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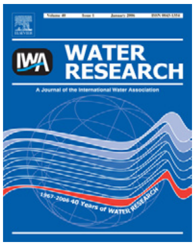

Search for basic relationships between "molecular size" and "chemical structure" of aquatic natural organic matter—Answers from ^{13}C and ^{15}N CPMAS NMR spectroscopy

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ABSTRACT

To investigate the structural composition of natural organic matter (NOM), a 3-step micro- and ultrafiltration procedure was applied to 3 surface waters from southern Germany, and fractions from all filtration steps were collected. The NOM was characterized using solid-state ^{13}C and ^{15}N nuclear magnetic resonance (NMR) techniques. Routine integration of the ^{13}C NMR spectra and extended data analysis procedures were carried out for a quantitative comparison of the structural components as well as for the elucidation of structural fractionation patterns. A common feature of the large molecular size fractions was the predominance of polysaccharide material, with the dissolved high molecular weight organics being mostly enriched in N-acetylated polysaccharides derived from microbial leftovers. Aromatic structures like lignin and tannin derivatives were most abundant in the intermediate size fraction. All membranes were found to be highly permeable for branched aliphatics, i.e. isoprenoids. Fouling layers of the ultrafiltration membrane were significantly enriched in long-chain aliphatics (lipids). Biofouling was not observed on any of the membranes. Overall, a strong interdependence between the chemical structural characteristics of NOM components and their size, shape, or interaction characteristics could be shown. The results provide the basis for a better understanding of water process technologies as treatment effectiveness is strongly dependent on the chemical composition and the "size" distribution of NOM.

1. Introduction

The structural composition of natural organic matter (NOM) is highly variable and depends mainly on the source of the precursor material as well as on the degree of its modification. A widespread concept for the advanced structural elucidation of NOM is the combination of sample fractionation with an analytical method. For the fractionation of aquatic NOM via membrane filtration, well-defined experimental protocols have not been developed yet. Thus, innumerable combinations of different filtration modes (tangential flow, dead-end), molecular weight cut-offs (MWCO), membrane materials, and filtration conditions (e.g. transmembrane pressure) are being used, each of them performing differently with respect to the separation of

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molecules according to size and shape. In the case of NOM the task of fractionation is further complicated by the sample itself because NOM represents a complex mixture of biomolecules and their degradation products. These molecules undergo inter- and intramolecular interactions and they interact with the filter membrane. Nevertheless, if the interactions are predominantly of weak type (hydrogen bonds, Van-der-Waals bonds, and hydrophobic interactions), then the application of membrane filtration will lead to a partial separation of molecules according to outer structure characteristics (size, shape, surface functionalities) since "small" molecules are more likely to permeate through the membrane than "large" molecules. In case of strong (electrostatic) interactions, the ionic strength in particular might affect the apparent molecular size of NOM and the likelihood for membrane permeation (Schäfer et al., 2002).

A measure for the likelihood of permeation during filtration time is dissolved organic carbon (DOC) rejection. The sum parameter "DOC", however, obscures information about the inner (chemical) structure. Such information can be extracted most powerfully via nuclear magnetic resonance (NMR) spectroscopy. Several NMR investigations of size-fractionated organic matter have already been carried out. They focused either on a more quantitative integral analysis (Baldock et al., 1992; Christl et al., 2000; Francioso et al., 2002; Wong et al., 2002; Assemi et al., 2004; Müller et al., 2004) or on more qualitative spectroscopic editing techniques and two-dimensional spectroscopy (Haiber et al., 2001; Mao et al., 2007).

NMR spectroscopic characterization of such size fractions remains somehow unsatisfactory because firstly the fractionation of biomolecular mixtures is incomplete due to a broad size distribution and physico-chemical interactions, and secondly the polymer mixtures yield a great signal overlap within the NMR spectra. Furthermore, some components such as branched and non-branched aliphatics are particularly challenging because they cannot be distinguished on the basis of integral regions only. In spite of these limitations detailed information on the structural components of NOM fractions can be obtained from NMR data, even more so if sophisticated data analysis procedures are applied. Additional improvements in the understanding of NOM structures can be achieved if background knowledge on natural compounds is considered: the most prominent building blocks of biopolymers are carbohydrates, amino acids, phenylpropanes, polyketides, isoprenes, and lipids from which homopolymers, e.g. polysaccharides, proteins, terpenoids as well as heteropolymers, e.g. mureins, lignocelluloses, tannins, meroterpenoids, are formed.

The aim of this work was to separate NOM according to outer structures and to further elucidate the selective enrichment of inner structures in the fractions by focusing on NMR spectroscopic details. This was achieved as follows:

- 3 surface waters were fractionated via 3 filtration steps, and a total of 6 size fractions were gained from each sample,
- the fouling layer from the ultrafiltration step was recovered and directly analyzed,
- ^{13}C CPMAS NMR spectra of the original sample and all of its fractions were recorded and a quantitative analysis was performed,
- the integral data were supplemented by dipolar dephasing (DD) spectra and ^{15}N CPMAS NMR spectra, and a detailed comparison of the spectra concerning the chemical shifts of the signal groups was made,
- an extended comparative analysis approach of the 3 water samples is presented to gain an improved insight into the systematic of structural fractionation.

The detailed structural insight into the composition of NOM and its fractionation during membrane filtration is necessary for a better understanding of the role of NOM in water treatment processes like membrane filtration, oxidation, or adsorption. Furthermore, molecular size and chemical structure are also important parameters of NOM with respect to contaminant transport through membranes (Dalton et al., 2005) or NOM bioreactivity (Amon and Benner, 1994).

2. Materials and methods

2.1. *Sample preparation and basic analysis*

Samples were taken from 3 surface waters in southern Germany: sampling site (1) is a Bog Pool in a peat bog ("Kulzer Moos", Bavarian Forest) consisting of high bog and transition bog areas. This peat bog has been weakly modified by drainage and peat bog mining during the past centuries. (2) The oligotrophic Forest Pond "Barmoosweiher" is situated in a mixed forest with near-natural cultivation in the Bavarian Forest. Summergreen broad-leaved trees alternate with coniferous trees. The pond has extended zones of terrestrialization. (3) Lake Hohloh ("Hohlohsee", Black Forest) lies in a former high bog area which has been anthropogenically changed by peat bog mining, drainage, and afforestation with a spruce forest. Sampling sites (1) and (3) are located in protected areas.

The water samples (48–54 L) were filtered through cellulose filters for the removal of larger particles, e.g. vascular plant residues and algae. The filtrate, the so-called original water sample (ORG), was filtered through a 0.45 μm polyethersulfone membrane to remove the particulate organic matter (POM). For the fractionation of the dissolved organic matter (DOM) two filtration modes were applied: firstly, dead-end filtration via a polyethersulfone membrane with a nominal pore size cut-off of 0.1 μm was carried out, and the membrane filter cake was collected as the L-DOM fraction (DOM of large molecular size). The feed pressure was 500 kPa; the transmembrane pressure difference was 400 kPa. The POM and L-DOM fractions were removed from the membrane surface (filter area 0.13 m^2) with a broad stainless-steel spatula. The permeate of the 0.1 μm membrane was collected and then separated via cross-flow filtration with a spiral wound membrane module (membrane material: regenerated cellulose, membrane area: 0.85 m^2) with a nominal MWCO of 10 kg/mol. The feed pressure was 300 kPa and the transmembrane pressure difference was 30 kPa. The retentate fraction was diluted 1 by 10 with deionized water. The cross-flow filtration was repeated 9 times with the diluted retentate fraction. Afterwards, the retentate was collected as the M-DOM fraction (DOM of medium molecular size). The