Science of the Total Environment 544 (2016) 525–534

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Coupling effects of abiotic and biotic factors on molecular composition of dissolved organic matter in a freshwater wetland

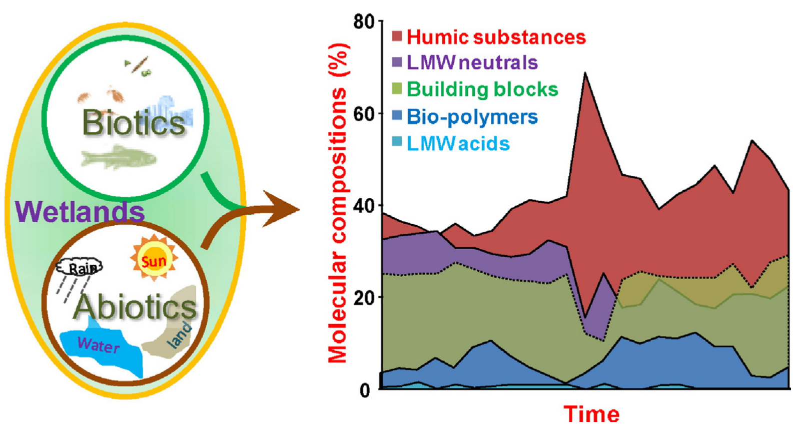
Wei He [a], Ilhwan Choi [b], Jung-Joon Lee [c], Jin Hur [a,*]

[a] Department of Environment and Energy, Sejong University, Seoul 143-747, South Korea
[b] Water Analysis and Research Center, K-water, 560 Sintanjin-ro, Daedeok-gu, Daejeon 307-711, South Korea
[c] Department of Biological Education, Daegu University, Gyungbuk 712-714, South Korea

HIGHLIGHTS

- Humic fractions varied seasonally and periodically in a freshwater wetland.
- The origin of humic substances was aquagenic in winter and pedogenic in summer.
- Humics and DOM aromaticity were associated with temperature, chl-a, and rainfall.
- Solar irradiation mainly affected the molecular weight of humic substances.
- Coupling effects of biotics and abiotics on DOM were implicitly observed.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 22 August 2015
Received in revised form 17 November 2015
Accepted 2 December 2015
Available online xxxx

Editor: D. Barcelo

Keywords:
Dissolved organic matter
SEC-OCD
Coupling effects
Wetland
Molecular size

ABSTRACT

In this study, temporal and spatial variations in five defined molecular size fractions of dissolved organic matter (DOM) were examined for a well preserved wetland (Upo Wetland) and its surrounding areas, and the influencing factors were explored with many biotic and abioic parameters. For each DOM sample, the five size fractions were determined by size-exclusion chromatography coupled with organic carbon detector (SEC-OCD). For 2-year long monthly monitoring, bio-polymers (BP), humic substances (HS), building blocks (BB), low molecular-weight (LMW) neutrals, and LMW acids displayed the median values of 264, 1884, 1070, 1090, and 11 μg-C L^{-1}, respectively, accounting for 6.2%, 41.7%, 24.5%, 26.4%, and 0.4% of dissolved organic carbon (DOC). The dominant presence of HS indicated that terrestrial input played important roles in DOM composition of the freshwater ecosystem, which contrasted with coastal wetlands in other reports. Both seasonal and periodic patterns in the variations were found only for HS and BB among the size fractions. It was also notable that the sources of HS were seasonally shifted from aquagenic origin in winter to pedogenic origin in summer. The correlations among the size fractions revealed that BB and LMW neutrals might be degradation products from HS and humic-like substances (HS + BB), respectively, while LMW acids, from LMW neutrals. Principle component analysis revealed that the humic-like substances and the aromaticity of DOM were associated with temperature, chlorophyll a, phosphorous, and rainfall, whereas the other fractions and the molecular weight of HS were primarily

* Corresponding author.
E-mail address: jinhur@sejong.ac.kr (J. Hur).

http://dx.doi.org/10.1016/j.scitotenv.2015.12.008

affected by solar irradiation. Significant correlations between DOM composition and some biotic factors further suggested that DOM may even affect the biological communities, which provides an insight into the potential coupling effects of biotic and abiotic factors on DOM molecular composition in freshwater wetlands.

1. Introduction

Wetland, a land seasonally or permanently saturated with water, plays significant roles in the global carbon cycle by pumping a large amount of atmospheric carbon dioxide (CO_2) into water and storing carbon as dissolved CO_2 and organic carbon in both vegetation and natural organic matter (Abril et al., 2014; Kayranli et al., 2010). The organic carbon stored in dissolved organic matter (DOM) is highly linked with many biotic and abiotic factors, and it exhibits more stable behavior than dissolved CO_2 in aquatic ecosystems (Azam and Malfatti, 2007; Battin et al., 2008; Post et al., 1990). It has been reported that the organic carbon cycling and the associated roles of DOM could be easily altered by natural disasters (e.g., hurricane) and/or anthropogenic activities (e.g., agricultural land use) (Osburn et al., 2012; Wilson and Xenopoulos, 2009). Such a complexity makes it necessary to identify the key factors responsible for the changes in the quantity and the quality of DOM with regard to wetlands.

To date, abiotic factors have been among the most concerning issues for DOM changes due to the relatively easy monitoring and the abundance of records (Chen et al., 2013; Franke et al., 2012; Jeong et al., 2012; Wilson and Xenopoulos, 2009). In particular, hydrologic factors, including water retention, flood, runoff, and hydrological connectivity, have been mostly investigated (Chen et al., 2013; Mazzuoli et al., 2005; Mladenov et al., 2005; Park et al., 2009; von Schiller et al., 2015; Yu et al., 2015). The meteorological parameters such as temperature, rainfall, wind, and sunlight have been considered to be important influencing factors, but also have been rather overlooked regarding the composition of DOM in wetlands (Chen et al., 2013; Park et al., 2009; Piirsoo et al., 2012; von Schiller et al., 2015). For example, photochemical transformation may lead to the changes in DOM (Franke et al., 2012), especially in shallow wetlands. Nearly the half of aromatic moieties can be removed by solar irradiation during summer (Waiser and Robarts, 2004). Anthropogenic activities, including water regimen, land use, and pollution discharge, attract much attention in recent years because this influence is much easier to be altered and controlled than natural factors (Wiegner and Seitzinger, 2004; Wilson and Xenopoulos, 2009; Yao et al., 2015). It was reported that aromatic fraction and bioavailability of DOM are much lower in an anthropogenically impacted wetland than a pristine one (Wiegner and Seitzinger, 2004). Wetland has been highlighted as the key land-use regulating the DOM export from the surrounding watershed, storing a part of DOM as carbon sink, and reducing carbon emission (Abril et al., 2014; Laudon et al., 2004).

In summer, algal- and microbial activities and the productivity may be more important than rainfall because significant correlations between terrestrial DOM and rainfall were observed in spring but not in summer in previous reports (Biber et al., 1996; Li et al., 2008; Zhang et al., 2011). Humic substances and free amino acids are known to be ingested by detritivorous invertebrates and other organisms associated with them (Thomas, 1997). In oligotrophic wetlands, the composition of DOM is more influenced by aquatic vascular plants (Chen et al., 2013) than algae and microbes. In an effort to explore roles of abiotic and biotic factors on DOM composition in wetlands, bulk dissolved organic carbon (DOC), spectral characterization (specific ultraviolet absorbance (SUVA), fluorescent indicators), and pyrolysis-GC-MS have been often employed to date, and the seasonal variations were monitored under given biotic and/or abiotic factors (Biber et al., 1996; Chen et al., 2013; Duan et al., 2007). However, the bulk DOC measurements and the spectroscopic methods are not sufficient to explain the compositional variation of the entire DOM. Pyrolysis-GC-MS offers more molecular information on bulk DOM, but it is very limited for the quantitative analyses of DOM due to the possibility of inaccurate assignments (Biber et al., 1996). Size-exclusion chromatography coupled with organic carbon detector (SEC-OCD) is a promising technique to overcome the aforementioned limitations (Huber et al., 2011). Despite its wide uses in water treatment fields (Ho et al., 2015; Kimura et al., 2015; Simon et al., 2013), unfortunately, only a few studies have investigated the DOM composition in natural environments such as coastal water, rivers, and reservoirs using the technique (Chen et al., 2015; Marie et al., 2015; Penru et al., 2013). It would be beneficial to extend the applicability of SEC-OCD into wetlands, an environmentally important compartment, to obtain a better understanding of DOM in natural environments.

As stated before, most related studies of wetlands have separately considered abiotic or biotic effects on DOM composition. However, it should be noted that the two factors are always coupled with each other in exerting their influences. The coupling effects are largely influenced by the balance between precipitation and biological factors within wetlands, and the temporal variance of DOC in the downstream of wetland is typically much higher than that of upstream (Goodman et al., 2011; Piirsoo et al., 2012). Therefore, the present study based on a long-term monthly monitoring of a well preserved freshwater wetland (Upo wetland; the largest wetland in South Korea) was targeted with two main goals: 1) to examine the seasonal and the spatial variations in DOM concentrations and the molecular composition by employing SEC-OCD, and 2) to explore the roles of biotic and abiotic factors in changing the DOM composition. The biotic factors considered for this study included biological communities and the primary production of aquatic vascular plants, while the abiotic factors were water quality and meteorology parameters (season, rainfall, temperature, and solar irradiation time).

2. Materials and methods

2.1. Study area and sampling sites

Upo Wetland (128°25′ E and 35°33′ N) is the largest freshwater wetland in South Korea. It is designated as an Ecological Conservation Area by the Ministry of Environment and registered to Ramsar. Many animals and plants live in the vast wetland of 231 ha. In the Upo Wetland watershed, there are five categories of land-use manly including forest land (54.6%), farmland (27.9%), building & roads (5.6%), bare land (5.4%), and water bodies (3.4%) (Landsat 8 OLI/TIRS image in May 13th, 2013). Surface water samples from Upo Wetland (W1), Mokpo Wetland (W2), Sajipo Wetland (W3), Jjogjibeol Wetland (W4), upstream rivers, including Topyeongcheon River (U1), Chogogcheon River (U2), Daehabcheon River (U4), and downstream Topyeongcheon River (D1), were collected monthly from October 27th, 2011 to September 28th, 2013 (Fig. S1).

2.2. Water physicochemical property, meteorological information, and biological communities

The water quality properties, including dissolved oxygen (DO), pH, conductivity, temperature, chlorophyll a (Chl-a), turbidity, chemical oxygen demand (COD), nitrate-nitrogen (NO3-N), ammonium-nitrogen (NH4-N), total nitrogen (TN), orthophosphate phosphorus (PO4-P), total phosphorus (TP), suspended solids (SS), were also monthly monitored from October, 2011 to September, 2013 in Upo Wetland. The meteorological information was monthly recorded by Changnyung Station of Korea Meteorological Administration (http://web.kma.go.kr/eng/