FluoroNet Newsletter 8

Welcome to the 8th Newsletter from FluoroNet, the regular newsletter containing information about member events, activities, publications, courses, projects, instruments, etc... This needs your input! Details on how to submit articles for the next issue can be found at the end of the Newsletter.

Workshop on ‘Fluorescence methodologies: instrumentation, quantification, standardisation’
University of the West of England, Bristol
THURSDAY 10 MAY 2007, 10.00 – 16.00

A workshop aimed at some of the more advanced issues in fluorescence analysis. With only one month to the meeting, we encourage delegates to register NOW!

Speakers

Sam Allshorn, University of Leeds
‘Applications of EEMs in multiple dye tests’

Andy Baker, University of Birmingham
‘Fluorescence thermal quenching’

Lucy Bolton, Environment Agency
‘Storage and stability issues in the fluorescence analysis of DOM’

Chris Brunsdon, University of Leicester
‘Visualisation of fluorescence data’

Lee Chapman, University of Birmingham
‘Using expert systems to classify fluorescence EEMS’

John Gilchrist, Gilden Photonics, Scotland
‘A review of state of the art fluorescence technologies’

Kate Murphy, University of New South Wales, Australia
‘The use of PARAFAC for the analysis of Fluorescence spectra’

Elfrida Pfeiffer, Optoelectronics, Romania
‘Water analysis using laser induced fluorescence’

Darren Reynolds, University of the West of England, Bristol
‘The standardisation of fluorescence measurements’

A registration form can be downloaded from: http://www.gees.bham.ac.uk/research/fluoronet/ and is also appended to this Newsletter. On-line bookings can alternatively be made via the website below and following the ‘Geography, Earth and Environmental Sciences’ link. http://www.ecommercegateway.co.uk/bham/webStore/

Selected Recent Journal Publications

Scientific publications that feature fluorescence analyses of waters and waste waters and which have been published in the last two months. As well as the publications with abstracts listed below, two review / commentary articles have recently been published which feature fluorescence applications in the water sciences. These have no abstracts, so only bibliographic details are possible. These are: Coble, PG (2007), Marine optical biogeochemistry: the chemistry of ocean color. CHEMICAL REVIEWS, vol 107, 402-418 and Granger, SJ et al. (2007) Processes affecting transfer of sediment and colloids, with associated phosphorus, from intensively farmed grasslands: tracing sediment and organic matter, HYDROLOGICAL PROCESSES, vol 21, 417-422.

Spencer, RGM, Baker, A, Ahad, JME, Cowie, GL, Ganeshram, R, Upstill-Goddard, RC and Uher, G
Discriminatory classification of natural and anthropogenic waters in two UK estuaries
SCIENCE OF THE TOTAL ENVIRONMENT, 2007, vol 373, p 305-323

The ability to distinguish water inputs from both natural and anthropogenic sources was investigated in the complex environment of an urban estuary (Tyne) and a relatively pristine estuary (Tweed). We used a data set from a total of 11 estuarine transects, comprising measurements of bulk dissolved organic matter (dissolved organic carbon and nitrogen), dissolved nitrogen (total dissolved nitrogen, ammonia, nitrate+nitrite and dissolved organic nitrogen), optical absorbance measurements (a(350), S290-350) and fluorescence excitation emission matrix measurements (fluorophores A, H, B and T intensity and A and H emission wavelength maxima). In order to investigate trends within the numerous parameters measured, multivariate statistics were employed. Principal components analyses showed 63.4% of the variability in the total data set can be explained by two sets of components and 74.9% of the variability by the spectrophotometric measurements alone. In both analyses the first component correlated to the mixing of terrestrial and marine waters and the second component was correlated to sources of pollution such as domestic sewage. Within the data set, river flow and terrestrially derived DOM were significantly correlated, and situations with high river input showed an increase in terrestrial signature in the estuary. Discriminant analyses were also carried out and indicated that 59.8% (total data set) and 53.3% (solely spectrophotometric data) of the samples can be correctly classified into their respective groups (water categories) assigned on the basis of salinity and sampling location. Overall the results clearly show...
the potential of spectrophotometric techniques to discriminate distinct water categories with different DOM characteristics. In particular, measurement of the fluorophore H emission maxima, the spectral slope parameter, S290-350, and fluorophores T and B intensity enabled discrimination of DOM from riverine, estuarine, marine, and sewage affected water categories. The results presented here indicate the ability of spectrophotometric data alone to distinguish between marine, anthropogenic and terrestrial DOM and distinguish terrestrial DOM from different catchments (Tyne vs. Tweed). With current advances in the in-situ deployment of absorbance and fluorescence spectroscopy it is anticipated that multivariate statistics will gain importance as a cost effective, powerful and diagnostic approach to assessing the distributions of water types and their associated DOM characteristics and fluxes at the land-ocean interface.

Hua, B, Dolan, F, Mcghee, C, Cleveenger, TE, Deng, BL
Water-quality protection and environmental forensics require rapid water monitoring and source identification. In this paper, parallel factor analysis (PARAFAC) of fluorescence excitation-emission matrix spectra (EEMS) was used to characterize and classify water samples from landfills, wastewater treatment plants, lakes, and rivers. The study showed that the optimal number of components was four to represent the data set. The fluorescence fingerprints for water samples from different sources were sufficiently different, so qualitative water classification could be achieved. Specifically, Component I was the major fluorescing centre in river waters, with characteristics consistent with humic-like fluorophores; Component 2 was the dominant fluorophore in the treated wastewaters; Component 3 was the characteristic fluorophore in landfill leachates; and Components 1, 3, and 4 existed in lake waters at comparable weight, among which Component 4 may be considered as a protein- or amino acid-like fluorophore.

Takahashi, M, Kawamura, K
Simple measurement of 4,4′-bis(2-sulfostyryl)-biphenyl in river water by fluorescence analysis and its application as an indicator of domestic wastewater contamination WATER AND SOIL POLLUTION, 2007, vol 180, p 39-49
A characteristic peak of fluorescent whitening agents (FWAs) was detected by fluorescence excitation spectrum (FES) measurement of river water samples. The main causative chemical was 4,4′-bis(2-sulfostyryl)-biphenyl (DSBP), which is commonly added to household detergents in Japan. As the fluorescence of DSBP overlaps with that of fulvic-like organic matter in the spectral fluorescent signatures, DSBP concentration was determined by the newly proposed calculation method, which uses fluorescence intensity at three excitation wavelengths of 320, 345 and 360 nm at emission wavelength of 430 nm for baseline correction. The concentration of DSBP calculated using this method showed strong correlation (correlation coefficient: r = 0.992) with that obtained by high-performance liquid chromatography analysis. The concentrations of DSBP detected in river water samples were 0.28 to 1.84 µg l⁻¹, with high concentrations observed at the stations with relatively high flow rates of upstream sources of treated domestic wastewater and untreated grey water (domestic wastewater excluding flush toilet wastewater). It was proved that the concentration of DSBP in river water is useful for giving rough estimation of the magnitude of domestic wastewater contamination in river water.

Sun, WL, Ni, JR, Xu, N, Sun, LY
Fluorescence of sediment humic substance and its effect on the sorption of selected endocrine disruptors CHEMOSPHERE, 2007, vol 66, 700-707
Humic substances (HS) have a critical influence on the sorption of organic contaminants by soils and sediments. This paper describes investigations into the sorption behavior of three representative endocrine disruptors, bisphenol A (BPA), 17 beta-estradiol (E2), and 17 alpha-ethynylestradiol (EE2), onto sediments and HS extracted sediments using a batch technique. The organic carbon-normalized partition coefficients (K-oc) for the extracted HS (K-oc(hs)) were calculated, and the fluorescence spectra of the HS extracted from different sediment samples were gained using excitation/emission matrix (EEM). Particular attention was paid to the correlations between the fluorescence characteristics of HS and the log K-oc(hs) of selected endocrine disruptors. The results show that the log K-oc(hs) values range from 3.14 to 4.09 for BPA, from 3.47 to 4.33 for E2, and from 3.65 to 4.32 for EE2. Two characteristic excitation-emission peaks were observed for HS samples extracted from sediments. They are located at Ex/Em = 250-260 nm/400-450 nm (peak α) and Ex/Em = 310-330 nm/390-400 nm (peak β) respectively. The α and β peak relative intensities (I-oc/I-α) vary from 0.46 to 1.64 for different extracted HS samples. The similarity between fulvic acids (FA) Ex/Em pairs and those observed for HS indicates that FA is the predominant fraction of HS extracted from sediments. Moreover, the K-oc(hs) values of BPA, E2, and EE2 have a negative linear correlation to I-oc/I-α values. Peak α is often attributed to relatively stable and high molecular weight aromatic fulvic-like matter. Therefore, the result presented here reveals that the abundance of aromatic rings in HS molecular structure plays a critical role in the sorption of selected endocrine disruptors.

Hall, GI Kenny, JE
Estuarine water classification using EEM spectroscopy and PARAFAC-SIMCA ANALYTICA CHIMICA ACTA, 2007, vol 581, p 118-124
The primary method for the prevention of the introduction of nonindigenous aquatic nuisance species in the U.S. is ballast water exchange (BWE). Our recent work focused on the use of the excitation emission matrix (EEM) spectroscopy of the colored dissolved organic matter (CDOM) to "fingerprint" water as a function of its port of origin, and therefore provide a forensic tool for the enforcement of BWE regulations. In that work, we utilized N-way partial least squares with discriminant analysis (NPLS-DA), which models the data with an emphasis on differences among classes (ports of origin). In this work, EEMs of samples from three different U.S. ports were analyzed by parallel factor analysis (PARAFAC) coupled with soft independent modeling of class analogy (SIMCA) to provide an effective classification method with a low false positive rate. This coupling, which is shown for the first time in this work, can be a useful alternative to NPLS-DA in that PARAFAC-SIMCA decomposes the EEM signal into chemical components and utilizes the scores for these components in the classification scheme. This gives the user the option of removing the contributions of interfering or unidentifiable fluorescent components prior to classification.

Pakou, C, Fountoulakis, M, Drillia, P, Kampioti, A, Stamataletou, K, Lyberatos, G
Occurrence and fate of polycyclic aromatic hydrocarbons in sewage treatment plants using microwave-assisted extraction followed by liquid chromatography coupled with fluorescence detector FRESENIUS ENVIRONMENTAL BULLETIN, 2007, vol 16, 127-132
Polycyclic aromatic hydrocarbons (PAHs) are highly persistent compounds in the environment, recalcitrant to biodegradation...
and highly lipophilic, while some of them cause acute carcinogenic and mutagenic toxicity. Due to the risk of soil contamination whenever sewage sludge is disposed to agricultural land, the investigation of their presence in sewage sludge is a priority need. This work concerns the occurrence of five PAHs, selected from the priority list of the US Environmental Protection Agency (phenanthrene, fluoranthene, pyrene, benzo[b]fluoranthene, and benzo[a]pyrene), in municipal sewage sludge and to assess their fate in a sewage treatment plant. An analytical method based on microwave-assisted extraction (MAE), followed by HPLC-UV coupled with a fluorescent detector (FD) was used for their measurement. The method efficiency was evaluated as to its linearity, repeatability, accuracy and sensitivity. The contamination levels of the PAHs were determined in sludge from the sewage treatment plants of three main Greek cities: Athens, Patras and Heraklion. PAHs ranged from 0.2 to 4 mg kg\(^{-1}\) d.m for each PAH in mixtures of primary and secondary sludge, while they were significantly lower in secondary sludge (less than 0.1 mg kg\(^{-1}\) d.m).

Maie, N, Scully, NM, Pisani, O, Jaffe, R
Composition of a protein-like fluorophore of dissolved organic matter in coastal wetland and estuarine ecosystems
WATER RESEARCH, 2007, vol 41, p 563-570
This study demonstrates the compositional heterogeneity of a protein-like fluorescence emission signal (T-peak; excitation/emission maximum at 280/325 nm) of dissolved organic matter (DOM) samples collected from subtropical river and estuarine environments. Natural water samples were collected from the Florida Coastal Everglades ecosystem. The samples were ultrafiltered and excitation-emission fluorescence matrices were obtained. The T-peak intensity correlated positively with N concentration of the ultrafiltered DOM solution (UDON), although, the low correlation coefficient (\(r^2 = 0.140, p < 0.05\)) suggested the coexistence of proteins with other classes of compounds in the T-peak. As such, the T-peak was unbundled on size exclusion chromatography. The elution curves showed that the T-peak was composed of two compounds with distinct molecular weights (MW) with nominal MWs of about > 5 x 10\(^4\) (T-1) and similar to 7.6 x 10\(^3\) (T-2) and with varying relative abundance among samples. The T-1 peak intensity correlated strongly with [UDON] (\(r^2 = 0.516, p < 0.001\)), while T-2 peak did not, which suggested that the T-peak is composed of a mixture of compounds with different chemical structures and ecological roles, namely proteinaceous materials and presumably phenolic moieties in humic-like substances. Natural source of the latter may include polyphenols leached from senescent plant materials, which are important precursors of humic substances. This idea is supported by the fact that polyphenols, such as gallic acid, an important constituent of hydrolysable tannins, and condensed tannins extracted from red mangrove (Rhizophora mangle) leaves exhibited the fluorescence peak in the close vicinity of the T-peak (260/346 and 275/313 nm, respectively). Based on this study the application of the T-peak as a proxy for [DON] in natural waters may have limitations in coastal zones with significant terrestrial DOM input. PY 2007

Fan, J, Guo, HQ, Liu, GG, Peng, PG, Fan, Jing, Guo, Huiqin, Liu, Guoqiang, Peng, Pingan
Simple and sensitive fluorometric method for determination of environmental hormone bisphenol A based on its inhibitory effect on the redox reaction between peroxy radical and rhodamine 6G
Peroxy radical produced by Fenton-like reagent (Fe(III) + H\(_2\)O\(_2\)) oxidizes Rhodamine 6G and produces the quenching of its fluorescence. It is also found that bisphenol A has an inhibitory effect on the redox reaction. Based on this observation, an inhibitory kinetic fluorometric method is proposed for the determination of trace bisphenol A. The fluorescent inhibition of rhodamine 6G is measured by fix-time method. Under the optimum experimental conditions, the detection limit and the quantification limit for bisphenol A is 2.0 and 6.7 ng mL\(^{-1}\), respectively; and the linear range of the determination is 0.024-0.4 mg mL\(^{-1}\). The proposed method has been used for the determination of bisphenol A in environmental waters, river bottom sediment, generic soil, polycarbonate products and teeth filling samples with recoveries of 92.5-110.0%. The possible mechanism of the reaction has also been discussed.

Brooks, ML, Meyer, JS, McKnight, DM
Photooxidation of wetland and riverine dissolved organic matter: altered copper complexation and organic composition
HYDROBIOLOGIA, 2007, vol 579, p 95-113
In natural waters, the uptake of transition metals such as copper (Cu) by aquatic biota depends on the activity of the free cupric ion ([Cu\(^{2+}\)]) rather than on total Cu concentration. Thus, an important ecological function of dissolved organic matter (DOM) in aquatic ecosystems is Cu-DOM complexation, which greatly decreases the [Cu\(^{2+}\)]. However, Cu bioavailability is greatly modified by source and environmental history of DOM because DOM affinity for Cu varies by orders of magnitude among DOM sources; moreover, DOM is photochemically unstable. During 72-h irradiation experiments at intensities approximating sunlight with DOM from a palustrine wetland and a third-order river, we investigated photooxidative effects on DOM complexation of Cu as well as spectral and chemical changes in DOM that might explain altered Cu complexation. Irradiation decreased Cu complexation by riverine DOM, but unexpectedly increased Cu complexation by wetland DOM, resulting in 150% greater [Cu\(^{2+}\)] in riverine DOM at the same dissolved organic carbon concentrations. The specific ultraviolet absorption (SUVA) and humic substances tracked photochemical changes in the conditional stability constants of Cu-DOM complexes, suggesting that the aromaticity of DOM influences its affinity for Cu. Carbonyl concentration in C-13 nuclear magnetic resonance spectra (C-13-NMR) covaried directly with Cu binding-site densities in DOM. However, no aspect of Cu-DOM complexation consistently covaried with fluorophores (i.e., the fluorescence index) or low molecular weight organic acids. Our results suggest that global increases in UV radiation will affect Cu-DOM complexation and subsequent Cu toxicity depending on light regime as well as DOM source.

Material for future issues
Your articles are needed! These can be sent at any time to:
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FLUORESCENCE FOR THE WATER SCIENCES

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Workshop on ‘Fluorescence methodologies: instrumentation, quantification, standardisation’

University of the West of England, Bristol

THURSDAY, 10 MAY 2007

10.00 – 16.00

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