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Unraveling Seasonal Dynamics of Dissolved Organic Matter in Agricultural Ditches Using UV-Vis Absorption and Excitation–Emission Matrix (EEM) Fluorescence Spectroscopy

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Abstract

Seasonal dynamics of dissolved organic matter (DOM) in agricultural ditches significantly impact carbon cycling and water quality in connected rivers. This study aimed to characterize seasonal variations in DOM composition and dynamics within hierarchical agricultural ditch systems in Tianjin, northern China. Surface water samples were collected from river channels, main ditches, branch ditches, lateral ditches, and field ditches during wet (June 2021) and dry (December 2021) seasons. DOM characteristics were analyzed using dissolved organic carbon (DOC) quantification, ultraviolet-visible (UV-Vis) absorption spectroscopy, and three-dimensional excitation–emission matrix spectroscopy (3D-EEMs) coupled with parallel factor analysis (PARAFAC). The concentration of DOC in ditch surface water exhibited significant seasonal variations, with significantly higher levels observed during the wet season (Huangzhuang: 6.72 $\pm$ 0.7 mg/L; Weixing: 13.15 $\pm$ 3.1 mg/L) compared to the dry season (Huangzhuang: 5.93 $\pm$ 0.3 mg/L; Weixing: 9.35 $\pm$ 2.6 mg/L). Both UV-Vis spectral and EEM-PARAFAC analysis revealed that DOM in ditch systems was predominantly composed of fulvic-like and tryptophan-like components, representing the portion of organic matter in water bodies that is highly biologically active, highly mobile, relatively "fresh", or "not fully humified". PARAFAC identified microbial humic-like (C1: wet season 40.36%, dry season 34.42%) and protein-like (C3: wet season 40.3%, dry season 49.87%) components as dominant. DOM sources were influenced by dual inputs from terrestrial and autochthonous origins during the wet season, while primarily deriving from autochthonous sources in the dry season. This study elucidates the advances of spectroscopic techniques in deciphering the composition, sources, and influencing factors of DOM in aquatic systems. The findings support implementing riparian buffer strips and optimized fertilizer management to mitigate seasonal peaks of bioavailable DOM in agricultural ditch systems.

Keywords: DOM; drainage networks; temporal dynamics; UV-Vis; EEMs-PARAFAC

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1. Introduction

Approximately 40% of global land is utilized for agricultural development, with agricultural activities constituting a significant source of riverine organic carbon (OC)

through migration processes [1]. Research indicates two primary pathways for agriculturally derived OC to enter river systems: (1) Direct transport by precipitation-induced surface runoff. Precipitation events generate overland flow that mobilizes topsoil particles and adsorbed OC, delivering them directly into ditches or rivers. (2) Indirect transport via leaching. Irrigation and rainfall percolate through soil profiles, carrying dissolved OC (DOC) to groundwater or tile drains that eventually discharge into ditches [2]. Land use and management practices within agricultural systems—including land conversion, tillage methods, and fertilizer application—disrupt OC transportation and storage in watersheds [3]. However, there remain critical knowledge gaps regarding the biogeochemical transformation processes experienced by organic carbon generated from these agricultural activities within drainage networks, particularly the transformation of its most active component—dissolved organic matter (DOM).

DOM, comprising a complex mixture of organic compounds including humic substances, proteins, carbohydrates, and organic acids, serves as a major vector for pollutants. DOM influences biogeochemical processes by facilitating the transport and transformation of nutrients, heavy metals, and organic contaminants, and by fueling microbial metabolism, thereby constituting a primary focus of research. The Haihe River Basin, heavily impacted by anthropogenic activities (industrial and agricultural), exhibits diverse and complex sources of dissolved organic carbon (DOC) in its fluvial systems—including wastewater, terrestrial vegetation, soils, and plankton—with external inputs contributing substantially to the basin's DOC pool [4]. Chromophoric dissolved organic matter (CDOM) constitutes a significant light-absorbing component of natural aquatic DOM, primarily absorbing ultraviolet and visible light [5]. CDOM, widely distributed in aquatic environments with complex composition, is mainly categorized into protein-like and humic-like substances. Its predominant sources include terrestrial inputs and secretions/degradation products of marine flora and fauna [6]. Spectroscopic techniques, particularly UV-Vis and fluorescence spectroscopy, have unique advantages to characterize CDOM components rapidly and effectively. Additionally, fluorescence spectroscopy emerges specifically to exploit the fluorescent properties of CDOM. When excited by external energy, fluorescent dissolved organic matter (FDOM) within CDOM (e.g., proteins, aromatic hydrocarbons, lignin) absorbs energy, causing electrons to transition to higher-energy orbitals and enter an excited state. Such an unstable state decays back to the ground state through electron emission and generates fluorescence [7,8]. Due to its high sensitivity, operational simplicity, and capacity to provide rich quantitative/qualitative data, excitation–emission matrix spectroscopy coupled with parallel factor analysis (EEMs-PARAFAC) has been extensively applied in environmental samples, particularly for large-scale spatiotemporal studies of FDOM.

Agricultural ditches (also termed drainage ditches) are artificial channels constructed in agricultural regions to deliver water to farmlands during drought or growing seasons for irrigation purposes [9] and to discharge excess water (e.g., floodwater) into river networks during rainfall events, thereby mitigating flood damage to crops and infrastructure [10]. Ditches, functioning as critical linkages between farmland and natural rivers, mitigate agricultural pollution through soil adsorption, plant uptake, bio- and photo-degradation, thereby reducing contaminant transfer to rivers and other aquatic ecosystems. As critical components of agricultural ecosystems, these ditches form essential intercepting wetlands between farmlands and freshwater bodies, performing multiple ecological functions including irrigation delivery, flood control, pollutant transformation, and soil-water conservation [11]. The global scale of agricultural ditches will inevitably expand, driven by the expansion of agricultural land, increased application of fertilizers, and irrigation to meet growing population and food demands [12–14]. Concurrently, increased application of chemical fertilizers and pesticides has led to excessive inputs of nutrients such as nitrogen

and phosphorus, exacerbating eutrophication in aquatic systems. Consequently, agricultural ditches serve as the initial collection sites for agricultural nonpoint source pollutants and are also sources of nutrient inputs to rivers and wetlands [15]. Seasonal variations alter the physicochemical properties and organic matter composition of agricultural ditch waters through temperature and precipitation changes. Research indicates that during summer, the decomposition of organic matter coupled with transformations in the organic nitrogen pool leads to a concurrent apex in ammonia nitrogen concentrations and dissolved organic nitrogen (DON). These dynamics accelerate DON transport rates to rivers through ditch systems [9,16]. Experimental studies have shown that the reduction rate of nitrate (NO_3^-) in ditches can reach 3~23% [17,18], with efficiency regulated by vegetation cover, hydraulic retention time, and sediment characteristics.

Systematic investigations of agricultural ecosystems remain relatively scarce in the Haihe River Basin, despite extensive studies on heavy metals, carbon, and nitrogen in water and sediments. Consequently, research on aquatic dissolved organic matter (DOM) dominated by agricultural activities is particularly imperative in this region. This study addresses this gap by exploring seasonal variations in DOM compositional characteristics within two typical agricultural ditches in Tianjin. We integrate DOC analysis, ultraviolet-visible absorption spectroscopy (UV-Vis), and three-dimensional excitation–emission matrix spectroscopy (3D-EEMs) to resolve DOM dynamics at the ditch system.

Current research has predominantly focused on the macro level, including changes in hydrological conditions, removal of pollutants, and maintenance of biodiversity. Research on the overall understanding of the ditch system still needs to be strengthened, and therefore, investigating DOM optical properties in such a system is crucial for elucidating its system-wide characteristics and influence on riverine dynamics.

2. Materials and Methods

2.1. Study Area

The study area (39°37′~39°68′ N, 117°30′~117°71′ E) belongs to North China Plant and encompasses artificial ditch systems distributed across northern Tianjin, primarily along the Chaobai New River and Yongding New River corridors (Figure 1a). The northern and western parts of the basin are occupied by the Yanshan Mountains, while the eastern and southern parts are plains. The river has a total length of 458 km, a natural drop of 1706 m, and a total basin area of 19,354 km^2. Within this area, mountainous regions account for 87%, and plains account for 13% [19]. Precipitation constitutes the dominant recharge source for Chaobai New River runoff, driving substantial intra-annual discharge variability with marked differences between flood and non-flood seasons. Summer and autumn represent periods of concentrated precipitation, collectively accounting for 59.21% to 76.03% of the annual runoff, with peak contributions occurring in July and August (32.59%~48.64% of total annual runoff). Hydrometric data confirm this seasonal dichotomy, documenting a mean flood season discharge of 2850 m^3/s, contrasted with a non-flood season average of merely 20 m^3/s. Thousands of ditches across the study area, featuring an engineered water management system including: rivers (R) serving dual functions of external water transfer and flood drainage, main ditches (MD), branch ditches (BD), lateral ditches (LD), and field ditches (FD) directly connected to croplands (Figures 1b and S1). Dominant cropping systems include wheat–maize rotation and rice monoculture, employing basal fertilization coupled with growth-stage topdressing. Climatically characterized as a temperate continental monsoon zone, it exhibits a mean annual temperature of 11.1 °C and receives 611 mm of precipitation (75% concentrated from June to September).

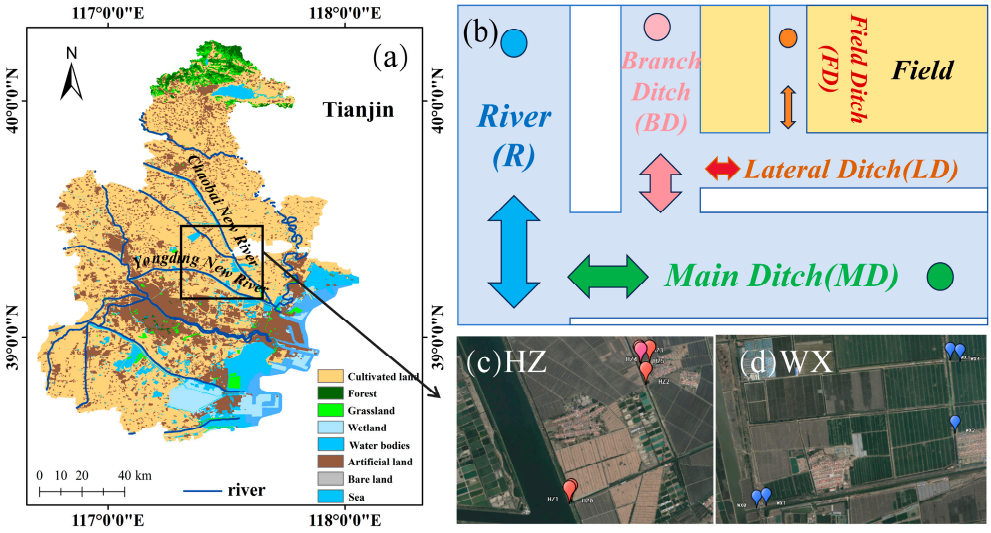

Figure 1. Study area and sampling sites. (**a**) Land use type of Tianjin, China, where the agricultural region is covered by numerous ditch systems, land use type data here was in 30 m resolution and obtained from the GlobeLand30 V2020 dataset; (**b**) the conceptual diagram of the ditch system [20]; sampling sites in (**c**) Huangzhuang Ditch (n = 6) and (**d**) Weixing Ditch (n = 5) in Tianjin.

Two representative ditch systems—comprising river channels and various ditch types were selected to investigate DOM characteristics across the agricultural ditch hierarchy. Eleven sampling sites representing different croplands were selected, including paddy fields (HZ group, Figure 1c) and wheat–maize rotation fields (WX group, Figure 1d). Note that the ditches remained essentially static except during intermittent irrigation and drainage periods.

2.2. Sample Collection and Treatment

To systematically analyze the organic matter characteristics of the ditch system, samples were collected from two typical agricultural channel systems: the Huangzhuang Ditch (6 sampling sites) and the Weixing Ditch (5 sampling sites). Two sampling sessions were conducted in summer (June 2021) and winter (December 2021). Sampling sites were set at depths of 0.1~0.3 m according to the grade of the agricultural ditches. Prior to sampling, the sample bottles were rinsed three times with river water from the sampling points. Sampling sites were sequentially designated from the river channel to field ditches as: River channel (R), Main ditch (MD), Branch ditch (BD), Lateral ditch (LD), and Field ditch (FD). Detailed site information was described in Table S1.

Samples for DOC analysis were stored in 50 mL amber glass bottles, which underwent high-temperature combustion to eliminate organic residues before sampling, and caps were triple-rinsed with ultrapure water and acid-washed in 1 mol/L hydrochloric acid baths. In addition, samples were filtered using glass fiber filters (GF/F, 0.7 μm pore size, pre-combusted at 450 °C for 6 h in a muffle furnace) and stored at 4 °C pending analysis. The hydrochloric acid used in this study was purchased from Merck (Darmstadt, Germany); primary analytical instrumentation was detailed in Table S2.

2.3. Basic Physicochemical Properties Detection

At each sampling site, water temperature (T), pH, dissolved oxygen (DO), salinity (Sal), and total dissolved solids (TDS) were measured using a portable Multi 3630 water quality meter (WTW GmbH, Weilheim, Germany) and a YSI-EXO multiparameter sonde (Xylem Inc., Yellow Springs, OH, USA). Both instruments were deployed 0.1~0.3 m below the water surface, with pH and DO probes calibrated according to manufacturer protocols

prior to measurements. Measurements were conducted in triplicate at each sampling point, and the average value was recorded to ensure data accuracy and reproducibility.

2.4. DOC Concentration Determination

The DOC concentration was determined using a TOC analyzer (Model 1030W+1088, OI Analytical, College Station, TX, USA). This analytical process initiates with acidification of the sample to pH < 2 to eliminate total inorganic carbon (TIC), followed by wet oxidation treatment, where persulfate digestion at 100 °C converts organic carbon into CO_2, which is ultimately quantified through non-dispersive infrared (NDIR) detection to measure DOC content. Blank and standard samples were prepared, and each sample was measured three times to ensure experimental accuracy. The instrument features a detection range of 2 ppb–30,000 ppm C and a limit of detection (LOD) of 2 ppb C, ensuring high sensitivity for environmental DOC analysis. All measured concentrations were well above the LOD.

2.5. CDOM Analysis and Optical Parameters Calculation

The UV-Vis spectrophotometer acts as a sensor for CDOM, detecting light-absorbing moieties like conjugated double bonds and aromatic rings. Its rapid scanning capability makes it an ideal tool for monitoring dynamic water quality changes in agricultural ditches following precipitation or irrigation events. The CDOM component of DOM was analyzed using a UV-2700 ultraviolet spectrophotometer (Shimadzu Corporation, Kyoto, Japan), where samples were measured in 1 cm pathlength quartz cuvettes with ultrapure water as the reference blank, scanning across the 200~800 nm wavelength range to ensure capture of the entire CDOM absorption spectrum, from the high-energy UV bands associated with aromatic compounds to the long-wavelength baseline essential for scattering correction at 1 nm intervals.

The initial test uses ultrapure water (18.2 MΩ cm) as a blank, which is inserted between every five samples. The baseline correction for all samples was performed using the average absorbance between 680 nm and 700 nm [21]. The resultant absorbance spectra were subsequently calibrated using the following Equations (1) and (2):

$$a\hat{}_\lambda = 2.303 \times A_\lambda / r, \quad (1)$$

$$a_\lambda = a\hat{}_\lambda - a\hat{}_{700} \times \lambda / 700, \quad (2)$$

where A_λ is the absolute absorbance at wavelength of λ; $a\hat{}_\lambda$ is the uncorrected absorption coefficient at wavelength of λ; a_λ is the scattering-corrected absorption coefficient at wavelength of λ; and r is the optical path length of 0.01 m. $SUVA_{254}$ is defined as the ratio of the CDOM absorption coefficient at 254 nm to the DOC concentration [22], with units of $L \cdot (mg \cdot m)^{-1}$, and the formula is expressed as Equation (3):

$$SUVA_{254} = a_{254} / DOC, \quad (3)$$

where a_{254} is the scattering-corrected absorption coefficient at 254 nm with units of m^{-1}; DOC is the dissolved organic carbon concentration of the sample measured in mg/L.

2.6. FDOM Analysis and Data Process

The fluorescence spectrophotometer will be framed as a highly sensitive and selective multi-dimensional sensor, capable of fingerprinting FDOM components (e.g., humic-like, fulvic-like, and protein-like substances). This non-destructive technique is exceptionally suited for tracing complex DOM mixtures and identifying pollution sources in agricultural watersheds, a key application for quality control in environmental monitoring. The FDOM component was characterized using an F-7000 fluorescence spectrophotometer (Hitachi,

Tokyo, Japan). The instrument undergoes absorption calibration and emission calibration prior to testing. Samples were analyzed in 1 cm four-window quartz cuvettes. Ultrapure water (18.2 MΩ cm) was used as a blank and inserted between every five samples. Instrumental parameters included excitation wavelength scanning from 220 to 400 nm at 5 nm intervals, emission wavelength scanning from 280 to 500 nm at 1 nm intervals, a scan speed of 1200 nm/s, and slit widths set to 5 nm, and the photomultiplier voltage was set to 700 V. For samples exhibiting CDOM absorbance at 254 nm (A_{254}) exceeding 0.3, inner-filter effect correction was applied using the specified mathematical formula Equation (4):

$$F^{Cor}_{Ex,Em} = F^{Obs}_{Ex,Em} \times 10^{[0.5\times(A_{Ex}+A_{Em})]}, \quad (4)$$

where $F^{Cor}_{Ex,Em}$ is the corrected fluorescence intensity at specific excitation (Ex) and emission (Em) wavelengths; $F^{Obs}_{Ex,Em}$ is the observed fluorescence intensity at specific excitation and emission wavelengths; A_{Ex} and A_{Em} indicate the absorbance at the specific excitation wavelength and emission wavelength, respectively.

PARAFAC was performed using the "MATLABR2024a N-way Toolbox for MATLAB" [23], with EEM data undergoing preprocessing through a custom Excel program prior to analysis. This involved subtracting Rayleigh and Raman scattering peaks measured from ultrapure water blanks from the experimental EEM spectra [24] and applying non-negativity constraints to the PARAFAC model [25], while all sample fluorescence intensities were calibrated using the integrated intensity of the Raman scattering peak (371~428 nm) in ultrapure water at 350 nm excitation wavelength [26]. The preprocessed fluorescence data were analyzed using PARAFAC with the DOMFluor toolbox in MATLAB, decomposing the EEMs spectra into three matrices of scores, excitation loadings, and emission loadings, with component identification and validation conducted through split-half analysis and residual analysis [27].

This study employed the FDOM (Fn355), fluorescence index (FI), biological index (BIX), and humification index (HIX) to further characterize the spectral properties, where Fn355 denotes the fluorescence intensity measured at 450 nm under 355 nm excitation, FI represents the ratio of fluorescence intensities at 470 nm to 520 nm emission under 370 nm excitation with values > 1.9 indicating predominantly microbial sources and values < 1.4 suggesting mainly terrestrial-derived contributions, BIX is calculated as the ratio of fluorescence intensities at 380 nm to 430 nm emission under 310 nm excitation, and HIX is defined as the ratio of integrated fluorescence intensities over 435~480 nm to those over 300~345 nm emission ranges at 255 nm excitation [28–30].

2.7. Statistical Analysis

Data presented using the ±symbol represents the mean value ± standard deviation. The number of significant figures reported for all analytical data was determined by the precision of the instrumentation and the standard deviation of replicate measurements. DOC concentrations, measured by the TOC analyzer, are reported to three significant figures, reflecting the instrument's precision of ±2% and the observed variability in replicate analyses. Absorption coefficients are reported to three significant figures, corresponding to the precision of the UV-Vis spectrophotometer. Values for calculated parameters (e.g., $SUVA_{254}$, SR, FI, BIX, HIX) are reported with a number of significant digits consistent with the least precise measurement used in the calculation. Mean values are presented alongside their standard deviations, with the number of decimal places in the standard deviation determining the rounding of the mean.

3. Results

3.1. Physicochemical Parameters in the Surface of Agricultural Ditches

The fundamental physicochemical parameters, including DOC concentration, DO content, pH, and TDS concentration, were exhibited in Figure 2, where DOC concentration reflects the overall abundance of dissolved organic carbon, pH and DO serve as biogeochemical indicators reflecting primary production processes and organic matter degradation in aquatic environments [31], respectively, and TDS represents a key water quality metric typically exhibiting positive correlations with electrical conductivity and salinity levels.

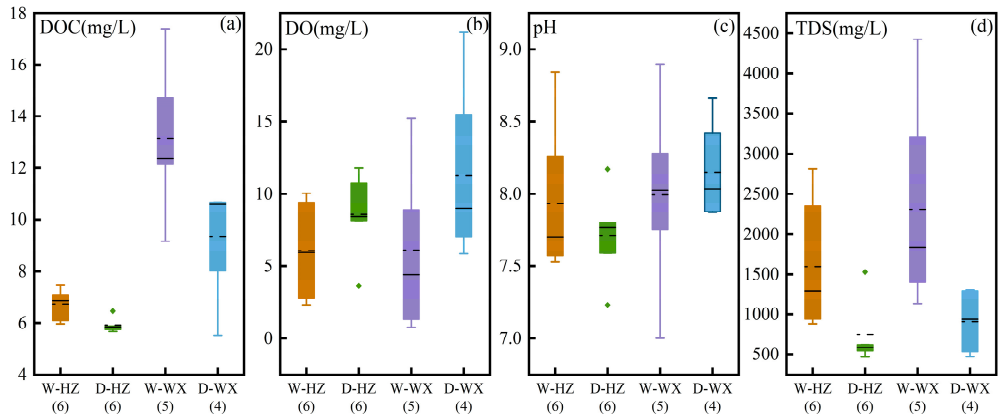

Figure 2. Concentrations of (**a**) DOC, (**b**) DO, (**c**) pH, and (**d**) TDS in agricultural ditches at different sampling times. In each box plot, the dashed line and solid line represent the median and mean values, respectively. W: Wet season; D: Dry season. The numbers on the horizontal axis represent the number of sample points.

Specifically, the mean DOC concentrations of Huangzhuang Ditch in the wet season and dry season were 6.72 ± 0.6 mg/L and 5.93 ± 0.3 mg/L, respectively, slightly higher than those in the Daqing River-Duliu Jian River (5.06 ± 3.3 mg/L) and Jiedi Jian River (6.14 ± 1.0 mg/L) in the Haihe River Basin [32], and comparable to DOC levels in agricultural catchments of Brandenburg, northern Germany (7.6 ± 2.8 mg/L) [33]. The mean DOC concentrations of Weixing Ditch in the wet season and dry season were 13.15 ± 3.1 mg/L and 9.35 ± 2.6 mg/L, approaching levels observed in the Baitapu River (Liaohe River Basin) with DOC concentrations of 10.51 ± 2.7 mg/L [34], which is primarily influenced by untreated livestock wastewater and domestic sewage. The DOC concentrations in both ditch systems were significantly lower than those in peatland agricultural ditches in the Qinghai region (mean value: 32.88 mg/L) [35] and agricultural catchment waters in Wangjiagou, Three Gorges Reservoir area (mean value: 21.19 mg/L) [36]. The DOC concentrations in both ditch systems exhibited clear seasonal variations, with significantly higher values during the wet season compared to the dry season. Specifically, in the Huangzhuang Ditch, the mean DOC concentration was 6.72 ± 0.6 mg/L in the wet season and decreased to 5.93 ± 0.3 mg/L in the dry season. This represents a decrease of approximately 11.8% from the wet season to the dry season. For the Weixing Ditch, the mean DOC was 13.15 ± 3.1 mg/L in the wet season and 9.35 ± 2.6 mg/L in the dry season, indicating a more pronounced reduction of about 28.9%.

During the sampling campaign, pH values exhibited minimal seasonal variation in ditch systems. Mean pH values in Huangzhuang Ditch measured 7.93 ± 0.5 (wet season) and 7.71 ± 0.3 (dry season), while Weixing Ditch recorded 7.99 ± 0.7 (wet season) and 8.15 ± 0.4 (dry season). These levels were comparable to the background pH (7.56 ± 0.4) in the mid-reach of Chaobai New River (Tongzhou segment) [37]. The DO values in

ditch systems were higher in the dry season than in the wet season, primarily due to temperature variations, while DO values demonstrated statistically significant correlation with pH values ($p < 0.05$). Additionally, TDS concentrations ranged from 883 to 2810 mg/L in the wet season and 464.9 to 1527.5 mg/L in the dry season across both ditches, with lower TDS values in the dry season resulting from halted irrigation and drainage activities, stagnant water conditions, and reduced disturbances from agricultural operations and environmental factors.

3.2. UV-Vis Characteristics in Surface Water of Agricultural Ditches

Clarifying the ultraviolet and fluorescence spectral characteristics of aquatic DOM can reveal the compositional features and sources of CDOM and FDOM. To explore the DOM seasonal variation and its corresponding influence factors in ditch systems of the study area, the optical properties of DOM were analyzed using four ultraviolet spectral indices—a_{355}, a_{254}, $SUVA_{254}$, and spectral slope ratio (S_R)—along with four fluorescence spectral indices: Fn355, FI, BIX, and HIX.

The absorption coefficient a_{355} is used to indicate the concentration of CDOM in DOM. As shown in Table 1, the a_{355} variation range in ditch systems was higher than that of the Daqing River-Duliu River (0.018~0.108 m^{-1}) and Jiedi River (0.064~0.097 m^{-1}) in the Haihe Basin, while being consistent with that of agricultural channels in the Three Gorges Reservoir Area (2.52~11.93 m^{-1}). The ratio of CDOM/DOC in Huangzhuang Ditch was 0.69 ± 0.07 $L\cdot(mg\cdot m)^{-1}$ during wet season and 0.95 ± 0.5 $L\cdot(mg\cdot m)^{-1}$ during dry season, while in Weixing Ditch, the corresponding values were 0.94 ± 0.4 $L\cdot(mg\cdot m)^{-1}$ (wet season) and 0.41 ± 0.2 $L\cdot(mg\cdot m)^{-1}$ (dry season). Compared to the CDOM/DOC ratios of 1.01 $L\cdot(mg\cdot m)^{-1}$ in the agricultural Wangjiagou watershed (Three Gorges Reservoir Area) and 2.03 $L\cdot(mg\cdot m)^{-1}$ in urbanized rivers, these ditch systems exhibited lower proportions of CDOM relative to total DOM.

Table 1. Seasonal variation of CDOM parameters in ditch systems.

Site	Season	a_{254} (m^{-1})	$SUVA_{254}$ ($L\cdot(mg\cdot m)^{-1}$)	S_R	a_{355} (m^{-1})
HZ	wet	19.88~30.17	3.27~4.10	0.89~1.28	3.79~5.30
		25.21 ± 3.5	3.74 ± 0.3	1.00 ± 0.2	4.62 ± 0.6
	dry	18.04~47.50	3.07~7.36	0.90~1.17	3.20~11.69
		26.97 ± 12.1	4.49 ± 1.8	1.04 ± 0.1	5.74 ± 3.5
WX	wet	36.34~82.56	2.99~5.58	0.81~1.48	6.33~19.60
		56.25 ± 19.9	4.24 ± 1.0	1.15 ± 0.2	12.73 ± 6.1
	dry	8.07~31.76	0.77~3.29	1.02~1.67	1.71~6.19
		18.89 ± 9.8	2.17 ± 1.2	1.27 ± 0.3	3.60 ± 1.9

Note: The upper part shows the numerical range, and the lower part shows the mean value ± standard deviation.

a_{254} represents the signal of unsaturated substances in CDOM. The mean a_{254} concentrations in Huangzhuang Ditch were 25.21 ± 3.5 m^{-1} (wet season) and 26.97 ± 12.2 m^{-1} (dry season), while those values in Weixing Ditch were 4.24 ± 1.0 m^{-1} (wet season) and 19.89 ± 9.8 m^{-1} (dry season). Overall, a_{254} values in Huangzhuang Ditch showed no significant difference between wet and dry seasons, whereas in Weixing Ditch, the values in the wet season were significantly higher than those in the dry season. The average a_{254} values in both ditches exceeded the values in the upstream area (Yanghe River, a tributary of Yongding River in the Haihe River Basin, with the mean a_{254} values of 14.4 ± 7.7 m^{-1}), but were comparable to its downstream with mean a_{254} values of 30.1 ± 4.4 m^{-1}, suggesting agricultural and anthropogenic influences on CDOM [38].

Higher $SUVA_{254}$ values indicate greater humification and aromaticity of CDOM [39]. In Huangzhuang Ditch, mean $SUVA_{254}$ values were 3.74 ± 0.3 $L\cdot(mg\cdot m)^{-1}$ (wet season)

and 4.49 ± 1.8 L·(mg·m)$^{-1}$ (dry season). Corresponding values in Weixing Ditch were 4.24 ± 1.0 L· (mg·m)$^{-1}$ (wet season) and 2.17 ± 1.2 L·(mg·m)$^{-1}$ (dry season). $SUVA_{254}$ exhibited relatively similar variation patterns to a_{254}. Compared with published $SUVA_{254}$ values, this study demonstrated more pronounced aromatic characteristics than those observed in the Tongzhou section of Chaobai New River (0.90~1.62 L·(mg·m)$^{-1}$) and the Wangjiagou agricultural sub-watershed in the Three Gorges Reservoir area (0.46~8.69 L·(mg·m)$^{-1}$) [36].

S_R ($S_{275-295}/S_{350-400}$) serves as a diagnostic parameter for the preliminary assessment of DOM sources and structural changes, reflecting CDOM aromaticity and average molecular weight, which also exhibits a negative correlation with DOM molecular weight. Theoretically, S_R values below 1 indicate higher CDOM aromaticity characteristic of terrestrial humic-like inputs or microbial transformation processes, whereas $S_R > 1$ suggests predominantly autochthonous organic pollution sources [40]. In this study, the mean S_R value in Huangzhuang Ditch was 1.00 ± 0.2 (wet season) and 1.04 ± 0.1 (dry season), while these values were 1.15 ± 0.2 (wet season) and 1.27 ± 0.3 (dry season) in Weixing Ditch. No significant seasonal differences were observed in either ditch, with values consistently exceeding 1, indicating endogenous organic pollution sources throughout both hydrological periods.

3.3. Fluorescence Characteristics

Fluorescence spectroscopy serves as a critical tool for characterizing the structural composition and sources of FDOM. Through EEM-PARAFAC, three distinct fluorescent components were identified: two humic-like components (designated Component 1 and Component 2, C1 and C2) and one protein-like component (Component 3, C3) (Figure 3). The fluorescence peaks and positions of different fluorescent components are shown in Table 2. The excitation and emission wavelength pairs of these components were systematically compared with literature references, confirming their prevalence across diverse aquatic systems [32,41]. This analytical approach revealed that the identified components—C1 and C2 representing terrestrial humic substances and microbial byproducts, respectively, and C3 corresponding to autochthonous biological activity. C1, characterized by two fluorescence peaks (Peak A and Peak M), represents a microbially derived humic-like substance. Peak A primarily indicates fulvic-like substances, which belong to aromatic amino acids and humic substances with relatively high molecular weights. These are predominantly formed through allochthonous inputs of humic and fulvic acids, but may also originate from photochemical degradation of autochthonous phytoplankton [42,43]. In addition, Peak M is generated by microbial metabolism and is typically observed in aquatic environments with high microbial activity [7]. Such a component has been identified in DOM analysis within the agricultural watershed of the Dianbu River—a major recharge source of Lake Chaohu [41]. C2, exhibiting two fluorescence peaks (Peak A and Peak C), represents a terrestrial humic-like substance primarily composed of high molecular weight and highly aromatic organic compounds. In natural environments, it is introduced through surface runoff carrying terrestrial organic matter, influenced by soil type, vegetation cover, and precipitation patterns. C3, characterized by dual fluorescence peaks (Peak T_{UV} and Peak T), predominantly originates from photodegradation of extracellular polymeric substances or microbial respiration. These components mainly consist of proteinaceous materials generated during autochthonous production processes of terrestrial plants or soil organic matter, along with minor peptide derivatives [44]. Such tryptophan-like protein substances were likewise identified in EEM of DOM within the agricultural watershed of Dianbu River [41]. The T peak represents a typical proteinaceous peak, generally associated with water-soluble amino acids. Some studies also suggest its correlation with low molecular weight and nitrogen-free aromatic compounds [45,46]. Concurrently, research indicates

that C3 constitutes the primary fluorescent component in untreated wastewater, serving as an effective indicator of organic pollution. And all three fluorescent components have been documented in DOM studies of rivers within the Haihe River Basin [4].

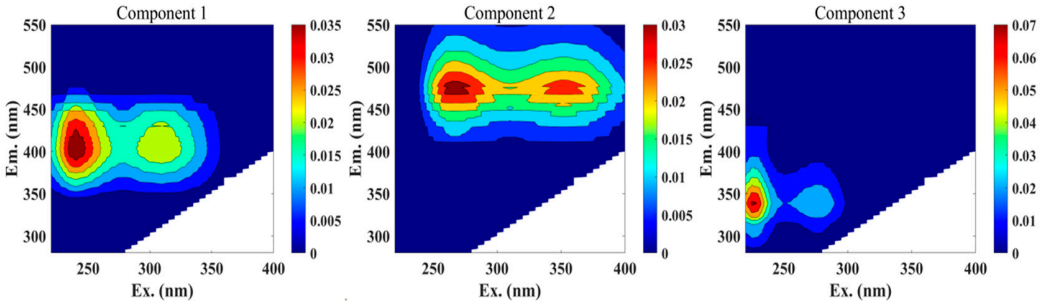

Figure 3. EEM-PARFAC results in ditch systems.

Table 2. EEMs-PARAFAC resolved the FDOM fluorescence components in ditch systems.

	Component	Fluorescence Peaks and Positions (nm)	Fluorescence Peaks and Positions (nm)	References
C1	Microbial humic-like (Humic-like)	A 240/406	M 305/410	Williams et al. [22]
C2	Terrestrial humic-like (Fulvic-like acid)	A 260/477	C 350/466	He and Hur. [47]
C3	Protein-like (tryptophan-like)	T_{UV} 225/337	T 275/337	Liu et al. [48]

FI serves as a robust indicator for distinguishing the relative contributions of terrestrial versus microbial sources of FDOM [49,50]. When FI values exceed 1.9, this signifies FDOM with predominant microbial origins, such as extracellular release and degradation of bacterial/algal leachates. Conversely, FI values below 1.4 indicate that FDOM is dominated by terrestrial inputs, primarily derived from degradation of plant and soil materials [51]. The average FI values in Huangzhuang Ditch during wet and dry seasons were 1.90 ± 0.02 and 1.98 ± 0.06, while those in Weixing Ditch were 1.88 ± 0.06 and 1.90 ± 0.06 (Figure 4). These values were slightly higher than the typical FI range for natural water bodies (1.2~1.8), but slightly lower than those of polluted water bodies (1.85~2.06), indicating that FDOM in these two ditches was subject to dual influences. During the wet season, the ditches were affected by both allochthonous inputs and autochthonous sources, whereas the dry season exhibited predominantly autochthonous characteristics. This pattern arose primarily because the study area experiences frequent rainfall with downpour events during the wet season, leading to significant external influences. Conversely, during the dry season, minimal or no rainfall results in reduced external inputs, and the relatively stable ecological conditions allow microbial activities to dominate DOM dynamics.

BIX is used to distinguish the contribution of fresh autochthonous organic matter [8]. Generally, when the BIX value exceeds 1, DOM undergoes significant degradation, and FDOM demonstrates a substantial autochthonous source with fresh organic matter being released into the water body. Values ranging between 0.8 and 1 indicate strong autochthonous contributions. And BIX values within the 0.6~0.8 range suggest limited autochthonous contributions. The average BIX values in Huangzhuang Ditch were 1.03 ± 0.05 and 1.08 ± 0.08 during the wet and dry seasons. Corresponding values for Weixing Ditch were 0.91 ± 0.08 (wet season) and 0.98 ± 0.11 (dry season). These high BIX values indicate substantial contributions from autochthonous materials and microbial processes to DOM. This further

demonstrates pronounced autochthonous characteristics in both ditch systems, exhibiting high bioavailability that promotes microbial community development and consequently enhances protein-like components in DOM.

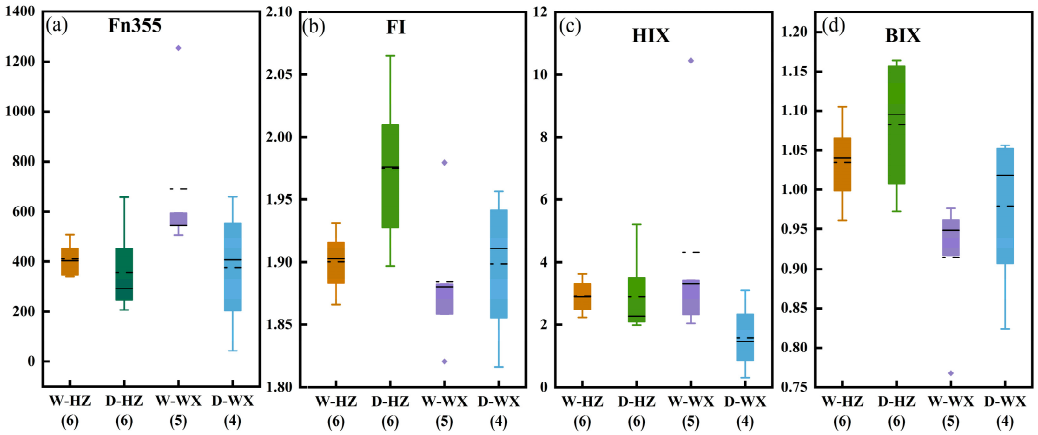

Figure 4. Levels of (**a**) Fn355, (**b**) FI, (**c**) HIX, and (**d**) BIX in agricultural ditches at different sampling periods. In each box plot, the dashed line and solid line represent the median and mean values, respectively. W: Wet season; D: Dry season. The numbers on the horizontal axis represent the number of sample points.

HIX serves as a quantitative indicator of the degree of DOM humification, reflecting the relative abundance of humic substances [8]. Higher HIX values denote greater humic content and more advanced humification processes. Conventionally, HIX values exceeding 10 indicate DOM with pronounced humic characteristics, typically derived from terrestrial plant decomposition, whereas values below 4 suggest weakly humified DOM predominantly originating from aquatic biological activity. In Huangzhuang Ditch, average HIX values were 2.91 ± 0.5 and 2.89 ± 1.3 during the wet and dry seasons. Corresponding values for Weixing Ditch were 2.78 ± 0.7 (wet season) and 1.58 ± 1.1 (dry season). Collectively, these results demonstrate weakly humified DOM characteristics across both systems. The moderately elevated HIX values observed during wet seasons in both ditches suggest enhanced humic signatures attributable to rainfall events and associated surface runoff inputs.

4. Discussion

4.1. Seasonal Dynamics of DOM Characteristics

Based on comparative analysis, it is preliminarily inferred that DOM in both Huangzhuang and Weixing Ditches is predominantly influenced by agricultural activities (farmland nutrients and rural sewage) with minimal industrial impact. Located in a temperate monsoon climate zone, water discharge in the Haihe River Basin primarily relies on surface runoff and groundwater recharge, while ditch water sources mainly derive from river replenishment and groundwater pumping for irrigation [52]. During wet season sampling, the sampling sites exhibited eutrophic conditions, and decaying phytoplankton released more organic matter and therefore resulted in high DOC values in both ditch systems [53]. The coefficients of variation (CV) for a_{355} in Huangzhuang and Weixing Ditches were relatively high in the dry season, with the values of 60.4% and 50.2%, while the corresponding CV values decreased to 11.9% and 48.0% in the wet season. The higher variability during dry periods is attributed to reduced external water replenishment in low-grade channels, coupled with diminished terrestrial input resulting from scarce rainfall in Tianjin. The $SUVA_{254}$ values in natural surface water typically range from 1.00 to 6.0 $L \cdot (mg \cdot m)^{-1}$, and samples exhibiting $SUVA_{254}$ > 6.0 indicate pronounced terrestrial signals [50]. In

the wet season, DOM in Huangzhuang Ditch and Weixing Ditch demonstrated higher aromaticity (3.74 ± 0.3 L·(mg·m)$^{-1}$, 4.24 ± 1.0 L·(mg·m)$^{-1}$). This phenomenon occurs because precipitation transports increased amounts of soil and plant-derived materials into the aquatic systems through surface runoff, resulting in greater terrestrial contribution to CDOM in ditch systems during wet seasons compared to dry seasons.

4.2. Seasonal Changes in DOM Components

In the wet season, the percentage content of microbial humic-like component C1 ranged from 35.2% to 42.3% at Huangzhuang Ditch and from 32.5% to 53.5% at Weixing Ditch. Correspondingly, in the dry season, the variation ranges were 33.6% to 47.5% and 33.3% to 40.1% for the two ditches (Figure 5). The reason for the highest value of C1 during the wet season may be that plant metabolism keeps organic matter in the ditch water at a relatively high level, while high temperatures promote increased microbial activity in the water, thereby accelerating organic matter decomposition. Furthermore, in the wet season, the percentage content of terrestrial humic-like C2 ranged from 14.3% to 18.8% at Huangzhuang Ditch and 15.8% to 37.2% at Weixing Ditch. Correspondingly, in the dry season, the variation ranges were from 14.4% to 24.5% and from 14.4% to 18.1% for the two ditches. Two primary factors influence terrestrial humic-like substances during the wet season: (1) rainfall-induced surface runoff facilitating the transport of terrestrial materials into ditch systems; (2) sluice gate operations triggering water exchange between internal ditch systems and external water bodies. Regarding the C3, the percentage content of protein-like C3 ranged from 38.9% to 50.6% at Huangzhuang Ditch and 9.3% to 51.7% at Weixing Ditch in the wet season, while the variation ranges were 28.0% to 52.0% and 41.8% to 52.3% for the two ditches in the dry season. Samples collected in the wet season exhibited high proportions of protein-like C3 in DOM. This phenomenon is likely attributed to concurrent agricultural fertilization practices, which rapidly increases organic fertilizer content in farmlands. Nitrogen fertilizers transported via agricultural runoff into drainage ditches can provide microorganisms with relatively abundant bioavailable carbon sources. Consequently, enhanced microbial metabolic activity further leads to substantial release of proteinaceous substances during metabolic processes, thereby increasing the relative abundance of protein-like substances. The observed high absolute abundance of C3 in this study may also originate from inputs of untreated wastewater. Accelerated urbanization and improved living standards in rural areas have generated increased domestic sewage, which lacks adequate treatment infrastructure in these regions. Notably, residents near shorelines often discharge wastewater directly onto banks, where it subsequently percolates into soil and enters ditches via surface runoff, or alternatively, dispose of it straight into ditches. Organic matter from such wastewater contains high levels of fluorescent constituents—including detergents, preservatives, and personal care products—contributing to the relative enrichment of C3 components in ditch systems [54].

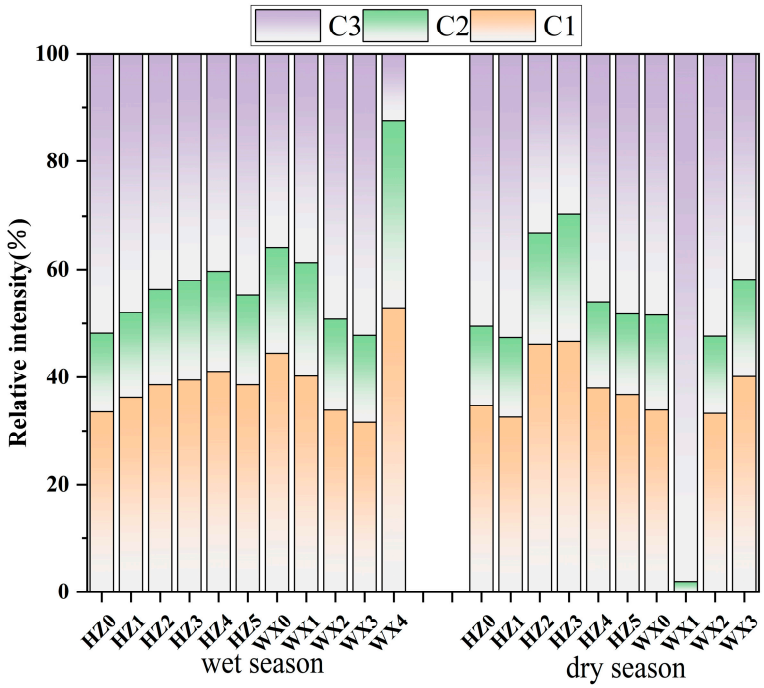

Figure 5. Relative abundance of each fluorescent component identified by the EEM-PARAFAC model in ditch systems, where C1 represents microbial humic-like, C2 represents terrestrial humic-like, and C3 represents protein-like components.

4.3. Correlation Between Physicochemical Parameters and Fluorescent Characteristics

Correlation analysis was performed on all fundamental physicochemical parameters and fluorescent spectral indices, both in Huangzhuang and Weixing ditches. Such an approach elucidates variations in CDOM and FDOM metrics, enabling source apportionment using these characteristic variables. Contributions of different DOM sources were determined through factor loadings on each variable. As shown in Figure 6, DO exhibited a significantly positive correlation with pH ($p < 0.05$), consistent with findings from a previous study [38]. DOM parameters, including a_{355}, $SUVA_{254}$, and Sal, demonstrated highly significant positive correlations ($p < 0.01$). Additionally, Fn355, C1, and C2 showed significant positive relationships with TDS ($p < 0.05$). These results indicate that fundamental physicochemical properties substantially influence the DOM characteristics in ditch systems.

Previous studies have documented significant correlations between DOC and CDOM in most aquatic systems [55,56]. In the present study, DOC concentration showed a significantly positive correlation with CDOM (DOC and a_{355}, $p < 0.01$), but no significant correlation with FDOM (DOC and Fn355). However, FDOM demonstrated a highly significant positive correlation with CDOM (a_{355} and Fn355, $p < 0.01$), indicating that variations in FDOM concentration can be inferred from CDOM dynamics. Besides, correlation analysis revealed that Sal exhibited highly significant positive relationships with both C1 and C2 components ($p < 0.01$), while TDS showed a significant opposite result ($p < 0.05$). These patterns suggest substantial contributions from terrestrial inputs to C1 and C2 components.

Correlation analysis among the three fluorescent components, DOC, and a_{355} revealed no significant relationships between DOC and components C1 or C2, whereas DOC exhibited a highly significant positive correlation with C3 ($p < 0.01$). This result indicates substantial influence of tryptophan-like constituents on ditch systems, confirming our hypothesis regarding the high proportions of protein-like substances in agricultural ditch systems. In addition, a highly significant positive correlation between C1 and C2 ($p < 0.01$) suggests shared origins or similar chemical structures. Fn355 showed highly significant pos-

itive correlations with both C1 and C2, demonstrating that terrestrial inputs predominantly generate more DOM in ditch systems. Furthermore, the FI displayed highly significant negative correlations with C3 ($p < 0.01$), while the BIX exhibited significantly negative correlations with C3 ($p < 0.05$). These patterns collectively indicate an allochthonous origin for the protein-like components.

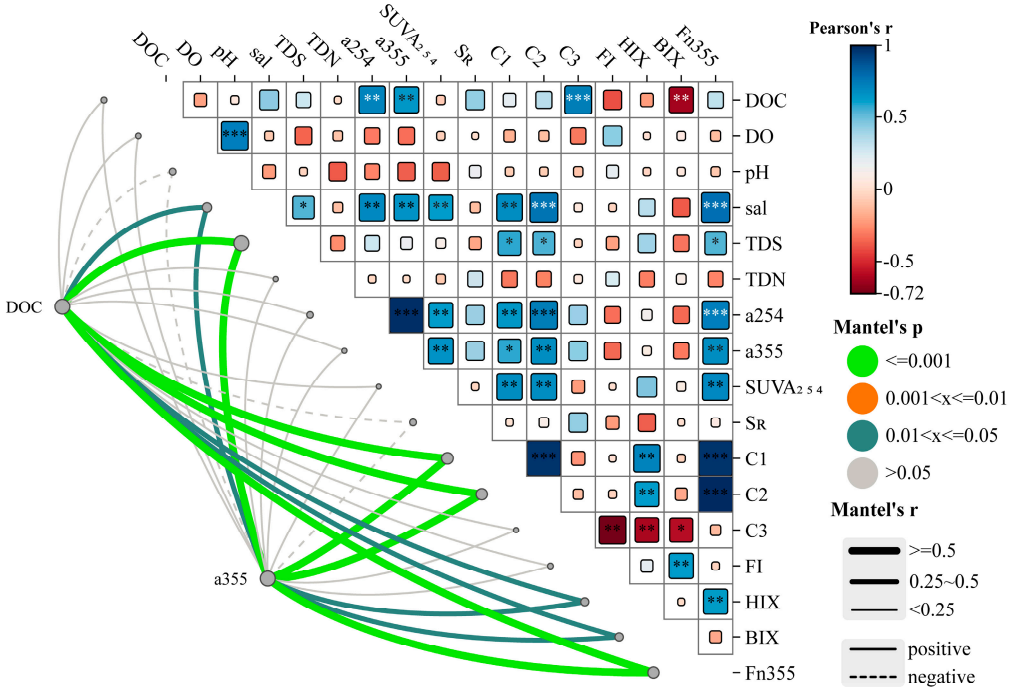

Figure 6. Correlation analysis among DOC concentrations, fluorescent components, and basic physicochemical parameters using the Pearson analysis, where the blue color represents a positive correlation, and the red color represents a negative correlation. The strength of the statistical significance is represented by the size of the dots, where * indicates significantly correlation ($p \leq 0.05$), ** indicates extremely significantly correlation ($p \leq 0.01$), *** indicates extremely significantly higher correlation ($p \leq 0.001$).

4.4. The Role of Chemical Sensors

This study highlights the pivotal role of advanced chemical sensing technologies, particularly optical sensors based on ultraviolet-visible and fluorescence spectroscopy, in unraveling the complex dynamics of DOM within agricultural ditch systems. These sensors enable rapid and sensitive characterization of DOM composition, sources, and bioavailability, factors that critically influence water quality and carbon cycling within agricultural landscapes. Parameters derived from spectral measurements, such as $SUVA_{254}$, FI, BIX, and HIX, serve as effective optical surrogates for assessing DOM aromaticity, sources, and humification levels. Such sensor metrics hold immeasurable value for high-frequency monitoring activities, enabling researchers to track DOM responses to precipitation events, seasonal variations, and agricultural management practices in near real time. Beyond agricultural ditches, these chemical sensors extend their application to diverse environmental monitoring scenarios, including rivers, lakes, wetlands, and coastal waters. Their capability to provide continuous multi-parameter data makes them particularly suitable for early warning systems detecting organic pollution, eutrophication, or sudden water quality changes caused by human activities or extreme weather events.

4.5. Limitations of the Study

It should be noted that this study has several limitations. Firstly, the sampling campaign, while capturing distinct wet and dry seasons, was conducted in two specific time windows (June and December 2021). Although this design revealed clear seasonal patterns, higher-frequency sampling throughout the year would provide a more continuous and detailed understanding of DOM dynamics in response to shorter-term weather events and agricultural practices. Secondly, while we characterized the ditch systems and their general setting, we did not perform quantitative monitoring of specific, localized human activities (e.g., precise timing of fertilizer application, wastewater discharge events, or ditch maintenance practices like dredging) during the sampling periods. These activities could introduce short-term pulses of organic matter and affect DOM composition. Furthermore, the potential influence of unexpected short-term climate anomalies (e.g., an unseasonal heavy rainfall or drought outside the typical monsoon period) was not specifically investigated, but could also impact the sampling results and DOM characteristics. Future studies would benefit from a more continuous monitoring design coupled with detailed logs of on-farm activities to better resolve these dynamics and minimize uncertainties.

5. Conclusions

5.1. Theoretical and Methodological Implications

This study explores the characteristics of DOM in Huangzhuang and Weixing ditches in both wet and dry seasons, and identifies the seasonal variation of DOM together with their potential sources and indicators with multiple spectroscopy techniques. The principal findings are summarized as follows: DOC concentrations in ditch systems exhibited seasonal variations, with significantly higher values in the wet season than in the dry season. UV-Vis and EEM-PARAFAC results reveal that both terrestrial inputs and autochthonous production contribute to the high DOM content: CDOM shows strong terrestrial signatures (e.g., from soils and riverine sources) and FDOM demonstrates substantial autochthonous production alongside terrestrial inputs. And fulvic-like and tryptophan-like substances are regarded as dominant components by PARAFAC analysis. Collectively, these results demonstrate multi-sourced DOM in Huangzhuang and Weixing ditch systems, which should increase attention to its further environmental impact.

Modern spectroscopic techniques, with high sensitivity, high specificity, rapid analysis, multi-component detection capability, and strong source elucidation power, have become indispensable tools in the field of water quality analysis. Such methods significantly enhance our capabilities to depict the DOM characteristics and deepen our understanding of the DOM fate in aquatic systems. The findings support implementing riparian buffer strips and optimized fertilizer management to mitigate seasonal peaks of bioavailable DOM in agricultural ditch systems. In practice, "smart management" of the aquatic environment can be achieved by deploying in-situ optical sensors for continuous, real-time monitoring of DOM quality and quantity. These sensors, integrated into IoT-based platforms, can provide early warnings of high DOM loadings. Furthermore, reduced fertilization should be implemented under the framework of precision agriculture, which is encouraged by local policies. Practical measures include site-specific nutrient management based on soil testing, use of slow-release fertilizers, and promotion of organic amendments. These strategies can effectively reduce the export of nutrient-rich runoff into ditches, thereby curbing autochthonous production of protein-like DOM and improving downstream water quality.

5.2. Perspectives for Future Studies

Based on our findings, we propose several key directions for future research. First, future work should combine longitudinal monitoring with incubation experiments to

quantitatively resolve the rates of key processes identified here, such as the microbial degradation of autochthonous DOM and the photochemical transformation of terrestrial inputs. Second, integrating optical techniques with stable isotope analysis ($\delta^{13}C$, $\delta^{15}N$) would provide a more robust tool for unmixing DOM sources and quantifying the contribution of specific sources like fertilizer, wastewater, and soil organic matter. Finally, investigating the link between DOM composition, as revealed by spectroscopy, and broader ecosystem functions (e.g., greenhouse gas emissions, denitrification potential) would bridge the gap between DOM character and its ultimate environmental impact.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/chemosensors13090346/s1, Figure S1. Photos of sampling areas; Figure S2. Land cover of the North China Plain; Figure S3. Correlation analysis among DOC concentrations, fluorescence components, and basic physicochemical parameters using the Pearson analysis, where the red color represents a positive correlation, and the blue color represents a negative correlation. The strength of the statistically significant is represented by the size of the dots, where * indicated a great significance ($p <= 0.05$); Figure S4. The instrument of the experiment, (a) Total Organic Carbon Analyzer; (b) UV-Vis Spectrophotometer; (c) Fluorescence Spectrophotometer; Figure S5. UV-Vis Absorption Spectra of Huangzhuang and Weixing Ditches from Wet and Dry Seasons; Figure S6. EEM-PARFAC analysis results in surface water of ditches; Figure S7. Principal component analysis load diagram and confidence interval graph based on the physicochemical parameters (DOC, DO, pH, Sal, TDS, TDN), UV indices (a355, a254, SUVA254, SR), and fluorescence indices (C1, C2, C3, FI, HIX and BIX) of the samples; Table S1 Basic information of samples [57]; Table S2 The instrument of the experiment.

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Abbreviations

The following abbreviations are used in this manuscript:

3D-EEMs	Three-dimensional excitation–emission matrix fluorescence spectroscopy
BIX	Biological index
CDOM	Chromophoric dissolved organic matter
DO	Dissolved oxygen
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
DON	Dissolved organic nitrogen
Em	Emission
Ex	Excitation
FD	Field ditch

FDOM	Fluorescent dissolved organic matter
FI	Fluorescence index
HIX	Humification index
LD	Lateral ditch
LOD	limit of detection
MD	Main ditch
NDIR	Non-dispersive infrared
OC	Organic carbon
PARAFAC	Parallel factor analysis
pH	Pondus hydrogenic
R	River
Sal	Salinity
TDS	Total dissolved solids
UV-vis	Ultraviolet-visible spectroscopy

References

1. Foley, J.A.; DeFries, R.; Asner, G.P.; Barford, C.; Bonan, G.; Carpenter, S.R.; Chapin, F.S.; Coe, M.T.; Daily, G.C.; Gibbs, H.K. Global consequences of land use. *Science* **2005**, *309*, 570–574. [CrossRef]
2. Woltemade, C. Ability of restored wetlands to reduce nitrogen and phosphorus concentrations in agricultural drainage water. *J. Soil Water Conserv.* **2000**, *55*, 303–309. [CrossRef]
3. Ogle, S.M.; Breidt, F.J.; Paustian, K. Agricultural management impacts on soil organic carbon storage under moist and dry climatic conditions of temperate and tropical regions. *Biogeochemistry* **2005**, *72*, 87–121. [CrossRef]
4. Wen, Z.; Song, K.; Liu, G.; Lyu, L.; Shang, Y.; Fang, C.; Du, J. Characterizing DOC sources in China's Haihe River basin using spectroscopy and stable carbon isotopes. *Environ. Pollut.* **2020**, *258*, 113684. [CrossRef]
5. Xu, J.; Wang, Y.; Gao, D.; Yan, Z.; Gao, C.; Wang, L. Optical properties and spatial distribution of chromophoric dissolved organic matter (CDOM) in Poyang Lake, China. *J. Great Lakes Res.* **2017**, *43*, 700–709. [CrossRef]
6. Stedmon, C.A.; Markager, S.; Kaas, H. Optical properties and signatures of chromophoric dissolved organic matter (CDOM) in Danish coastal waters. *Estuar. Coast. Shelf Sci.* **2000**, *51*, 267–278. [CrossRef]
7. Coble, P.G. Characterization of marine and terrestrial DOM in seawater using excitation-emission matrix spectroscopy. *Mar. Chem.* **1996**, *51*, 325–346. [CrossRef]
8. Huguet, A.; Vacher, L.; Relexans, S.; Saubusse, S.; Froidefond, J.-M.; Parlanti, E. Properties of fluorescent dissolved organic matter in the Gironde Estuary. *Org. Geochem.* **2009**, *40*, 706–719. [CrossRef]
9. Herzon, I.; Helenius, J. Agricultural drainage ditches, their biological importance and functioning. *Biol. Conserv.* **2008**, *141*, 1171–1183. [CrossRef]
10. Clarke, S.J. Conserving freshwater biodiversity: The value, status and management of high quality ditch systems. *J. Nat. Conserv.* **2015**, *24*, 93–100. [CrossRef]
11. Kalita, P.K.; Kanwar, R.S. Effect of water-table management practices on the transport of nitrate-N to shallow groundwater. *Trans. ASAE* **1993**, *36*, 413–422. [CrossRef]
12. Dollinger, J.; Dagès, C.; Bailly, J.-S.; Lagacherie, P.; Voltz, M. Managing ditches for agroecological engineering of landscape. A review. *Agron. Sustain. Dev.* **2015**, *35*, 999–1020. [CrossRef]
13. Siebert, S.; Kummu, M.; Porkka, M.; Döll, P.; Ramankutty, N.; Scanlon, B.R. A global data set of the extent of irrigated land from 1900 to 2005. *Hydrol. Earth Syst. Sci.* **2015**, *19*, 1521–1545. [CrossRef]
14. Tilman, D.; Cassman, K.G.; Matson, P.A.; Naylor, R.; Polasky, S. Agricultural sustainability and intensive production practices. *Nature* **2002**, *418*, 671–677. [CrossRef]
15. Borin, M.; Bonaiti, G.; Giardini, L. Controlled drainage and wetlands to reduce agricultural pollution: A lysimetric study. *J. Environ. Qual.* **2001**, *30*, 1330–1340. [CrossRef]
16. Klick, S.A.; Pitula, J.S.; Bryant, R.B.; Collick, A.S.; Hashem, F.M.; Allen, A.L.; May, E.B. Seasonal and temporal factors leading to urea-nitrogen accumulation in surface waters of agricultural drainage ditches. *J. Environ. Qual.* **2020**, *50*, 185–197. [CrossRef]
17. Moore, M.; Kröger, R.; Locke, M.; Cullum, R.; Steinriede, R., Jr.; Testa Iii, S.; Lizotte, R., Jr.; Bryant, C.; Cooper, C. Nutrient mitigation capacity in Mississippi Delta, USA drainage ditches. *Environ. Pollut.* **2010**, *158*, 175–184. [CrossRef]
18. Smith, D.R.; Pappas, E.A. Effect of ditch dredging on the fate of nutrients in deep drainage ditches of the Midwestern United States. *J. Soil Water Conserv.* **2007**, *62*, 252–261. [CrossRef]
19. Zhijun, Y.; Yanping, G.; Yingchun, G. Analysis of distribution regulation of annual runoff and affection to annual runoff by human activity in the Chaobaihe River. *Prog. Geogr.* **2003**, *22*, 599–606.

20. Wu, W.; Niu, X.; Yan, Z.; Li, S.; Comer-Warner, S.A.; Tian, H.; Li, S.-L.; Zou, J.; Yu, G.; Liu, C.-Q. Agricultural ditches are hotspots of greenhouse gas emissions controlled by nutrient input. *Water Res.* **2023**, *242*, 120271. [CrossRef]
21. Li, P.; Chen, L.; Zhang, W.; Huang, Q. Spatiotemporal distribution, sources, and photobleaching imprint of dissolved organic matter in the Yangtze Estuary and its adjacent sea using fluorescence and parallel factor analysis. *PLoS ONE* **2015**, *10*, e0130852. [CrossRef]
22. Williams, C.J.; Yamashita, Y.; Wilson, H.F.; Jaffé, R.; Xenopoulos, M.A. Unraveling the role of land use and microbial activity in shaping dissolved organic matter characteristics in stream ecosystems. *Limnol. Oceanogr.* **2010**, *55*, 1159–1171. [CrossRef]
23. Stedmon, C.A.; Bro, R. Characterizing dissolved organic matter fluorescence with parallel factor analysis: A tutorial. *Limnol. Oceanogr. Methods* **2008**, *6*, 572–579. [CrossRef]
24. Mostofa, K.M.; Wu, F.; Liu, C.-Q.; Fang, W.L.; Yuan, J.; Ying, W.L.; Wen, L.; Yi, M. Characterization of Nanming River (southwestern China) sewerage-impacted pollution using an excitation-emission matrix and PARAFAC. *Limnology* **2010**, *11*, 217–231. [CrossRef]
25. Mohinuzzaman, M.; Yuan, J.; Yang, X.; Senesi, N.; Li, S.-L.; Ellam, R.M.; Mostofa, K.M.; Liu, C.-Q. Insights into solubility of soil humic substances and their fluorescence characterisation in three characteristic soils. *Sci. Total Environ.* **2020**, *720*, 137395. [CrossRef]
26. Lawaetz, A.J.; Stedmon, C.A. Fluorescence intensity calibration using the Raman scatter peak of water. *Appl. Spectrosc.* **2009**, *63*, 936–940. [CrossRef]
27. Tang, J.; Wang, W.; Yang, L.; Qiu, Q.; Lin, M.; Cao, C.; Li, X. Seasonal variation and ecological risk assessment of dissolved organic matter in a peri-urban critical zone observatory watershed. *Sci. Total. Environ.* **2020**, *707*, 136093. [CrossRef]
28. Wilson, H.F.; Xenopoulos, M.A. Effects of agricultural land use on the composition of fluvial dissolved organic matter. *Nat. Geosci.* **2009**, *2*, 37–41. [CrossRef]
29. Vignudelli, S.; Santinelli, C.; Murru, E.; Nannicini, L.; Seritti, A. Distributions of dissolved organic carbon (DOC) and chromophoric dissolved organic matter (CDOM) in coastal waters of the northern Tyrrhenian Sea (Italy). *Estuar. Coast. Shelf Sci.* **2004**, *60*, 133–149. [CrossRef]
30. Del Vecchio, R.; Blough, N.V. Photobleaching of chromophoric dissolved organic matter in natural waters: Kinetics and modeling. *Mar. Chem.* **2002**, *78*, 231–253. [CrossRef]
31. Yi, Y.; Zhong, J.; Bao, H.; Mostofa, K.M.; Xu, S.; Xiao, H.-Y.; Li, S.-L. The impacts of reservoirs on the sources and transport of riverine organic carbon in the karst area: A multi-tracer study. *Water Res.* **2021**, *194*, 116933. [CrossRef]
32. Xu, A.; Han, X.; Liu, M.; Guo, L.; La, W.; Ding, H.; Guo, Q.; Lang, Y. Spectral characteristics and influencing factors of dissolved organic matter in two rivers and their coastal waters in the Bohai Bay. *Earth Environ.* **2022**, *50*, 526–536. [CrossRef]
33. Graeber, D.; Gelbrecht, J.; Pusch, M.T.; Anlanger, C.; von Schiller, D. Agriculture has changed the amount and composition of dissolved organic matter in Central European headwater streams. *Sci. Total Environ.* **2012**, *438*, 435–446. [CrossRef]
34. Yu, H.; Song, Y.; Du, E.; Yang, N.; Peng, J.; Liu, R. Comparison of PARAFAC components of fluorescent dissolved and particular organic matter from two urbanized rivers. *Environ. Sci. Pollut. Res.* **2016**, *23*, 10644–10655. [CrossRef]
35. Wang, D.; Li, Z.; Li, Z.; Ma, W.; Nie, X. Response of organic carbon in drainage ditch water to rainfall events in Zoige Basin in the Qinghai-Tibet Plateau. *J. Hydrol.* **2019**, *579*, 124187. [CrossRef]
36. Wang, Q.-L.; Jiang, T.; Zhao, Z.; Liang, J.; Mu, Z.-J.; Wei, S.-Q.; Chen, X.-S. Spectral characteristics of dissolved organic matter (DOM) in waters of typical agricultural watershed of Three Gorges Reservoir areas. *Huan Jing Ke Xue Huanjing Kexue* **2016**, *37*, 2082–2092.
37. Zhang, L.; Sun, Q.; You, Y.; Zhang, K.; Gao, C.; Peng, Y. Compositional and structural characteristics of dissolved organic matter in overlying water of the Chaobai River and its environment significance. *Environ. Sci. Pollut. Res.* **2021**, *28*, 59673–59686. [CrossRef]
38. Ge, J.; Qi, Y.; Li, C.; Ma, J.; Yi, Y.; Hu, Q.; Mostofa, K.M.; Volmer, D.A.; Li, S.-L. Fluorescence and molecular signatures of dissolved organic matter to monitor and assess its multiple sources from a polluted river in the farming-pastoral ecotone of northern China. *Sci. Total Environ.* **2022**, *837*, 154575. [CrossRef]
39. WeishaarJL, A.; BergamaschiB, A. E-valuation of specific ultravio let absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. *Environ. Technol.* **2003**, *37*, 4702–4708. [CrossRef]
40. Helms, J.R.; Stubbins, A.; Ritchie, J.D.; Minor, E.C.; Kieber, D.J.; Mopper, K. Absorption spectral slopes and slope ratios as indicators of molecular weight, source, and photobleaching of chromophoric dissolved organic matter. *Limnol. Oceanogr.* **2008**, *53*, 955–969. [CrossRef]
41. Yang, X.; Wu, Z.; Ye, Y.; Chen, X.; Yuan, Z.; Wang, J. Parallel factor analysis of fluorescence excitation emission matrix spectroscopy of DOM in waters of agricultural watershed of Dianbu River. *Spectrosc. Spectr. Anal.* **2022**, *42*, 978–983.
42. Zhou, S.; Sun, Y.; Huang, T.; Zhan, J.; Wang, H.; Li, Z. Characteristics of nitrogen, phosphorus and dissolved organic matter in atmospheric wet deposition of Zhoucun Reservoir. *Water Resour. Prot.* **2020**, *36*, 52–59. [CrossRef]
43. Stedmon, C.A.; Markager, S.; Bro, R. Tracing dissolved organic matter in aquatic environments using a new approach to fluorescence spectroscopy. *Mar. Chem.* **2003**, *82*, 239–254. [CrossRef]

44. Wang, H.; Wang, Y.; Zhuang, W.-E.; Chen, W.; Shi, W.; Zhu, Z.; Yang, L. Effects of fish culture on particulate organic matter in a reservoir-type river as revealed by absorption spectroscopy and fluorescence EEM-PARAFAC. *Chemosphere* **2020**, *239*, 124734. [CrossRef]
45. Yamashita, Y.; Tanoue, E. Chemical characterization of protein-like fluorophores in DOM in relation to aromatic amino acids. *Mar. Chem.* **2003**, *82*, 255–271. [CrossRef]
46. Hermes, R.G.; Molist, F.; Ywazaki, M.; Nofrarías, M.; Gomez de Segura, A.; Gasa, J.; Pérez, J. Effect of dietary level of protein and fiber on the productive performance and health status of piglets. *J. Anim. Sci.* **2009**, *87*, 3569–3577. [CrossRef]
47. He, W.; Hur, J. Conservative behavior of fluorescence EEM-PARAFAC components in resin fractionation processes and its applicability for characterizing dissolved organic matter. *Water Res.* **2015**, *83*, 217–226. [CrossRef]
48. Liu, Q.; Jiang, Y.; Tian, Y.; Hou, Z.; He, K.; Fu, L.; Xu, H. Impact of land use on the DOM composition in different seasons in a subtropical river flowing through a region undergoing rapid urbanization. *J. Clean. Prod.* **2019**, *212*, 1224–1231. [CrossRef]
49. McKnight, D.M.; Boyer, E.W.; Westerhoff, P.K.; Doran, P.T.; Kulbe, T.; Andersen, D.T. Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity. *Limnol. Oceanogr.* **2001**, *46*, 38–48. [CrossRef]
50. Cory, R.M.; McKnight, D.M. Fluorescence spectroscopy reveals ubiquitous presence of oxidized and reduced quinones in dissolved organic matter. *Environ. Sci. Technol.* **2005**, *39*, 8142–8149. [CrossRef]
51. Nebbioso, A.; Piccolo, A. Molecular understanding of a humic acid by "humeomic" fractionation and benefits from preliminary HPSEC separation. In *Functions of Natural Organic Matter in Changing Environment*; Xu, J., Wu, J., He, Y., Eds.; Springer: Berlin/Heidelberg, Germany, 2012; pp. 89–94.
52. Xu, H.; Zheng, H.; Chen, X.; Ren, Y.; Ouyang, Z. Relationships between river water quality and landscape factors in Haihe River Basin, China: Implications for environmental management. *Chin. Geogr. Sci.* **2016**, *26*, 197–207. [CrossRef]
53. Danhiez, F.; Vantrepotte, V.; Cauvin, A.; Lebourg, E.; Loisel, H. Optical properties of chromophoric dissolved organic matter during a phytoplankton bloom. Implication for DOC estimates from CDOM absorption. *Limnol. Oceanogr.* **2017**, *62*, 1409–1425. [CrossRef]
54. Yao, W.; Qi, Y.; Han, Y.; Ge, J.; Dong, Y.; Wang, J.; Yi, Y.; Volmer, D.A.; Li, S.-L.; Fu, P. Seasonal variation and dissolved organic matter influence on the distribution, transformation, and environmental risk of pharmaceuticals and personal care products in coastal zone: A case study of Tianjin, China. *Water Res.* **2024**, *249*, 120881. [CrossRef] [PubMed]
55. Ferrari, G.M.; Dowell, M.D.; Grossi, S.; Targa, C. Relationship between the optical properties of chromophoric dissolved organic matter and total concentration of dissolved organic carbon in the southern Baltic Sea region. *Mar. Chem.* **1996**, *55*, 299–316. [CrossRef]
56. Zhang, Y.L.; Qin, B.Q.; Chen, W.M.; Zhu, G.W. A preliminary study of chromophoric dissolved organic matter (CDOM) in Lake Taihu, a shallow subtropical lake in China. *Acta Hydrochim. Hydrobiol.* **2005**, *33*, 315–323. [CrossRef]
57. Davies, B.; Biggs, J.; Williams, P.; Whitfield, M.; Nicolet, P.; Sear, D.; Bray, S.; Maund, S. Comparative biodiversity of aquatic habitats in the European agricultural landscape. *Agric. Ecosyst. Environ.* **2008**, *125*, 1–8. [CrossRef]

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