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Dissolved organic matter in pore water of freshwater sediments: Effects of separation procedure on quantity, quality and functionality

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Abstract

Pore water was separated either with or without water extraction prior to centrifugation (7600 or 20000 × *g*) in order to investigate the effects of separation procedure on the amount and properties of dissolved organic matter (DOM i.e. the material passing through a 0.45-μm filter) in three freshwater sediments. On the basis of solubility in alkaline, organic matter was concluded to compose of humic substances in two (S1 and S3) and of humin (S2) in one of the sediments. DOM in the samples was quantified by total organic carbon measurement. Specific UV-absorption (SUVA) and high performance size exclusion chromatography (HPSEC) analyses were used to characterize DOM. Sorption of pyrene was used as a measure for functionality of DOM. Both water extraction and centrifugation speed were shown to affect the properties of DOM; however, the effects were sediment dependent. Water extraction increased the amount of DOM separated from the two sediments that had humic character (S1 and S3). In most cases water extraction increased SUVA and shifted the molecular size distribution of DOM towards larger sizes. The separation procedure had also an effect on the functionality of DOM. In water extracted samples of S2 and S3 the sorption of pyrene was higher than in the corresponding samples separated without water extraction, whereas in S1 similar effect was not found. Generally, centrifugation speed had smaller effects on the properties of DOM than water extraction. The fact that the effects of separation procedure on DOM depend on the sediment characteristics complicates the comparison between samples and evaluation of functionality in field conditions.

Keywords: Filtration; Water extraction; Pyrene; NOM; Sediment; Pore water; Centrifugation

1. Introduction

Sediments are both major sinks and sources for hydrophobic organic contaminants (HOC). In the sediments HOCs are distributed between particulate and dissolved phases depending on the characteristics of the sediment and HOC. In the dissolved phase HOCs are partitioned between water and the dissolved and colloidal organic matter (DOM). Several studies have indicated that DOM can increase solubility (Chiou et al., 1986; Danielsen et al., 1995; Cho et al., 2002) and decrease bioavailability (Kukkonen and Oikari, 1991;

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Haitzer et al., 1998; Akkanen and Kukkonen, 2001) of HOCs in water. In order to understand the speciation of HOCs in sediments it is necessary to study the association of HOCs with DOM in pore waters. However, ediment is a complex matrix and therefore several difficulties can be encountered during studies concerning pore water and DOM.

In order to study the properties of DOM in the pore water of sediments the pore water (and DOM in it) must be separated from the solid phase. This separation may be achieved by means of different treatments, but knowledge on the effects of different separation procedures on the properties of DOM is still limited. In the laboratory, the most common way to isolate pore water from sediment is by centrifugation with subsequent filtration. However, centrifugation speed varies greatly between studies and often only the rpms (i.e. rounds per minute) are given, which does not tell what the actual centrifugal force is. Although high speed centrifugation (i.e. $20000 \times g$) would remove particles more effectively from the solution, some authors avoid it because possible cell rupture may increase the concentration and distort the quality of DOM (Raber et al., 1998; Zsolnay, 2003). Some authors have separated pore water by squeezing and high speed centrifugation without subsequent filtration (Chin et al., 1998). Apparently this method produces DOM that differs from DOM separated by methods utilizing filtration. This in turn complicates comparison between studies.

In sediment samples it is often difficult to obtain reasonable volume of pore water for further analyses and therefore the sample volume must be increased. In these situations the first step for pore water isolation from sediment or soil samples is extraction with water (dilute electrolyte solution) to increase the sample volume. However, availability of DOM varies among sediments and thus the extraction can alter the quantity of DOM (Zsolnay, 2003). Furthermore, the DOM mobilized by the water extraction is likely to have different quality and functionality. This complicates comparison between studies as well as extrapolation of the laboratory results to field conditions (Zsolnay, 2003).

DOM has been defined in several ways but mostly the definition is connected to physical size (Gustafsson and Gschwend, 1997). The most common definition for DOM is the material that passes through a 0.45-μm pore size filter (Zsolnay, 2003). Thus the definition is operational and the material consists of truly dissolved molecules and colloidal organic matter (Buffle and Leppard, 1995a,b; Gustafsson and Gschwend, 1997). However, this matter is considered to be the mobile, available and ecologically important fraction of natural organic matter (NOM) present in water phase (Gustafsson and Gschwend, 1997; Zsolnay, 2003). The macromolecular (also referred to as tertiary) structure of DOM has been shown to be sensitive to several factors, such as pH, ionic strength and composition as well as concentration of DOM (Ghosh and Schnitzer, 1980; Engebretson and von Wandruszka, 1994; Myneni et al., 1999; Zsolnay, 2003). Subsequently these structural changes also affect the functionality (e.g. sorption capacity for HOCs) of DOM (Kukkonen, 1991; Schlautman and Morgan, 1993; Akkanen and Kukkonen, 2001). Therefore, it is possible that the properties of DOM change during the separation but the nature of these changes is still largely unknown.

The purpose of this study was to investigate the effects of water extraction and centrifugation on the quantity, quality and functionality of DOM, i.e. the material passing through the 0.45-μm filter in pore water of three different freshwater sediments. In addition, some analyses were made on the unfiltered samples to investigate the properties of the samples before the filtration step. This study is part of a larger project (ABACUS) funded by EU studying speciation and bioavailability of organic contaminants in sediments.

2. Materials and methods

2.1. Study sediments

Three lake sediments were chosen for this study to represent a variety of different sediment characteristics. The sediment samples were from Lake Höytiäinen (S1), Lake Ketelmeer (S2) and Lake Mekrijärvi (S3) (Table 1). For more detailed information on the sediments see Cornelissen et al. (2004). Sediment organic carbon (OC) content was analyzed with Elemental analyzer (Carlo Erba Strumentazione 1106, Italy). In order to evaluate the proportion of humic substances in OC the sediments were extracted with NaOH. A sediment sample (1.5 g ww) was placed into a test tube followed by 3.5 ml of 0.5 M NaOH. The samples were incubated at 80 °C for 30 min. The aliquot was separated by centrifugation and the extraction was repeated with another portion of NaOH. The organic carbon concentration in the combined extracts was determined (Shimadzu TOC-5000 A, Kyoto, Japan).

2.2. Experimental water

Artificial freshwater, which was used to extract the sediments, was prepared in MilliQ-grade water (Millipore, Bedford, MA, USA) by adding the following inorganic salts; $CaCl_2 \times 2H_2O$ 58.8 $mg l^{-1}$, $MgSO_4 \times 2H_2O$ 24.7 $mg l^{-1}$, $NaHCO_3$ 13.0 $mg l^{-1}$, and KCl 1.2 $mg l^{-1}$. Conductivity of the experimental water was 14.0 $mS m^{-1}$ and pH was adjusted to 7. The sediment samples were extracted (sediment: water ratio of 1:4 v.v.) by shaking on a rotary shaker for an hour at 6 rpm at 20 ± 0.5 °C. After the extraction the samples were centrifuged in 50-ml