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Short communication

Identification and characterization of dissolved organic matter sources in Kushiro river impacted by a wetland

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ABSTRACT

The characterization of dissolved organic matter (DOM) is an important parameter for the management of water resources. In this study, physical and chemical characteristics of DOM in Kushiro river, and its territory (Eastern Hokkaido, Japan) were analyzed using multiple analytical tools. Multiple samples were collected from diverse locations (Kushiro river, Kushiro wetland, compost fertilizer, forest and treated sewage) and compared them against their DOM characteristics. Among the samples, Kushiro wetland samples presented higher specific ultraviolet absorbance (SUVA) values demonstrating DOM derived from vascular plants which are rich in aromatic-components. The SUVA values of the two samples of the Kushiro river were relatively close to those of the wetland samples implying the fact that the river contains high amount of plant derived aromatic DOM compounds, originating from the wetland. The excitation–emission matrix (EEM) fluorescence results showed that generally all water samples have two peaks namely, A and C. These two peaks are related to humic-like substance typically derived from the breakdown of organic matters. The excitation–emission matrix (EEM) fluorescence results of the river samples were also similar to those of the wetland samples, characterized by no appearance of protein, amino acid, polysaccharide, and fluvic like matter, but more pronounced to the aromatic component rich humic acid. Principal component analysis revealed that approximately 88% of the variance in the DOM characteristics might be explained by the type of different sources. From the loadings on PC1 and PC2 in the scores plot, the properties of the DOM of the wetland appeared to be similar to those of the river DOM. Combined results exhibited that the quality of the Kushiro river water is fundamentally inherited from the Kushiro wetland, and the main structure of the river water is characterized by poly-aromatic humic like matter and higher molecular weight.

1. Introduction

Aquatic ecosystems in many countries around the world show rapidly rising trend in dissolved organic matter (DOM) (Reynolds and Fenner, 2001; Monteith et al., 2007). A steady increase in DOM has also been observed in several rivers in Japan (Imai et al., 2001). At the point when the main source of potable water is from a river, it is significant to distinguish the source and characterization of DOM (Fernando et al., 2007). The increase in DOM presents a serious challenge for drinking-water management in light of the fact that intractable DOM impacts the optimization and efficiency of water treatment unit operations, including coagulation and membrane treatment, and serves as the main substrate for the formation of disinfection by-products (DBPs) (Lee et al., 2004; Gough et al., 2012, 2014). Therefore, prior knowledge of the nature and potential sources of DOM would benefit utilities during the process optimization and evaluation of the characteristics of DOM in a river.

Kushiro river, a class A river originating in Kussharo Lake (43°33′35″ N, 144°20′20″ E) in eastern Hokkaido, Japan, flows gently winding through the big Kushiro wetland area in Kushiro

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plain, into the Pacific Ocean. Kushiro city, whose fundamental drinking water source is the Kushiro river, located on the downstream basin of the Kushiro wetland and the Kushiro river. The primary drinking water source of the Kushiro city is the Kushiro river.

Dissolved organic matters in natural waters are a complex mixture of various compounds and they comprise majority of the reduced carbon in aquatic ecosystems (Swietlik and Sikorska, 2005) The characteristics of DOM in a river are a function of allochthonous sources (i.e. dissolved vegetation debris carried by storm runoff and snowmelt), autochthonous production (i.e. organic matter originating from biological processes within the water column) and other anthropogenic sources such as effluent organic matter from wastewater treatment and urban runoff. Once in water, these materials can be subsequently modified by physicochemical processes (Na and Park, 2006; Hur et al., 2009; Park et al., 2009). Wetlands are considered a significant supplier of organic matters if it is located within a river's catchment area. During rain events wetlands might flood to close by rivers leading to a significant increase in DOM values in the rivers.

Numerous investigations have been made in identifying the major sources of DOM in rivers, in which the chemical structures, molecular sizes, and spectral features of potential DOM sources in upstream areas were compared with those of the targeted DOM values (Imai et al., 2001; McDonald et al., 2004). Characterization techniques popularly employed for DOM include UV–vis and fluorescence spectroscopy (Lu et al., 2003; Wei et al., 2009; Hur, 2011; Guo et al., 2014), resin fractionation (Imai et al., 2001; Park et al., 2008), pyrolysis-gas chromatography/mass spectrometry (Py-GS/MS) (Wickland et al., 2007), and ^{13}C NMR (Lu et al., 2003; Wickland et al., 2007). Previous DOM source identification studies used simple comparison techniques to compare between different DOM sources. However, the information which results from such techniques was not self-explanatory and was hard to interpret. The use of multivariate statistical tools, based on a number of analytical results, is more desirable in light of the fact that they help to eliminate possible errors associated with the analyses and the bias arising from the limited number of the collected samples (Wickland et al., 2007). There is still a lack of studies on applying a multivariate statistical tool to identify the sources of the DOM in watersheds or drinking water supply. The primary goal of this study is to characterize the DOM inflowing into Kushiro river, a major source of drinking water supply at Kushiro city, Hokkaido, Japan. The characterization was performed to understand the differences in DOM among the source waters. The secondary objective is to identify the primary sources of DOM in Kushiro river using principal component analysis (PCA) as a systematic approach.

2. Materials and methods

2.1. Study area

Kushiro river, a class A river originating in Kussharo Lake (43°33′35″ N, 144°20′20″ E) in Akan National Park in eastern Hokkaido, flows gently winding through the big Kushiro Swamp range in Kushiro Plain, into the Pacific Ocean. It is 154 km in length and has a drainage area of 2510 km^2. The river is joined by two tributaries, the Kuchoro River (60.2 km) and the Setsuri River (59.8 km), before it discharges into the Pacific Ocean at the port at Kushiro. The lower reaches of the Kushiro river, running through the Kushiro Wetland, providing water resources for its population. The Kushiro wetland is the largest wetland in Japan. It is the first wetland registered under the Ramsar Convention in Japan and is designated as a national park. It has an abundance of natural scenery and serves as a significant habitat for wildlife.

2.2. Sample collection

A map of sampling locations and details of collected samples and their characteristic are presented in supplementary data Figure S.1 and Table S.1, respectively. All samples with the exception of compost fertilizer (CP) and wetland 3 (WL3) were collected in September, 2011. CP and WL3 were collected in May, 2011. Three water samples from Kushiro river (RW1, RW2 and RW3) were collected from three different locations. RW1 was taken from the location where Kushiro river enters into the wetland. RW2 was taken from the location where the Kushiro river is surrounded by the wetland. RW3 was taken from the influent point of the water treatment plant. Again, one of the purposes of this study is to suggest a systematic approach to identify the possible source of DOM in the Kushiro river water from many other potential sources. The potential DOM sources include wetland (WL), compost fertilizer (CP), forest (FS) and wastewater treatment plant effluent (WWTP). Wetland sample represents the decomposition of wetland plants, for example, reed. Three wetland samples (WL1, WL2 and WL3) were collected from different locations of Kushiro wetland. WL1 and WL2 were taken from a location around the RW2 sampling point. WL3 was collected from the point where the Setsuri river meets with the Kushiro river. A significant area of the upstream of the Setsuri river is occupied by a forest. FS sample was collected from the Setsuri river when it passes through the forest. CP sample was taken from an agricultural field spotted within the wetland, where organic fertilizers have been used for agricultural purposes. WWTP sample was taken from the outflow of a membrane bioreactor process (MBR) waste water treatment plant, which is located at the east of the wetland. The outflow of the plant is directed to a small stream that at the end meets the Kushiro river at the south. All samples were collected as liquid stage. Collected samples were filtered (0.45 μm) and stored at 4 °C.

2.3. Analytical methods

All samples were filtered through 0.45 μm filter before analyzing. Dissolved organic carbon (DOC) was determined by a Shimadzu V-CPH analyzer. UV absorbance was measured by a UV–vis spectrophotometer (Shimadzu) with 1 cm quartz cuvette. Fluorescence measurements were conducted using a spectro-fluorometer (FP-6500, Jasco, Japan) equipped with a 150 W xenon lamp at ambient temperature of 24 °C. A 1-cm quartz cuvette with four optical windows was used for the analysis. Emission scans were performed from 220 to 550 nm at 5 nm steps, with excitation wavelengths from 220 to 450 nm at 5 nm intervals. The detector was set to high sensitivity, and the scanning speed was maintained at 2000 nm/min in this study; the slit widths for excitation and emission were 5 nm and 3 nm respectively. Under the same conditions, fluorescence spectra for Milli-Q water were subtracted from all the spectator eliminate water Raman scattering and to reduce other background noise. Fluorescence ratios can be adopted as a good gauge for the relative contributions of organic substances, which are derived from animals, plants, soils and microorganisms to DOM found in natural waters via specific spectral regions of an EEM. Supplementary data Table S.2 presents fluorophores EEM regions with peak abbreviation (Coble, 1996). Specific UV absorbance (SUVA) values were determined by taking the ratio of the UV absorbance at 254 nm to the DOC concentration. The spectral slope ($S_{290-350}$) was obtained by a best-fit regression line from the natural log-transformed absorption spectra of the samples at the wavelengths between 290 and 350 nm (Spencer et al., 2007). The fluorescence