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Preliminary Assessment of Chemical Characteristics of Dissolved Organic Carbon in Surface Waters of the Hulugou Watershed, Qinghai-Tibetan Plateau

ZHOU Min¹, Kale M. CLAUSON², SUN Ziyong³, ZHENG Chunmiao¹ and ZHENG Yan^{1,2,4*}

1 Center for Water Research, Peking University, Beijing, 100871, PR China

2 Queens College, City University of New York, Flushing, NY 11367, USA

3 School of Environmental Studies, China University of Geosciences, Wuhan, 430074, P R China

4 Lamont-Doherty Earth Observation of Columbia University, Palisades, NY 10964, USA

Climate warming induced permafrost melting has begun to exert considerable impact on watershed hydrology, including water quality. The concentration and characteristics of dissolved organic carbon (DOC) in stream water are expected to respond or may even be sensitive indicators of such changes. Optical properties of the light absorbing or chromophoric fraction of DOC can provide information on the amount, source, and quality of chemically distinct moieties within the DOC pool. Recent research has demonstrated that combined measurements of ultraviolet-visible (UV-Vis) and fluorescence spectra with multivariate statistical techniques have transformed our understanding of biogeochemical dynamics in aquatic systems. Such methods were employed in this study to provide a preliminary assessment of DOC characteristics in a low latitude alpine watershed with an area of 25 km² in the northeastern part of the Qinghai-Tibetan Plateau (Fig. 1). Water samples ($n=22$, Table 1) were collected from streams, flow seepage from shallow soils, and thermokarst ponds in July, 2012.

DOC concentration was determined through measuring the non-purgable organic carbon (NPOC) fraction for all samples using a TOC-5000 Analyzer (Shimadzu). UV-vis absorbance was measured by obtaining broad range spectra on an Agilent 8453 UV-Vis spectrophotometer with a 1 cm path length quartz cuvette. Carbon-specific UV absorbance (SUVA; Table 1) was calculated as the UV absorbance at 254 nm (UV254) normalized to the DOC concentration (L m⁻¹ mg⁻¹). Excitation emission matrices (EEMs) were collected for filtered liquid samples by scanning over an excitation range of 240 to 460 nm at 10 nm increments, and an emission range of 350 to 550 nm at 2 nm increments on a JY-Horiba

Fluoromax-3 spectrofluorometer with instrument-specific corrections, Raman normalization, inner filter correction, and blank subtraction applied. To minimize inner filter effects prior to fluorescence measurements, samples were diluted to UV254 absorbance less than 0.2 (Miller et al., 2009). The fluorescence index (FI, Table 1) as calculated as the ratio of intensities emitted at 470 and 520 nm at 370 nm excitation (Cory and McKnight, 2005). The EEMs were fit to a parallel factor analysis (PARAFAC) model developed by Cory and McKnight (2005), which resolves the EEMs into 13 components including quinone-like, protein-like, and other undetermined components. The percentage of protein-like fluorescence is calculated as the ratio of tryptophan-like and tyrosine-like components to the total components (Cory and McKnight, 2005). The components can be grouped to assess the redox state of the DOC or fulvic acids, with four components representing semi-quinones and hydroquinone-like compounds or reduced DOC and another three representing quinones or oxidized DOC (Miller et al., 2006). A redox index (RI) is calculated as the percentage of the four reduced components.

For samples collected within the boundary of the watershed (Fig. 1), the mean concentrations of DOC are 14.2, 0.6 and 0.14 mg/L for thermokarst water, seepage and stream waters, respectively (Table 1). The FI provides information on organic matter source (McKnight et al., 2001), with a value of 1.8~1.9 for microbially-derived fulvic acids and a value of 1.2~1.4 for terrestrially derived fulvic acids. SUVA determined at 254 nm is strongly correlated with percent aromaticity determined by ¹³C NMR (Weishaar et al., 2003). The thermokarst water, with high DOC content and SUVA values, displayed the lowest FI values with a mean close to 1.40 - characteristics indicative of terrestrially-sourced DOC. The increasing FI

* Corresponding author. E-mail: yzheng@coe.pku.edu.cn

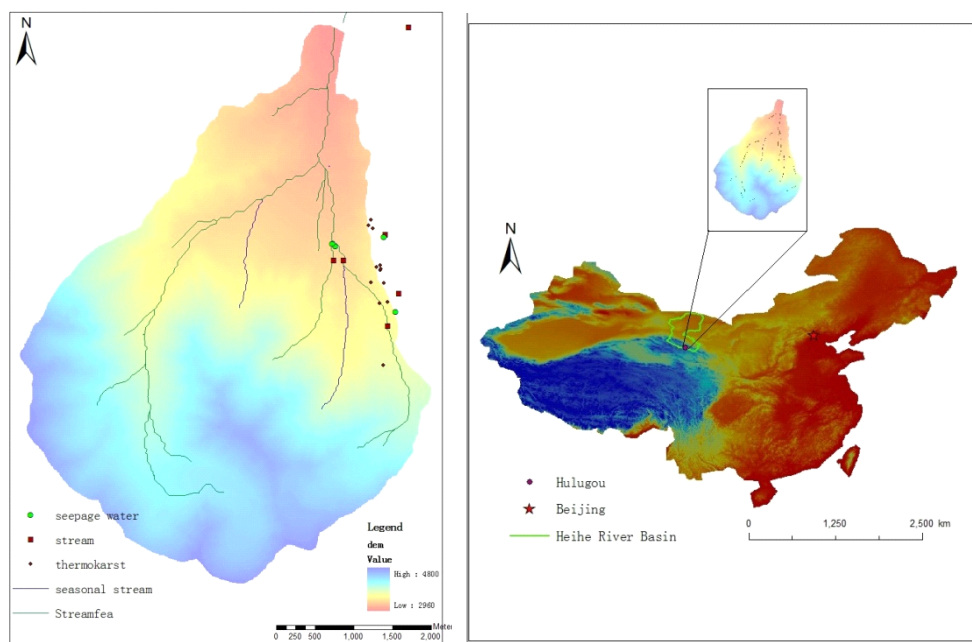


Fig. 1 Location of Hulugou watershed

Table 1 Characteristics of DOC in Hulugou watershed, July 2012

	Location (n)	SUVA L.mgC ⁻¹ .m ⁻¹	DOC mgC.L ⁻¹	spCond uScm	pH	FI	MaxEm nm	RI	Protein %
Stream	Inside (4)	1.36±0.29	0.56 ±0.13	194.3±0.17	7.89±0.04	1.57±0.04	459	0.77 ±0.05	21~49
	Outside (2)	3.11±0.03	3.78±1	348.5±22	8.19±0.04	1.47±0.01	466	0.76 ±0.03	7~13
Thermokarst	Inside (11)	3.87±0.17	13.8±7.1	380.91±40	7.52±0.44	1.41±0.13	469	0.73 ±0.04	6~9
	Outside (1)	10.55	6.19	383	7.25	1.48	424	0.71	11
Seepage water	Inside (2)	0.97±0.4	0.62±0.14	398.5±1	8.09±0.06	1.67±0.00	454	0.7 ±0.01	20~39
	Outside (2)	2.51±0.05	2.12±1.4	319.5±90	7.79±0.17	1.53±0.01	462	0.75 ±0.01	11~18

For each property, values are mean and 1 standard deviation, respectively.

values of the stream water collected within the watershed suggests increasing degree of influence of DOC from microbial processing (Table 1). The pH, SUVA, DOC levels are comparable for seepage and stream waters (Table 1), suggesting that they are of similar sources. However, seepage water had higher FI, suggesting that microbial processing of DOC that influenced stream and seepage water may have occurred in the subsurface. The high RI values observed support our assumption that the DOC in the stream and seepage waters are influenced by subsurface biogeochemical processes, because hyporheic exchange has likely brought reduced fulvic acids into the stream.

A limitation of this dataset is that no shallow groundwater samples representing the hyporheic zone were collected hence the biogeochemical processes responsible for the range of DOC characteristics observed could not be assessed. Nevertheless, the data suggest the permafrost melt water not only has high concentrations of

DOC but also displays a unique chemical signature. Further work combined with stable isotope analysis will help to illuminate the processes and to resolve the contribution of water and DOC from permafrost melting to streams.

Key words: dissolved organic carbon (DOC), UV-Vis absorbance, fluorescence, permafrost, alpine, low latitude, Qinghai-Tibet Plateau, Heihe River Basin

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