Investigation of Pollution in Rivers and Groundwater by Fluorescence

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Organic molecules that contain conjugated aromatic constituents have the potential to fluoresce. Both natural and anthropogenic organic matters may contain fluorescent molecules, and river and groundwater organic matters can be understood as a complex mixture of fluorescent and nonfluorescent organic molecules. The investigation of pollution in rivers and groundwaters, therefore, requires the differentiation of multiple fluorescent molecules from multiple sources. The fluorescence spectra of both natural and pollutant organic matters are increasingly well known. Fluorescent pollutants in rivers and groundwaters are typically identified by high levels of fluorescence in the shortwave ultraviolet spectra associated with high levels of microbiological activity and biochemical oxygen demand (BOD); the presence of polycyclic aromatic hydrocarbons from landfill leachates or petroleum products; or the presence of fluorescent whitening agents (FWAs) from industrial, landfill, or sewerage pollution. These fluorescence signals can be distinguished from natural organic matter fluorescence by analyzing either of the differences in spectral properties, often using multiway analysis such as parallel factor analysis, or the investigation of their sensitivity to microbial or photodegradation. Examples of the investigation of pollution in rivers and groundwaters by fluorescence using both laboratory instrumentation and in situ probes are discussed.

1 INTRODUCTION

Light-absorbing organic substances, ubiquitously present in rivers, may emit this absorbed energy in the form of fluorescence. Such intrinsic fluorescence has long been recognized, for example as background interference for fluorescent dye traces[1] and as an observed signal in satellite remote sensing images.[2] The source of this natural organic matter (NOM) fluorescence is ascribed to terrestrially derived, humic-like substances, and their transformation products. Rivers are increasingly viewed as organic carbon processors, with this terrestrial-derived NOM being the source of energy for within-river microbial processing, driving the riverine ecosystem.[3] NOM fluorescence in rivers is, therefore, a mixture of fresh and reprocessed humic-like substances, with reprocessing due to either biological (microbial degradation) or chemical (e.g. photochemical, sorption, and freeze-thaw) processes, as well as the fluorescent exudates of the microbiological communities that are processing the humic-like substances. NOM is similarly transported and transformed in groundwater, affected by microbial degradation, sorption, and redox processes. For a general overview of fluorescent NOM in aquatic systems, the reader is referred to the books by Hudson et al.[4] and Fellman et al.[5]

The investigation of pollution in rivers and groundwaters by fluorescence therefore relies on the detection of intrinsic fluorescence which is either (i) at a different wavelength than that observed in rivers or aquifers of good water quality, (ii) fluorescent in the same wavelengths but at a significantly higher intensity or fluorescence efficiency, or (iii) rapidly bio- or photodegradable and is identified by different rates of change of fluorescence intensity to that of an unpolluted sample. Such fluorescence measurements can be undertaken using grab-samples, in situ probes or

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remotely sensed systems. This article outlines some of the fundamental principles of fluorescence and sampling protocols and the nature and interpretation of aquatic organic matter fluorescence data with specific focus on river and groundwater pollution.

2 ORGANIC MATTER FLUORESCENCE IN RIVERS AND GROUNDWATERS

2.1 Theory and Environmental Interferences

Organic matter transported by rivers and groundwaters can fluoresce if its chemical structure is such that energy can be absorbed and subsequently emitted as fluorescence. In both the field and the laboratory, the excitation energy is provided by photons using a light source of appropriate wavelength, and the emitted fluorescence is detected by an appropriate device such as a charge-coupled device (CCD) or photomultiplier tube (PMT). Typical excitation light sources include xenon bulbs, which generate a wide range of excitation energies, and light-emitting diodes (LEDs), which provide a fixed-wavelength light source. Laser light sources can also be utilized but are relatively impractical compared to off-the-shelf instrumentation available using LED and xenon sources. The relatively low energy emitted by xenon bulbs and LEDs typically excites fluorescent dissolved organic matter in river and groundwater systems causing fluorescence. The fluorescence signatures of both natural and pollutant organic matters are dominated by that from conjugated aromatic molecules with polar functional groups. Their semi-rigid structure and presence of electron donating groups in the conjugated aromatic molecules promote the ability of the molecule to fluoresce.(6) Molecules that are attributed to fluorescence in both polluted and good quality river and groundwaters are presented in Figure 1.

Probably the most important factor behind the increasing use of fluorescence analysis to measure the concentration and characters of river and groundwater organic matters is the technological advances, which has led to an increase in the speed of analysis, with an associated miniaturization and ease of quantification of the data produced. For more than a decade, the ability to rapidly measure fluorescence for a range of excitation and emission wavelengths has permitted the rapid identification of organic matter fluorescence signatures in aquatic environments. The resulting output is typically called an excitation–emission matrix (EEM), and a large body of research has resulted in a good knowledge of the optimal instrument configuration required for useful analyses of dissolved organic matter. Typically, this is an excitation and emission wavelength range within 200–500 nm, and excitation and emission wavelength increments less than the expected region of excited and emitted fluorescence (typically <3 nm). Example EEMs from rivers and groundwaters of good water quality are presented in Figure 2, which clearly show the presence of several regions of fluorescence within the excitation wavelengths of 200 and 400 nm [short-ultraviolet (UV) to violet wavelengths] and emitted fluorescence at 280–500 nm (short UV to visible wavelengths). Following the pioneering work of Coble,(8,9) the aquatic organic matter fluorescence community has largely followed a naming protocol, which is based on her original observations, and these peak-naming conventions are presented in Figure 2. Peaks A and C fluorescence are both ubiquitously found in all humic-like substances, including International Humic Substances Society (IHSS) standards, with peak A exciting at a shorter wavelength than peak C. In rivers of good water quality, a first-order correlation exists between peak C fluorescence and dissolved organic carbon (DOC) concentration.(10) Our most recent understanding is that peaks A and C comprise a mixture of ‘fresh’ and reprocessed humic-like material. Decomposition of the fluorescence signal using multivariate techniques (Section 2.2) universally separates these peaks into two components emitting fluorescence at longer (‘fresh’) and shorter (reprocessed) wavelengths.(7) Peak T is located in the same location as the aromatic amino acid tryptophan and is referred to as being tryptophan-like, as many substances can fluoresce in this wavelength. However, a ubiquitous relationship between peak T fluorescence intensity and BOD (Section 3.1) suggests that there is a strong relationship between fluorescence in this region and microbiological activity. Figure 2 demonstrates that some fluorescence in this region is likely in river systems of good water quality because of microbiological processing of NOM.

The analysis of organic matter fluorescence in rivers has to consider the fundamental principles of fluorescence analyses, and for a detailed consideration, the reader is referred to the book by Lakowicz.(11) The process of fluorescence requires electrons to be excited to a higher energy level in a molecule with this energy emitted as fluorescence when the electrons return to the original state. In an ideal system, the Beer–Lambert law can be applied, where the amount of fluorescence is proportional to concentration. The use of cuvettes of known path-length in laboratory spectrometers permits the conversion of fluorescence intensity to concentration through the use of linear calibration curves. Such a linear relationship holds only for relatively low concentrations of organic matter: at high concentrations, emitted fluorescence can be reabsorbed and excitation light might not penetrate the cuvette, leading to a nonlinear relationship between fluorescence intensity and concentration. Fluorescence is also sensitive to the environmental conditions, in

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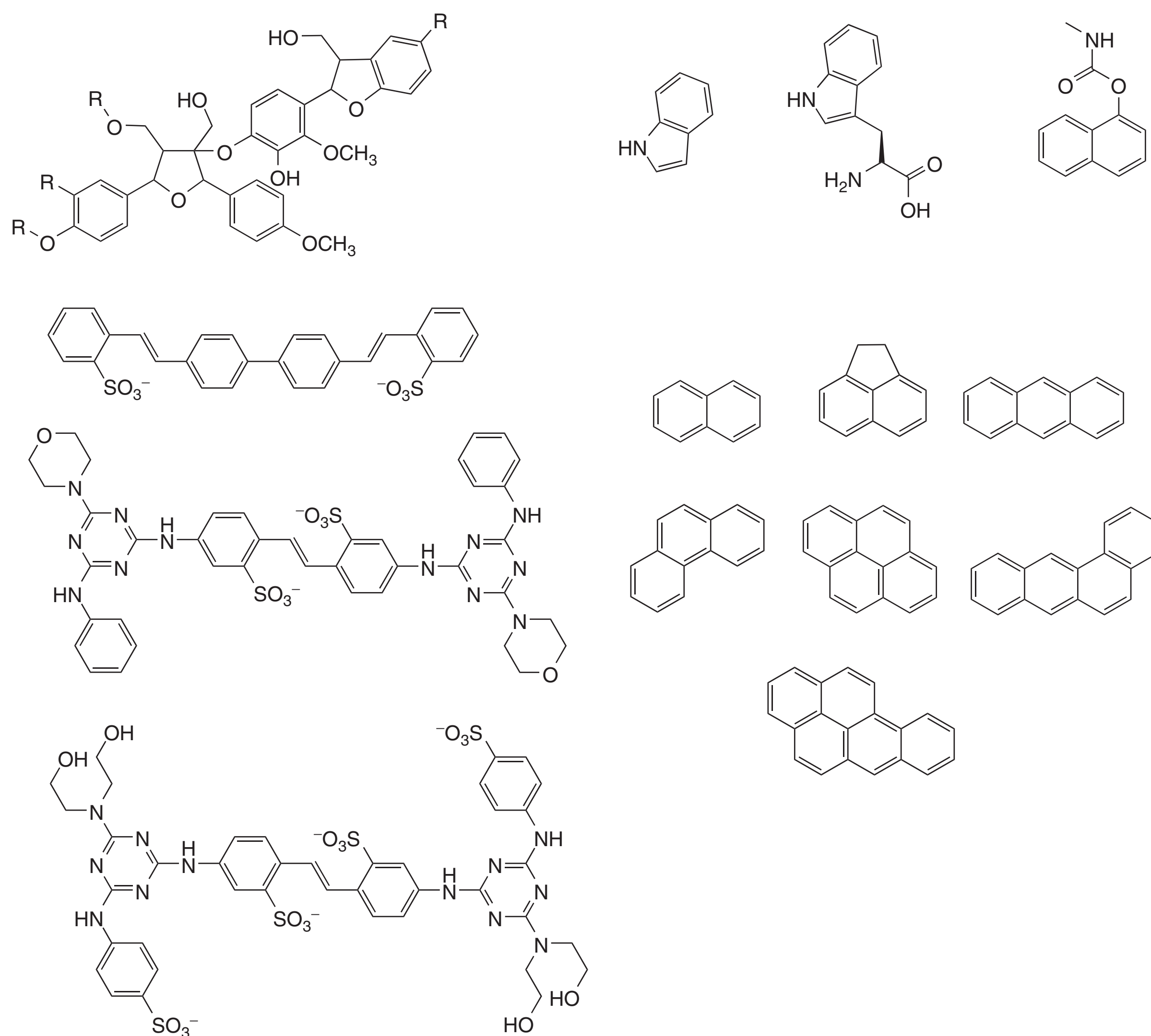

Figure 1 Examples of fluorescent structures within organic molecules. Clockwise from top-left: a hypothetical lignin macromolecule, indole, tryptophan, carbaryl (1-naphthyl methylcarbamate), seven polycyclic aromatic hydrocarbons of differing aromacity, three fluorescent whitening agents. Hydrogen on aliphatic carbons is implied with 'R' groups representing additional organic residues.

this case, the water matrix surrounding the fluorescent organic matter. Relevant to the analysis of pollutants in river and groundwaters are the effects of temperature and pH and interactions with colloids and dissolved metals. Inter-instrument configuration differences mean that fluorescence spectra should also be corrected for instrument-specific effects if comparison with data from other instruments is desired.

In river and groundwater samples, all of these fundamental fluorescence phenomena have to be considered and either controlled or quantified. Within the research community, the effect of concentrated solutions on fluorescence is often referred to as the inner-filter effect (IFE). The IFE leads to both a nonlinear relationship between fluorescence and concentration as well as a change in the excitation and emission wavelengths of fluorescence. The presence of an IFE in a river water sample can be easily identified by checking for linearity through analysis of a dilution series. The literature is less clear on the upper limit of riverine organic matter concentration above which IFE becomes problematic. Hudson et al.[4] reviewed the literature and reported upper limits which range from 1 to 15 $mg\,L^{-1}$, which are within the range of DOC concentrations in most rivers and groundwaters. Removal of the IFE often relies on an empirical correction based on absorbance spectra measurements and the assumption that the IFE at a particular wavelength is proportional to the absorbance at that wavelength.[12,13] Corrections are usually less than 10% if absorbance at 254 nm is less than 0.1 units.[14]

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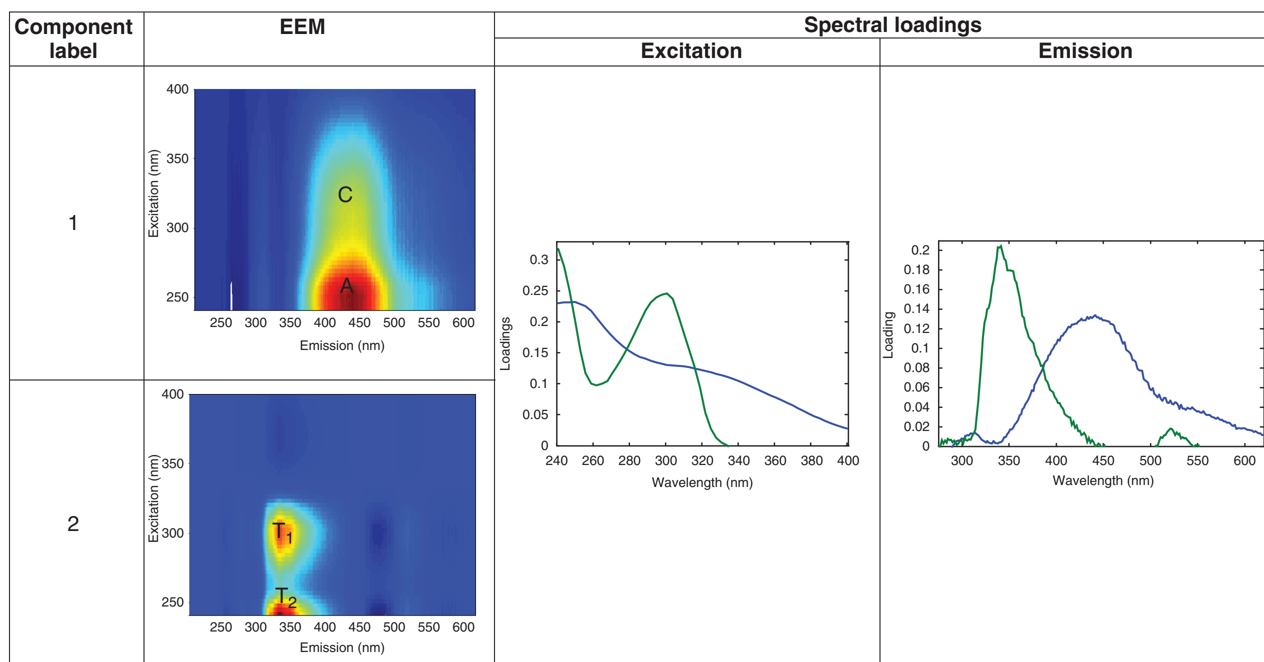

Figure 2 Examples of natural organic matter fluorescence signatures of unpolluted river and groundwaters. The EEMs are modeled PARAFAC components. In this model of river and groundwaters in the Namoi catchment, Murray–Darling Basin, Australia, two components are resolved. In many models, component 1 is resolved into two components.(7) 'Peak-picking' labels are also shown. (Ishii and Boyer.)

IFE correction is relatively automated for laboratory analyses; however, for in situ river fluorescence analyses, nonlinear calibrations that include reabsorption may be more appropriate. A similar consideration has to be made for correction of effects of temperature and pH on fluorescence. In the laboratory, these effects can be controlled by undertaking analyses at a constant temperature and pH; however, in the field, it requires independent measurement of temperature and pH, knowledge of the pH sensitivity, and thermal quenching of the NOM or pollutant being analyzed. Vodacek and Philpot,(2) Baker,(15) and Seredyńska-Sobecka et al.(16) have all considered the thermal quenching properties of riverine organic matter fluorescence, and Vodacek and Philpot,(2) Patel-Sorrentino et al.,(17) and Spencer et al.(18) the effects of pH on riverine organic matter fluorescence. In summary, thermal quenching is specific to a fluorescent chemical compound (fluorophore), with fluorescence in the peak T regions more temperature sensitive than that in the peak C region: further thermal quenching research is needed for pollutant fluorescence. pH quenching of fluorescence is comparatively well understood and within the pH range 5–9, relatively little quenching of fluorescence is observed.

Turbidity is also a potentially significant interference, preventing light penetration and causing scatter of excitation light into the fluorescence detector. In laboratory samples, this is simply overcome by prior filtration of the samples; however, for in situ analyses, this requires correction through the simultaneous measurement of turbidity. In situ measurements are considered in more detail in Section 2.3. Finally, fluorescence quenching by metal-ions in solution has been widely reported in controlled laboratory experiments, typically using extracted humic substances standards (see the review by Hudson et al.(4)). However, in the river and groundwater environments, such quenching is rarely observed. Presumably this is due to the ubiquitous presence of dissolved metals and colloids in the natural environment, such that organic matter fluorescence is always quenched to some degree; however, further research in this area is warranted.

2.2 Laboratory Analyses of River and Groundwater Fluorescence: Sampling Protocols and Excitation–Emission Matrix Data Processing

Sampling protocols for river and groundwater fluorescence analyses are based on the requirements to not contaminate the water sample with fluorescent material and to preserve the sample to prevent any processing of the organic matter between sampling and analysis. In practice, this means that river and groundwater samples should be stored at low temperature and in the dark to limit microbial degradation and photodegradation. Storage temperature should not be so low as to freeze the

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samples, as this can break down the organic matter and change the fluorescence signal.[19] To prevent interactions with any sediment or colloidal material in the sample, the water sample should be filtered as soon as possible, ideally in the field as part of the sampling routine. Filtration must be undertaken using nonfluorescent filter papers. Many possible combinations of sample containers and filters are possible, and a pragmatic approach of testing for background fluorescence from equipment is recommended. Pre-aged (washed in dilute acid solution) plastic containers have been reported to be useful, which helps remove possible contaminants from the containers. In general, polyethylene terephthalate (PET), high-density polyethylene (HDPE), or low-density polyethylene (LDPE) plastic sample containers combined with glass microfiber or polysulfone filters are widely utilized by the community. Filtering with a range of filter sizes can be insightful: filtering at 0.1 or 0.2 μm removes the majority of particulate microbial material and can help elucidate the organic matter properties or nature of a river or groundwater pollution source.[16,20]

Additional sample preservation is not recommended as this will alter the environmental conditions of the organic matter and therefore its fluorescence signal. For example, lowering the pH of the solution to less than 2 is recommended for DOC analyses; however, this will lead to a quenched fluorescence signal. The addition of preservatives and poisons such as sodium azide likewise change the environment and fluorescence, although further research in this area is warranted. Freezing is not recommended for reasons given earlier. The limited possibilities of sample preservation methods means that analysis should be undertaken as soon as possible after sampling, ideally within 24 h, although this may be impractical for remote field sites. With increased portability of laboratory instruments, field deployment is a practical option. If holding times greater than 24 h is unavoidable, fluorescence degradation tests can be undertaken to assess the possible changes in fluorescence over time. A thorough understanding of appropriate sampling protocols is particularly necessary for investigation of pollution in rivers and groundwaters, as many organic pollutants are either more biologically reactive or more sensitive to photodegradation than NOM. This is discussed further in Section 3.

Assuming that laboratory analyses are undertaken to produce an EEM, a significant amount of data can be produced rapidly in a data matrix form: an EEM from 200 to 500 nm at 5 nm steps produces a matrix of 3600 data points. Several data analysis, modeling, and mining techniques are routinely applied to reduce the data into an interpretable format, each with advantages and disadvantages. Data analysis is routinely preceded by data treatment which can include IFE correction, removal of scatter features, and data normalization. Widely utilized are parallel factor analysis (PARAFAC), a modeling approach that decomposes a set of EEMs into constituent components[21,22]; principal component analysis (PCA), a statistical approach that produces components that maximize the variance of the data but potentially at the expense of physical meaning[23]; regional integration approaches, which are basic summations of fluorescence within defined regions of optical space[24]; and basic 'peak picking' or 'fluorescence index' approaches, which identifies the wavelengths and intensity of a fluorescence peak, or ratio of intensities.[8,25] The choice of data processing technique for the analysis of fluorescence for river pollution investigations will partly depend on the nature of the pollutant being investigated, the sample size, and the speed of data analysis required. For example, PARAFAC would be very useful if a complex mixture of overlapping fluorescence spectra is suspected; however, it requires a large data set of EEMs to build a model. PARAFAC has been widely used, especially in NOM fluorescence research, and a series of components are widely recognized as reviewed in Ishii and Boyer.[7]

2.3 In Situ Analyses and Instrumentation

In situ analysis of river and groundwater, fluorescence has become increasingly practical in recent years, with a fundamental step-change in LED technology permitting the increased miniaturization of in situ probes and the availability of probes that excite at shorter UV wavelengths.[26–28] In situ probes are currently limited to fluorescence analyses at fixed excitation and emission wavelengths, and a useful approach is to identify regions of fluorescence using a laboratory spectrometer and the analysis of EEMs, followed by in situ analyses using fluorescence probes at appropriate fixed wavelengths. Probes that detect within the peak C region (exciting between 300 and 400 nm and detecting emitted fluorescence between 400 and 500 nm) are widely available, as are those calibrated to detect chlorophyll fluorescence (excitation of 465 nm and emitted fluorescence detected at 650 nm). Probes within the peak C region have some utility in detecting landfill leachate plumes in groundwaters, where there is increased fluorescence in this region from biodegradation products, as shown in Figure 3.

Most recently, in situ probes with LED excitation below 300 nm have become commercially available, permitting fluorescence in the 'peak T' region. These will become of great relevance owing to the large number of pollutants that fluoresce in this region (Section 3). The measurement of in situ fluorescence of pollutants permits continuous monitoring of rivers and groundwaters and overcomes any difficulties of sample degradation during transport before laboratory analysis. However, in situ analyses

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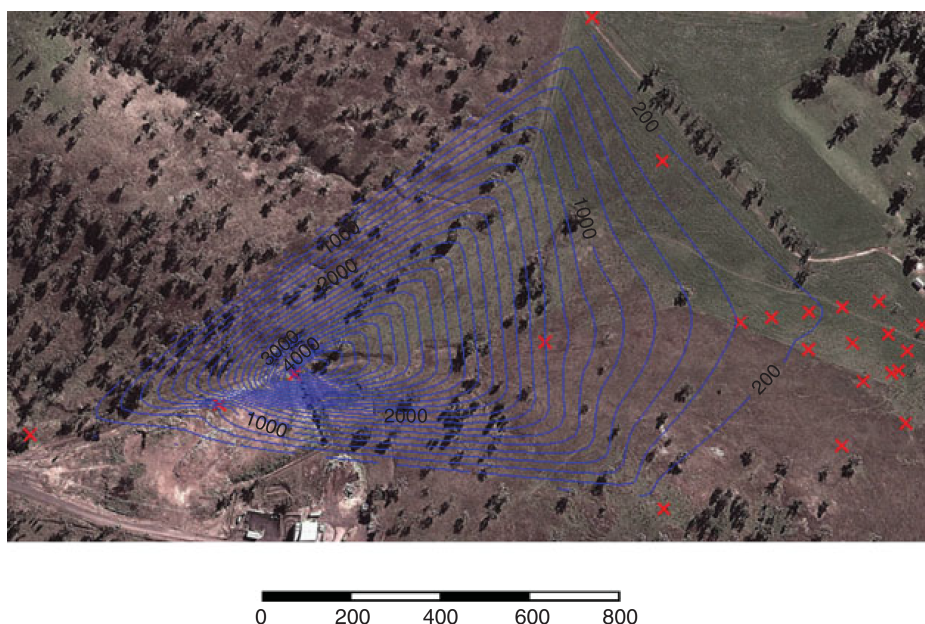

Figure 3 Contours of organic matter fluorescence in groundwater downgradient of a landfill cell. Contours are of PARAFAC component C1, which has maximum excitation at 320 nm and maximum emission of 400 nm. For more details on this case study see Ref. 29. (Graham et al.[29])

are unable to constrain many of the environmental factors that affect fluorescence, such as changes in pH, temperature, turbidity, and the potential of IFE occurring. The deployment of platforms with multiple probes, along with an in-line filter, permits the empirical correction of the fluorescence signal, and this has been undertaken for long wavelength probes in the peak C region.[30,31] However, any corrected in situ fluorescence signal is likely to be site specific, with new corrections necessary at each sample location. Calibration against grab samples that are filtered and analyzed under controlled laboratory conditions can also be useful. Quantification of the relative contribution of environmental effects versus the intrinsic fluorescence signal of an organic substance is essential for the application of in situ probes in the investigation of pollution.

3 POLLUTANT FLUORESCENCE SIGNATURES IN RIVERS AND GROUNDWATERS

Although pollution sources are likely to be similar for both rivers and groundwaters, in general, groundwater has a lower organic carbon concentration and therefore lower NOM background fluorescence. In principle, this means that pollutants are likely to be more easily detected in groundwater than in river systems. The groundwater environment also helps limit photodegradation and is more likely to be geochemically buffered in comparison to a river environment. On the other hand, pollutants that are susceptible to photodegradation will tend to persist for longer in a groundwater environment. Thus, when polluted groundwaters are sampled, changes in pollutant concentration due to photodegradation can be more dramatic for groundwater samples if care is not taken to keep the samples out of sunlight.

3.1 Biochemical Oxygen Demand and Microbial Health

A large body of research has identified the relationship between the BOD of a water sample and its fluorescence. Initial research on wastewaters[32,33] was followed by regional scale river investigations that demonstrated links between peak T fluorescence and BOD.[30,34–37] Further research within the wastewater treatment process suggests that the BOD versus peak T fluorescence relationship is robust over the range of BOD from 1 to 1000 mg L^{-1}(Figure 4). Intriguingly, BOD is notoriously difficult to measure precisely and reproducibly, whereas fluorescence provides the possibility of relatively precise analyses and the extrapolation of fluorescence intensities to obtain a measure of BOD at low BOD values.

The relationship between BOD and peak T fluorescence is due to the direct link between fluorescence and microbiological activity in this region of fluorescence, although the precise source of fluorescence in the peak T region is rarely demonstrated. Numerous laboratory

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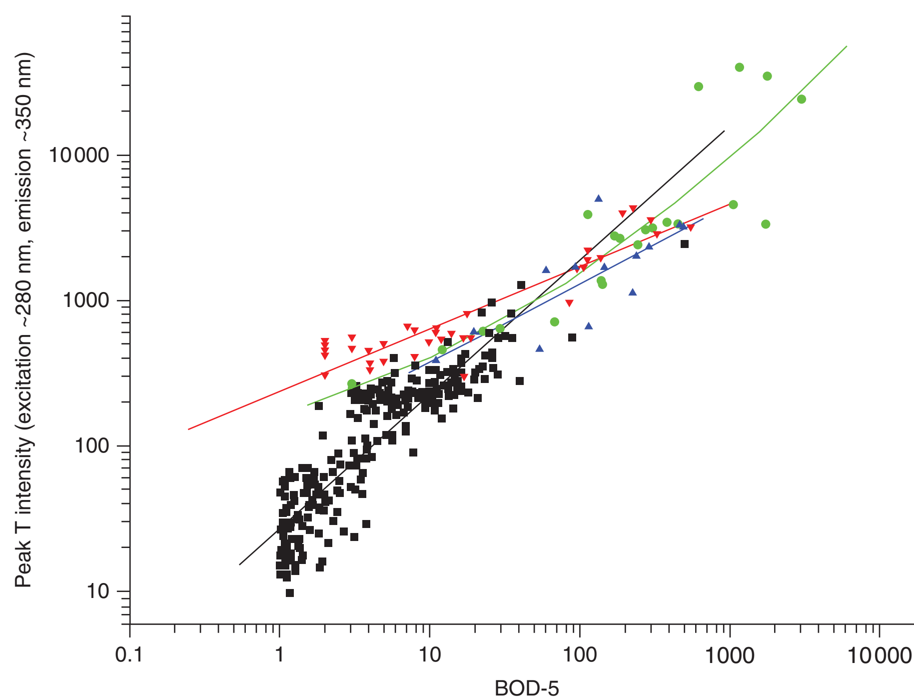

Figure 4 Relationship between BOD and peak T fluorescence. Data are from rivers and final treated effluents (squares)[35] and at different stages in the wastewater treatment process (circles, upward triangle, and downward triangle for each works[38] and unpublished data). All fluorescence intensities were determined using 'peak picking' the highest intensity in the peak T region, collected using an Agilent Cary Eclipse with data normalized to a Raman intensity of 20 at 348 nm excitation. (Hudson et al.)

incubation and microbiological studies have identified a direct relationship between microbial cell numbers and fluorescence.[38–45] Using end-member samples, Baker[46] demonstrated the link between peak T fluorescence and farm wastes including silage effluent and slurries, demonstrating potential pollution applications in rural catchments. Ohno and Bro[47] analyzed a wide range of soil amendment fluorescence EEMs and determined that the resultant soil organic matter EEMs were relatively homogeneous despite the diversity of amendments. Naden et al.[38] and Old et al.[48] utilized peak T fluorescence and the peak T to peak C ratio to track slurry pollution from an agricultural catchment. They noted that the slurry fluorescence signature was only ubiquitously present in the first runoff event after slurry application, after which slurry decomposition had progressed to such a degree that the slurry fluorescence signature was not distinguishable from background.

In wastewater, Bridgeman et al.[49] observed that the peak T–BOD signal is less than 0.2 µm fraction in wastewater effluents, and therefore an indirect measurement of living cellular material in these waters. Goldman et al.[50] used a multivariate approach that utilizes all fluorescence peaks, as well as UV absorbance and the fluorescence index of McKnight et al.[25] to develop a model that predicted the amount of wastewater in river catchments. Hudson et al.[35] had previously shown that the strength of the BOD–peak T relationship varied between river catchments, and a multivariate approach will help in the cases where there are several sources of fluorescence in the peak T region. River and groundwater microbial activities will also depend on temperature, and in cold climates, in situ fluorescence may remain low (low microbiological activity), whereas a sample obtained for BOD analysis demonstrates a significant BOD (owing to the standard methods requiring incubation at 20 °C). In situ analysis of peak T fluorescence, therefore, can be argued to be a more representative measure of actual microbiological activity in a river or groundwater system at its current temperature. With the availability of hand-held fluorimeters[49,50] and the most recent commercialization of in situ fluorescent probes in the peak T region, it will now be possible to investigate the temporal variability of BOD and provide the possibility of real-time BOD measurements as opposed to the classical 5-day test.

The possibility of fluorescence analysis as a rapid surrogate method for the 36-h incubation in *Escherichia coli* standard method also exists. Laboratory studies have demonstrated a correlation between fluorescence and *E. coli* blends of river and wastewaters.[42,51,52] In the natural environment, the presence of a large number of different microbial communities means that this

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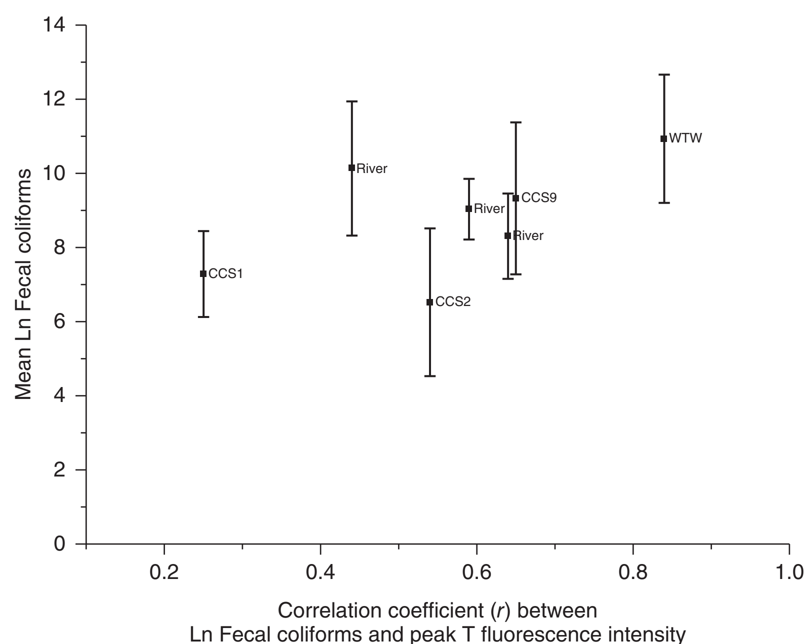

Figure 5 Relationship between Fecal coliform numbers and the correlation coefficient between fecal coliforms and peak T fluorescence. CCS, cross-connected storm sewer; WTW, wastewater treatment works final effluent; and river, urban river receiving cross-connect storm sewerage and combined sewer overflows.

relationship is only likely to be maintained in simple river and groundwater systems with a single pollutant source, which is high in *E. coli*. Figure 5 demonstrates the loss of correlation between peak T fluorescence and coliform numbers between the single source scenario (a wastewater effluent), cross-connected storm sewers (storm sewers with accidental wastewater connections), and river samples in an urban river.

3.2 Fluorescent Whitening Agents

FWAs or optical brighteners (Figure 1) are commonly found in potential pollutants such as industrial effluents, landfill leachates, and sewerage. For an example of FWAs and their degradation in sunlight, see Kramer et al.[53] These compounds are designed to have high fluorescence efficiency and to absorb UV light and emit in the UV/blue spectra; to whiten the appearance of products such as tissue, paper, and sanitary products; and for use in detergents. Their region of fluorescence strongly overlaps with the peak C region representing humic-like substances; however, FWAs can be distinguished from this source by a number of techniques. Being highly photodegradable, repeated measurements of fluorescence during controlled light exposure can elucidate their presence.[54] Owing to their high fluorescence efficiency, a comparison of fluorescence normalized to DOC concentration or UV absorbance can identify their presence[52] by means of the higher fluorescence per gram C or absorbance. Thanks to their subtly different shape of the emission peak compared to natural humic-like substance fluorescence, careful ratio measurements or PARAFAC analyses should separate out FWA fluorescence from background.[55]

Hartel et al.[56,57] used hand-held fluorimeters to investigate the relationship between fluorescence in the peak C fluorescence region and the presence of optical brighteners and then inferred from that the presence of sewerage pollution and *E. coli*. However, results were inconclusive because of the presence of peak C fluorescence from NOM giving false positives. Further developmental methods utilized the measurement of fluorescence decay over time using hand-held fluorimeters. Making repeated fluorescence measurements under conditions of photodegradation, the rate of change of fluorescence decay over time can distinguish the different rates of fluorescence decay of NOM and FWAs in the peak C region.[54,58] The detection of FWAs through analysis of fluorescence decay in the peak C region was successfully applied to sewerage impacted river systems.[54]

3.3 Polycyclic Aromatic Hydrocarbons

Polycyclic or polyaromatic hydrocarbons (PAHs) strongly fluoresce because of the presence of two or more aromatic carbon rings in the chemical structure (Figure 1). The

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fluorescence signature of a wide range of PAHs has been reported,[59,60] normally in the context of providing end-members for fingerprinting petroleum pollution sources,[61] as in the marine environment.[62] Petroleum products are complex mixtures that include PAHs. Pharr et al.[61] produced 21 fluorescence fingerprints of petroleum products diluted 10 000 times in a water solution using synchronous scan fluorescence, which demonstrated a wide range of fluorescence spectra emitting in the short UV. Alostaz et al.[60] report the fluorescence spectra of nine PAHs and used an EEM and PARAFAC approach to identify the fluorescent components of various petroleum products. In general, PAH fluorescence occurs in the shortwave UV and overlaps that of microbial activity (peak T), and in some cases can also extend into the longwave UV and overlap in the peak C region (Figure 6). Therefore, PARAFAC or other decomposition approaches can be useful to distinguish these pollutants from other fluorescent organic materials.

Examples of the use of fluorescence to detect organic pollution in the aquatic environment relate to the presence of PAHs in both petroleum and landfill leachates. Christensen et al.[62] utilized fluorescence EEMs and PARAFAC to identify the petroleum contamination from the Baltic Carrier oil spill in 2001. In an urban river pollution event, Carstea et al.[63] identified a diesel spill in a river that was also polluted by sewerage pollution by identifying increased fluorescence in the ~225-nm excitation and ~350-nm emission region. In an oil-tar producing region, Kabanagh et al.[64] report the use of fluorescence to detect oil-sand process-affected waters, identifying naphthalene fluorescence as the probable cause of the observed fluorescence. Baker and Curry[65] also report naphthalene fluorescence as a fingerprint of some landfill leachates and associated pollutant plumes. PAHs

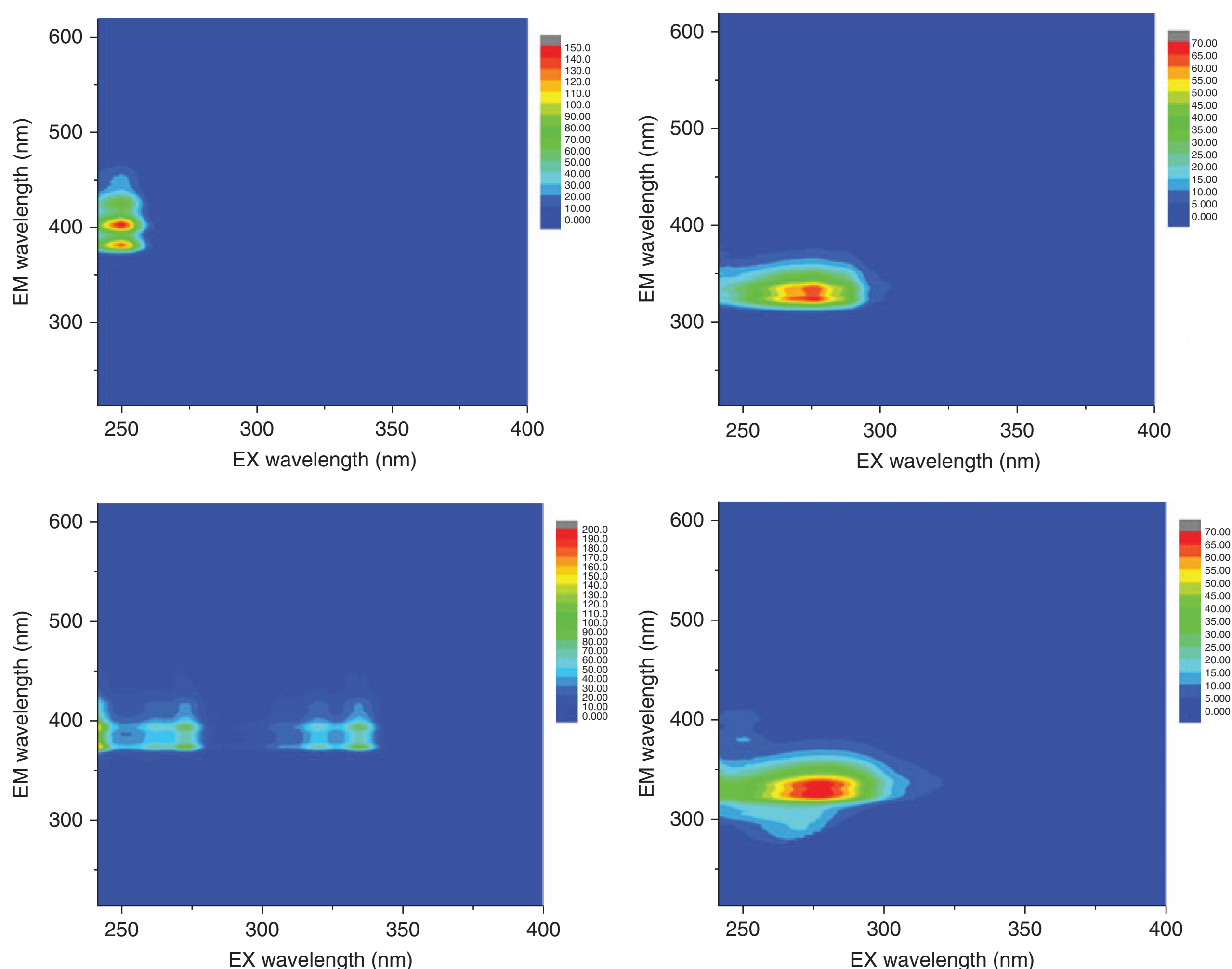

Figure 6 EEMs of PAHs and petroleum. Clockwise from top left: anthracene, naphthalene, pyrene, and aviation fuel. All samples are diluted to avoid IFE, with final fluorescence intensity chosen to give optimal visual appearance of the EEM.

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are a likely component of landfills that contain industrial wastes and owing to their low solubility and high fluorescence efficiency, they are likely to be persistent pollutants that can be detected at low concentrations in rivers and groundwaters. Baker[15] demonstrated the use of this fluorescence signature to identify landfill leachate in an urban river system also contaminated by sewerage pollution, and Tedetti et al.[66,67] utilized and developed in situ shortwave UV fluorimeters in an attempt to detect PAH pollution in wastewaters and coastal waters. Dahm et al.[68] characterized fluorescence signatures in groundwater samples as a method to identify well contamination from coal-bed methane operations.

4 CONCLUSIONS

Many organic pollutants contain the aromatic ring structures that permit fluorescence. However, overlaps in fluorescence spectra exist, and care has to be taken to correctly identify the pollution source for a successful investigation. Forensic river investigations, with regular samples taken while working upstream; and samples taken from the main stem, major tributaries, and potential pollution sources, are a good sampling framework. This may be followed by appropriate multivariate techniques, especially in the case of detecting multiple pollutants against a variable NOM fluorescence background. In general, relatively high fluorescence in the short UV region (excitation <300 nm and emission <370 nm) appears to be indicative of anthropogenic pollutants,[69] and river and groundwaters of poor water quality. This fluorescence derives both from microbiological activity such as that observed in urban sewerage impacted rivers[70,71] and rural agriculturally impacted rivers,[43,48] as well as from PAHs from petroleum product and some landfills. Pesticides with aromatic groups also fluoresce[72–74]; however, their fluorescence characteristics and fate in rivers and groundwaters require further research. Repeat analysis of water samples under controlled conditions that permit photodegradation and microbial degradation can help elucidate a fecal versus a PAH source of the fluorescence signal. High fluorescence intensity in the peak C region can be attributed to a contribution of fluorescence from FWAs; however, in this region, there is a possibility of overlap with NOM fluorescence. Again the analysis of fluorescence photodegradation over time in this region of optical space permits the identification of highly photodegradable FWAs over NOM background.

The combination of fluorescence analysis with other geochemical measurements can be highly informative. The identification of stormwater, gray-water, and foul-water sewerage pollution in an urban river was undertaken by the analysis of fluorescence and ammonia.[75] In the same study, de-icer pollution from propylene glycol was identified in an urban river through the lack of increase in fluorescence with an associated increase in DOC downstream of a pollution source.

Recent research continues to develop the use of fluorescence in river and groundwater pollution. Analysis of different suspended particle size fractions of waters has been demonstrated to improve the uniqueness of the fluorescence fingerprint, with Wei et al.[76]suggesting that less than 5 kDa HPOA fraction had a more unique signal of peak T for polluted urban waters. We made similar findings for the BOD versus peak T relationship for the less than 0.2 μm fraction in wastewater treatment.[49] Hur and Cho[77] and Bridgeman et al.[49] demonstrate relationships between fluorescence and chemical oxygen demand (COD) in rivers and wastewaters; however, this is done with peaks A and T respectively. Further research should permit the identification of a fluorescence signal for river COD. Continued development of in situ fluorimeters with excitation into the short UV will permit the real-time monitoring of pollutants such as PAHs and the separation of PAH and microbial fluorescence signals in that region.[67]

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ABBREVIATIONS AND ACRONYMS

BOD	Biochemical Oxygen Demand
CCD	Charge-coupled Device
COD	Chemical Oxygen Demand
DOC	Dissolved Organic Carbon
EEM	Excitation–Emission Matrix
FWA	Fluorescent Whitening Agent
HDPE	High-density Polyethylene
IFE	Inner-filter Effect
IHSS	International Humic Substances Society
LDPE	Low-density Polyethylene
LED	Light-emitting Diode
NOM	Natural Organic Matter
PAH	Polyaromatic Hydrocarbon
PARAFAC	Parallel Factor Analysis
PCA	Principal Component Analysis

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PET Polyethylene Terephthalate
PMT Photomultiplier Tube
UV Ultraviolet

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