

유기물 형광분석법을 활용한 유역 오염 진단 및 오염원 추적: 문헌 연구

칸다따라 니푸니 디니샤^a · 허진² · 이병준^{b,3,*}

¹경북대학교 미래과학기술융합학과 · ²세종대학교 환경에너지공간융합학과 · ³경북대학교 에너지환경연구소

Application of Fluorescence Excitation Emission Matrices for Diagnosis and Source Identification of Watershed Pollution : A Review

Kandaddara Badalge Nipuni Dineesha^{1a} · Jin Hur² · Byung Joon Lee^{1b,3,*}

¹Department of Advanced Science and Technology Convergence, Kyungpook National University

²Department of Engineering Environment, Energy and Geoinformatics, Sejong University

³Energy Environment Institute, Kyungpook National University

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Abstract

The constituents of a watershed control a wide range of ecosystem processes, such as, carbon sequestration, nutrient retention, and biodiversity preservation. Maintenance of a healthy watershed is advantageous to humans in many direct and indirect ways. Dissolved organic matter fluorescence analysis is one of the most commonly utilized parameters for water quality measurement, pollution source tracking, and determination of the ecological state of a watershed. Throughout the recent decades, the advancement in data processing, instrumentation, and methods has resulted in many improvements in the area of watershed study with fluorescence analysis. The current trend of coupling advanced instrumentations and new comparative parameters, such as, microplastics of different types, antibiotics, and specific bacterial contaminants have been reported in watershed studies. However, conventional methodologies for obtaining fluorescence excitation emission matrices and for calculating the fluorescence and spectral indices are preferred to advanced methods, due to their easiness and simple data collection. This review aims to gain a general understanding of the use of dissolved organic matter fluorescence analysis for diagnosis and source identification of watershed pollutions, by focusing on how the studies have utilized fluorescence analysis to improve existing knowledge and techniques in recent years.

Key words : Fluorescence, Organic matter, Pollution, Watershed, Water quality

^{1a} 석사과정(Master Student), kbndineesha@knu.ac.kr, <https://orcid.org/0000-0002-6314-1391>

² 교수(Professor), jinhur@sejong.edu, <https://orcid.org/0000-0001-6735-1946>

^{1b,3} Corresponding Author, 교수(Professor), bjlee@knu.ac.kr, <https://orcid.org/0000-0002-8338-5238>

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1. Introduction

Natural aquatic ecosystems such as marine and freshwater ecosystems are crucial for maintaining the general balance of the environment (Band et al., 2012). Human population is the main beneficiary of these aquatic ecosystems as they provide clean water for drinking and irrigation, habitats for fisheries, maintenance of biogeochemical cycles. Watersheds or drainage basins contain these aquatic ecosystems, which are directly responsible for nutrient cycling, carbon storage (Allan, 1995), soil formation, wildlife corridor (Clipp and Anderson, 2014) sediment filtration, flood and erosion control.

In a simple explanation, a watershed is a land area that drains into a water body. This can be a river, lake, or stream, and the watershed can be small in size with a single waterway or very large, comprising one or more streams and a main water body. Watersheds extensively affect surface water quality. The land area of the watershed is connected through the movement of water, and collectively, all the chemical, physical, and biological processes occurring in the area are responsible for the functionality of the ecosystems. The rapid growth of the human population and the increasing rate of urbanization negatively affect watershed maintenance and health. In particular, the degradation of water quality has been a key focus for decades (Bolan et al., 2011; Chen et al., 2015; Chen et al., 2007; Grimm et al., 2008). Human activities such as urban development, agriculture, and animal husbandry are strongly reflected in water quality parameters, such as total nitrogen (TN) and total phosphorus (TP) concentration (Chen et al., 2007). Dissolved organic matter (DOM) has shown a tendency to reflect water quality because it is closely related to the basic water quality parameters of a water body, such as biological oxygen demand (BOD) and chemical oxygen demand (COD) (Lee et al., 2020). The type and abundance of DOM provide valuable information concerning human impacts on aquatic ecosystems (Clayton et al., 2017). For example, an obscene proportion of protein-like organic matter or the presence of microbial humic-like substances in DOM within the ecosystem is associated with the presence of anthropogenic activities and is utilized as an indicator to assess human impact on water pollution (Clayton et al., 2017; Petrone et al., 2011; Tanaka et al., 2014).

The composition of DOM can also be considerably altered by effluents from wastewater treatment plants (Zhu et al., 2020) and/or by unintentional residential wastewater discharge (Kim et al., 2012). The efficiency of the wastewater treatment process can be assessed by investigating the change in the DOM composition of downstream water (Meng et al., 2013; Stolpe et al., 2014).

DOM has been commonly used as an indicator of the land use of watersheds and a predictor of pollution sources in surface water bodies (Derrien et al., 2019; Lozovik et al., 2007; Retelletti Brogi et al., 2018). The spectral fingerprint of humic substances (HS) generated from agricultural land use and forest watersheds has been distinguished by DOM analyses (Graeber et al., 2012). The DOM in a watershed is affected in multiple ways by human disturbances, which can be verified because *in situ*-produced DOM shows unique signals and differences in its spectroscopic indices from terrestrially derived DOM (Stanley et al., 2012).

DOM characterization mainly employs a three-dimensional fluorescence spectrum (3D-EEM) along with ultraviolet-visible spectroscopy (Arguelho et al., 2017; Li, Lu et al., 2021). Only a certain fraction of DOM absorbs light and produces a signal, and even a minor fraction fluoresces (Gilchrist and Reynolds, 2014). However, optical measurements of these DOM sub-fractions have provided useful insights into DOM composition, which has been used extensively in recent years as a reliable parameter (DeVilbiss et al., 2016; Kamjunke et al., 2017; Li, Zhang et al., 2022). There is a range of technical methods besides spectroscopy, such as isotope analysis (Guo et al., 2009) and chromatographic methods (high-performance liquid chromatography (HPLC)-size exclusion chromatography (SEC)) (Her et al., 2003). However, spectroscopic methods are prevalent owing to the many conveniences of these complex methodologies and their comparatively high sensitivity, ease of use, fast responses, and low-cost instrumentation and processing (Conmy et al., 2014; Li and Hur, 2017).

The inherent chemical complexity and heterogeneity of DOM make it necessary to resolve the overlapped fluorescence signals and to remove other spectral interferences from the samples during fluorescence spectroscopic analysis (Gilchrist and Reynolds, 2014). This makes the fluorescence excitation-emission matrix (FEEM) itself low in accuracy and reliability for directly identifying the source or composition of the DOM (Ma and Li, 2020). This hurdle was overcome by using mathematical techniques, specifically decomposition methods and multivariate analyses. The most commonly utilized tool in watershed studies is parallel factor analysis (PARAFAC), in which the 3D-EEM is separated into individual components (Gu et al., 2020). Combining fluorescence spectroscopy with mathematical tools such as PARAFAC has heightened its application potential (Bro, 1997; Stedmon and Bro, 2008; Stedmon et al., 2003). Built-in programming tools such as the DOMFluor open toolbox in MATLAB software and staRdom package in R programming make PARAFAC more convenient to use for research purposes and it has been extensively utilized in the majority of the watershed studies

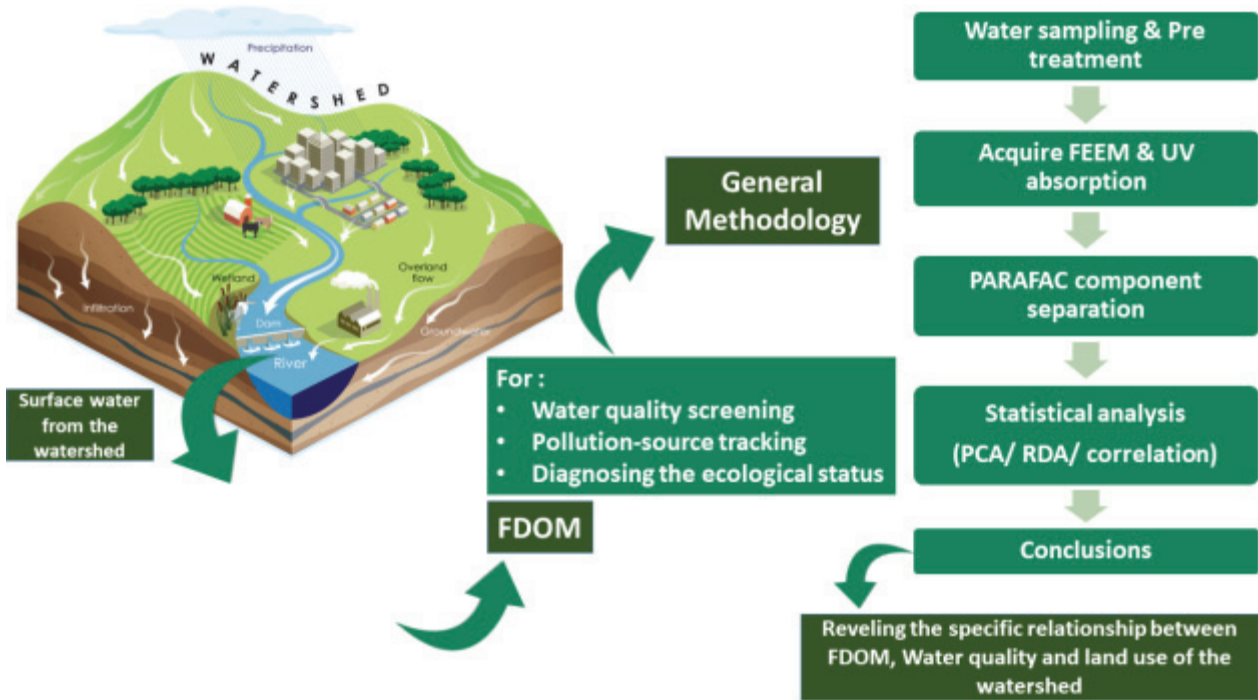


Fig. 1. Schematic diagram of the utilization of FDOM characterization with Fluorescence Excitation Emission Matrices (FEEM) and statistical analysis for diagnosis and source identification of watershed pollution.

(DeVilbiss et al., 2016; Lee et al., 2020; Li, Zhang et al., 2022; Stanley et al., 2012).

In order to understand DOM optical property measurements in depth, it is necessary to consider the environmental context and the diversity of production, transformation, transport, and storage mechanisms involved in the process (D'Andrilli et al., 2022). Because the applicable ecosystems are versatile, the range of available literature in the field is also plentiful. This review aims to gain a general understanding of the use of DOM fluorescence analysis in watershed studies, focusing on recent years and how the field of watershed studies has utilized DOM fluorescence to improve existing knowledge and techniques.

2. Separation of Independent DOM fluorescent Components

The different fluorescent components present in DOM samples can be differentiated by the distinct wavelengths of each peak separated in the PARAFAC. Moreover, source determination can be performed based on the specificity of these components (Murphy et al., 2014). The peak representation of the relevant DOM components provides a better understanding of the collected data. However, it is notable that the peak positions can shift with changes in the ionic strength, pH, and other solvent properties (Osburn et al.,

2014). Owing to the diverse uses of the FEEM approach in DOM studies, PARAFAC models have now been applied to natural systems such as freshwater, marine, and soil-derived waters alongside engineered systems (D'Andrilli et al., 2022; Ishii and Boyer, 2012; Stedmon et al., 2003; Wu et al., 2022).

There are commonly occurring PARAFAC components that are defined by a range of excitation and emission wavelengths across a range of studies (Ishii and Boyer, 2012). The most commonly occurring fluorescent dissolved organic matter (FDOM) can be categorized as either humic-like type or protein-like type (Stedmon and Cory, 2014). Humic-like components are very versatile. They show a wide range of excitation and emission wavelengths, as well as different chemical qualities mainly related to their natural origin. Researchers have observed the three most commonly occurring humic-like components in both natural and engineered systems. The first component has an excitation peak at approximately 260 nm or less with a broad emission band centered at 400 - 500 nm (Ishii and Boyer, 2012). This component is most commonly abundant in DOM dominated by terrestrial precursor material from soil extractions, soil solutions, forested streams, wetlands, and tree leaves, especially during warm months in spring and summer (Ohno and Bro, 2006; Stedmon and Markager, 2005; Stedmon et al., 2003). This peak position is classified as humic-like peak A in the Coble peak nomenclature (1996) (Coble, 2007; Coble et al., 1998).

The second humic-like component consists of a primary excitation peak wavelength of approximately 260 nm or less, with a broad emission band centered at 400 - 500 nm. It is similar to the first humic-like component; however, this second component also has a secondary excitation peak at 340 - 420 nm (Ishii and Boyer, 2012). The secondary peak is labeled as peak C (humic-like peak C) in the Coble peak nomenclature (Murphy et al., 2014). In a natural environment, peaks C and A are always observed together, but their ratio exhibits some variability. This humic-like component has been identified in DOM from a wide variety of aquatic systems, including those dominated by terrestrial and potential secondary sources of microbial input (Lapierre and Frenette, 2009; Stedmon and Markager, 2005).

Another fluorescent component, the microbial humic-like component, has a primary and secondary excitation peak, occurring at 260 nm or less and 295 - 380 nm, respectively secondary excitation peak at 295 - 380 nm and a single emission peak at 374 - 450 nm. Studies have suggested that microbial humic-like fluorophores are similar to those of terrestrial and marine precursors, which are traditionally classified as humic-like peaks A and M, where peak M implies a marine humic-like component (Coble et al., 1998; Ishii and Boyer, 2012). Peak M was originally derived from bloom conditions in the Gulf of Maine (Coble, 1996) and the Arabian Sea (Coble et al., 1998). The M peak of microbial humic-like components has also been observed in non-marine environments (Stedmon and Markager, 2005) and has been found associated with recent microbial activity, rather than arising exclusively from a marine source. These are a family of humic-like compounds that share a common fluorophore backbone with a different ring substitution, which can fluoresce at slightly different excitation and emission maxima (Coble et al., 2014). Therefore, within any given sample, the position of the humic-like peak provides reliable information regarding chromophoric dissolved

organic matter (CDOM) composition, organic matter source, and environmental conditions (D'Andrilli et al., 2022; Ishii and Boyer, 2012).

The peak positions for protein-like components are much less variable than those for humic-like components (Ishii and Boyer, 2012). These peaks were found to be more readily resemble the pure compounds and unlikely to be influenced by the environment or source (Coble et al., 1998; Ishii and Boyer, 2012). These amino acid-like peaks are similar to tyrosine and tryptophan, presenting their respective positions in FEEM for tyrosine and tryptophan at an excitation/emission of 230, 275/305 nm and 230, 275/340 nm, respectively. Protein-like fluorescence in natural waters tends to arise from a combination of free and combined amino acids rather than pure compounds. This is reflected in the PARAFAC output, which has a border range of emission maxima for tyrosine and tryptophan-like component separation (peaks B and T in the Coble peak nomenclature) (Coble, 1996; Coble et al., 2014). The fluorescence emission maximum for proteins also depends on the hydrophobicity of the molecular sites surrounding the amino acid moiety (D'Andrilli et al., 2022; Stedmon and Cory, 2014).

Multiplex fluorescence peaks have been observed in areas of active biological productivity, other than the protein-like (amino acid-like) peaks. These include chlorophyll-like pigment peaks, quinone-like peaks, (Cory and McKnight, 2005) as well as several unidentified compounds such as fluorophore N (Coble, 1996) and many more newly found unspecified components (e.g., Component 9 in Murphy et al., 2009). The earliest peak nomenclature defined by Coble et al. (1990) (Coble, 1996; Coble et al., 1990, 1998) and Stedmon et al. (2003) (Stedmon et al., 2003) has been the most widely used, and the peak distinction is clear. The common labels for the identified regions of the observed fluorescence peaks with excitation-emission wavelengths of aquatic DOM are summarized in Table 1.

Table 1. Labels for identified regions of commonly observed fluorescence peaks in an excitation-emission spectrum of aquatic DOM

Peak label	Excitation maximum (nm)	Emission maximum (nm)	Description of fluorophores
B	275	305	Tyrosine-like, protein-like ^a
T	275	340	Tryptophan-like, protein-like ^a
A	260	400-460	Humic-like ^a
M	290-310	370-410	Marine humic-like ^a
C	320-360	420-460	Humic-like ^a
D	390-455	509-512	Soil fulvic acid ^b

a: Coble, 2007; b: Stedmon et al., 2003

Note: Peak M has subsequently been observed in nonmarine environments.

3. Fluorescence and Spectral Indices

The DOM composition and sources in watersheds are often correlated with fluorescence indices calculated from 3D-EEM data. These indices can simply be defined as the ratio of the fluorescence intensity measured at two different regions in the optical space that should be chemically reasonable (Gabor et al., 2014). For decades, researchers have developed these fluorescence indices concurrent with their studies (Chen et al., 1977; Weishaar et al., 2003; Zsolnay et al., 1999). Hence, the fluorescence indices were targeted to address system-specific questions, such as the identification of soil organic matter in groundwater (Kalbitz et al., 2000), predicting the inactivation of bacteria during ozonation in the wastewater treatment process, (Wu et al., 2018) and many more source-detection and pollution-detection applications throughout the years (Chaves et al., 2020; Li, Zhao et al., 2022; Shi et al., 2022; Zhang et al., 2021).

More recently, researchers have been able to develop fluorescence indices on a system-specific scale, where they can be applied in a wide range of systems (Gabor et al., 2014). The humic-like peak in NOM is mostly the key focus in developing fluorescence indices, but the intensities associated with humic-like and protein-like peaks have also been extensively studied (Kalbitz et al., 2000; Ohno and

Bro, 2006; Zsolnay et al., 1999). The general interpretations of fluorescence indices are most likely to vary with solution properties, such as salinity, pH, and organic matter source (Gabor et al., 2014). The commonly used fluorescence indices for freshwater systems are described along with their relative wavelength ratios and references in Table 2.

Alongside fluorescence spectroscopy, UV-Vis spectroscopic studies have also prominently utilized spectral parameters to analyze CDOM. UV-Vis absorption spectra have a rather low sensitivity compared to fluorescence spectra, and the gathered information is insufficient to conclude only from the UV-Vis spectra (Li and Hur, 2017). However, these spectra are still widely used as common and easy measurement methods to estimate CDOM abundance, reactivity, quality, and source tracking. Researchers have previously used UV spectral parameters in a site-specific manner. For examples, natural system studies mostly applied the results of absorption coefficients and spectral slope parameters, whereas engineered systems more frequently used absorbance and differential absorbance spectra (Li and Hur, 2017; Peacock et al., 2014). Similar to fluorescence indices, spectral indices require generalization for applicability. The most commonly observed UV indices in watershed studies are listed in Table 3.

Table 2. Fluorescence indices for freshwater systems with their relative wavelength ratios and references.

Fluorescence Indices	Parameters	Comments	Reference
Humification Index (HIX _{EM})	The area under the em spectra at 435 - 480 nm divided by the peak area at 300 - 345 nm + 435 - 480 nm, at ex of 254 nm	Indicator of humic substance or extent of humification. Higher values indicate an increasing degree of humification	(Ohno and Bro, 2006; Zsolnay et al., 1999)
Freshness Index (β/α) (BIX)	The ratio of em intensity at 380 nm divided by the maximum em intensity between 420 nm and 435 nm at ex of 310 nm	β peak: recently created (likely microbial) organic matter α peak: older, more decomposed organic matter. β/α : Indicates the proportion of recently produced DOM. Developed for and mostly used in estuarine environments.	(Huguet et al., 2009; Parlanti et al., 2000; Wilson and Xenopoulos, 2008)
Fluorescence Index (FI)	The ratio of em wavelengths at 470 nm and 520 nm, obtained at ex of 370 nm	Indicates if precursor material for DOM is more microbial (FI~1.8) in nature or more terrestrially derived (FI~1.2).	(Cory et al., 2010; Cory and McKnight, 2005; McKnight et al., 2001)
Peak T/Peak C ratio	The ratio of maximum fluorescence at ex 275 nm/em 350 nm (Peak T) to max intensity of the region at ex 320 - 340 nm/em 410 - 430 nm (Peak C).	Used to identify the impact of sewage effluent on a river. Indicates biochemical oxygen demand relative to dissolved organic carbon (BOD/DOC)	(Baker, 2001)

Note: em = emission wavelengths, ex = excitation wavelengths

Table 3. Most commonly observed UV indices in freshwater-related watershed studies.

Absorbance index	Calculation	Purpose	Reference
A_{254} , A_{280} , A_{300}	Absorption value (arbitrary units) of the given excitation wavelength in nm	Absorptivity at 254 nm that is very readily absorbed by organic matter in the water. UV ₂₅₄ parameter to other water quality parameters that provide a measure of organic matter in the water.	(Edzwald et al., 1985; Lawrence, 1980; Mcknight et al., 1997)
		Absorptivity at 300 nm and 280 nm strongly correlated with the aromatic carbon content for seven aquatic fulvic acids	
Specific ultraviolet absorbance at 254 nm [SUVA ₂₅₄ (L mg-C ⁻¹ m ⁻¹)]	Absorption coefficient at 254 nm divided by DOC concentration	Absorbance per unit carbon. Typically, a higher number is associated with greater aromatic content	(Weishaar et al., 2003)
Spectral slopes ($S_{275-295}$, $S_{290-350}$, $S_{350-400}$) (nm ⁻¹)	Nonlinear fit of an exponential function to the absorption spectrum over the wavelength range	Higher S values indicate low molecular weight material and/or decreasing aromaticity	(del Vecchio and Blough, 2002; Helms et al., 2008)
Spectral slope ratio (S_R) $S_{275-295}$ (nm ⁻¹): $S_{350-400}$ (nm ⁻¹)	Spectral slope $S_{275-295}$ divided by spectral slope $S_{350-400}$	Negatively correlated to DOM molecular weight and a general increase in CDOM	(Helms et al., 2008)

Note: em = emission wavelengths, ex = excitation wavelengths

4. Applications of DOM Fluorescence for Watershed Studies

The watershed mostly consists of a large land area and a related water body. In such cases, point sampling can be inconvenient and overconsume resources. Therefore, a strategy for developing easy and alternative methods should be considered, where the research area of watershed pollution source tracking is mostly associated with DOM fluorescence studies (Li and Hur, 2017). DOM analytical tools in watershed studies have attracted the attention of the water research community for more than 20 years, and such high attractiveness has led to the publication of several related review articles (Andrade-Eiroa et al., 2013; D'Andrilli et al., 2022; Ishii and Boyer, 2012; Stedmon and Bro, 2008; Stedmon et al., 2003).

It is important to study how DOM fluorescence has been utilized and interpreted in watershed studies because using such new technology has resulted in precise outcomes compared to those of earlier studies. To obtain a basic idea of the general demographics in research publications on DOM fluorescence for the field of watershed studies, a literature search was conducted using the keywords dissolved organic matter, watershed, and fluorescence. As per the results, the United States of America (USA) was the leading publisher for the past 10 years (218 articles), followed by China (124 articles), Canada (64 articles), South Korea (32 articles), and Japan (18 articles) (Figure 2). For the past five years, a total of 197 publications have directly mentioned the use of DOM fluorescence in the field of watershed

studies. Specifically, there were 50, 47, 39, and 39 articles published in 2021, 2020, 2019, and 2018, respectively (Figure 3).

The literature review revealed that EEM-PARAFAC is a promising alternative method for tracing water quality linked with DOM composition while tracking organic matter sources in natural aquatic systems. DOM spectroscopy displayed the potential to be a simple and fast tool for pollution-source tracking alongside water quality indices, which were eventually utilized to diagnose the environmental and ecological status of the watershed. In a recent correlation study of water quality indices and DOM fluorescence data, Tang et al. (2019) demonstrated good correlations between DOM components and water quality parameters in peri-urban and urban river watersheds (Zhangxi River and Lu River in Ningbo, East China, respectively). From the PARAFAC, DOM was separated into two terrestrial humic-like components and a protein-like component. The urban watershed revealed higher terrestrial humic-like components with a lower percentage of protein-like components (39% and 30%, respectively), whereas the peri-urban watershed displayed an inverse trend (33% and 37%, respectively). A correlation study with fluorescence components and water quality parameters (COD, TN, TP, and dissolved organic carbon (DOC)) was conducted by applying redundancy analysis (RDA). A significant linear relationship between COD and the terrestrial humic-like component was found in both watersheds, suggesting that the terrestrial humic-like component can be used as a good COD indicator. Tang et al. (2019) demonstrated that the pollution sources and water quality correlated with the DOM fluorescent components and that

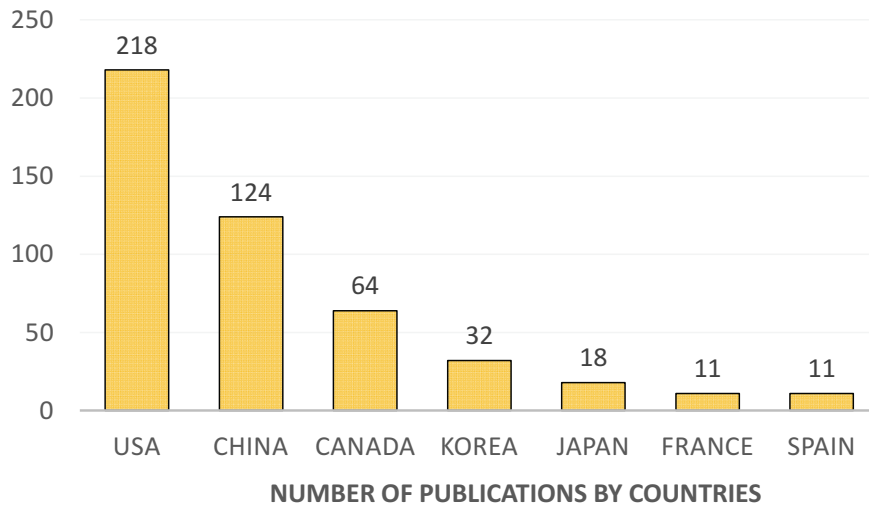


Fig. 2. The general demographics of research publications where dissolved organic matter fluorescence has been used for watershed studies, based on the country of the research. (Clarivate: Web of Science; Analyze Results: dissolved organic matter AND watershed (All Fields) AND fluorescence (All Fields), Accessed date: 2022/09/02)

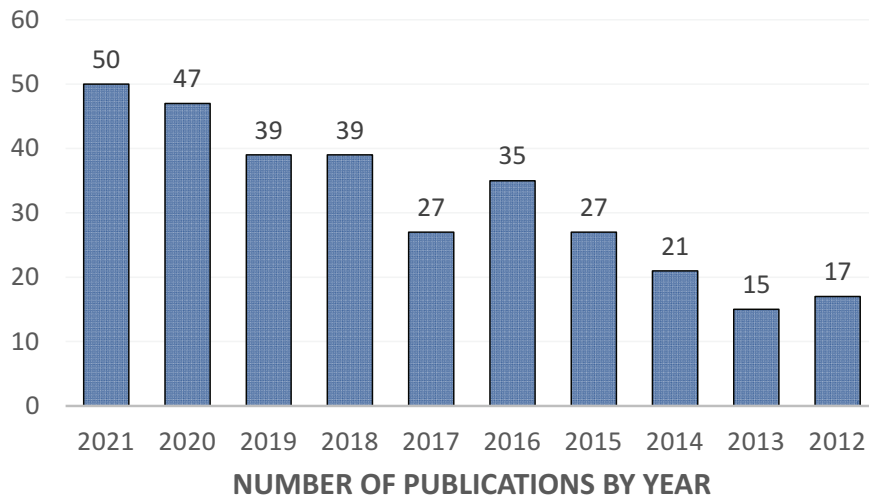


Fig. 3. The general demographics of research publications over the past 10 years where dissolved organic matter fluorescence has been used for watershed studies. (Clarivate: Web of Science; Analyze Results: dissolved organic matter AND watershed (All Fields) AND fluorescence (All Fields), Accessed date: 2022/09/02)

water quality assessment can be performed to a certain extent using DOM fluorescence components (Tang et al., 2019). DOM fluorescence was also successfully used in a Yellow River-based study conducted by Li et al. in China in 2021, where the relationships of CDOM with water quality indicators and trophic state were analyzed. PARAFAC was separated into six components, with the majority comprising four humic-like components (85.6%) and the minority comprising two protein-like components (15.8%). Li, Pan et al. (2021) suggested that the use of the fluorescence index (FI) had a good predictive ability for pollution detection, especially for pollutants related to nitrogen and phosphorus nutrients in the

basin (Li, Pan et al., 2021). Using DOM fluorescence as a diagnostic tool to study the environmental and ecological status of watersheds in this aspect was also noted. This is crucial in situations where the ecosystem is delicate and pollution traces are found at low concentrations. Early pollution detection will ensure the safety of endemic flora and fauna as well as the costs of management strategies. In a study on the Tibetan Plateau in 2021, Li et al. suggested the importance of DOM fluorescence indicators as potential highly suitable measurement parameters for the characterization of low-concentration DOM in alpine areas (Li, Xiao et al., 2021).

Many researchers have broadened their DOM fluorescence

studies not only to track the pollution source but also to explore the spatiotemporal variation in DOM to determine whether it will provide insight into the land use gradient of the watershed. The spatial variation in DOM and land use gradient studies have always provided a general trend of a higher ratio of humic-like components when anthropogenic activity is limited, along with a moderate or low ratio of protein-like components in the presence of human activities. In an FDOM analysis study of a coastal river basin in eastern North Carolina, USA; Bhattacharya and Osburn (2020) discussed the effect of land use and land cover morphology reflect on DOM composition using FEEM-PARAFAC. During the study period, the large coastal river network was subjected to rapid and intense land-use and land-cover changes. The results indicated prominent terrestrially derived DOM, with the most significant control on DOM composition and concentration in the wetland area of the study. The DOM in the wetland areas and agricultural coastal streams were abundant in humic-like substances and structurally complex. In comparison, mixed urbanized and forested streams were found to have abundant less complex, low-molecular-weight DOM, along with higher concentrations of DOC and nitrogen due to higher urban runoff and higher DOM production. From the correlation studies, the authors concluded that increasing anthropogenic alterations had a higher tendency to increase the abundance of reactive DOM in coastal rivers and estuaries, resulting in severe water quality issues and that DOM could be used as an effective tool to analyze land-use gradients in larger river systems (Bhattacharya and Osburn, 2020).

Lyu et al. (2021) carried out a four-year observation dataset of EEMs from urban and non-urban waters in Jilin Province, northeastern China. Being one of the longest continuations of data collection for FEEM PARAFAC studies, this study was significant. The authors compared two watersheds and classified them into urban and non-urban areas to analyze the impact of nonpoint source urban inputs on the DOM amount, composition, and source. The results indicated that urbanization had an important influence on DOM concentration and composition, specifically that urban areas had higher DOM content, CDOM absorption, DOM fluorescence intensity, and a greater proportion of protein-like components (26% > 21.3%). In addition, the observed proportion of humic-like components was smaller in the urban water samples than in the non-urban samples (51.9% < 57.6%). The study revealed that the continuous increase in impervious artificial surfaces caused by urban expansion contributed to the increase in DOM quantity, which altered the DOM to contain more protein-like components (Lyu et al., 2021). In a study of Three Gorges

Reservoir (TGR) regions in China, Ma and Li investigated the spatial variations in DOM compositions and sources using EEM-PARAFAC. In the samples of forest-affected river areas, DOM revealed higher terrestrial sources and weaker microbial sources, irrespective of hydrological seasonality. In contrast, the DOM in farmland-affected rivers showed a more protein-like signal. The investigators concluded that anthropogenic activities and land use were the driving factors of DOM quality variation in the TGR region (Ma and Li, 2020).

The trend in seasonal DOM variation is affected by sunlight availability and the general increase in temperature. Therefore, in the wet season, higher levels of overall DOM concentration, as well as a comparatively lower ratio of protein-like components, are typically observed if there is no recognized point source of pollution. In Lyu et al. (2021), using a four-year observation dataset of EEMs from Jilin Province, northeast China, long-term observations of urbanized DOM reflected the response to regional climate. Summer seasons are characterized by high overall concentrations of DOM and mixed DOM sources. For example, the FI values revealed both the presence of autochthonous production originating from algal growth and allochthonous input resulting from rainfall (Lyu et al., 2021). Similarly, data from the TGR region (Ma and Li, 2020) implied a higher ratio of humic acid to fulvic acid (more terrestrial origin), aromaticity, molecular weight, and CDOM proportion in the wet season than in the dry season. The study concluded that monsoonal precipitation was one of the driving factors of DOM quality variation in the TGR region.

Jin et al. (2022) found that DOM in the North Canal River (China) watershed was composed of two humic acid-like components (excitation 230 nm, emission 335/400 nm and excitation 260 nm, emission 360/450 nm) and a tryptophan-like component (excitation/emission 280/290 - 350 nm). The study was conducted across four seasons throughout the year to determine the source of DOM and its relationship to water quality parameters, along with the spatiotemporal variation in DOM fluorescence. The intensity of DOM showed obvious seasonal variations, with the overall DOM concentration in winter being significantly higher than that in hotter months. The authors explained the reasons for this temporal variation in the overall water volume and temperature factors that can chemically change DOM. The spatial variation in the tryptophan-like component showed a significantly higher concentration in the mainstream. The main DOM sources were human habitation and agricultural nonpoint sources in the main channel, as well as terrestrial and microbiological in the tributaries. The DOM composition was associated with water quality indicators such as TN and

TP concentrations ($r = 0.38 - 0.91$) (Jin et al., 2022).

Close associations between total nutrient concentration (mostly TN and TP) and fluorescent humic-like components were observed in multiple watershed studies. This reoccurring relationship is common in open water sources with significant human impact. Zhao et al. (2017) conducted a correlation analysis between the spatial distribution of CDOMs and water quality in 19 lakes across the Songhua River Basin, situated in the semi-arid regions of northeastern China. The data imply a positive linear correlation between the fluorescent component C1 (humic-like) and TN ($R^2 = 0.76$ and 0.81 , $p < 0.01$) because organic nitrogen was derived from terrestrial humic-like substances. Similar correlation was also observed in the lakes of the Yungui Plateau in China, which has been reported by Zhang et al. (2010) in the Ebinur Lake watershed ($r = 0.61$), and by Wang et al. (2017) in the Northeastern Basin ($r = 0.60 - 0.84$) in China. These results indicate that large amounts of nitrogen are connected to carbon in the form of organic nitrogen by chemical bonding to form the molecular structures of the humic-like components (Wang et al., 2017; Zhang et al., 2010).

UV spectroscopy has also been widely used to estimate the composition and sources of DOM. A study conducted in Sanggou

Bay, China, by Wang et al. in 2017 suggested a strong correlation between the amount of bioavailable DOC and protein-like components separated using FEEM-PARAFAC. This study demonstrates the reliability of estimating DOC concentration using the absorption at 280 nm (A_{280}) in protein-like component-rich ecosystems, such as aquaculture systems (Wang et al., 2017). A five-river-based optical analysis in Japan indicated that the main types of fDOM observed in the rivers were terrestrial humic-like and tryptophan-like substances. The river flowed mainly through an urban area that was found to be contaminated with other compounds, such as fluorescent whitening agents, autochthonous humic-like substances, and extracellular polymeric substances. The slope ratio was strongly correlated with the land use gradient and river flow. Therefore, the slope ratio $S_{275-295}$ can be used as an index of pollution levels in these Japanese rivers (Ayeni et al., 2022). Similarly, a Yellow River-based study in China (2022) suggested the use of a combination of the CDOM absorption at 254 nm (A_{254}), spectral slope ratio (SR), specific UV absorbance at 254 nm ($SUVA_{254}$), and FI as good predictive tools for the key water quality indicators TN, dissolved total nitrogen, TP, and dissolved total phosphorus. This research implies the use of UV spectral parameters for rapid water quality monitoring and pollution source indication, especially for pollutants related to nitrogen and phosphorus nutrients in polluted river basins (Li, Pan

Table 4. Summary of key research studies discussed in this review

List of publication	Location	Watershed type	Purpose	Key outcomes and conclusions of the research
Jin et al. (2022)	The North Canal River watershed, northern China	Forest- and industrial -dominated land use	To investigate the content, spatiotemporal fluctuations, and major sources of DOM To study the relationship between DOM composition, concentration, and water quality	Temporal variation: DOM concentration in winter is the highest Spatial variation: Tryptophan-like components were significantly higher in the mainstream and the humic-like components were higher in the tributaries Source tracking: Main-stream - human-derived point sources and agricultural nonpoint sources Tributaries - terrestrial nonpoint sources DOM composition is significantly related to WQ indicators, especially TN and TP
Li, Xiao et al. (2021)	Namco Lake, Niyaqu basin in the Tibetan Plateau	Watershed with the land cover gradient of the ice sheet, through the wetland to the estuary	To investigate the content, spatiotemporal fluctuations, and major sources of DOM To evaluate the potential of fDOM as a detector for nonpoint source pollution	Humic-like signals: natural organic matter background or degradation products Tyrosine-like signals: pollution traces Tryptophan-like signals: microbial byproducts Wetlands can absorb or degrade the organics to regulate water quality and buffer the environmental impact. Fluorescence indicators: for characterization of low-concentration DOM in alpine areas; Has a potential use in environmental assessment and modeling.

List of publication	Location	Watershed type	Purpose	Key outcomes and conclusions of the research
Lyu et al. (2021)	Jilin province, northeastern China	Urban and non-urban watersheds with significantly different land use and land cover gradients	To characterize DOM and CDOM absorption in urban water bodies To investigate the content, spatiotemporal fluctuations, and major sources of DOM	DOM responds to the regional climate. Higher DOM amount and FI appeared in the summer due to autochthonous production from algae growth and allochthonous input from rainfall. Urbanization influences DOM concentration and composition; urban areas had higher DOM content, CDOM absorption, and DOM fluorescence intensity (FI), higher protein-like fluorescence components
Li, Lu et al. (2021)	The Yellow River, Northern China	Natural sediment-laden river segments and reservoirs	To identify possible CDOM sources in the mainstream To study the potential use of CDOM as a WQ indicator	Prominent humic-like component: nonpoint source erosion origin Minor protein-like components: point source discharges, anthropogenic activities The fluorescence index (FI) is a good predictor of TN in the basin
He et al. (2021)	Southern Qinling mountains in southern Shaanxi province, China	A series of hilly ponds with different eutrophication levels and adjacent watersheds	To study the potential use of FDOM as a WQ and eutrophication level indicator To identify the effects of land-use changes on aquatic DOM concentration and composition	A majority of humic-like components: derived from terrestrial plant decomposition or soil organic matter Microbial humic-like component: produced by microbial decomposition Protein-like components: point source pollution, sewage discharge Farmlands are the major contributors to DOC concentration rather than forest and grassland Humic-like fluorescence components in A_{254} could be used as indicators to reflect the eutrophication level
Ma and Li (2020)	Three Gorges Reservoir (TGR) region, the upper reach of the Yangtze River, China	Farmland and forested land use	To investigate the content, spatiotemporal fluctuations, and major sources of DOM To identify the effects of land-use changes on aquatic DOM concentration and composition	Land use and monsoonal rainfall affect DOM composition. Dry season: Lower ratio of humic acid to fulvic acid, DOM aromaticity, humification, the molecular weight of humic substances Wet season: weaker microbial and stronger terrestrial sources in DOM regardless of land use Forest-affected rivers (dry season): A higher degree of humification and aromaticity, the molecular size of DOM, and a higher proportion of CDOM Farmland-affected rivers: lower molecular weight of DOM, higher FI and BIX, regardless of hydrological seasonality
Tang et al. (2019)	Zhangxi River and Lu River watershed, Ningbo, China	Peri-urban and urban watershed	To identify the effects of urbanization on aquatic DOM concentration and composition	COD concentration is positively correlated with humic-like fluorescent components: humic-like components are a good COD predictor. Urban: higher terrestrial humic-like components than protein-like components Peri-urban: inverse trend compared to urban

List of publication	Location	Watershed type	Purpose	Key outcomes and conclusions of the research
Bhattacharya and Osburn (2020)	Neuse River Basin, North Carolina, USA	Coastal river basin with a variation in land use; urban, agricultural, forested, and wetland	To investigate the molecular complexity and molecular weight change of aquatic DOM across the land-use gradient	Terrestrially derived the overall DOM composition and concentration Wetland and agricultural coastal streams have abundant structurally complex DOM
			To identify the effects of urbanization on the spatial variation in aquatic DOM concentration and composition	Mixed urbanized and forested streams have abundant less complex, low molecular weight DOM; higher concentrations of DOC and TN caused by urban runoff; and higher DOM production
Zhang and Liang (2019)	Quanchengwu Village, Luniao Town, Yuhang District, Hangzhou, Zhejiang, China	The East Tiaoxi River watershed	To evaluate the potential of FDOM as a detector for nonpoint source pollution	Agricultural and rural nonpoint sources contribute a substantial organic pollution load to downstream watersheds
		This river originates from the hills within this watershed: a closed watershed Agricultural and non-urban	To study the potential use of FDOM as a disinfected byproduct formation potential (DBP FP) indicator	FDOM can replace the labor-intensive and time-consuming routine parameters of pollution detection When combined with the support vector machine (SVM), it can be used to indicate pollution and predict DBP FP
Zhao et al. (2017)	Songnen Plain and Hulun Buir Plateau in semiarid regions of northeastern China	Fresh water and brackish water lakes: various land use/cover (e.g., cropland, grassland, forest, and residents)	To characterize CDOM composition	No significant differences in CDOM components between freshwater and brackish-water lakes DOM components were affected by the spatial variation in land cover and pollution sources in hypereutrophic brackish-water lakes.
			To investigate CDOM differences between freshwater and brackish-water lakes	A positive linear correlation between the humic-like fluorescent component and TN ($R^2 = 0.76$ and 0.81 , $p < 0.01$): organic nitrogen was derived from terrestrial humic-like substances
			To assess the effects on FDOM components by land cover and a point source of pollution	

Note: WQ indicates Water Quality.

et al., 2021).

In recent years, many watershed analyses have been conducted using methodologies related to FDOM analysis. In this review, a few recent studies are discussed in terms of their usage and significance. A summary of the outcomes of this review is presented in Table 4. It is crucial to note that researchers tend to highlight the applicability of research outcomes to specific watershed systems because relevance on the universal scale still needs to be studied.

5. Conclusion

DOM is an important parameter for watershed studies. The practice of using DOM in watershed studies has been known to the scientific community for decades and is still utilized to a great extent. The advancement of data processing/management instrumentation and methods has resulted in many improvements in the field of DOM fluorescence analysis. Research results

provide convincing scientific evidence for water quality monitoring and pollution control in watersheds using DOM fluorescence as an analytical tool. A number of results implied a unique correlation between water quality parameters, DOM fluorescent components, and optical indices. As DOM displays unique compositional characteristics, it is crucial to verify the environmental relevance of each study in accordance with the focused DOM types in terms of comparisons, correlations, and concluding. Most of the recent watershed research studies compared environments to reveal distinct varieties of DOM, as in urban vs. non-urban, urban vs. forest, or agricultural vs. forest, without focusing on a single watershed. Research from the past five years has shown the tendency to attribute more fluorescence and spectral indices to a wide array of new parameters, such as microplastics of different types, antibiotics, and specific bacterial contaminants. Most novel approaches have considered machine learning and model development for easier predictions to improve sustainable watershed management in the future.

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