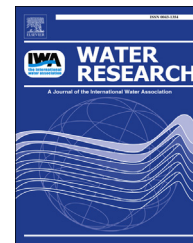




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# Disinfection byproduct formation from lignin precursors

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## ABSTRACT

Lignin is the most abundant aromatic plant component in terrestrial ecosystems. This study was conducted to determine the contribution of lignin residues in natural water to the formation of disinfection byproducts (DBPs) in drinking water. We investigated the formation of different classes of DBPs from lignin model compounds, lignin polymers, and humic substances using two common disinfection techniques, chlorination and chloramination. The contributions of lignin to the overall formation of DBPs from these organic products were determined based on the observed abundances of individual lignin phenols and their DBP yields. Model lignin phenols generally produced higher trichloroacetic acid (TCAA) yields than chloroform and dichloroacetic acid (DCAA) during chlorination. Lignin phenols generally produced higher DBP yields but lower percentages of unknown total organic halogen compared to bulk humic substances and lignin polymers. The relative significance of lignin phenols as chlorination DBP precursors generally follows the order of TCAA > DCAA & chloroform. The relative significance of lignin phenols to DBP formation by chloramination follows the order: TCAA > DCAA & DCAN > chloroform. Overall, lignin phenols are more important as TCAA precursors than as chloroform and DCAA precursors.

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## 1. Introduction

Disinfection byproducts (DBPs) are a group of chemical compounds formed during the disinfection process. The formation of DBPs in drinking water has caused serious public health concerns since the discovery of chloroform in chlorinated waters (Rook, 1974; Krasner et al., 1989; Singer, 1994; Xie, 2003). Trihalomethanes (THMs) and haloacetic acids (HAAs) are the two major halogenated DBPs that are regulated by the US Environmental Protection Agency. Natural organic matter (NOM) is the major organic precursor to the formation

of halogenated DBPs during drinking water treatment. Aquatic NOM is a complex mixture of many chemical groups, including humic substances, simple carboxylic acids, amino acids, proteins, and carbohydrates (Croue et al., 2000). Recently, the importance of autochthonous organic input from algae on drinking water DBP formation has also been recognized (Wert and Rosario-Ortiz, 2013). It is critical to understand the nature of DBP precursors in order to control the DBPs in drinking water.

Researchers have used model organic compounds as surrogates of NOM to investigate the DBP formation mechanisms. The early work on chlorination of model compounds focused

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on aromatic species that are believed to resemble aquatic humic substances. Resorcinol, substituted phenols and substituted benzenes are examples of aromatic model compounds that have been used in many investigations (Larson and Rockwell, 1979; Norwood et al., 1980; Boyce and Hornig, 1983; Norwood et al., 1987). Recently, aliphatic compounds such as  $\beta$ -dicabonyl acids and amino acids have been evaluated for the formation of carbonaceous and nitrogenous DBPs during chlorination and chloramination (Dickenson et al., 2008; Yang et al., 2012). The model compounds studies have produced useful information regarding the specific reaction mechanisms and kinetics of DBP formation, but the relevance of any particular model compound to DBP formation in drinking water remains uncertain.

The humic substances in terrestrial NOM are largely lignin derived with a high aromatic content (Ertel et al., 1984). Lignin is the second most abundant naturally occurring polymer after cellulose. It is also the most abundant aromatic plant component in terrestrial ecosystems (Crawford, 1981). Lignin is a complex natural polymer found in the cell walls of vascular plants, and the exact chemical structure is not well understood. It is generally accepted that lignin is composed of alkylmethoxy phenols with carbon to carbon linkages between the alkyl units. This irregular structure makes it relatively resistant to biodegradation (Sakakibara and Sano, 2001). Lignin and its decomposition products play a key role in the soil formation and carbon cycle because of its natural abundance, wide distribution, and resistance to biological and chemical degradation (Thevenot et al., 2010).

The alkaline CuO oxidation method is probably the most commonly used for the characterization and quantification of lignins in environmental matrices such as soils, sediments and dissolved organic matter (Hedges and Ertel, 1982; Lobbes et al., 1999). Mild CuO oxidation of lignin macropolymers yields a number of single-ring phenolic compounds (vanillyl, syringyl, cinnamyl and hydroxyl) with their aldehyde, ketone and acid substitutes (Hedges and Ertel, 1982; Lobbes et al., 1999). Louchouart et al. (2000) applied the CuO oxidation method to several natural river samples and the measured lignin-derived phenol concentrations were 3–10  $\mu\text{g/L}$ .

Lignin structures in NOM have often been associated with the tendency to form halogenated DBPs upon chlorination (Conrad and Huck, 1996; Pellerin et al., 2010). This association has been widely advanced because of the ubiquitous presence of lignin in the terrestrial environment, its recalcitrant nature, and its activated aromatic structures which are known to react readily with chlorine. Forested catchments have been identified as major sources of dissolved organic carbon (DOC) in natural water systems (Dalva and Moore, 1991; Kraus et al., 2010). High lignin content in the DOC may lead to high production of DBPs in drinking water. Despite all of this circumstantial evidence, few studies have established a causal link between DBP formation and the presence of lignin-based precursors. Moreover, the majority of model compounds studies have focused on the formation of THMs and HAAs. Few studies have examined the formation of total organic halogen (TOX) along with individual DBPs from model compounds precursors. Different types of DBPs are known to have different toxicities and health concerns. Simultaneous analysis of TOX and specific DBPs will help determine the amount of unknown DBPs

and identify halogenation reaction pathways of model compounds. Studies have shown that THMs, HAAs, and other identifiable DBPs collectively account for approximately 50% of the chlorination TOX and 20% of the chloramination TOX under typical drinking water disinfection conditions (Diehl et al., 2000; Zhang et al., 2000; Hua and Reckhow, 2007, 2008a, 2008b). There is a lack of quantitative evaluation in the literature regarding the formation of unidentified DBPs from lignin-based precursors. We need to acquire a better understanding of the role of lignin in the formation of DBPs to better manage DBP precursors in source water and reduce the DBP formation during drinking water treatment.

The objectives of this study were to investigate the yields of different classes of DBPs from lignin model compounds and to determine the contribution of lignin-based precursors to the formation of DBPs during chlorination and chloramination of selected lignin polymers and humic substances. In this study, we used the CuO oxidation method coupled with high performance liquid chromatography (HPLC) to determine the yields of key lignin phenols of selected NOM products. Then, DBP formation tests were performed on each lignin phenol using chlorine or chloramines under controlled conditions. The contributions of lignin phenols to the formation of specific DBPs and TOX were determined based on the occurrence in the NOM products and DBP yields of each lignin phenol. The results of this study can be used to quantitatively evaluate the contribution of lignin residues in natural water to the formation of DBPs in drinking water. This study improves our understanding of the role of lignin in the formation of DBPs which can help better manage DBP precursors in source water.

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## 2. Experimental methods

### 2.1. Lignin phenols and NOM products

A total of 11 key lignin phenols (Fig. 1) were purchased from Sigma-Aldrich (Milwaukee, WI) for this study. These lignin phenols are frequently reported as lignin products generated by CuO oxidation of soils, sediments, and organic matter in aquatic environments (Hedges and Ertel, 1982; Thevenot et al., 2010). Two commercial lignin polymers were acquired in purified forms from Sigma-Aldrich. The organosolv lignin is largely based on hardwoods and is extracted using ethanol, without the assistance of strong acids or bases. The alkali lignin is produced from a gymnosperm using high-pH digestion. Organosolv and alkali processes are widely used to solubilize lignin from wood materials (Pla et al., 1986). Table S1 shows the characteristic of the two commercial lignins. The organosolv lignin is smaller in weight averaged and number averaged molecular weight than the alkali lignin. In addition, two commercial humic substances were also used in this study. The two humic substances comprised a terrestrial humic acid obtained from Sigma-Aldrich and the Suwannee River fulvic acid obtained from the International Humic Substances Society.

### 2.2. The CuO oxidation and HPLC method

Lignin-derived CuO oxidation products were determined using a slight modification of the method of Hedges and Ertel

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