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Hydrological changes of DOM composition and biodegradability of rivers in temperate monsoon climates



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ARTICLE INFO

Article history: Received 3 July 2015 Received in revised form 20 March 2016 Accepted 1 June 2016 Available online 16 June 2016 This manuscript was handled by Laurent Charlet, Editor-in-Chief, with the assistance of Ewen James Silvester

Keywords:
Dissolved organic matter (DOM)
Dissolved organic carbon (DOC)
Fluorescence
UV-Vis spectroscopy
Parallel factor analysis (PARAFAC)
Biodegradable DOC (BDOC)

SUMMARY

The spatial and hydrological dynamics of dissolved organic matter (DOM) composition and biodegradability were investigated for the five largest rivers in the Republic of Korea (South Korea) during the years 2012-2013 using incubation experiments and spectroscopic measurements, which included parallel factor analysis (PARAFAC). The lower reaches of the five rivers were selected as windows showing the integrated effects of basin biogeochemistry of different land use under Asian monsoon climates, providing an insight on consistency of DOM dynamics across multiple sites which could be difficult to obtain from a study on an individual river. The mean dissolved organic carbon (DOC) concentrations of the five rivers were relatively low, ranging from 1.4 to 3.4 mg L^{-1} , due to the high slope and low percentage of wetland cover in the basin. Terrestrial humic- and fulvic-like components were dominant in all the rivers except for one, where protein-like compounds were up to ~80%. However, terrestrial components became dominant in all five of the rivers after high precipitation during the summer monsoon season, indicating the strong role of hydrology on riverine DOM compositions for the basins under Asian monsoon climates. Considering that 64% of South Korea is forested, our results suggest that the forests could be a large source of riverine DOM, elevating the DOM loads during monsoon rainfall. Although more DOM was degraded when DOM input increased, regardless of its sources, the percent biodegradability was reduced with increased proportions of terrestrially derived aromatic compounds. The shift in DOM quality towards higher percentages of aromatic terrestrial compounds may alter the balance of the carbon cycle of coastal ecosystems by changing microbial metabolic processes if climate extremes such as heavy storms and typhoons become more frequent due to climate change.

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1. Introduction

Dissolved organic matter (DOM) of rivers can be a major energy source for aquatic biota (Findlay et al., 1998), and riverine dissolved organic carbon (DOC) is an important component of the global carbon cycle, linking the two major carbon pools, *i.e.*, terrestrial and oceanic ecosystems (Cole et al., 2007; Raymond and Bauer, 2001). The primary source of DOM in streams and rivers is soil organic matter which can be connected to a riverine network when hydrologic flow paths change from groundwater to near-surface runoff or DOM-rich riparian sources (Aitkenhead and McDowell, 2000; Boyer et al., 1997; Sanderman et al., 2009). The riverine DOM composition as well as concentrations can vary both locally

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and globally due to the spatiotemporal variation of hydrology with the heterogeneous DOM sources (Aitkenhead and McDowell, 2000; Hernes et al., 2008; Oh et al., 2013; Sanderman et al., 2009).

Strong seasonal variation in precipitation and temperature is observed in South Korea under Asian monsoon climates which can directly influence watershed hydrology and riverine DOM dynamics (Jeong et al., 2012; Kim et al., 2013; Park et al., 2007). Similar to other studies on headwater streams in U.S. and Canada (Boyer et al., 1997; Hinton et al., 1997), studies on headwater streams in South Korea also demonstrated significantly increased terrestrial DOC inputs to streams following rain events (Jeong et al., 2012; Kim et al., 2010). However, the DOC pulse due to storms in the headwater stream can be integrated with the pulses from other subwatersheds within the basin, resulting in dampened response of DOC concentration ([DOC]) to hydrologic changes near the mouth of the river basin (Kim et al., 2013).

The lower reaches of rivers, where DOM has passed through microbial- and photo-degradation, can be considered as windows

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showing the integrated effects of basin biogeochemistry. Changes in the amount and composition of riverine DOM may play an important role in coastal biodiversity and productivity (Diaz and Rosenberg, 2008). Thus, research using multiple rivers at the mouths of basins can provide an insight on DOM dynamics which could be difficult to obtain from a study on an individual river (Butman et al., 2012). Although higher frequency measurements at a single location can provide insight into DOM dynamics not possible to obtain from lower frequency measurements, a study on multi-river systems can be useful to identify common patterns of DOM dynamics over a larger area. We investigated the DOM composition and biodegradability of the five largest rivers of South Korea to understand characteristics of DOM released into the seas from South Korea. The five largest rivers, the Han River (HR), the Geum River (GR), the Youngsan River (YR), the Sumiin River (SR), and the Nakdong River (NR) drain 57% of the area of South Korea (Fig. 1). The five rivers provide \sim 31 million people water for drinking, agricultural irrigation, and industrial use. Due to the regional importance of these rivers, the concentrations (Jeong et al., 2012; Kim et al., 2013; Yoon et al., 2003) and characteristic (Hur et al., 2008, 2014; Nguyen et al., 2010; Park et al., 2007) of DOC have been studied. However, these studies were mostly conducted to subwatersheds of large basins or only during a certain period of a year such as storm events. To our knowledge, no systematic study has been conducted to simultaneously compare and contrast the hydrological changes of DOM composition and the biodegradability of all five major river systems. Although limited due to relatively low frequency sampling, this concurrent work is crucial for a better understanding of changes in DOM sources and dynamics of the whole system.

Thus, the specific objectives of this study were to investigate the changes of DOM composition of the five largest rivers in South Korea in various hydrological conditions, and to examine correlations between optical properties and the reactivity of the DOM through incubation experiments. South Korea is one of the densely populated regions in Asia that shares the characteristics of the East Asian summer monsoon systems (Wang et al., 2008). Therefore, this study could be beneficial to understand the effects of monsoon climates on the riverine DOM of other rivers in Asia where inputs of riverine DOM and nutrients to estuaries and local oceans are clo-

sely related with productive fisheries and regional hypoxia (Kim et al., 2015; Song, 2010).

2. Methods

2.1. Site descriptions

The five largest rivers of South Korea are drained from \sim 61,000 km² of the area, releasing \sim 40 km³ yr⁻¹ of water (Fig. 1 and Table 1). The monthly mean temperatures of the basins ranged from -6 (Ian.) to 26 °C (Aug.) between 1981 and 2010 (Korea Meteorological Administration, www.kma.go.kr). The mean annual precipitation from 2000 to 2009 was similar, at 1300-1500 mm yr⁻¹ among the basins (www.kma.go.kr), and most of the precipitation (55–76%) fell during the monsoon rainfall season (Jun.–Sep.) when the region was also affected by several typhoons (www.hrfco.go. kr). Subsequently, the discharge (Q) was the largest during the monsoon period, accounting for up to 78% of the annual Q in South Korea. Annual O of the five rivers ranged from $1.9 \text{ km}^3 \text{ yr}^{-1}$ in the YR to $20.3 \text{ km}^3 \text{ yr}^{-1}$ in the HR for 2012-2013 (Table 1). Daily Q and land use/land cover data on the five rivers were downloaded from the Water Management Information System of Korea (WAMIS: http:// www.wamis.go.kr) and the Ministry of Environment (http://egis. me.go.kr). Mean basin slopes were calculated by ArcGIS spatial analyst using digital elevation model (30 m \times 30 m resolution).

Forest is the most dominant land use in the five river basins, ranging from 52% for the YR to 75% for the HR, followed by agricultural and urban land uses (Table 1). In order to compare the integrated effects of basin biogeochemistry on DOM composition, water samples were collected at the lower reaches of the five rivers (Fig. 1) where the salinity was 0–0.2‰. We selected these sampling points with no influence of sea water to avoid interference of salinity on the microbial activity (Fellman et al., 2010).

2.2. Sample collection and preparation

A total of 10–13 river water samples were collected in 2012–2013 from \sim 50 cm below the surface using a 2 L glass bottle from the middle of a bridge at each location. The sampling design is better for comparing sites than for identifying temporal dynamics

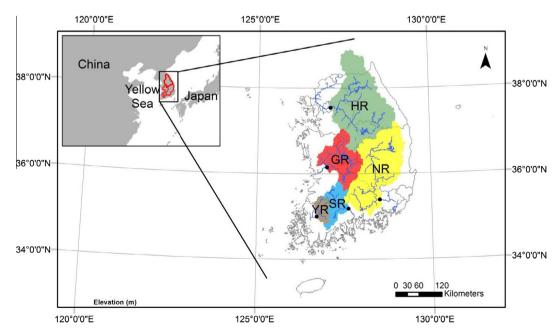


Fig. 1. Locations of the study sites in South Korea. The five river basins are presented in colored polygons and rivers in blue lines. Black circles represent the sampling locations. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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