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Optical property of dissolved organic matters (DOMs) and its link to the presence of metal ions in surface freshwaters in China

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HIGHLIGHTS

- The deprotonation property of DOM in wide range of surface waters in China was tracked.
- Binding capacities of DOMs could be quantified by spectral parameter and NICA Model.
- The presence of dissolved Zn, Hg and Ni correlate with total binding sites in DOMs.
- Absorbance titration can help understand the speciation and bioavailability of metals.

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ABSTRACT

It is believed that dissolved organic matter (DOM) plays an important role in carrying metal ions through global cycle and distribution, while this point has not yet been elucidated clearly as DOM is extremely heterogeneous and site-specific. In this study, optical properties of DOM in 53 surface freshwater sites all over China were recorded by UV–Vis absorbance spectroscopy in pH range 3–11. The subtle processes of protonation-deprotonation of DOM were quantified by tracking the changes of DOM spectra. The binding capacities of DOMs-binding sites and affinity constants-were interpreted by introducing a spectral parameter, differential log-transformed differential absorbance at 400 nm ($DlnA_{400}$) in combination with Non-Ideal Competitive Adsorption (NICA) Model. It is found that the presence of dissolved Zn, Hg and Ni in the examined waters show strong correlation with total binding sites in DOMs. However, the presence of some other metals with high affinities to DOM, e.g. Cu, Fe and so on, have not demonstrated strong correlation with the total binding sites in DOMs. This indicates the presence of these metals may be seriously influenced by other factors besides DOM. This study demonstrates that the spectroscopic titration approach could potentially provide more structure-specific *in situ* information about DOM and help to understand the role of DOM in the speciation and bioavailability of toxic metal ions.

1. Introduction

Dissolved organic matter (DOM) is ubiquitous in the aquatic environment, and plays important roles in natural and artificial environmental processes, including acting as a carrier of metal ions through global cycle and distribution (Benedetti et al., 1996; Lofts and Tipping, 2011; Mazrui et al., 2016; Wang et al., 2016). While as a metal-binding substrate, the behavior will depend on its nature, i.e. source and composition. DOM is a complex mixture of disordered and polyelectrolytic molecules generated from plant, microbial and animal products at various stages of decomposition (Leenheer and Croué, 2003). It consists of a range of organic molecules comprising oxygen (O)-containing acid functional groups such as carboxyls and phenols, and nitrogen (N)- and sulfur (S)-containing functional groups at relatively low abundance, but these groups display strong binding affinities to trace metals (Craven et al., 2012; Croue et al., 2003; Frenkel et al., 2000; Laglera and van den Berg, 2003; Rozan et al., 2000).

Several geochemical speciation models, e.g. NICA-Donnan

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Model and Model VII, have been developed to interpret metal-DOM interaction. These can model the inherent complexity of DOM properties, assuming the presence of discrete binding sites with no-continuous or continuous distribution of affinities (Benedetti et al., 1995; Lofts and Tipping, 2011; Luo and Millero, 2007). These models are well suited to interpreting the laboratory data on the binding of protons and metals to isolated humic substances, but are much less successful when used to predict metal speciation in natural waters (Ahmed et al., 2013; Hartland et al., 2011; Lofts and Tipping, 2011; Unsworth et al., 2006). One of the challenges involved in applying these models to natural water is the need to estimate the concentration of "active" fulvic or humic acid present in the natural water. Often, the only available information of DOM is the concentration of dissolved organic carbon (DOC) (Mueller et al., 2011).

DOM optical indices are nonetheless expected to be useful descriptors of DOM property in natural water because they are relatively simple and sensitive, and their measurement is rapid and non-destructive (Chen et al., 2003; Spencer et al., 2012). For example, Weishaar et al. (2003) demonstrated that the specific $SUVA_{254}$ value (the absorbance at 254 nm in inverse meters (m^{-1}) by the concentration of DOC measured in milligrams of carbon per liter (mg C L^{-1})) correlates well with the aromatic characteristics of DOM. Spencer et al. (2012) further showed a strong correlation between $SUVA_{254}$ and the amount of hydrophobic fraction of DOM in a study of 30 US rivers. $SUVA_{254}$ has been used to estimate the quality and proportion of DOM that is present as fulvic or humic acid, which participates in the complexation of metal ions, e.g., Cu, Fe and Cd (Amery et al., 2007; Baken et al., 2011; Cornu et al., 2011; Fujii et al., 2014; Kikuchi et al., 2017; Mueller et al., 2011, 2012; Richards et al., 2001). However, the utility is limited because the structural basis of optical properties of DOM remains unclear (Muresan et al., 2011; Pernet-coudrier et al., 2008).

Recent studies have shown that a subtle change in purified DOMs caused by proton and/or metal cations complexation and other aquatic reactions can be tracked by the concept of differential absorbance (Yan et al., 2013, 2014; Yan and Korshin, 2014). Differential absorbance spectra are deemed to be manifestations of

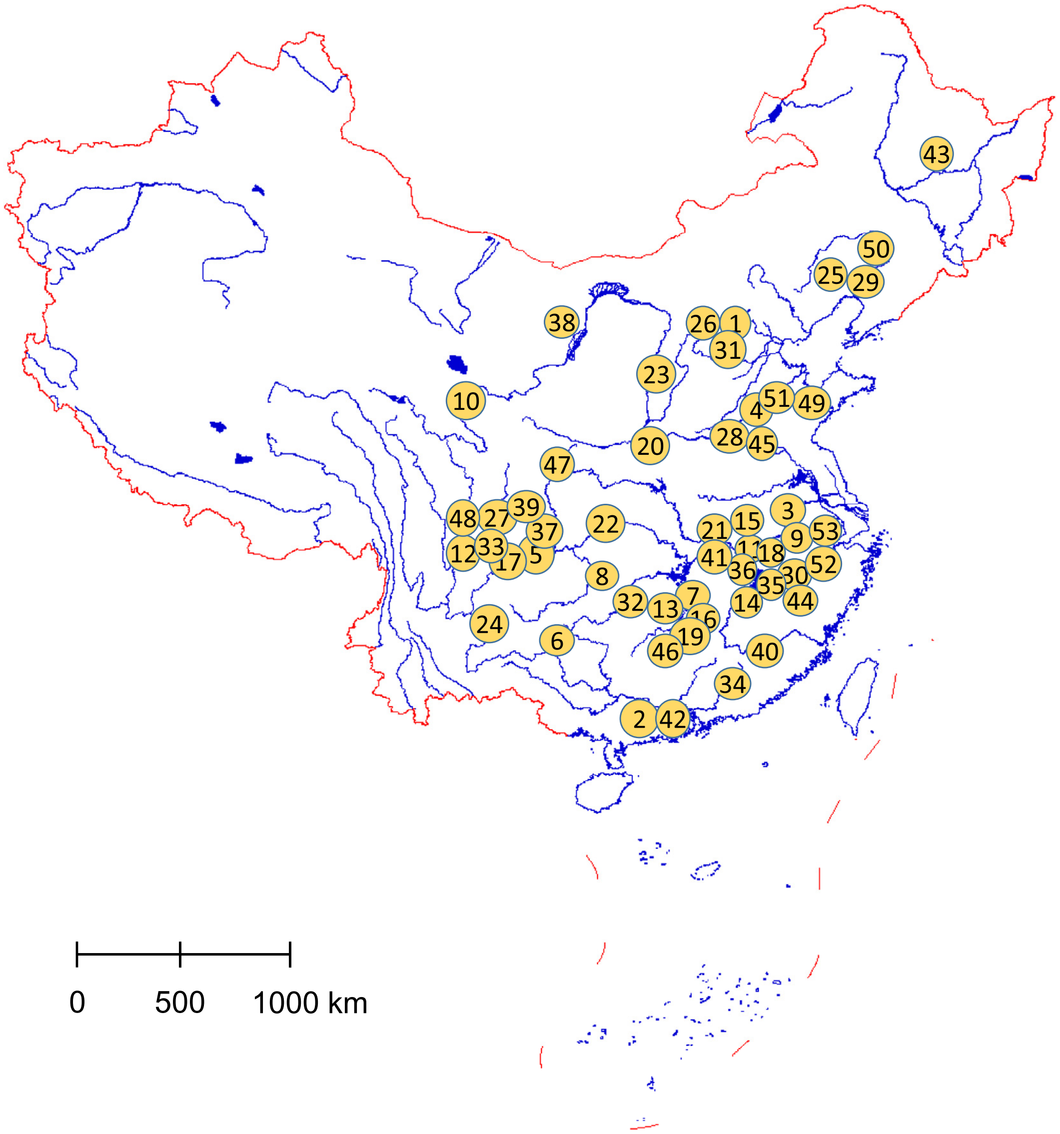

Fig. 1. Sampling site locations across China.