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Dynamics and ecological risk assessment of chromophoric dissolved organic matter in the Yinma River Watershed: Rivers, reservoirs, and urban waters

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ABSTRACT

The extensive use of a geographic information system (GIS) and remote sensing in ecological risk assessment from a spatiotemporal perspective complements ecological environment management. Chromophoric dissolved organic matter (CDOM), which is a complex mixture of organic matter that can be estimated via remote sensing, carries and produces carcinogenic disinfection by-products and organic pollutants in various aquatic environments. This paper reports the first ecological risk assessment, which was conducted in 2016, of CDOM in the Yinma River watershed including riverine waters, reservoir waters, and urban waters. Referring to the risk formation theory of natural disaster, the entropy evaluation method and DPSIR (driving force-pressure-state-impact-response) framework were coupled to establish a hazard and vulnerability index with multisource data, i.e., meteorological, remote sensing, experimental, and socioeconomic data, of this watershed. This ecological vulnerability assessment indicator system contains 23 indicators with respect to ecological sensitivity, ecological pressure, and self-resilience. The characteristics of CDOM absorption parameters from different waters showed higher aromatic content and molecular weights in May because of increased terrestrial inputs. The assessment results indicated that the overall ecosystem risk in the study area was focused in the extremely, heavily, and moderately vulnerable regions. The ecological risk assessment results objectively reflect the regional ecological environment and demonstrate the potential of ecological risk assessment of pollutants over traditional chemical measurements.

1. Introduction

Chromophoric dissolved organic matter (CDOM) in surface waters, as the colored fraction of dissolved organic matter (DOM), could potentially be estimated via remote sensing (Kutser et al., 2005; Organelli et al., 2014; Song et al., 2012, 2013; Zhu et al., 2013, 2014). CDOM, a complex mixture of organic matter in compounds, can produce carcinogenic disinfection substances and is significantly related to biological oxygen demand (BOD), chemical oxygen demand (COD), and organic pollutants (Kowalczuk et al., 2010; Liu et al., 2014; Zhang et al., 2011). Absorption and fluorescence technology can be a potentially viable approach in tracing, detecting, and understanding the mobility, degradability, and bioavailability of CDOM and anomalous changes in waters (Baghoth et al., 2011). CDOM-specific ultraviolet absorbance ($a_{\mathrm{CDOM}}(350)$ and $a_{\mathrm{CDOM}}(440)$) and spectrum slope ($S_{275–295}$, $S_{350–400}$, and S_r) are used to represent CDOM concentration and relative molecular weight and to differentiate sources. CDOM fluorescence at wavelength 275/342 nm could serve as a key indicator for detention of point source contamination (Zhou et al., 2016). Hence, CDOM may be recognized as a major threat to the environment and the health of humans and other organisms. Human activities increase pollutant emissions, particularly during rapid industrialization and economic development and in regions that utilize low efficiency energy. In fulfilling the role as the medium of remote sensing reflection and DOM concentration, CDOM represents organic compounds especially in highly polluted waters. Previous studies have focused on the ecotoxicological risk assessment of organic compounds, pollution control, and pollution prevention (Nakata et al., 2014; Sun et al., 2015). However, routine water pollutant monitoring and ecotoxicological risk assessment methods may not satisfy the need for large scale and low cost. Remotely sensed imagery, spatial technologies, and computer processing are increasingly useful in the monitoring of environmental pollutants and in ecological risk assessment especially in the big data era and have the advantages of being long term and free and having geography spatial extensiveness and a high level of spectral classification. CDOM can be seen as an indirect medium evaluating ecotoxicological risk. For

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the geographical extent of the terrestrially dominated inland rivers and streams, terrestrial factors that control the seasonal concentration and physicochemistry of CDOM strongly show spatial and temporal characteristics (Monteith et al., 2007; Miller et al., 2002). Hydrological, geological, biological, and anthropic factors can control the seasonal flux of CDOM in waters (Arvola et al., 2016; Brezonik et al., 2015; Minor et al., 2006). Quantitative understanding of seasonal CDOM dynamics would be beneficial to understanding biogeochemical carbon cycles and conducting the ecological risk assessment in highly polluted waters.

The Songhua River, the seventh longest river in China, flows through four provinces, i.e., Jilin, Liaoning, Heilongjiang, and Neimenggu. About 100 t of benzene was discharged into the Songhua River from the Jilin chemical plant explosions in 2005. This incident of Songhua pollution has affected the Russian people downstream. In addition, the Yinma River and Yitong River, which are part of the Songhua River in Jilin Province, as well as the Songhua River itself, flow through the drinking water sources (e.g., Xinlicheng Reservoir and Shitoukoumen Reservoir) that supply water to the city of Changchun. Shitoukoumen Reservoir supplies the daily water for 8 million residents and agricultural and fish products. According to the Chinese environmental state bulletin in 2014, the Yinma and Yitong Rivers were the most polluted watersheds within the Songhua River watershed. Wang et al. (2012) have shown that COD, ammonia nitrogen (NH_3-N), total nitrogen (TN), and total phosphorus (TP) accounted for 44.14%, 53.14%, 82.15%, and 78% of total pollutants, respectively, in the Yinma River. Large amounts of organic matter from the sewage of industrial plants, agriculture, and aquaculture have been poured into the Songhua fluvial system. The great environmental pressure from agriculture, rapid development of industry, and urban construction over the last 20 years has had widespread influence on the watershed ecological security and human health. Practically, ensuring safe drinking water for human health is a global problem (Williamson et al., 2014). In this study, riverine water, reservoir water, and urban water samples were collected in the Yinma River watershed in different seasons. Our objective was to investigate and evaluate the dynamics of CDOM and ecological risk in the Yinma River watershed. The results lay the foundation of ecological risk assessment based on remote sensing. Likewise, quantitative estimation and monitoring of CDOM in highly polluted watershed waters provides early warning of contamination and management measures for water resource protection.

2. Materials and methods

2.1. Study area

The Yinma River watershed (124°8′–126°4′E, 43°2′–44°3′N), located in central Jilin Province, China, is an important polluted tributary of the Songhua River fluvial system (Fig. 1). This watershed has two main rivers, the Yinma River and the Yitong River, and a total area of about 1.74×10^4 km^2. The Yinma River originates in southeast Yitong County and merges with the Yitong River in Nong'an County. Shitoukoumen Reservoir (125°43'–125°51'E, 43°47'–43°57'N) and Xinlicheng Reservoir (125°43'–125°50'E, 43°51'–43°57'N) are the primary water sources for Changchun (the capital city of Jilin Province), and are utilized for irrigation and fishing. Urban Yitong River is the unique river flow through Changchun and has a length is 23 km. The Yinma watershed lies within a typical North Temperate Zone continental monsoon climate, with mean annual temperature of 5.3 °C. The yearly average precipitation ranges from 370 to 668 mm and evaporation is 1438.4 mm.

2.2. Sampling collection

Coordinates for water sample stations were recorded using a global positioning system (GPS). In 2016, 34 riverine samples were collected from the Yinma River (YM) and Yitong River (YT); 56 reservoir samples in Shitoukoumen Reservoir (STKM), Xinlicheng Reservoir (XLC), and Kalun Lake (KLH); and 38 urban water samples from the urban Yitong River (UYT) and several landscape lakes, i.e., Beihu Lake (BH), Youyi Lake (YY), Changchun Lake (CC), and Tianjia Lake (TJ). Detailed sampling information regarding each field survey from the various water bodies can be found in Fig. 1. The sampling locations in the riverine and urban waters were fixed. The Perspex water sampler, Niskin bottles, and brown glass bottles needed to be rinsed with Milli-Q water, and then with sample water. At each station, 2 L water samples were collected from a depth of 0–0.2 m from the surface. The collected samples were stored at 4 °C in coolers and then transported to the laboratory immediately. Physical and chemical parameters were determined within 6 h.

2.3. Measurement of absorbance and three-dimensional fluorescence

Water samples were filtered first through a precombusted Whatman GF/F (1825-047) filter (0.7 μm pore size) under low vacuum, then through a prerinsed 25 mm diameter Millipore membrane cellulose filter (0.22 μm pore size) into brown glass bottles (Li et al., 2016). The twice-filtered were measured between 200 nm and 800 nm at 1 nm intervals using a Shimadzu UV-2600 spectrophotometer with Milli-Q water as a reference. The CDOM absorption coefficient ($a_{\mathrm{CDOM}}(\lambda)$) was calculated using the measured water optical density (OD) as follows:

$$a_{CDOM}(\lambda') = 2.303 \cdot OD_{\lambda}/L \tag{1}$$

where $a_{\mathrm{CDOM}}(\lambda')$ is the uncorrected CDOM absorption coefficient at given λ (nm), $OD(\lambda)$ is the optical density at the same wavelength, and L is the cuvette path length in meters (Li et al., 2016). According to Bricaud et al. (1981), the absorbance at 700 nm was used to correct the absorption coefficients after internal backscattering. OD(null) is the average optical density over 740–750 nm where the absorbance of CDOM can be assumed to be zero (Song et al., 2012). Spectral slope coefficient S can be calculated using a nonlinear fit of an exponential function to the absorption spectrum (Bricaud et al., 1981) as follows.

$$aCDOM(\lambda) = aCDOM(\lambda_0) \times e^{S(\lambda_0-\lambda)} \tag{2}$$

Excitation-emission (0) matrix (EEM) fluorescence spectra of the CDOM were determined by a Hitachi F-7000 fluorescence spectrometer (Hitachi High-Technologies, Tokyo, Japan) with a 700-voltage xenon lamp. The scanning ranges of excitation and emission were 220–450 nm (5 nm intervals) and 250–600 nm (1 nm intervals), respectively, with scanning speed of 2400 nm min^{-1}. Milli-Q water, as the blank of the EEM fluorescence spectra, was subtracted to eliminate water Raman scatter peaks (Stedmon et al., 2011). To eliminate the inner-filter effect, the EEM fluorescence spectra need to be corrected for absorbance (Zhang et al., 2011). More details can be found in Zhang et al. (2011). Parallel factor analysis (PARAFAC) was performed in MATLAB 7.0 with the DOM Fluor toolbox (N-way toolbox) (http://www.models.life.ku.dk), which could separate the EEM fluorescence spectra of the CDOM mixture into separate fluorescence signals. Because of the influence of scatter peaks, the region of the spectra influenced by scatter peaks ($Ex-20 \le Em \le Ex+20$ and $2Ex-20 \le Em \le 2Ex+20$) of all the EEMs needs to be cut. The fluorescence intensity of components was represented by Fmax (QSU). More details can be found in Zhang et al. (2011).

2.4. Water quality

Referring to the Environmental Quality Standards for Surface Water (GB3838-2002, China) (http://kjs.mep.gov.cn/), dissolved oxygen (DO) was measured via iodometry, COD using dichromate, NH_3-N via Nessler's reagent colorimetry, Fe via flame atomic absorption spectrometry, Mn via potassium periodate spectrophotometry, Zn via atomic absorption spectrometry, Hg via atomic absorption spectrophotometry,