Photo-stability of iron-phenolic complexes derived from peatland upon irradiation in waters under simulated sunlight

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ABSTRACT

Phenolics from peatlands have been proven to enhance the solubility of iron, even under alkali or saline conditions, by forming iron-phenolic complexes. However, the photo-stability of these complexes has received little attention thus far. Based on the investigation of water and peat samples in Jinchuan peatland, in northern China, simulated experiments – using Gallic acid (GA) as a structural analog of peat-derived phenolic acid – were carried out to clarify the mechanisms of photo-stability of iron-phenolic complexes. Our research confirmed that when the molar ratio of GA to Fe reaches 0.1:1, photolysis led to some Fe deposition. By comparing GA concentrations under aerobic/anaerobic conditions, we demonstrated that dissolved oxygen plays a key role, not only in GA autoxidation but also in photo-degradation of GA through direct and indirect photolysis. Besides, adding coexisting phenolic acids into GA/iron systems showed various effects, depending on the different functional groups, while the dominant species of phenolic acids in peatlands, such as p-cumaric acid and p-hydroxybenzoic acid, may still act as reactive oxygen species scavengers, protecting over 99% of the dissolved iron under solar irradiation. Our results indicate that by forming iron-organic complexes with certain phenolics from peatlands, dissolved iron can be effectively protected from precipitation during freshwater transport under solar irradiation, which has profound implications for controlling the limited primary production in certain marine areas.

1. Introduction

Iron is an essential element as well as a main factor limiting primary production in HNLC (high-nutrient, low-chlorophyll) marine areas (Martin, 1990; Hutchins, 1995; Witter and Luther, 1998; Biller and Bruland, 2014). The growth of phytoplankton is retarded with lower concentrations of DFe and the extreme unavailability of insoluble iron species in these areas (Martin, 1990; Martin and Fitzwater, 1988). Many large-scale, ocean iron fertilization experiments have shown that the growth rate of phytoplankton could be increased significantly by increasing bioavailable iron in seawater (Martin, 1990). In most cases, the predominant iron form, under high pH and ionic strength in the ocean, is the oxidized iron state, Fe(III) (Rose and Waite, 2002). In a seawater environment, the theoretical solubility of inorganic iron, due to the formation of its hydrolysis and insoluble ferric (Fe(III)) oxyhydroxide, is 1.0×10^{-11} mol/l. However, field investigations revealed a significantly greater concentration of inorganic iron of 0.09–0.77 mol/l in sea water (Liu and Millero, 1999; Liu and Millero, 2002). Many studies have demonstrated that > 99% of the DFe in the ocean is bound to organic ligands, which makes Fe(III) become more

bioavailable to aquatic microorganisms (Rue and Bruland, 1995; Gledhill et al., 1998; Nolting et al., 1998; Witter and Luther, 1998; Kondo et al., 2012). Although some iron-organic complexes might not be taken up by phyto-plankton directly, these complexes can be converted into available forms of iron through other processes, such as photochemical reactions (Zuo, 1995; Kuhn et al., 2013). Therefore, the input of iron-organic complexes has become an important factor determining primary production in certain ocean areas, and thus carbon dioxide fixation, on a global scale.

As a main source of terrigenous dissolved organic matter (DOM), rivers carry large amounts of iron-organic complexes (Raiswell, 2006; Saitoh et al., 2008). Because of the higher pH values and ionic strength of estuaries, sedimentation occurs in most estuarine mixing zones, capturing DFe and limiting its actual input into the ocean (Forsgren et al., 1996; Windom et al., 1999). However, rivers can still input approximately 26×10^9 mol of total DFe each year (de Baar, 2001). The main reason for this is that rivers contain humic substances, which have a stronger capacity to carry dissolved iron through mixing zones. For example, 3300 nmol/l DFe was found in rivers drained from peat swamps (a large reservoir containing DOM), while the global average
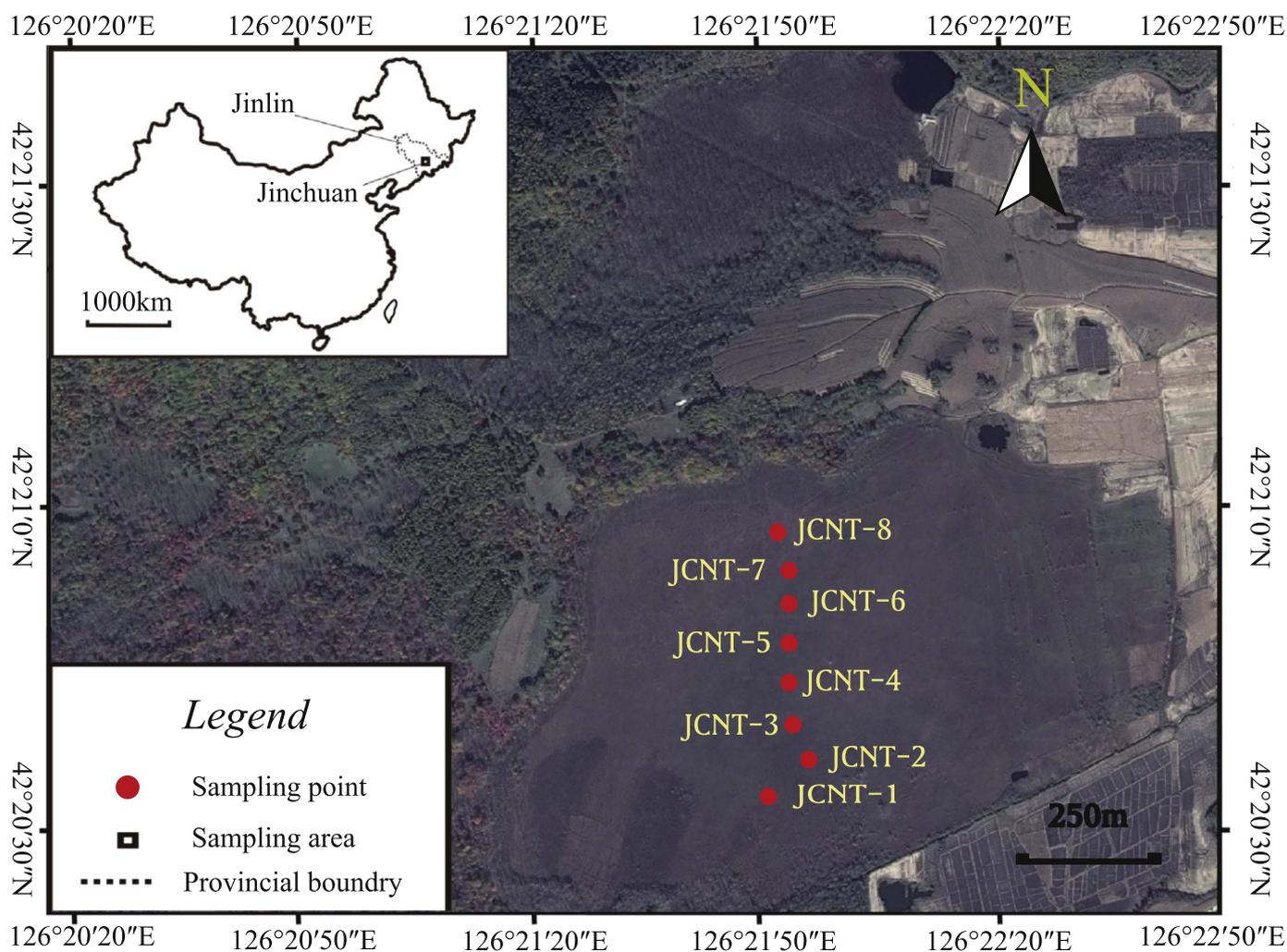
Fig. 1. Sampling area. The peat samples were marked with "JCNT-1~JCNT-8" and the water samples were collected in the exact same sites.

concentration of DFe is just 40 nmol/l (van Schaik et al., 2008; Karlsson and Persson, 2010; Krachler et al., 2010; Stolpe et al., 2013). Some of the recalcitrant DOM, such as aromatic rings in phenolic acids derived from lignin, may retard the degradation of DOM during freshwater transport (Harwood and Parales, 1996). Consequently, the peat-derived phenolic acids, with their strong iron complexing ability, play an important role in transporting DFe long distances and retaining the bioavailability of iron (White et al., 2011; Wan et al., 2013). Upon entering the ocean, they can be effectively used by phytoplankton through direct or indirect pathways.

Different phenolic acids have been identified and measured in peat swamps. According to Wu et al. (2016), 10 phenolic acids were identified in the Hani Peatland, in Northeast China, including gentistic acid, ferulic acid, salicylic acid, syringic acid, p-coumaric acid, caffeic acid, vanillic acid, p-hydroxybenoxic acid, protocatechuic acid, and gallic acid. Similar phenolic acids were also found in other peatlands, especially those with p-hydroxyphenyl compounds, vanillyl compounds, syringic compounds, cinnamyl compounds, galloyl and catechol groups (Tsutsuki and Kondo, 1995; Djurdjević et al., 2003; Philben et al., 2014). Based on simulated experiments, our previous work indicated that phenolic acids with gallyol or catechol groups, under dark and alkali (pH = 8) conditions, protected more iron (total DFe) from precipitation after 72 h, compared with other phenolic acid species (Wu et al., 2016), which might be related to the different negative change density on the ligand sites (Andjelković et al., 2006). Among 10 phenolic acids, caffeic acid, gallic acid, and protocatechuic acid have successfully protected 69%, 64%, and 33% of initial DFe, respectively,

under alkali conditions. And even in different salinities, this protective mechanism still operated (Wu et al., 2016). However, photochemical processes may significantly influence the stability of these iron-organic complexes (Zuo and Hoigne, 1992), which should be taken into account when evaluating the stability of iron-organic complexes in surface waters.

In fact, the photochemistry of phenolics and iron-organic complexes has been studied extensively (Faust et al., 1993; Zuo and Hoigné, 1994; Jeong and Yoon, 2005). According to Hernes and Benner (2003), the total dissolved lignin phenol concentration decreased 72% over ten days of exposure to sunlight, compared to a reduction of only 21% of the same chemical concentration in a dark, control sample. The photoreactions of iron-organic complexes mainly include the photo-reduction process of Fe(III), which is known as the Ligands to Metal Charge Transfer (LMCT) process, and the degradation of organic ligands. Some secondary reactions are induced by the generation of ROS, such as $\cdot$OH, $O_2\cdot^-$, which lead to the re-oxidation of iron (Patterson and Perone, 1973; Zuo and Hoigne, 1992; Zuo and Deng, 1997). Kuma et al. (1995) studied the photolysis of iron-organic acid complexes in marine environments (pH = 8.1) and found that the iron reduction rate, as well as the degradation rate of organic ligands, varied with different organic ligands in the order of gluconic acid > tartaric acid > citric acid > malic acid. Also, under simulated solar irradiation, Yang et al. (2005) found that when the ratio of amino acid to iron concentration is greater than two, both the reduction and the re-oxidation processes of iron can be observed during the whole experiment. However, the photochemical stability of iron-phenolic acid complexes