Article

Evaluation of Organic Matter Contribution Using Absorbance and Chromatographic Parameters in Lake Paldang, Republic of Korea

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Abstract: Organic matter in lakes is categorized into allochthonous organic matter, such as leaves and sewage effluent, and autochthonous organic matter, generated by microorganisms within the water system. In this study, organic matter composition was analyzed using UV-vis spectroscopy and liquid chromatography-organic carbon detection (LC-OCD). Several allochthonous natural organic matter substances were collected including leaves, green leaves, forest soils, and paddy soils. The organic matter composition analysis in our study sites revealed that humic substances comprised the highest proportion (36.5–42.3%). Also, individual samples at each site exhibited distinct characteristics. This study used a humic substance-diagram (HS-diagram) and principal component analysis (PCA) to trace the sources affecting the river water quality and identify their origins. The humic substances of soil origin predominantly influenced the water quality, with the impact of organic matter significantly pronounced during the July rainfall period. Compared with the PCA results, the contribution of the humic substance (HS, 48.9%) and building block (BB, 42.0%) indices appeared higher between June and July in summer, likely due to non-degradable substances released by heavy rain. In fall, the contribution of low molecular weight neutrals increased from 71.2% to 85.2%, owing to a humic substance influx and decomposition. This study demonstrated the application of estimating the relative contributions of source materials in lakes utilized for drinking and agricultural water to identify sources, aiding in the development of efficient watershed management plans.

Keywords: dissolved organic matter; UV-vis spectroscopy; LC-OCD; HS-diagram; statistical analysis; principal component analysis

1. Introduction

Organic matter forms a basic carbon skeleton and is present in water systems rich in suspended solids, engaging in complex interactions. It is synthesized by photosynthetic organisms using light energy and represents the stored energy resulting from the conversion of solar energy into chemical energy [1,2]. Energy in an ecosystem is introduced as chemical energy, which circulates through the food chain and undergoes breakdown processes [3]. While increasing organic matter in a water system can enhance aquatic resource production, excessive or prolonged accumulation may promote underwater oxygen depletion [4], causing the death of aquatic animals, the formation of carcinogenic disinfection by-products during water purification, and increased water purification costs [5].

In lakes, organic matter is categorized into two types based on its source: allochthonous organic matter from outside the watershed, and autochthonous organic matter generated within the lake. Allochthonous materials originating from terrestrial plant photosynthesis include leaves and rice straw, which naturally break down into detritus or are leached as dissolved organic matter [6]. Populated catchments may introduce manufactured organic
matter such as untreated sewage and livestock excrement. Autochthonous organic materials produced through photosynthesis within the lake (primary productivity) are mainly generated by phytoplankton and occasionally by lakeside and underwater plants [7]. Organic matter from various sources entering the water system absorbs inorganic and organic pollutants, thereby influencing the behavior of complex pollutants within the system [8]. Further studies are necessary to explore the impact of incoming aquatic organic matter on the behavior of complex organic and inorganic pollutants in water systems [9].

Previous organic matter studies used ultraviolet-visible and fluorescence spectroscopy [10–12]. Recent studies have employed Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) and liquid chromatography-organic carbon detection (LC-OCD) to identify their source characteristics, including source analysis during the dry and wet seasons and analysis based on riverine organic matter sources [13]. DOM discrimination focuses on forested or agricultural watersheds that engage in various farming activities [14]. This study presented a method to track allochthonous organic matter that affects water quality during rainfall in drinking water and agricultural water reservoirs using the latest organic matter composition analysis, LC-OCD.

Lake Paldang in South Korea is an important domestic water supply and a multipurpose dam used for various activities such as fisheries, agriculture, and hydroelectric power [15]. Urban areas, farmland, and forests in the watershed have the greatest implications for the water quality of the lake and the sustainable management of water resources [16]. Increasing industrial units, intensive urbanization, and agricultural activities in the upstream areas of the basin introduce large amounts of organic matter and nutrients, and the management of eutrophication and algal blooms is necessary [17].

For this study, Lake Paldang, a significant water source in the capital area of Seoul, was selected as the study site. Advanced analytical techniques were employed to examine the organic matter components. The molecular composition of the DOM (dissolved organic matter) was investigated using adsorbance spectroscopy and LC-OCD. The data were analyzed using an HS-diagram to trace river water and organic matter sources and to identify the contribution of organic matter originating from humic substances. Additionally, principal component analysis using R was conducted to identify the factors contributing to local and seasonal changes. These findings can be used to trace sources and serve as foundational data for watershed management [18].

2. Materials and Methods

2.1. Study Sites and Sample Collection

Lake Paldang, a primary drinking and agricultural water source in the Seoul Capital Area, has an area of 20,432 km$^2$. Positioned at the confluence of the North Han River and South Han River, which are forested areas, and the Gyeongan Stream, featuring rice paddies, agricultural fields, and facility cultivation areas, it receives 52.1% of inflow from the South Han River, 45.8% from the North Han River, and 1.7% from Gyeongan and other streams, with the South Han River contributing the most. Rainfall influences the average inflow rate and organic matter load of Lake Paldang [19,20].

For this study, river water quality data were collected weekly from 14 February to 12 December 2022, by monitoring Lake Paldang (PD) and Sambong-ri (SB) in the North Han River basin, the Gangsang (GS) site in the South Han River basin, and the Gwangdonggyo (KK) site in the Gyeongan Stream. Samples were collected at different depths (PD (0, 10, 20 m) SB, GS, KK (0, 4, 8 m)) at each site from a boat using a Van Dorn water sampler (Niskin Water Sampler, DAIHAN CHEMLAB, Incheon-si, Republic of Korea). The collection and preservation adhered to the Water Pollution Standard Method of the Ministry of Environment (MOE, 2023). Organic materials, including soil, green leaves, and leaves, were collected from Ungilsan (US), a forested area unaffected by precipitation in the North Han River Basin [13]. Soil from crop cultivation areas such as rice paddies and agricultural fields was collected from Toechon-Myeon (TC) and Chowol-Eup (CW) in the Gyeongan Stream Basin to assess the contribution of organic matter sources from paddy fields (Figure 1).
were filtered using a 0.7 µm filter paper (GF/F, Whatman, Maidstone, UK) and then diluted for analysis. All the samples were stored at a temperature of 4 °C throughout the experiment. Data were collected in triplicate, and the average values were used for analysis.

2.4. Elemental Analysis

To assess the physical and chemical characteristics of the organic matter samples, particulate organic carbon and nitrogen were analyzed using an elemental analyzer (Elementar, Hanau, Germany). For the removal of inorganic carbon, the samples were reacted with a sulfuric acid solution (5–6% H₂SO₄; Wako, Osaka, Japan) and combusted at high temperatures. The quantities of carbon and nitrogen were then determined by measuring the CO₂ and N₂ gases generated during the combustion (O₂, 99.999%, electrolysis). Samples were analyzed using the Sediment Standard Method of the Water Pollution Standard Method of the Ministry of the Environment [21].
2.5. UV-Vis Spectroscopy

To investigate the photolytic characteristics of the NOM in the Paldang Watershed, UV-vis absorption analysis was conducted using a UV-2600 spectrophotometer (Shimadzu, Kyoto, Japan). Because of its ease of use and ability to provide extensive information on various organic components, this analytical method is commonly employed to determine the characteristics of dissolved organic matter (DOM) [23]. To minimize the interference caused by the inherent light absorption of DOM, the samples were diluted to achieve an absorbance below 0.05 [24]. The analysis was performed in scan mode, covering a wavelength range of 200–700 nm. The scan mode conditions were as follows: operation peak, 0.0001; scan speed, slow; and sampling interval, 1.0 nm. A wavelength of 254 nm, which is highly correlated with organic carbon, was identified. The ratios at specific wavelengths were used to calculate \( E_2/E_3 \), \( E_2/E_4 \), and the spectral slope ratio (\( S_R \)) as follows [10,25]:

\[
E_2/E_3 = \frac{250 \text{ nm}}{365 \text{ nm}} \\
E_2/E_4 = \frac{254 \text{ nm}}{436 \text{ nm}} \\
S_R = \frac{\text{Slope}(275-295) \text{ nm}}{\text{Slope}(350-400) \text{ nm}}
\]

Absorbance coefficients can reveal the sources and chemical compositions of dissolved organic matter. An increase in the \( E_2/E_3 \) values indicates a decrease in the average molecular weight and aromatic substances in aquatic DOM [26,27], whereas \( E_2/E_4 \) indicates the level of condensation of organic molecules [28]. The \( S_R \), which represents a negative correlation with the molecular weight of NOM, indirectly confirmed the molecular weight distribution of organic carbon [23,29].

2.6. Liquid Chromatography-Organic Carbon Detection (LC-OCD)

LC-OCD (model 9, DOC-LABOR, Karlsruhe, Germany) is a chromatographic analysis method used to identify the molecular weight distribution of DOM. Using a Protein-Pak column (TSK HW 50(S), 250 × 20 mm, Toso Haas, Tokyo, Japan) for molecular weight fractionation in general HPLC, the analysis was performed using a mobile phase (2 g/L \( \text{KH}_2\text{PO}_4 \); Wako, Osaka, Japan, 1.2 g/L \( \text{Na}_2\text{HPO}_4 \); Merck, Darmstadt, Germany) and a sulfuric acid solution (2 g/L \( \text{K}_2\text{S}_2\text{O}_8 \); Merck, Darmstadt, Germany, 2 mL/L \( \text{H}_2\text{SO}_4 \); Merck, Darmstadt, Germany) set at 2 mL/min. Five substances were quantified based on their molecular weights: biopolymers (BP, 10,000 g/mol < Mw), humic substances (HS, 500 g/mol < Mw < 1200 g/mol), building blocks (BB, 350 g/mol < Mw < 500 g/mol), low molecular weight acids (LMWA, Mw < 350 g/mol), and low molecular weight neutrals (LMWN, Mw < 350 g/mol). The specific ultraviolet absorbance of the total organic matter (SUVA) and humic substances (aromaticity) was analyzed using a UV detector (UVD, 254 nm, S-200, Knauer, Berlin, Germany) attached to the LC-OCD. An Organic Carbon Detector (OCD; DOC-LABOR, Karlsruhe, Germany) was employed to identify the factors that elucidate the characteristics of the organic matter, including the molecularity and aromaticity of humic substances [30]. The aromaticity of the aquatic humic substances was plotted against nominal molecular weights; this plot was called the HS-diagram.

2.7. Statistical Analysis

The statistical program R (version 4.3.1) was used to compute the correlation coefficient between each pair of indices pertaining to the water quality and organic matter components. Among the results, the parameters with a high correlation were selected, and principal component analysis (PCA) was conducted to analyze multiple variables simultaneously using the prcomp function in R. The prcomp function applies PCA to the transformed data after conducting a centered log-ratio (clr) transformation on the input data.
3. Results and Discussion

3.1. Water Quality Characteristics of the Paldang Watershed

The BOD, TOC, T-N, T-P, and Chl-a of Lake Paldang (PD) and its tributaries (SB, GS, and KK) were investigated weekly from 14 February to 15 December 2022 (Figure 2a).

![Graphs showing water quality parameters for PD, SB, GS, and KK](image)

Figure 2. Variations of water quality in (a) PD, (b) SB, (c) GS, (d) KK.

In PD, BOD was the highest in spring at 1.9 mg/L, presumably attributable to the rapid increase in algal biomass due to abundant nutrients [31]. TOC peaked in the summer at 3.4 mg/L, possibly due to the influx of particulate organic matter from heavy rainfall during the monsoon season (≥85% of the annual precipitation) accompanied by increased turbidity [32]. The T-N and T-P concentrations mainly increased under the influence of sewage discharge or non-point source pollution, contributing to a slight nutrient increase in the PD post-rainfall [33,34]. Chl-a increased in spring to 27.7 mg/L along with BOD and peaked in July at 28.8 mg/L. The Paldang Watershed experiences a significant blue-green algae (Cyanophyta) surge post-rainfall during the high-temperature months of July and August (24.4 ± 1.6 °C), likely leading to high Chl-a [35].

BOD and TOC in SB peaked in June at 2.6 and 4.1 mg/L, respectively, possibly influenced by the preceding week’s rainfall of 37.4 mm per event (Figure 2b). TN remained relatively consistent throughout the year, with occasional slight increases following rainfall. The TP was highest in October. This spike, coupled with a marginal increase in TOC, suggests an influx of particulate organic matter, including phosphorus, during the substantial rainfall of 84.1 mm per event in early October [36]. Similar to PD, Chl-a in SB reached its
peak in July, consistent with previous studies that correlated heightened algal biomass with nutrient influx during rainfall [37].

GS, representing the South Han River, showed the highest BOD, TOC, and Chl-a values in spring (Figure 2c). An increased algal mass may explain this due to a relative decrease in precipitation and an increase in water temperature after the thawing period [38]. T-N and T-P peaked in July, showing higher concentrations than in the SB, probably influenced by larger cropland and urban areas, as shown in Table 1 [39].

| Table 1. Land use types of the Paldang Watershed, Republic of Korea. |
|---|---|---|---|---|---|
| PD | 71.1 | 13.0 | 6.9 | 6.1 | 0.3 | 2.6 |
| SB | 76.0 | 8.4 | 5.5 | 9.2 | 0.2 | 0.8 |
| GS | 71.5 | 14.5 | 6.0 | 5.7 | 0.4 | 2.0 |
| KK | 66.2 | 10.8 | 11.2 | 5.5 | 0.2 | 6.1 |

Note(s): National pollutant survey data, land use type (2021), units: %.

KK, located in the Gyeongan Stream Basin, occupied the smallest basin area among all sites (Table 1) and showed the highest concentration in most assessment indices owing to its low flow rate (Figure 2d). The analysis of the seasonal characteristics revealed that the concentrations of BOD, T-N, and Chl-a were the highest in spring. TP peaked in September at 0.202 mg/L after a rainfall of 216.5 mm/event. Considering that the influx of TP is largely influenced by non-point source pollution, the influx of TP into KK is likely to be associated with the inflow of turbid water from sewage discharge or crop debris and soil during rainfall [21], especially in the Gyeongan Stream Basin, which has a relatively large percentage of urban areas (11.2%, Table 1).

In 2022, the Paldang Watershed recorded a total precipitation of 2143.4 mm, with strong rainfall over the past decade (KMA, 2022). Due to such impacts, the chemical parameters of the water quality showed seasonal variations \( p < 0.05 \), mainly due to rainfall events, similar to studies from Mediterranean rivers in Europe affected by monsoon climates [40].

3.2. Organic Matter Characteristic Analysis

The analysis of the riverine organic matter characteristics resulted in these findings: (1) In PD, humic substances were most widely distributed in the surface layer with BP at 8.9%, HS at 41.9%, BB at 22.5%, and LMWN at 26.7% (Table 2); (2) SB revealed a slightly lower percentage of BP at 7.5%; (3) GS showed a similar organic matter distribution to PD and indicated by the highest E2/E4 value of 22.16, presumably influenced by autochthonous microorganisms [28,41]; (4) KK showed a reduced distribution of humic substances and an increased distribution of LMWN compared to other sites, with BP at 8.8%, HS at 36.5%, BB at 23.4%, and LMWN at 31.3%. Despite KK having the lowest distribution of HS, the highest UV254 value of 0.064 suggested the significant presence of aromatic organic matter compared to PD, SB, and GS [42]. The presence of LMWA or low molecular weight organic acids was negligible across all study sites, with values below 0.1%. In the Paldang Watershed, encompassing the PD, SB, GS, and KK sites, seasonal variations generally displayed hydrophilic (SUVA < 3) characteristics. An exception was noted in July and August, when a hydrophobic trend (3 < SUVA) was observed at all sites except KK [43]. This was presumed to result from a significant influx of aromatic high molecular weight substances or particulate organic matter (POM), likely due to heavy rainfall events [44,45].
Table 2. Characteristics of the DOM water sample in Paldang Watershed, South Korea.

<table>
<thead>
<tr>
<th>Group</th>
<th>UV-Vis Parameters</th>
<th>Chromatographic Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E2/E3</td>
<td>E2/E4</td>
</tr>
<tr>
<td>PD</td>
<td>6.22</td>
<td>18.84</td>
</tr>
<tr>
<td>SB</td>
<td>6.33</td>
<td>19.18</td>
</tr>
<tr>
<td>GS</td>
<td>6.76</td>
<td>22.16</td>
</tr>
<tr>
<td>KK</td>
<td>6.75</td>
<td>18.75</td>
</tr>
</tbody>
</table>

Allochthonous NOM was categorized into leaves, green leaves, forest soil, and paddy soil. Table 3 presents the analysis results for each index. The elemental analysis revealed that leaves and green leaves were composed of more carbon and nitrogen compared to soil samples, especially deciduous trees (bracken and maple leaves), which had higher nitrogen contents of 31.7% and 34.1% [46]. Regarding soil samples, paddy soil showed a higher C/N ratio (0.11–0.339) than forest soil (0.071–0.077), which might be associated with the use of fertilizers containing nutrients.

Table 3. Characteristics of natural organic matter in the US, TC, CW.

<table>
<thead>
<tr>
<th>Group</th>
<th>NOM</th>
<th>Elemental Composition</th>
<th>UV-Vis Parameters</th>
<th>Chromatographic Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C (%)</td>
<td>N (%)</td>
<td>C/N Ratio</td>
<td>E2/E3</td>
</tr>
<tr>
<td>Leaves</td>
<td>Mixture</td>
<td>43.9</td>
<td>11.8</td>
<td>0.027</td>
</tr>
<tr>
<td></td>
<td>Broadleaf tree</td>
<td>46.1</td>
<td>10.7</td>
<td>0.023</td>
</tr>
<tr>
<td></td>
<td>Conifer</td>
<td>46.9</td>
<td>13.5</td>
<td>0.029</td>
</tr>
<tr>
<td>Green leaves</td>
<td>Maple leaf</td>
<td>42.6</td>
<td>34.1</td>
<td>0.080</td>
</tr>
<tr>
<td></td>
<td>Bracken</td>
<td>41.2</td>
<td>31.7</td>
<td>0.077</td>
</tr>
<tr>
<td></td>
<td>Conifer</td>
<td>46.1</td>
<td>11.6</td>
<td>0.025</td>
</tr>
<tr>
<td>Forest soil</td>
<td>Tample soil</td>
<td>11.3</td>
<td>8.0</td>
<td>0.071</td>
</tr>
<tr>
<td></td>
<td>Red clay</td>
<td>3.9</td>
<td>3.0</td>
<td>0.077</td>
</tr>
<tr>
<td>Paddy soil</td>
<td>TC soil</td>
<td>0.4</td>
<td>1.2</td>
<td>0.339</td>
</tr>
<tr>
<td></td>
<td>CW soil</td>
<td>5.6</td>
<td>6.2</td>
<td>0.111</td>
</tr>
</tbody>
</table>

The analysis of the NOM characteristics in Table 3 reveals that allochthonous organic matter leached from leaves, particularly from the broadleaf tree, had higher UV$_{254}$ (15.415 and 6.344) and SUVA (3.83 and 0.25) values compared to conifers, indicating a relatively higher aromatic content with a humic substance proportion of 49.1% in the broadleaf tree and 71.8% in mixed leaf samples [22]. The conifers showed the highest E2/E3 and E2/E4 values of 22.4 and 1691.6, respectively. Additionally, with a high proportion of LMWN at 73.7%, conifers had the highest percentage of biodegradable organic matter among the leaf samples [47]. For green leaves, bracken had the highest biodegradability, with E2/E3 and E2/E4 values of 18.58 and 174.82, respectively, and an LMWA and LMWN of 16.5% and 65.1%, respectively [6]. With SUVA values below 1, all green leaves were easily biodegradable, unlike non-degradable aromatic substances [48]. In conifers, all biodegradability parameters, along with SR, increased during the transition period from green to leaf. Soil samples, primarily composed of humic substances, showed the highest distribution of HS (≥50%) and SUVA (≥3). While forest and paddy soils generally had high percentages of HS [13], the former showed higher BP than the latter (11.4%, 12.8% > 2.2%, 9.9%). The paddy soils exhibited a slight difference between TC (Teochon-Myeon) and CW (Chowol-Eup), with CW showing a higher (BP + HS + BB)% than TC (84.2% vs. 77.6%), indicating a higher content of high molecular weight organic matter. The qualitative analysis of the water sample DOM and NOM revealed the characteristics of organic matter.
distribution, but it has limited scope for determining the influence and contribution of organic matter on riverine water quality [22].

3.3. Contribution of Organic Matter Originating from Humic Substances

While the Paldang Watershed (PD, SB, GS, and KK) had no significant rainfall exceeding 100 mm/event in spring, the summer had a very high rainfall, with a total of 1612 mm (June was 408.7 mm, July was 255.9 mm, August was 947.4 mm), showing a typical monsoon climate with frequent and intense rainfall [49]. In the fall, in early September, a large rainfall event of 255.9 mm was observed. Figure 3 shows the changes in the characteristics of the humic substances of allochthonous organic matter entering riverine water during rainfall. Green leaves, which had low humic substance distribution, were excluded from the HS-diagram analysis. The HS-diagram, which is a diagram of the SUVA (aromaticity) and average molecular weight (molecularity), provides information regarding the sources of humic substances in the NOM [30]. It primarily provides the traceability in three categories: aquagenic FA (autochthonous origin), pedogenic FA (soil origin), and pedogenic HA (allochthonous origin).

The analysis of riverine water revealed a low aromaticity and molecularity during the dry season in spring, highlighting the characteristics of aquagenic and pedogenic FA, which are of autochthonous origin (Figure 3a). The dominant distribution of aquagenic FA due to algal growth and pedogenic FA, indicating the contribution of humic substances originating from the soil, was observed in spring [50]. In summer, the appearance of the pedogenic HA range was noted, attributed to the influx of humic substances with high aromaticity (≥4) and molecularity (≥700), influenced by the introduction of turbid water, sewage discharge, and crop debris [2]. Subsequently, the characteristics shifted back to aquagenic and pedogenic FA, with a similar distribution of humic substances observed at other sites (SB, GS, and KK).

The analysis of allochthonous materials from NOM showed that PD was predominantly distributed with soil-origin HS rather than leaves during the dry season and that the HS components of soil and leaves entered the basin during the wet season. Overall, riverine water during the wet season inclined more towards the range of NOM compared to the dry season and was more strongly influenced by allochthonous organic matter. This observation is similar to that of a study on the Yeongju Dam watershed, where the contribution by source was higher during the wet season [22]. The SB and GS sites showed similar sources of humic substances to PD, whereas KK was more influenced by soils from cultivation, such as paddies and fields, than by forestland (Figure 3b). Even during the wet season, the soil origin exerted a greater impact than the leaves, showing significant site-dependent differences.

3.4. Correlation Analysis and Principal Component Analysis

Correlation and principal component analyses (PCA) were conducted to determine the relative contributions of the indices related to water quality and organic matter (Figure 4).
The organic matter index with a high correlation with the water quality indices, namely, BOD, TOC, DOC, and Chl-a, was selected as the principal component coefficient.

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Figure 4. Correlation coefficients for water quality factor, absorbance, and chromatographic parameters in (a) PD, (b) SB, (c) GS, (d) KK.

BOD primarily refers to organic matter that is easily biodegradable. In the PD (Table S1), high correlations were observed with Chl-a (r = 0.784, p < 0.01) and the B/T ratio (BOD/TOC ratio) (r = 0.854, p < 0.01). In addition to Chl-a and the BOD/TOC ratio, SB also showed a high correlation with BP, a substance with a high molecular weight (r = 0.638, p < 0.01) (Table S2). BP, known for its high biodegradability, is composed of large molecules such as carbohydrates and proteins. An increase in organic materials, including nutrients such as nitrogen, can increase their value [51]. GS exhibited a trend similar to that of the other sites, whereas KK had a marginally higher correlation with E2/E4 (r = 0.542, p < 0.01) (Table S3). E2/E4, related to microbial autochthonous sources [28], exhibited the highest correlation with biodegradable substances similar to microorganisms at KK compared to the other sites (Table S4).

TOC was highly correlated with UV$_{254}$ (r = 0.759, p < 0.01), HS (r = 0.763, p < 0.01), and BB (r = 0.795, p < 0.01) in the PD, and similar trends were observed for the SB and GS. KK showed a relatively high correlation with the spectral slope ratio $S_R$ (r = 0.491, p < 0.01), indicating a positive correlation with the molecular weight of nonbiodegradable organic matter such as DOC [52]. Additionally, the BP (r = 0.751, p < 0.01) and LMWN (r = 0.582, p < 0.01) were highly correlated.
In PD, Chl-a showed a relatively high correlation coefficient with the BOD/TOC ratio \(r = 0.480, p < 0.01\), which is a measure of biodegradability, LMWN \(r = 0.447, p < 0.01\), and BB \(r = 0.485, p < 0.01\), which is a breakdown form of humic substances. In SB, Chl-a showed a high correlation with HS \(r = 0.446, p < 0.05\), GS with the BOD/TOC ratio \(r = 0.747, p < 0.01\) and BP \(r = 0.614, p < 0.01\), and in KK with the BOD/TOC ratio \(r = 0.788, p < 0.01\), E2/E4 \(r = 0.562, p < 0.01\), and BP \(r = 0.376, p < 0.05\) in descending order. At all four sites, Chl-a was highly correlated with the BOD/TOC ratio.

PCA was performed using the following parameters: the BOD/TOC ratio selected from among the organic matter indices derived through correlation analysis; UV254, E2/E4, and SR as spectral parameters; and BP, HS, BB, and LMWN as chromatographic parameters (Figure 5). PCA is a method for reducing the dimensions of data based on the correlations between variables [53]. In this study, the variables were linearly transformed, and the first principal component (PC1) and second principal component (PC2) were derived [54]. The data used were the means of the weekly analysis outcomes, and missing data were excluded from the study sites. As a result of the analysis, no evident contribution was confirmed among the spectral parameters, except for the E2/E4 index, and most of the chromatographic parameters showed a high contribution. The graph shows the correlation between the parameters with high contributions and the monthly river water samples.

Figure 5. Scores of the two dominant principal components: (a) PD, (b) SB, (c) GS, and (d) KK (season identification: spring (March–May), summer (June–August), autumn (September)).
In PD, PC1 and PC2 accounted for 72.3% and 24.9%, respectively, resulting in a cumulative contribution of 97.2% (Figure 5a). For PC1, we selected the principal component with the highest contribution that had a cumulative contribution of 90% or higher in data analysis [55]. In spring, a high contribution was observed from BP, a parameter of high molecular weight organic materials such as algae and proteins. Between June and July, high contributions were observed from HS (48.9%) and BB (42.0%), factors of nonbiodegradable organic matter, possibly due to the impact of the organic matter originating from humic substances caused by substantial rainfall exceeding 100 mm/event, as shown in the HS-diagram. In July and August, LMWN had the highest contribution of 71.2%, presumably because of the influx of organic materials rich in LMWN or the decomposition of particulate organic matter after entering the water system [32,56].

In SB, PC1 and PC2 accounted for 68.0% and 22.9%, respectively, resulting in a cumulative contribution of 90.9% (Figure 5b). Generally, a trend similar to that of the PD was observed in spring. However, in summer, SB showed a higher contribution from the E2/E4 index (4.3%), associated with autochthonous organic matter, compared to other sites. This observation suggests that the SB is more profoundly influenced by heavy rainfall, generating autochthonous biodegradable organic matter, such as algal growth [52,57,58]. In the fall, the LMWN contribution increased to 85.2%, indicating the significant influence of low molecular weight organic matter in SB’s water system post-rainfall [56].

In GS, the cumulative contribution was as high as 96.6%, with PC1 and PC2 accounting for 72.2% and 24.4%, respectively (Figure 5c). The contribution of the parameters was similar to that of PD, with a high contribution of BP in spring and chromatographic parameters HS, BB, and LMWN in summer.

In KK, PC1 and PC2 accounted for 91.2% and 6.9%, respectively, resulting in a cumulative contribution of 98.1% (Figure 5d). Unlike the other sites, KK exhibited no clear correlation between the samples and parameters. The correlation analysis revealed that KK had higher correlations across all spectral and chromatographic parameters than the other sites, which may have impacted the distinction in the PCA. This phenomenon may be attributed to Gyeongancheon having the lowest flow rate among the three tributaries in Lake Paldang because it is a relatively urban area (Table 1), consequently increasing the concentration of organic matter [59].

4. Conclusions

This study employed advanced analytical techniques to characterize the distribution of organic matter in the Paldang Watershed, focusing on the major source materials entering Lake Paldang. Spectral and chromatographic analyses were used to explore the chemical quality parameters within the watershed, including Lake Paldang (PD) and its tributaries (SB, GS, and KK), in 2022. This study identified seasonal variations induced by heavy rainfall events. The wet season analysis, represented in the HS-diagram, highlighted the significant influence of humic substances originating from forests and paddy soils during the dry season. Soil and humic substances related to leaves entered the watershed more prominently during the wet season. The correlation and principal component analyses revealed a substantial contribution from biodegradable organic matter in spring, which was attributed to microorganisms such as plankton. In contrast, summer showed notable contributions from non-biodegradable substances with a (HS + BB) fraction of 90.9%. After August, low molecular weight neutrals (LMWN) surged by more than 70% owing to the influx of humic substances and their subsequent decomposition into water systems.

This study provides insights into the composition of riverine and natural organic matter using advanced analytical techniques. The HS-diagram and PCA revealed the contributions of humic substances and various organic matter factors, facilitating the tracing of the source samples impacting the watershed. These results are expected to serve as foundational data for quantitatively analyzing the organic carbon components present in the watershed and the inflow of organic carbon, thereby facilitating source tracking.
Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/agronomy13112766/s1, Table S1: Correlation coefficients for water Quality factor, absorbance and chromatographic parameters in PD; Table S2: Correlation coefficients for water Quality factor, absorbance and chromatographic parameters in SB; Table S3: Correlation coefficients for water Quality factor, absorbance and chromatographic parameters in GS; Table S4: Correlation coefficients for water Quality factor, absorbance and chromatographic parameters in KK.

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