Quantification and characterization of dissolved organic carbon and iron in sedimentary porewater from Green Bay, WI, USA

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Abstract. Both dissolved organic carbon (DOC) and iron play an important role in biogeochemical processes in lacustrine benthic environments. Moreover, recent evidence has shown that both substances can act as active reductants in the redox transformation of organic pollutants. This paper examines the nature and abundance of DOC and dissolved ferrous iron (Fe$^{II}$) in porewaters from a sediment core collected in Green Bay, WI, USA. The concentration of dissolved Fe$^{II}$ and the abundance, absorbance at 280 nm ($A_{280}$), molar absorptivities ($e_{280}$), molecular weights, and polydispersities of DOC were measured as a function of depth in porewaters. Dissolved Fe$^{II}$ concentrations increased from 3.6 µM near the sediment–water interface to 163 µM at a depth of 11 cm, then gradually declined. The DOC distribution varied with sediment depth, with the greatest variation in porewater DOC content and properties occurring in the transitional zone between oxic and suboxic conditions. The down-core porewater DOC profile was characterized by an increase in DOC concentration with depth from 0.64 mM OC at 1 cm to 1.23 mM OC at 13 cm, below which it remained relatively constant. A strong correlation was observed between Fe$^{II}$ and DOC concentrations, suggesting that these constituents co-accumulate in these porewaters. The correlation between the DOC concentration of the porewaters and $A_{280}$ was significant, making this parameter a good predictor for DOC concentrations in these waters. The molecular weight distributions of the porewater DOC were primarily monomodal, with relatively low polydispersivities. Weight-average molecular weights ranged from 1505 to 1949 Da. This data set is unique in that it is the first detailed study of a relatively highly resolved DOC profile of benthic porewater in surficial sediment from the Laurentian Great Lakes.

Introduction

Dissolved organic carbon (DOC) in sedimentary porewater plays a significant role in many biogeochemical processes in aquatic environments, including the flux of sedimentary organic carbon to the overlying water (Alperin et al. 1999; Burdige et al. 1999); the remineralization and preservation of organic matter (Alperin et al. 1994; Hedges and Keil 1995; Burdige et al. 1999); and the distribution (Brownawell and Farrington 1986; Capel and Eisenreich 1990;
Chin and Gschwend 1992; Mitra and Dickhut 1999), mobility (Thoma et al. 1991; Valsaraj and Sojitra 1997; Skrabal et al. 2000), and bioavailability (Harkey et al. 1994; Forbes et al. 1998) of contaminants. The porewater DOC pool is composed of an array of organic compounds that are often operationally grouped on the basis of their molecular weights. The low-molecular-weight components (< 1 kDa) typically include fatty acids and free sugars and amino acids. The majority of porewater DOC, however, is contained in the high-molecular-weight (> 1 kDa) fraction (Krom and Sholkovitz 1977; Orem et al. 1986; Burdige 2001), which consists largely of humic substances (Krom and Sholkovitz, 1977; Burdige, 2001) with minor amounts of soluble proteins, carbohydrates, and other non-humic macromolecules.

The humic and fulvic acid components of porewater DOC are believed to have significant effects on many geochemical processes in sediments, including influences on the fate and transport of organic and inorganic contaminants and on iron cycling. Aquatic humic substances can complex/bind many metallic (Cabanis 1992; Wood 1996), organometallic (O’Loughlin et al. 2000; Amirbahman et al. 2002), and organic compounds (Chiou et al. 1986; Chin et al. 1997; Perminova et al. 1999), leading to an apparent increase in the solubility of contaminants; however, the potential risks of increased solution-phase concentrations are often offset by the decreased bioavailability of many complexed/bound contaminants (Landrum et al. 1985; Hutchinson and Sprague 1987; Ortego and Benson 1992). Humic substances (and in some cases bulk DOC) are effective electron transfer mediators in abiotic and microbially mediated redox transformations of many contaminants (Curtis 1991; Dunnivant et al. 1992; Fredrickson et al. 2000; O’Loughlin and Burris 2000; Kappler and Haderlein 2003; O’Loughlin et al. 2003). Humic substances can also serve as electron donors or terminal electron acceptors for anaerobic respiration by a phylogenetically diverse array of microorganisms including iron-reducing, sulfate-reducing, and halorespiring bacteria, as well as methanogenic archae (Coates et al. 1998; Lovley et al. 1999; Cervantes et al. 2002; Coates et al. 2002). Moreover, humic substances can act as electron mediators for dissimilatory iron reduction (Lovley et al. 1998), a key process in the biogeochemical cycling of iron in aquatic environments.

The reactivity of DOC with respect to a given process often varies with the source of the DOC, reflecting changes in its chemical and structural properties (Chin et al. 1997; Perminova et al. 1999; O’Loughlin and Burris 2000; Ma et al. 2001; and many others). Therefore, proper characterization of both the physical and chemical properties of porewater DOC is crucial for understanding its many roles in the biogeochemical processes involved in the cycling of major and minor elements and in the fate and transport of both organic and inorganic contaminants. Several studies have examined changes in the abundance and physicochemical properties of DOC in marine sediment porewater as a function of sediment depth (Orem and Gaudette 1984; Brownawell and Farrington 1986; Chen et al. 1993; Alperin et al. 1994; Burdige and Gardner 1998; Papadimitriou et al. 2002); however, similar studies of sediment porewater DOC from freshwater systems have been limited (Chin and Gschwend