of Yangtze River Water Environment of Ministry of Education, Tongji University, Shanghai, China); Ling CHEN (State Key Laboratory of Pollution Control and Resources Reuse, Tongji University, Shanghai, China)</p>	<p>CHARACTERISTICS OF DISSOLVED ORGANIC MATTER FROM DIFFERENT BIOTOPES IN A BRACKISH LAKE AND ITS EFFECT ON PHAEODACTYLUM TRICORNUTUM GROWTH North Lake is a brackish lake in the north branch of the Yangtze estuary. Four sediment samples and one plant sample were collected from deep water zone, shallow water zone, mudflat and reed marshes in North Lake. Dissolved organic matter (DOM) was extracted with water and characterized by using three-dimensional excitation emission matrix (EEM) fluorescence spectroscopy. The components of DOM extracted from different biotopes showed large variation. Effects of DOM extracted from reed and sediment on Phaeodactylum tricornutum (<i>P. tricornutum</i>) were analyzed by using chlorophyll fluorescence technology. The concentrations of chlorophyll a and the maximum quantum yield (F_v/F_m) tended to decrease in DOM treatments after four days of incubation. Growth and photosynthesis efficiency of <i>P. tricornutum</i> were inhibited significantly. Parallel factor analysis (PARAFAC) on fluorescence spectra revealed that one protein-like component of DOM in algae filtrate significantly strengthened during incubation. Therefore, natural DOM derived from salt marsh could have much influence on the adjacent aquatic systems.</p>

AUTHORS	TITLE AND ABSTRACT
<p>Monika Zabłocka, Piotr Kowalczyk; Institute of Oceanology, Polish Academy of Sciences, Sopot, Poland</p>	<p>PRELIMINARY ASSESSMENT OF THE DISSOLVED ORGANIC MATTER COMPOSITION IN THE SOUTHERN BALTIC SEA WATERS WITH USE OF FLUORESCENCE SPECTROSCOPY AND PARALLEL FACTOR ANALYSIS.</p> <p>This study presents results of the Parallel Factor Analysis (PARAFAC) applied to Dissolved Organic Matter fluorescence excitation emission spectra collected during 8 cruises between May 2002 and May 2004 in the different regions of the Southern Baltic Sea. The PARAFAC model was successfully applied to identify 5 fractions of DOM and assess their spatial and seasonal changes in the study area. The PARAFAC model identified 3 terrestrial humic-like substances: two primary ones - component C1 and component C3 and one secondary humic-like component C2. Component C4 represented marine humic materials or microbial reprocessed organic material. Spectral characteristics of component C5 could be associated with combination of fluorophores containing tyrosine and tryptophan. Identified PARAFAC components of EEM spectra occurred in different proportions in studied regions of the Baltic Sea. These proportions fluctuated during the year. An average DOM composition pattern of samples collected in the open waters of Southern Baltic was: C1>C2>C5>C4>C3. In the Gulf of Gdansk the average pattern of the DOM composition was: C1>C2 >C4>C3>C5 and the intensities of components C3 and C5 were nearly equal. The DOM composition in the Gulf of Gdansk in winter was similar to one observed in open waters. We have performed the regression analysis to test the relationships between CDOM absorption coefficient $a_{CDOM}(350)$, total fluorescence intensity, I_{tot} ($R^2=0.79$, $N=138$) and fluorescence intensities of each identified components. We correlated fluorescence intensities of components identified by PARAFAC with integrated fluorescence intensities of respective EEMs peaks defined by Coble, 1996. There were very high values of the linear Pearson's correlations coefficients between respective fluorescence intensities calculated independently with use of those two techniques. Our results proved that PARAFAC can be used both for qualitative and quantitative studies of DOM fluorescence properties distribution in marine environment. We have shown how changes in DOM composition influence the values of the CDOM carbon specific absorption coefficient $a_{CDOM}(350)$.</p>
<p>Huiyu Zhao, Roland Redon, Cedric Garnier and Stephane Mounier</p>	<p>PARAFAC TREATMENT TO 3D-FLUORESCENCE QUENCHING (FQ) OF DISSOLVED ORGANIC MATTER (DOM)</p> <p>The DOM-Metal complexation propriety is accessible by fluorescence quenching (FQ). FQ spectrum can determine the fluorescent DOM composition by parallel factor analysis (PARAFAC) with excitation-emission matrix (EEM). [Cu²⁺] titration onto a tropical river water sample from Brésil: [C]=5mg/L, initial [Cu²⁺]=1.68 nM, pH=4.5, [Cu²⁺] 10⁻⁹M~10⁻³M is done with 50 EEM analyzed by PARAFAC, which has extracted 2 fluorescent components from all EEM: C1 ($\lambda_{ex}=235nm/\lambda_{em}=420-425nm$) and C2 ($\lambda_{ex}=250-260nm$ and $345-355nm/\lambda_{em}=470-480nm$) of which corresponding to the interferences obtained by this new approach. This observation has confirmed that the modelling fluorophores values of FQ are better distinguished from the whole matrix by the help of PARAFAC. Following the precedent work of 3D-FQ treated by PARAFAC, a phenomenon has interested us: the fluorescence intensity of component 1 increased sharply at the beginning of the titration. In order to find out the reason of this phenomenon, an experiment of FQ with two concentrations of DOM, of which one group at low concentration and the other at high concentration with surely inner filter effect, has been programmed. If the results correspond to the precedent work, the sharp increasing of fluorescence intensity was probably an influence of inner filter effect.</p>