



Review

An overview of the methods used in the characterisation of natural organic matter (NOM) in relation to drinking water treatment

Anu Matilainen^a, Egil T. Gjessing^c, Tanja Lahtinen^d, Leif Hed^e, Amit Bhatnagar^f, Mika Sillanpää^{a,b,*}

^a Laboratory of Applied Environmental Chemistry, Department of Environmental Sciences, University of Eastern Finland, Patteristontie 1 FI-50100 Mikkeli, Finland

^b Faculty of Technology, Lappeenranta University of Technology, Patteristontie 1 FI-50100 Mikkeli, Finland

^c Department of Chemistry, University of Oslo, P.O. Box 1033, Oslo 0315, Norway

^d Department of Chemistry, University of Jyväskylä, P.O. Box 35, FIN-40014 University of Jyväskylä, Finland

^e Technology Centre Ketek LTD, Korpintie 8, FI-67100 Kokkola, Finland

^f LSRE – Laboratory of Separation and Reaction Engineering, Departamento de Engenharia Química, Faculdade de Engenharia da Universidade do Porto (FEUP), Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

ARTICLE INFO

Article history:

Received 27 August 2010

Received in revised form 5 January 2011

Accepted 5 January 2011

Available online 11 February 2011

Keywords:

Natural organic matter (NOM)

Characterisation

Drinking water

Water treatment

Water analysis

ABSTRACT

Natural organic matter (NOM) is found in all surface, ground and soil waters. During recent decades, reports worldwide show a continuing increase in the color and NOM of the surface water, which has an adverse affect on drinking water purification. For several practical and hygienic reasons, the presence of NOM is undesirable in drinking water. Various technologies have been proposed for NOM removal with varying degrees of success. The properties and amount of NOM, however, can significantly affect the process efficiency. In order to improve and optimise these processes, the characterisation and quantification of NOM at different purification and treatment processes stages is important. It is also important to be able to understand and predict the reactivity of NOM or its fractions in different steps of the treatment. Methods used in the characterisation of NOM include resin adsorption, size exclusion chromatography (SEC), nuclear magnetic resonance (NMR) spectroscopy, and fluorescence spectroscopy. The amount of NOM in water has been predicted with parameters including UV–Vis, total organic carbon (TOC), and specific UV-absorbance (SUVA). Recently, methods by which NOM structures can be more precisely determined have been developed; pyrolysis gas chromatography-mass spectrometry (Py-GC-MS), multidimensional NMR techniques, and Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS). The present review focuses on the methods used for characterisation and quantification of NOM in relation to drinking water treatment.

© 2011 Elsevier Ltd. All rights reserved.

Contents

1. Introduction	1432
2. Different methods for characterisation of NOM	1434
2.1. Some general parameters	1434
2.1.1. UV–Vis	1434
2.1.2. Total organic carbon (TOC)/dissolved organic carbon (DOC)	1434
2.1.3. Specific UV-absorbance (SUVA)	1434
2.1.4. Fluorescence	1434
2.2. Biological tests	1435
2.3. Isolation and concentration	1435
2.4. Fractionation	1435
2.4.1. Resin fractionation	1435
2.4.2. Size exclusion chromatography (SEC)	1436
2.4.3. Membrane filtration	1437
2.4.4. Other fractionation methods	1437
2.5. Elemental composition and some structural features determination	1437

* Corresponding author. Tel.: +358 40 020 5215; fax: +358 15 336 013.

E-mail addresses: mika.sillanpaa@uef.fi, mika.sillanpaa@lut.fi (M. Sillanpää).

2.5.1.	Py-GC-MS	1437
2.5.2.	NMR	1438
2.5.3.	FTIR	1439
2.5.4.	LC-MS	1439
2.5.5.	FTICR-MS	1439
3.	Summary	1439
	Acknowledgement	1440
	References	1440

1. Introduction

Natural organic matter (NOM) is a complex mixture of organic compounds present in all fresh water, particularly surface waters. NOM consists of a range of different compounds, from largely aliphatic to highly colored aromatics. Some of this organic matter is negatively charged consisting of a wide variety of chemical compositions and molecular sizes (Thurman, 1985; Swietlik et al., 2004). Thus, NOM present in waters consists of both hydrophobic and hydrophilic components. The hydrophobic part is rich in aromatic carbon, having phenolic structures and conjugated double bonds, while hydrophilic NOM contains a higher proportion of aliphatic carbon and nitrogenous compounds, such as carbohydrates, proteins, sugars and amino acids. Hydrophobic acids constitute the major fraction of aquatic NOM, accounting for more than half of the dissolved organic carbon (DOC) in water (Thurman, 1985; Swietlik et al., 2004). These hydrophobic acids may be described as humic substances.

The amount and characteristics of NOM in surface water depends on climate, geology and topography (Fabris et al., 2008; Wei et al., 2008). Achievement of the desired drinking water quality requires the removal of this organic matter. Thus, designing and operating a drinking water treatment plant requires emphasis on the evaluation of removal technologies for NOM. A number of investigations, in the literature, discuss these NOM removal technologies. Among the various available technologies, the most common and economically feasible method is coagulation and flocculation followed by sedimentation/flotation and filtration. Most of the NOM can be removed by the coagulation method, although, the hydrophilic, low molecular weight (LMW) fractions of NOM is apparently removed less efficiently than the hydrophobic, high molecular weight (HMW) compounds (Jacangelo et al., 1995; Matilainen et al., 2010). This preference may be due to more aromatic character, and therefore more hydrophobic nature of the latter (Sharp et al., 2006). Moreover, the hydrophobic fraction has, in general, a higher specific colloidal charge; more charged fractions are more amenable to remove (Sharp et al., 2006; Bose and Reckhow, 2007). Hence, after the coagulation process LMW and hydrophilic NOM dominate the residual organic matter (Zhao et al., 2009; Liu et al., 2010).

Other treatment options for NOM removal include magnetic ion exchange resin (MIEX[®]) technique, activated carbon filtration, membrane filtration techniques, and advanced oxidation processes (Jacangelo et al., 1995; Singer and Bilyk, 2002; Matilainen et al., 2006; Zularisam et al., 2006; Toor and Mohseni, 2007; Matilainen and Sillanpää, 2010). Despite the MIEX[®] technique reportedly is removing even the hydrophilic NOM, none of the above stated alternative treatment methods successfully remove all the NOM fractions present in raw water.

In late 1980s, an increase in color (NOM) was first reported in Swedish surface waters (Forsberg and Petersen, 1990). During the last few decades, several other reports confirm that NOM occurrence in water is a worldwide phenomenon (Eikebrokk et al., 2004; Worrall and Burt, 2007). Change in the climate (tem-

perature, quality, and amount of precipitation) and the decline in acid deposition are reasonable explanations for the increasing NOM concentrations (Delpla et al., 2009). The increased levels of NOM and changes in the quality of the matter present major challenges to the drinking water industry. The presence of NOM, as already indicated, creates serious problems to drinking water quality and its treatment processes. These problems include: (i) negative effect on water quality due to color, taste, and odor, (ii) increased coagulant and disinfectant dose requirements, which in turn results in increased sludge and potential harmful disinfection by-product (DBP) production, (iii) promoted biological growth in distribution system, and (iv) increased levels of complexed heavy metals and adsorbed organic pollutants (Jacangelo et al., 1995).

Especially DBP production has been of increasing concern due to their adverse health affects (Singer, 2006). New compounds have been discovered as detection methods and detection levels are improving (Krasner et al., 2006; Richardson et al., 2007). The most common, and among the first identified, were the trihalomethanes (THM) and haloacetic acids (HAA). More than 600 different compounds have already been identified in drinking water as a consequence of disinfection of water containing NOM (Krasner et al., 2006). All methods used for disinfection (chlorine, ozone, chlorine dioxide, chloramines, and UV-radiation) reportedly produce their own suite of DBPs and bio-reactive compounds in drinking water (Richardson et al., 2007). Present knowledge and experience show that the hydrophobic and HMW compounds of NOM are the most important pre-cursors for DBP formation (Hua and Reckhow, 2007; Chen et al., 2008). Hydrophilic matter may also play a significant role in the formation of new compounds during disinfection, especially in waters with low humic components. Some of these are also reactive in iodine and bromine containing DBPs formation, which in turn may be even more toxic than their chlorinated counterparts (Krasner et al., 2006; Singer, 2006; Ates et al., 2007; Hua and Reckhow, 2007; Richardson et al., 2008).

Due to water quality problems and stricter regulations for drinking water quality, more efficient, yet economically feasible, water purification methods are needed (Rämö and Sillanpää, 2001; Pirkanniemi and Sillanpää, 2002; Pirkanniemi et al., 2007; Bhatnagar and Sillanpää, 2009, 2010; Tuutijärvi et al., 2009; Vilhunen and Sillanpää, 2009; Ambashta and Sillanpää, 2010). The requirement for more efficient removal of NOM necessitates more knowledge of the organic matter present. New methods have been developed for the characterisation of the organic compounds present in the raw water. Existing methods and techniques have simultaneously been improved. These updated collections of characterisation methods are used to study the composition of NOM prior to the treatment and during the different steps of treatment processes (Chen et al., 2007; Sarathy and Mohseni, 2007; Her et al., 2008a; Liu et al., 2008, 2010; Tercero Espinoza et al., 2009; Zhao et al., 2009). The diversity of molecules that constitute NOM and the relative low concentrations of NOM in water often makes characterisation difficult. Thus, methods that can either accurately characterise NOM in these dilute solutions, or isolated or concentrated NOM, are essential.

Table 1

Methods used to characterise different features of NOM, with their positive and negative sites.

Method (references)	Detected features	Positive	Negative
<i>Spectroscopic methods</i>			
Fluorescence (Liu et al., 2007; Seredynska-Sobecka et al., 2007; Spencer et al., 2007; Wu et al., 2007b; Baker et al., 2008; Hudson et al., 2008; Zhang et al., 2008; Bierzo et al., 2009; Peiris et al., 2010)	Molecules of the sample are excited by irradiation at a certain wavelength and the emitted radiation is measured at a different wavelength. Conjugated double bonds and aromatic rings, –OH and –NH ₂ enhance fluorescence, while –COOH diminishes. Three major groups: tryptophan-, humic- and fulvic-like fluorophores	Sensitivity, specificity, speed	Sensitive to chemical environment, e.g. pH
UV–vis (Korshin et al., 1999; Hur et al., 2006; Ates et al., 2007; Spencer et al., 2007; Li et al., 2009; Roccaro and Vagliasindi, 2009)	Quantitative measurement of all compounds in the sample which adsorb UV-light. Conjugated C–C multiple bonds, aromatic carbon, –COOH and –OH increase adsorption	Simple and fast, not too sophisticated instrumentation	Not all of the compounds of NOM can be detected. Wavelength specific adsorption. Under estimation of LMW compounds. Sensitive to chemical environment, e.g. pH and ionic strength
FTIR (Kanokkantarapong et al., 2006b; Hay and Myneni, 2007; Her et al., 2008a)	Aromatic and aliphatic hydrocarbon, different bonds and functional groups, e.g. OH in carboxylic and alcoholic groups	Sample can be measured both in liquid and solid phases, instruments nowadays small, reliable and easy to use	Interpretation of the analysis may be difficult because of overlapping of characteristic spectral features due to the complexity and polyfunctionality of NOM
¹ H NMR (Ma et al., 2001; Kim et al., 2006; Kim and Yu, 2007; Mao et al., 2007a)	Determine the structure with respect to hydrogen-1 nuclei within the molecules of a substance	Very sensitive. Powerful tool especially together with ¹³ C NMR in structural analysis	Interpretation of spectra can be limited
¹³ C NMR (Chen et al., 2002; Wong et al., 2002; Mao et al., 2007a,b; Lankes et al., 2008)	Carboxylic structures of NOM, as well as aliphatic carbon, o-alkyl carbon, aromatic carbon and carbonyl carbon. Can be done both on solid or liquid sample	Powerful tool especially together with ¹ H NMR in structural analysis	Less sensitive to carbon than ¹ H NMR to hydrogen. NOM sample needs to be isolated in solid state NMR measurements. Parameter sensitive
¹⁵ N NMR (Mao et al., 2007b; Lankes et al., 2008; Thorn and Cox 2009)	Identifies carbons bonded to nitrogen	Broader view to NOM structure	Nuclear quite insensitive, ¹⁵ N appears in low percentage in natural nitrogen
2-D NMR (Deshmukh et al., 2007; Mao et al., 2007a,b)	Spreads the spectrum in two dimensions and allow the observation of cross peaks. Structural environments of, e.g. carboxyls in detail	Multidimensional NMR techniques can be used to resolve contributions that overlap strongly in a 1 D NMR experiment	Very large molecules may not be detected
<i>Chromatographic methods</i>			
HP-SEC (Wu et al., 2007a; Chow et al., 2008; Fabris et al., 2008; Her et al., 2002, 2008b; Zhang et al., 2008, 2009; Korshin et al., 2009)	Fractionates NOM on basis of molecular sizes of organic compounds present	Rapid, sensitive, no pre-extraction needed, equipment not too sophisticated or expensive but rather available in research laboratories	Charge effects during measurement (column/NOM, eluent/NOM), choice of detector and proper standards
FIFFF (Moon et al., 2006; Messaud et al., 2009; Alasonati et al., 2010).	Chromatography like separation technique. Fractionate NOM by size and MWD	No stationary phase	Choice of proper standards
<i>Mass spectrometric methods</i>			
LC–MS (Reemtsma and These, 2005; Mawhinney et al., 2009)	Chemical formulae of compounds in NOM	ESI is a soft ionisation technique	Dependent on chemical properties of the analyte. Not so sensitive to all of the species (e.g. with HMW). Matrix effects
FTICR MS (Reemtsma et al., 2006, 2008; Stenson, 2008; Kunenkov et al., 2009; Reemtsma, 2009)	Molecular species, exact masses and molecular formulae of compounds on NOM	The full scale of molecular complexity of NOM has been revealed. Can be combined with SEC or RPHPLC	Data interpretation is difficult, because of complexity of NOM
GC–MS (Templier et al., 2005; Parsi et al., 2007)	Structural and molecular properties of compounds in NOM	Sensitive, specific, quick	Unwanted thermal reactions. Data interpretation is difficult, because of complexity of NOM
<i>Bulk parameters</i>			
TOC (Koprivnjak et al., 2006; Liu et al., 2007; Seredynska-Sobecka et al., 2007; Spencer et al., 2007)	Total organic carbon content in water	Easy to use, analytical equipment not too expensive. Can be used as on-line method	Give only information on quantity of NOM, not quality
DOC (Koprivnjak et al., 2006; Liu et al., 2007; Seredynska-Sobecka et al., 2007; Spencer et al., 2007)	Dissolved organic carbon in water, after filtration through 0.45 µm filter		
SUVA (Edzwald and Tobiasson 1999; Archer and Singer, 2006; Bose and Reckhow, 2007; Ates et al., 2007; Jung and Son, 2008; Wei et al., 2008)	High SUVA-value >4 refers to hydrophobic, aromatic compounds, while low SUVA <3 indicates mainly hydrophilic material	Easy to determine, analytical equipments not too sophisticated	High nitrate content in low DOC waters may interfere the measurement

Our objective is to summarise the methods which have been used in the studies of NOM related to drinking water treatment. Most of the methods used in NOM characterisation, and their advantages and disadvantages are listed in the Table 1.

Another approach for the characterisation of NOM is the study of its reactivity towards DBP formation and the occurrence of different DBPs in drinking water (Culea et al., 2006; Kanokkantapong et al., 2006b; Chen et al., 2008; Cooper et al., 2008; Richardson et al., 2008; Blodau et al., 2009). The binding-potential of NOM with inorganic and organic micro-pollutants may also be important topics in relation to drinking water treatment (Gjessing et al., 2007; Laborda et al., 2009; Park, 2009). These issues are, however, not dealt in this review.

2. Different methods for characterisation of NOM

2.1. Some general parameters

In practice, NOM is usually represented by the measurement of total organic carbon (TOC), dissolved organic carbon (DOC), adsorption of UV-light (UV_{254}) or chemical oxygen demand (COD). NOM is also the major contributor of the brownish yellow color in water. Measurement of color, therefore, can give some indication of the amount of NOM in water (Uyguner et al., 2007). All these tests are fast and do not require sophisticated sample pre-treatment or analytical equipment. These analyses, however, provide information mostly about the amount while offering limited information on the character of NOM.

2.1.1. UV–Vis

2.1.1.1. Single wavelength measurements. Ultraviolet and visible (UV–Vis) absorption spectroscopy is the measurement of the attenuation of a beam of light after it passes through a sample or after reflection from a sample surface. The concentration of an analyte in a solution can be determined by measuring the absorbance at a certain wavelength applying the Beer–Lambert Law. Absorption measurements can be done at a single wavelength or over an extended spectral range. The UV absorbance spectra of NOM decrease monotonically with increasing wavelength (Hur et al., 2006). Any wavelength from 220 to 280 nm has been considered to be the most appropriate for NOM measurements, although the molar absorptivities will vary due to the range of chromophores in NOM structure. The different wavelengths are believed to identify different chromophores of NOM. For example, absorbance at 220 nm is associated with both the carboxylic and aromatic chromophores, whereas, absorbance at 254 nm is typical for the aromatic groups with varying degrees of activation (Korshin et al., 2009). UV_{254} has been identified as a potential surrogate measure for DOC despite tendency to only represent the aromatic character.

Ratios between two different wavelengths such as: A_{254}/A_{204} , A_{254}/A_{436} , or A_{250}/A_{365} , have also been reported to be useful in NOM characterisation (Hur et al., 2006; Spencer et al., 2007; Li et al., 2009). For example the ratio of A_{253}/A_{203} correlates with the formation of DBPs (Kim and Yu, 2007). Significant errors, however, might emerge due to interference at 200 nm through 230 nm by inorganic ions such as nitrates or sulfates (Her et al., 2008b).

2.1.1.2. Differential absorption. An alternative approach is measurement of differential absorbance defined as the change in the absorbance of a sample in response to any forcing function, e.g. chlorination (Korshin et al., 1999; Ates et al., 2007). The differential absorbance at 272 nm has been suggested for the evaluation of DBPs formation. This differential absorbance has strong correlations with total THM and HAA concentrations (Roccaro and Vagliasindi, 2009). Differential absorbance at 254 nm (ΔA_{254}),

however, has no correlation with total THM or HAA formations (Ates et al., 2007).

2.1.2. Total organic carbon (TOC)/dissolved organic carbon (DOC)

Total organic carbon (TOC) is the sum of the particulate and dissolved organic carbon (DOC), existing inorganic carbon is removed by acidification. A widely accepted operational definition of DOC is the organic carbon in the water sample filtered through a 0.45 μm filter (Danielsson, 1982). TOC and DOC are the most convenient parameters for use in the overall study of treatment processes and effects on NOM removal. Basically all methods for quantification of organic carbon in water involve oxidation. Previously, before TOC-analysers, an oxidising agent was added and the amount of agent used expressed the concentration of carbon present (COD). In modern techniques and instrumentation, various kinds of oxidation steps are used (burning, radiation and oxidising agents). The resulting CO_2 is measured mostly by infra red (IR) spectroscopy.

2.1.3. Specific UV-absorbance (SUVA)

SUVA (UV-adsorption $A_{254\text{nm}(1\text{cm})}/\text{mg C L}^{-1}$) is defined as the UV absorbance of a given sample at 254 nm divided by the DOC concentration of the sample. This ratio describes the nature of NOM in the water in terms of hydrophobicity and hydrophilicity; a SUVA >4 indicates mainly hydrophobic and especially aromatic material whilst a SUVA <3 illustrates mainly hydrophilic material (Edzwald and Tobiason, 1999). Several researchers have emphasised that a good agreement may exist between the ability for NOM removal by coagulation and a high SUVA-value (Archer and Singer, 2006; Bose and Reckhow, 2007). Accordingly, SUVA and A_{254}/A_{204} correlate relatively well because both relate well with the amount of aromatic carbon present in NOM (Hur et al., 2006). Jung and Son (2008) also reported a good correlation between the SUVA-value and THM-formation potential. The latter relationship has, however, not been confirmed by others (Ates et al., 2007; Wei et al., 2008).

2.1.4. Fluorescence

Fluorescence is a spectrochemical method in which the analyte molecules are excited by irradiation at a certain wavelength and the emitted radiation is measured at a different wavelength. Fluorescence spectroscopy has received increased attention in the water industry, particularly due to its potential application as a monitoring technique. The main advantage of fluorescence techniques compared to traditional methods, including UV–vis, is the better sensitivity and selectivity (Bieroza et al., 2009; Peiris et al., 2010). The specific excitation and emission wavelengths are the characteristics of a particular molecular conformation, called fluorophore. These fluorophores are helpful in describing the structural compositions of the humic materials (Datta et al., 1971; Uyguner et al., 2007; Wu et al., 2007b; Baker et al., 2008; Zhang et al., 2008; Bieroza et al., 2009). Fluorescence has also been recommended as a tool for estimating the presence of biodegradable NOM, since strong correlations are found between fluorescence and biological oxygen demand values (Hudson et al., 2008).

The 3-D fluorescence excitation–emission matrix (EEM) spectrophotometric technique has been developed during the last decade. The EEM spectra visualises a range of different fluorophores covering the excitation and emission wavelengths range from ~200 nm to ~500 nm. Thus, it is more informative in comparison to the traditional single-scan technique (Spencer et al., 2007). Typical raw water may contain two major fluorescence peaks described as humic-like and protein-like fluorescence maxima (Wu et al., 2007b; Bagthoth et al., 2009) or three peaks referred to as tryptophan-like, fulvic-like, and humic-like fluorophores (Liu et al., 2007; Seredynska-Sobecka et al., 2007; Spencer et al., 2007; Baker et al., 2008; Hudson et al., 2008). The fluorescence

intensity peaks for different NOM fractions of natural waters are listed in Table 2 (Coble, 1996; Leenher and Croue, 2003; Spencer et al., 2007; Bagtho et al., 2009). The spectral fluorescent signature technique has been developed by Marhaba (2000) to model the NOM characteristics. Multivariate data analysis methods have been used to analyse the full fluorescence EEMs to characterise water samples obtained from different sources or different stages of the purification process, including, e.g. principal component analysis (Marhaba et al., 2009; Peiris et al., 2010).

2.2. Biological tests

Several biological tests have been developed to assess the level of biodegradable organic matter in water. These bioassays are generally based on two concepts: (1) the assimilable organic carbon (AOC), that measures the growth of bacterial inoculum in response to the amount of nutrients in the water and (2) the biodegradable dissolved organic carbon (BDOC) that measures the fraction of DOC assimilated and mineralised by heterotrophic microbes (Escobar and Randall, 2001).

The AOC is believed to be mostly LMW compounds which are the most difficult to remove. They are also readily degradable, thus indicating the potential for bacterial growth in the distribution system (Escobar and Randall, 2001; Kang et al., 2006; Matilainen et al., 2006; Chen et al., 2007; Chow et al., 2009a). The BDOC methods have been developed and used for the determination of biological stability of raw and treated water (Escobar and Randall, 2001; Chen et al., 2007; Soh et al., 2008; Zappia et al., 2008; Yapsakli and Cecen, 2009).

2.3. Isolation and concentration

A number of different methods for isolation and concentration of NOM are available, of which the most commonly used are reverse osmosis (RO), evaporation under reduced pressure (vacuum distillation) and freeze-drying. In addition, there are some sorption

methods (Aiken, 1985; Aiken et al., 1992; Croue, 2004). The disadvantage with most of these methods is that they also concentrate the salts, which are always present in natural waters (Croue, 2004). RO has been used in many NOM isolation studies (Croue, 2004; Koprivnjak et al., 2006; Song et al., 2009), since it has a relatively small alteration affect on the physicochemical properties of NOM (Song et al., 2009; Alasonati et al., 2010). In the RO method, the water is passed through a cation exchanger (mostly Na- or H-saturated) prior to the RO filtration. Recovery of NOM (mass recoveries 80–99%) from waters with high SUVA-value is more efficient than with water with low SUVA. The ambient pH will also have an affect on the recovery (Song et al., 2009).

2.4. Fractionation

NOM molecules are generally unique. They, however, also share many common properties. One of the major analytical difficulties in the characterisation of aqueous NOM is the lack of a suitable fractionation procedure, which will yield pure components that can subsequently be characterised by standard techniques (Leenher, 1985). Commonly used chemical fractionation methods include precipitation, solvent extraction, and adsorption chromatography. Available physical fractionation methods include electrophoresis, ultrafiltration, size exclusion chromatography (SEC), and ultracentrifugation (Leenher, 1985; Leenher and Croue, 2003; Chow et al., 2005).

2.4.1. Resin fractionation

The most common approach for distinguishing between hydrophobic and hydrophilic NOM is to define them as organic matter that is adsorbed or not adsorbed to Amberlite XAD resins (Table 3). This is a commercially available synthetic resin introduced by Malcolm et al. at the US Geological Survey in Denver for isolation of humic substances from water. Many researchers have developed and modified the resin adsorption methods (Leenher, 1981; Thurman and Malcolm, 1981; Malcolm and MacCarthy, 1992;

Table 2
Major fluorescence peaks for water samples.

Range of excitation (nm)	Range of emission (nm)	Component type	References
270–280	310–320	Tyrosine-like, protein like	Coble (1996) and Bagtho et al. (2009)
270–285 (220–235)	340–360	Tryptophan-like, protein like	Coble (1996), Spencer et al. (2007), Baker et al. (2008), Hudson et al. (2008), and Bagtho et al. (2009)
320–350	400–450	Fulvic-like	Spencer et al. (2007) and Baker et al. (2008)
310–320	380–420	Humic-like (marine humic-like)	Coble (1996) and Bagtho et al. (2009)
330–390	420–500	Humic-like	Coble (1996), Spencer et al. (2007), and Bagtho et al. (2009)

Table 3
Proposed composition of NOM fractions separated using fractionation techniques (adapted from Swietlik et al., 2004).

Fraction	Organic compound class	References
Humic acid	Portion of humic substances precipitated at pH 1	Peuravuori et al. (1997)
Hydrophobic acid	Soil fulvic acids, C ₅ –C ₉ aliphatic carboxylic acids, 1- and 2-ring aromatic carboxylic acids, 1- and 2-ring phenols	Leenher (1981), Aiken et al. (1992), Marhaba et al. (2000), and Barber et al. (2001)
Hydrophobic base	1- and 2-ring aromatics (except pyridine), proteinaceous substances	Leenher (1981), Marhaba et al. (2000), and Barber et al. (2001)
Hydrophobic neutral	Mixture of hydrocarbons, >C ₅ aliphatic alcohols, amides, aldehydes, ketones, esters, >C ₉ aliphatic carboxylic acids and amines, >3 ring aromatic carboxylic acids and amines	Leenher (1981), Marhaba et al. (2000), and Barber et al. (2001)
Hydrophilic acid	Mixtures of hydroxy acids, <C ₅ aliphatic carboxylic acids, polyfunctional carboxylic acids	Leenher (1981), Aiken et al. (1992), Marhaba et al. (2000), and Barber et al. (2001)
Hydrophilic base	Pyridine, amphoteric proteinaceous material (i.e. aliphatic amino acids, amino sugars, <C ₉ aliphatic amines, peptides and proteins)	Leenher (1981), Marhaba et al. (2000), and Barber et al. (2001)
Hydrophilic neutral	<C ₅ aliphatic alcohols, polyfunctional alcohols, short-chain aliphatic amines, amides, aldehydes, ketones, esters, cyclic amides, polysaccharides and carbohydrates	Leenher (1981), Marhaba et al. (2000), and Barber et al. (2001)

Marhaba et al., 2003), and it is still used in NOM fractionation studies (Swietlik et al., 2004; Kanokkantapong et al., 2006a,b; Sharp et al., 2006; Her et al., 2008a; Jung and Son, 2008; Wei et al., 2008; Zhang et al., 2008). This technique was adopted by International Humic Substances Society (IHSS) as a standard method for isolating fulvic acid (FA) and humic acid (HA). These fulvic and humic acid are, however, not in accordance with the Svein Odeñs classical definition (Odén (1919)). This so-called XAD-method involves the Amberlite resins XAD-8 and XAD-4. The XAD-8 resin favours the isolation of hydrophobics, containing NOM of HMW matter with aromatic character. The hydrophilic fraction does not adsorb onto either of the resins. XAD-4 resin adsorbs weakly hydrophobic acid fractions, which is commonly defined as transphilic NOM (Sharp et al., 2006; Croue, 2004; Wei et al., 2008). The IHSS Standard Method for FA is based on the matter adsorbed on XAD-8 after reducing pH to 2 and prefiltrating with 0.45 µm. The hydrophilic fraction can be further separated by using, e.g. AG-MP-50 cationic resin and WA-10 a weak anionic resin (Marhaba et al., 2003).

The rapid resin fractionation technique, based on XADs, has been described by Chow et al. (2004). It separates DOC into four fractions based on character and molecular weight. Fractions are defined as very hydrophobic acids (VHA), slightly hydrophobic acids (SHA), charged hydrophilics, and neutral hydrophilics (NEU). According to Chow et al. (2004), the VHA is composed of HMW HAs, whereas SHA represents FA components, and the NEU fraction contains substances that do not adsorb to any of the applied resins. A number of different studies use this method (Fabris et al., 2008; Liu et al., 2008, 2010; Soh et al., 2008). A new fractionation technique based on NOM polarity in combination with a XAD-8 adsorption chromatography technique involving gradient elution also reportedly separates different hydrophobic and hydrophilic moieties (Li et al., 2009).

Although fractionation methods, based on different kinds of resins, have been widely used and accepted, disadvantages may still influence the results. These discrepancies include possible chemical or physical alterations of NOM due to extreme pH levels and changes in pH during fractionation, irreversible adsorption of NOM compounds to the resin, contamination from resin bleeding, and size-exclusion effects. Different operational conditions during the fractionation procedures may also influence the results (Song et al., 2009).

2.4.2. Size exclusion chromatography (SEC)

2.4.2.1. Fractionation of NOM with SEC. SEC is a fractionation method based on the molecular size; the bigger the molecules, the shorter the retention time. The molecule shape and some interaction characteristics may, however, influence the results (Lankes et al., 2009). The SEC fractionation of NOM has been used since the early 1960s (Posner, 1963; Gjessing, 1965), however, these soft gels had some major disadvantages (Gjessing, 1973), such as poor separation. Hence, techniques were developed for SEC column application to high-performance liquid chromatography (HPLC), thus called HPSEC (Fukano et al., 1978). HPSEC, in particular, has become very useful for NOM characterisation during different steps in drinking water treatment (Matilainen et al., 2006; Allpike et al., 2007; Fabris et al., 2008; Chow et al., 2009a,b; Tercero Espinoza et al., 2009; Zhao et al., 2009).

2.4.2.2. Different eluents and columns used for HPSEC measurements. In NOM studies using HPSEC, the choice of a proper eluent is important since its ionic strength and pH significantly impact results. The surface charge characteristics of the gel, the charge and structure of the NOM, and NOM-gel interactions are affected by the eluent (Specht and Frimmel, 2000). Many different kinds of

eluents have been used as a mobile phase in the studies of NOM characterisation by HPSEC, such as a phosphate buffer solution with ionic strength adjustment using sodium chloride, or sodium acetate solution. The columns are of different silica-based and polymer-based supports (Swietlik et al., 2004; Matilainen et al., 2006; Sarathy and Mohseni, 2007; Wu et al., 2007a,b; Fabris et al., 2008; Her et al., 2008a; Liu et al., 2008, 2010; Soh et al., 2008; Zhang et al., 2008; Chow et al., 2009b; Korshin et al., 2009; Zhao et al., 2009). According to the study of Specht and Frimmel (2000), however, both polymer-based and silica-based columns have specific interactions with NOM.

2.4.2.3. Different detectors used for HPSEC measurements. Detectors used in different HPSEC systems include Fourier transform infrared (FTIR) (Allpike et al., 2007), on-line DOC analysers (Her et al., 2008a), and excitation emission fluorescence detection (Wu et al., 2007a). The most widely used detectors in HPSEC fractionation are, however, the single and variable wavelength UV–vis detectors or diode array detectors (Matilainen et al., 2006; Ates et al., 2007; Sarathy and Mohseni, 2007; Wu et al., 2007b; Fabris et al., 2008; Her et al., 2008a,b; Liu et al., 2008, 2010; Zhang et al., 2008; Chow et al., 2009b; Korshin et al., 2009). UV–Vis detectors are simple and rapid to use and available in the majority of laboratories. Limitations of the UV–Vis detectors are that they only respond to or detect analytes that absorb at the wavelength at which they are operating. Since NOM structures contain a range of chromophores with varying molar absorptivities, the MW calculated may not involve all of NOM compounds present (ÓLoughlin and Chin, 2001; Wu et al., 2007b; Soh et al., 2008; Tercero Espinoza et al., 2009). The decrease in the wavelength results in an increase in the absorbance (ÓLoughlin and Chin, 2001; Lankes et al., 2009). On the other hand, the LMW compounds reportedly show a weak response with UV–Vis due to the lack of conjugated double bonds.

Despite the success of on-line specific Ex/Em fluorescence detection used in the characterisation of NOM fractions, it only provides limited information and somewhat poorer separation resolution compared to UV–Vis absorbance detection (Wu et al., 2007a). Wu et al. demonstrated, however, that compared to UV–Vis, on-line 3D EEM fluorescence detection gives more insight about the chemical qualitative and structural features of NOM in addition of molecular size (Wu et al., 2003, 2007a).

On-line organic carbon detectors (OCD) may offer better quantification than UV–Vis detectors (Her et al., 2002; Soh et al., 2008; Lankes et al., 2009; Tercero Espinoza et al., 2009). During the last 20 years, a combination of LC–OCD has been developed, which give information on the amount of NOM as well as compound information (Huber and Frimmel, 1992a,b). Using LC–OCD, it is also possible to evaluate the content of HMW polysaccharides and biopolymers in the sample, which are not generally visible or traceable by UV–detectors.

High resolution mass spectrometry (MS) has also been coupled with HPSEC, thereby giving more information about the molecules in complex mixtures of NOM fractions. An application that has been recently developed, includes electrospray ionisation Fourier transform ion cyclotron resonance mass spectrometry (ESI–FTICR–MS) (Reemtsma, 2009).

An increasing number of reports couple multiple detectors on-line, such as UV–Vis and spectrofluorometer (Wu et al., 2007a), or UV–Vis and OCD (Her et al., 2002; Allpike et al., 2007; Soh et al., 2008; Baghoth et al., 2009; Lankes et al., 2009; Tercero Espinoza et al., 2009), because better quantitative and qualitative evaluation of NOM is needed. Accordingly, a SEC set-up that uses a UV detector followed by a TOC module and finally an MS as the detector has been described (Warton et al., 2008). Results from these combined detector systems seem promising.

2.4.2.4. Determination of MW by HPSEC. The size and the MW of the NOM may be indicated by comparing with known molecular mass standards. The selection of proper standards to characterise MWs of organic substances in NOM using HPSEC is based mostly on a hypothesised structure of NOM. Poly-styrene sulphonate (PSS) standards have been widely used in this connection (Zhou et al., 2000; Swietlik et al., 2004; Ates et al., 2007; Wu et al., 2007a; Fabris et al., 2008; Chow et al., 2009b; Korshin et al., 2009; Zhao et al., 2009; Liu et al., 2010). NOM in water can, however, be more branched and cross-linked than PSS. The resulted MWs are, therefore, approximations. Polyethylene glycols are also used to determine molecular weight distribution (MWD) of NOM (Her et al., 2008a; Zhang et al., 2008). The MW magnitudes determined by HPSEC reportedly correlate well with other MW measuring techniques (Egeberg et al., 2002; Assemi et al., 2004).

2.4.2.5. HPSEC determinations vs. removal of NOM. SEC-profiles provide valuable information in the study of the removal mechanism of HMW-NOM during coagulation. Several studies compare changes in both the quality of NOM during different stages of the treatment process (Matilainen et al., 2006; Fabris et al., 2008; Baghth et al., 2009; Chow et al., 2009b; Zhao et al., 2009) and the actual degree of removal (Wu et al., 2007b). These SEC profiles do not, however, contain sufficient information to evaluate the disinfection by-products formation potential (DBPFP) of the remaining NOM molecules. Despite Korshin et al. (2009) reported a good correlation between DBPFP and HPSEC multiwavelength UV results based on spectroscopic index calculations (Korshin et al., 2009).

2.4.3. Membrane filtration

Filtration is used extensively in studies related to water and water research. For instance, the present international definition of dissolved matter in water is “the matter that passes a filter with a cut-off of 0.45 μm ” and RO is the most used method for isolating NOM from water in relation to NOM research. As early as 1970, it was demonstrated that NOM (aquatic humus) could be fractionated by means of membranes with different cut-off ranges (Gjessing, 1970). Further use and development of this technique confirm that NOM is a mixture of organic matter with different sized molecules (Aiken, 1984; Liu et al., 2007; Lankes et al., 2008; Wei et al., 2008; Zhao et al., 2009). The separation by membranes may, however, be dependent on molecular structures in NOM as well as the size (Assemi et al., 2004). The separation of molecules according to size and shape by membrane filtration is also influenced by the methodical conditions.

A problem associated with the method is the adherence of macromolecules to the sides of membrane pores, thus affecting its permeability. Flow restriction, also known as concentration polarisation, in which the deposition of macromolecules results in a gel layer that becomes the dominant resistance to flow may also have an impact on the results (Amy et al., 1987). In general, a reasonably good agreement exists between this fractionation technique and SEC regarding size and MW (Gjessing, 1973). It should be emphasised, however, that accurate size and shape is not essential, the reproducibility of the characterisation method is more important.

2.4.4. Other fractionation methods

Reversed-phase high-performance liquid chromatography (RPHPLC) is used in fractionation studies of NOM, although its use is rather limited, especially compared to HPSEC (Stenson, 2008; Reemtsma, 2009). The RPHPLC is based on a non-polar stationary phase and an aqueous moderately polar mobile phase, thus fractionating NOM based on the polarity of the matter.

The field-flow fractionation (FFF) is a chromatography-like method for separation of macromolecules, colloids and particles

(Messaud et al., 2009). The flow field-flow fractionation (FIFFF) is a sub-technique of FFF. This is also a molecular size fractionation method and is used to determine the MWD of NOM (Moon et al., 2006; Rosario-Ortiz et al., 2007; Alasonati et al., 2010). Detectors used in FIFFF, include UV-Vis, fluorescence, inductively coupled plasma atomic emission spectroscopy (ICP AES), and ICP MS (Moon et al., 2006; Alasonati et al., 2010). Results obtained by the FIFFF are comparable to values obtained by other techniques (e.g. HPSEC) (Assemi et al., 2004). The drawback of FFF analysis, however, is that the method currently lacks the maturity of the technique, and published reports are also limited (Messaud et al., 2009).

2.5. Elemental composition and some structural features determination

A number of different analytical methods have been used during the last few decades to gain insight into the compositions of NOM. Many of these methods are, however, rather complex and time consuming, and require access to sophisticated analytical instrumentation. Even though these characterisation techniques for NOM are not routinely used, this kind of information may be useful to describe and understand its quality and characteristics at various water treatment process steps. The behaviour of NOM in various treatment processes can be better explained and understood if data of structural features involved in NOM are available.

The elemental composition is often used for calculation of the atomic ratios such as O/C, H/C, or N/C. In addition to the classical Elemental Analyser (Li et al., 2009; Zhao et al., 2009) elemental composition determination methods include ICP AES (Blodau et al., 2009) measurements. Another approach related to structural analysis is to measure the size and conformation of NOM under different surrounding conditions with photon correlation spectroscopy, transmission electron microscopy, or atomic force microscopy (AFM) (Baalousha et al., 2006; Abu-Lail et al., 2007). Recent advances in AFM are providing better chemical and structural information on NOM, in relation to bacteria-NOM adhesion forces (Abu-Lail et al., 2007). Scanning electron microscope images are also used to study adsorbent layers and foulants in membrane surfaces during drinking water treatment (Kim et al., 2010). Determination of the electrical character and surface charge of the NOM fractions may also provide valuable information about the nature of the NOM during water treatment processes (Sharp et al., 2006).

2.5.1. Py-GC-MS

In pyrolysis, large complex molecules, included in NOM, are broken apart to more analytically available fragments by the application of heat and under anoxic conditions. These fragments are then swept into the analytical column of the gas chromatography (GC) and detected by MS. Pyrolysis combined with gas chromatography-mass spectrometry (Py-GC-MS) is a useful technique for producing structural information about the molecular building blocks of NOM (Bruchet et al., 1990; Christy et al., 1999; Leenher and Croue, 2003; Templier et al., 2005; Chow et al., 2009b). Some limitations exist, however, for analysing complex oxygen-containing macromolecules. Polar pyrolysis products are poorly GC-amenable and undergo undesirable thermal reactions (Templier et al., 2005). The development of the pyrolysis technique has made it possible to overcome some of these analytical limitations (Parsi et al., 2007).

Microscale sealed vessel pyrolysis is a promising new approach for NOM characterisation. This technique promotes the reduction of polar NOM moieties and significantly increases the yields of GC amenable products (Greenwood et al., 2006; Berwick et al., 2007, 2010). Important additional pyrolysis information can be found with this analytical method which represents an excellent

complement to conventional flash pyrolysis techniques where chromatographic resolution of polar biochemicals can be limited. The technique, however, needs further development for more advanced NOM characterisation.

Major pyrolysis fragments, most commonly yielded from aquatic NOM pyrochromatograms, have been listed by Leenher and Croue (2003) and are summarised in Table 4. Besides pyrolysis-MS, the molecular level structural information can also be obtained with chemical degradation methods, such as reduction with a reducing agent (e.g. *n*-butylsilane) in combination with MS (Nimmagadda and McRae, 2007).

2.5.2. NMR

Nuclear magnetic resonance (NMR) spectroscopy has been used for decades to study the functional groups in NOM (Barron and Wilson, 1981). The NMR technique is especially useful in combination with elemental composition data, apparent molecular weight data, or IR spectroscopy data of fractionated NOM (Gjessing et al., 1998; Assemi et al., 2004; Templier et al., 2005; Deshmukh et al., 2007; Mao et al., 2007a,b; Lankes et al., 2008; Ritchie and Perdue, 2008; Li et al., 2009). The heterogeneity and complexity of NOM limit the practical value of the NMR data. Thus, to improve the practical availability of the NMR information, the different fractionation methods (SEC, resin fractionation) prior to analysis has been found to be rather useful. In some cases the prefractionation of NOM has not produced any simplified spectra when compared to the spectra of unfractionated NOM (Wong et al., 2002).

NMR spectroscopy of NOM can be done on both solid and aqueous-phase samples. Solution state NMR is applicable to soluble samples like humic and fulvic acids, however, the solid sample enables various ^{13}C NMR experiments, including spectral editing of strongly overlapping bands, because of higher NOM concentration in the solid sample (Mao et al., 2007a; Lankes et al., 2008). In addition to ^1H and ^{13}C NMR techniques, ^{15}N NMR has also been used in NOM research. Peptides and other nitrogen containing structures can be identified by ^{15}N NMR techniques (Thorn and Cox, 2009).

2.5.2.1. ^{13}C NMR. Solid-state ^{13}C NMR is used to study NOM structure. Several specific pulse techniques are available for improving the quality and quantity of ^{13}C NMR spectra of NOM. This technique is useful for determining details of carbon structures (Peuravuori et al., 2003). A cross polarisation magic-angle spinning solid state nuclear magnetic resonance (CP/MAS ^{13}C NMR) spectroscopy is used to determine the functional groups of carbon in the NOM (Chen et al., 2002; Wong et al., 2002; Mao et al., 2007b). According to Peuravuori et al. (2003) quantitative analysis with solid-state ^{13}C NMR is difficult, but qualitative analysis and relative compositions of NOM can be determined. Though this technique offers good results concerning the gross chemical compositions, specific compounds are rarely identified (Peuravuori et al., 2003). As the NOM is chemically and structurally heterogeneous, the chemical shift dispersion of the NMR spectrum can be

relatively large. The obtained ^{13}C chemical shift range is divided into aliphatic, alkoxy, unsaturated, and carbonyl carbon regions (Wong et al., 2002; Lankes et al., 2008). The general assignments for structural features of NOM obtained by solid-state ^{13}C NMR are shown in Table 5 (Chen et al., 2002; Mao et al., 2007b).

2.5.2.2. ^1H NMR. The ^1H NMR provides information on non-exchangeable structural proton distributions in NOM, basic structural information. Structural features of NOM obtained this way are listed in Table 6 (Ma et al., 2001; Kim et al., 2006; Kim and Yu, 2007). The ^1H NMR results can support elemental data interpretation in the quantification of aromaticity and degree of humification (Kim et al., 2006). ^1H high resolution magic-angle spinning (HR-MAS) spectroscopy is an innovative NMR method allowing examination of samples that are semi-solid using liquid state NMR methods. In NOM research, HR-MAS is used in studying soil–water interface (Simpson et al., 2006).

2.5.2.3. New NMR techniques. New two- or multidimensional NMR techniques may have more potential than the traditional 1 D method. Two- and multidimensional NMR spectra are especially useful in determining the structures of complicated molecules, such as NOM. Two- or multidimensional NMR, is therefore more appropriate for NOM characterisation compared to both one-dimensional ^1H NMR and ^{13}C NMR (Deshmukh et al., 2007; Mao et al., 2007a,b). Other techniques include correlation spectroscopy, nuclear overhauser effect spectroscopy, total correlation spectroscopy, and heteronuclear multiple bond correlation (HMBC) (Cook, 2004; Deshmukh et al., 2007). For example, the ^1H – ^{13}C HMBC reveals couplings between protons and carbon atoms separated by 2–3 bonds, with the potential to examine the structural environments of carboxyls in more detail. The method, however, still requires improvement to be useful in NOM research (Deshmukh et al., 2007).

Different kinds of advanced spectral editing techniques have also been developed to obtain more specific structural information, thus probing molecular connectivity or functional group identification for NOM compounds. Techniques which have been used, include $^{13}\text{C}\{^{14}\text{N}\}$ SPIDER NMR, which selects signals of carbons bonded to nitrogen (Mao et al., 2007b).

Table 5

Chemical shift regions for integration of peak areas in solid-state ^{13}C NMR spectra of NOM and their respective assignments according to Chen et al. (2002).

Chemical shift (ppm)	Carbon assignment
0–50	Aliphatic or paraffinic carbon chains
50–75	Methoxyl groups
75–112	Carbohydrate RC–OH or RC–OR functional groups
112–145	Aromatic carbons
145–163	Phenolic groups
163–180	Carboxylic, carbonyl, amine and ester carbons

Table 4

The predominant pyrolysis by-products from aquatic NOM (adapted from Leenher and Croue, 2003).

Type	Common fragments
Polysaccharides	Methylfuran, furfural, acetylfuran, methylfurfural, levoglucosenone, hydroxypropanone, cyclopentanone, methylcyclopentenone, acetic acid
Aminosugars	Acetamide, N-methylacetamide, propionamide, acetic acid
Proteins	Acetonitrile, benzonitrile, phenylacetone, pyridine, methylpyridine, pyrrole, methylpyrrole, indole, methylindole (from tryptophan), toluene, styrene (from phenylalanine), phenol, p-cresol (from tyrosine)
Polyphenolic compounds	Phenol; o-, m-, p-cresol; methylphenols; dimethylphenols
Lignins	Methoxyphenols
Tannins	Catechol
DNA	Furfuryl alcohol
Polyhydroxybutyrate	Butyric acid

Table 6General assignments of the ^1H NMR spectra of humic substances.

Chemical shift (ppm)	General assignment	References
0.0–1.6	Protons on methyl and methylene carbons directly bonded to other carbons	Ma et al. (2001), Kim et al. (2006) and Kim and Yu (2007)
1.6–3.2	Protons of the methyl and methylene carbons alpha to aromatic rings, carboxyl and carbonyl groups	Ma et al. (2001), Kim et al. (2006) and Kim and Yu (2007)
3.2–4.3	Protons on carbon of hydroxyl, ester and ether and protons on methyl, methylene and methyne carbons directly bonded to oxygen and nitrogen	Ma et al. (2001), Kim et al. (2006) and Kim and Yu (2007)
6.0–8.5	Protons attached to unsaturated carbons. Aromatic protons including quinones, phenols, oxygen containing hetero-aromatics	Ma et al. (2001), Kim et al. (2006) and Kim and Yu (2007)

2.5.3. FTIR

FTIR has been widely used for the characterisation of NOM (Kanokkantarapong et al., 2006a; Kim and Yu, 2007; Hay and Myneni, 2007; Her et al., 2008a). Samples exposed to infrared light absorb energy corresponding to the vibrational energy of atomic bonds. The resulting absorption spectrum is a unique fingerprint of compounds, allowing the identification of both inorganic and organic functional groups. The interpretation of the analysis may be difficult, however, because of severe overlapping of characteristic spectral features due to the complexity and polyfunctionality of NOM. The main characteristics of NOM obtained from several analysis of FT-IR spectra has been listed in Table 7 (Howe et al., 2002; Kanokkantarapong et al., 2006a; Kim and Yu, 2007; Rodrigues and Núñez, 2009; Berwick et al., 2010).

Traditionally, IR spectrometers are used to analyse solids or liquids by means of transmitting the infrared radiation directly through the sample. In many cases, however, to obtain good quality spectrum sample pretreatment is required. Hence, dilute aqueous NOM samples are analysed by drying the samples to thin films on the attenuated total reflection (ATR) crystals, and thereby avoiding the different artefacts that may develop with other concentration methods (Howe et al., 2002; Hay and Myneni, 2007). The ATR-IR technique has revolutionised solid and liquid sample analysis, because it combats the most challenging aspects of IR analysis, namely the sample preparation and consequently the spectral reproducibility.

2.5.4. LC–MS

Liquid chromatography–mass spectrometry (LC–MS, or alternatively HPLC–MS) is a technique that combines the physical separation capabilities of liquid chromatography (or HPLC) with the mass analysis capabilities of MS. LC–MS is one of the main recent innovations regarding NOM structure research. The possibility to couple the LC by an advanced technique called electrospray ionisation (ESI) with MS made the need for derivatisation of

NOM molecules unnecessary (Reemtsma, 2009). The LC–MS system is used in combination with SEC in describing LMW FAs (Reemtsma and These, 2005). According to Reemtsma and These (2005) the ESI-MS is a better and more sensitive method in the characterisation of LMW FAs compared to HMW humics. Tandem MS, such as ion trap, triple quadrupoles, or quadrupole time-of-flight (e.g. LC–MS/MS) are also used in the investigation of NOM structures (Reemtsma and These, 2005; Mawhinney et al., 2009).

2.5.5. FTICR-MS

Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS) is the latest approach within NOM research. This method separates thousands of ions from each other and fairly accurately determines molecular formulae. Thus, according to the review article by Reemtsma (2009), two inventions in mass spectrometry have dramatically changed the situation and have given MS the prime position in NOM research. The first invention was the ESI, which allowed the infusion of aqueous solutions into the MS, and furthered the coupling of MS with LC. This circumvented the need to destruct and derivatise NOM molecules, allowing their direct analysis by MS. The second invention was ultra-high-resolution in the form of Fourier transform ion cyclotron resonance.

More specified information is obtained by coupling the ESI-FTICR-MS method with SEC (Reemtsma et al., 2006, 2008; Reemtsma, 2009) and RPHPLC (Stenson, 2008; Reemtsma, 2009), thereby producing different fractions of NOM, which are easier to determine with ESI-FTICR-MS. Moreover, an application of the universal algorithm for automatic treatment of mass spectra, based on total mass difference statistics, has been developed and implemented to help with data interpretation of the complex NOM structures (Kunenkov et al., 2009).

3. Summary

Surface water is the main drinking water source in many regions of the world. Due to contact with the soil surface, fresh water will always contain some inorganic and organic matter. The quality of all fresh water, therefore, will depend on the nature of the catchment. In the northern hemisphere, surface water often has a high NOM content. Based on international research over the last 3–4 decades, the knowledge on this matter has considerably increased and the general conclusion is that NOM should be removed from drinking water. This is important for practical and hygienic reasons. The nature and character, as well as the amount of NOM in raw water, depends on geology, topography, and climate. Climate change clearly impacts this matter, demonstrated by a number of reports from various parts of the world showing a significant increase in the amount and most probably the quality of the NOM in the water.

In removing NOM from water, optimisation of the treatment process by controlling water quality change during the purification

Table 7

Main characteristics of the FT-IR spectra of humic substances (adapted from Rodrigues and Núñez, 2009).

Band (cm^{-1})	Assignment
3400	Associated O–H stretch (alcohols, phenols and carboxylic groups)
2850–2960	C–H stretch (CH_3 and CH_2)
2620	O–H stretch (hydrogen-bonded carboxylic groups)
1720	C=O stretch (carboxylic groups)
1630	C=C stretch (alkenes and aromatic rings)
1540	N–H bend (N–H structures)
1455	C–H bend (CH_3 and CH_2)
1410	O–H bend (carboxylic groups)
1375	C–H bend (CH_3)
1260 and 1220	C–O stretch (carboxylic groups, phenols, aromatic/unsaturated ethers)
1095 and 1030	C–O stretch (alcohols, aliphatic ethers)
805	C–H bend (tri- and tetra-substituted aromatic rings)

process is important. A number of different methods have been introduced during recent years to describe the nature of NOM. These new advanced characterisation techniques are useful for selecting of the best way to remove NOM from raw water. The main aim is to produce quality water that in turn will create fewer problems during further treatments, such as disinfection and alkalisation and during transport to the tap.

Isolation, concentration, and fractionation of NOM are often implemented before performing analytical procedures. Resin isolation and fractionation are widely accepted as pretreatment methods before further analysis with HPSEC or FTIR. HPSEC has been very popular for size fractionation of NOM with a number of different detection procedures. The NMR spectroscopy has also been extensively used during the last decades for the study of NOM structures and other properties.

The role of MS has considerably increased since coupling with HPLC, allowing direct analysis of NOM with MS, without prior destruction or derivatisation of the NOM molecules. Recently the development of FTICR-MS has allowed the analysis of NOM at the molecular level, enabling the separation of molecular species from very complex NOM structures. The multidimensional NMR techniques together with FTICR-MS are new and apparently promising set of methods that may characterise the major fractions of NOM. Through these methods new insights into the structural and functional features of NOM and fractionated NOM can be illustrated. Finally, regarding the need for better knowledge about the practical, hygienic and ecological consequences, it is important to have reproducible characterisation methods, rather than aiming at the chemical structure of NOM.

Acknowledgement

The authors thank EU and City of Mikkeli for financial support.

References

- Abu-Lail, L.I., Liu, Y., Atabek, A., Camesano, T.A., 2007. Quantifying the adhesion and interaction forces between *Pseudomonas aeruginosa* and natural organic matter. *Environ. Sci. Technol.* 41, 8031–8037.
- Aiken, G.R., 1984. Evaluation of ultrafiltration for determining molecular weight of fulvic acid. *Environ. Sci. Technol.* 18, 978–981.
- Aiken, G.R., 1985. Isolation and Concentration Techniques for Aquatic Humic Substances. In: *Humic Substances in Soil, Sediment and Water*. John Wiley & Sons, pp. 363–385.
- Aiken, G.R., McKnight, D.M., Thorn, K.A., Thurman, E.M., 1992. Isolation of hydrophilic organic acids from water using non-ionic macroporous resins. *Org. Geochem.* 18 (4), 567–573.
- Alasonati, E., Slaveykova, V.I., Gallard, H., Croué, J.-P., Benedetti, M.F., 2010. Characterization of the colloidal organic matter from Amazonian basin by asymmetrical flow field-flow fractionation and size exclusion chromatography. *Water Res.* 44, 223–231.
- Allpike, B.P., Heitz, A., Joll, C.A., Kagi, R.I., 2007. A new organic carbon detector for size exclusion chromatography. *J. Chromatogr. A* 1157, 472–476.
- Ambashta, R., Sillanpää, M., 2010. Water purification using magnetic assistance: a review. *J. Hazard. Mater.* 180, 38–49.
- Amy, G., Collins, M., Kuo, C., King, P., 1987. Comparing gel permeation chromatography and ultrafiltration for the molecular weight characterization of aquatic organic matter. *J. Am. Water Works Assoc.* 79 (1), 43–49.
- Archer, A.D., Singer, P.C., 2006. An evaluation of the relationship between SUVA and NOM coagulation using ICR database. *J. Am. Water Works Assoc.* 98 (7), 110–123.
- Assemi, S., Newcombe, G., Hepplewhite, C., Beckett, R., 2004. Characterization of natural organic matter fractions separated by ultrafiltration using flow field-flow fractionation. *Water Res.* 38, 1467–1476.
- Ates, N., Kitis, M., Yetis, U., 2007. Formation of chlorination by-products in waters with low SUVA – correlations with SUVA and differential UV spectroscopy. *Water Res.* 41, 4139–4148.
- Baalousha, M., Motelica-Heino, M., Le Coustumer, P., 2006. Conformation and size of humic substances: effects of major cation concentration and type, pH, salinity, and residence time. *Colloid Surf. A* 272, 48–55.
- Bagtho, S.A., Dignum, M., Grefte, A., Kroesbergen, J., Amy, G.L., 2009. Characterization of NOM in a drinking water treatment process train with no disinfectant residual. *Water Sci. Technol.* 9 (1), 379–386.
- Baker, A., Tipping, E., Thacker, S.A., Gondar, D., 2008. Relating dissolved organic matter fluorescence and functional properties. *Chemosphere* 73, 1765–1772.
- Barber, L.B., Leenher, J.A., Noyes, T.I., Stiles, E.A., 2001. Nature and transformation of dissolved organic matter in treatment wetlands. *Environ. Sci. Technol.* 35, 4805–4816.
- Barron, P.F., Wilson, M.A., 1981. Humic soil and coal structure study with magic-angle spinning ^{13}C CP NMR. *Nature* 289, 275–276.
- Berwick, L., Greenwood, P., Kagi, R., Croué, J.-P., 2007. Thermal release of nitrogen organics from natural organic matter using micro scale sealed vessel pyrolysis. *Org. Geochem.* 38, 1073–1090.
- Berwick, L., Greenwood, P.F., Smernik, R.J., 2010. The use of MSSV pyrolysis to assist the molecular characterisation of aquatic natural organic matter. *Water Res.* 44, 3039–3054.
- Bhatnagar, A., Sillanpää, M., 2009. Applications of chitin- and chitosan-derivatives for the detoxification of water and wastewater – a short review. *Adv. Colloid Interface* 152, 26–38.
- Bhatnagar, A., Sillanpää, M., 2010. Utilization of agro-industrial and municipal waste materials as potential adsorbents for water treatment – a review. *Chem. Eng. J.* 157, 277–296.
- Bierzo, M., Baker, A., Bridgeman, J., 2009. Relating freshwater organic matter fluorescence to organic carbon removal efficiency in drinking water treatment. *Sci. Total Environ.* 407, 1765–1774.
- Blodau, C., Bauer, M., Regenspurg, S., Macalady, D., 2009. Electron accepting capacity of dissolved organic matter as determined by reaction with metallic zinc. *Chem. Geol.* 260, 186–195.
- Bose, P., Reckhow, D.A., 2007. The effect of ozonation on natural organic matter removal by alum coagulation. *Water Res.* 41, 1516–1524.
- Bruchet, A., Rousseau, C., Mallevialle, J., 1990. Pyrolysis-GC-MS for investigating high-molecular-weight THM precursors and other refractory organics. *J. Am. Water Works Assoc.* 82 (9), 66–74.
- Chen, J., Gu, B., LeBoef, E.J., Pan, H., Dai, S., 2002. Spectroscopic characterization of the structural and functional properties of natural organic matter fractions. *Chemosphere* 48, 59–68.
- Chen, C., Zhang, X., He, W., Lu, W., Han, H., 2007. Comparison of seven kinds of drinking water treatment processes to enhance organic material removal: a pilot test. *Sci. Total Environ.* 382, 93–102.
- Chen, C., Zhang, X., Zhu, L., Liu, J., He, W., Han, H., 2008. Disinfection by-products and their precursors in a water treatment plant in North China: seasonal changes and fraction analysis. *Sci. Total Environ.* 397, 140–147.
- Chow, C.W.K., Fabris, R., Drikas, M., 2004. A rapid fractionation technique to characterise natural organic matter for the optimisation of water treatment processes. *J. Water Supply Res. Technol.* 53, 85–92.
- Chow, A.T., Dahlgren, R.A., Gao, S., 2005. Physical and chemical fractionation of dissolved organic matter and trihalomethane precursors: a review. *J. Water Supply Res. Technol.* 54, 475–507.
- Chow, C.W.K., Fabris, R., Van Leeuwen, J., Wang, D., Drikas, M., 2008. Assessing natural organic matter treatability using high performance size exclusion chromatography. *Environ. Sci. Technol.* 42, 6683–6689.
- Chow, C.W.K., Kuntke, P., Fabris, R., Drikas, M., 2009a. Organic characterisation tools for distribution system management. *Water Sci. Technol.* 9 (1), 1–8.
- Chow, C.W.K., von Leeuwen, J.A., Fabris, R., Drikas, M., 2009b. Optimised coagulation using aluminium sulfate for the removal of dissolved organic carbon. *Desalination* 245, 120–134.
- Christy, A.A., Bruchet, A., Rybacki, D., 1999. Characterization of natural organic matter by pyrolysis/GC-MS. *Environ. Int.* 25, 181–189.
- Coble, P.G., 1996. Characterization of marine and terrestrial DOM in seawater using excitation-emission matrix spectroscopy. *Mar. Chem.* 51, 325–346.
- Cook, R.L., 2004. Coupling NMR to NOM. *Anal. Bioanal. Chem.* 376, 1484–1503.
- Cooper, W.J., Song, W., Kalnina, D., Gonsior, M., Mezyk, S.P., Peake, B.M., 2008. Recent advances in structure and reactivity of dissolved organic matter in natural waters. *Water Sci. Technol.* 8 (6), 615–623.
- Croue, J.-P., 2004. Isolation of humic and non-humic NOM fractions: structural characterization. *Environ. Monit. Assess.* 92, 193–207.
- Culea, M., Cozar, O., Ristoiu, D., 2006. Methods validation for the determination of trihalomethanes in drinking water. *J. Mass Spectrom.* 41, 1594–1597.
- Danielsson, L.G., 1982. On the use of filters for distinguishing between dissolved and particulate fractions in natural waters. *Water Res.* 16, 179–182.
- Datta, C., Ghosh, K., Mukherjee, S.K., 1971. Fluorescence excitation spectra of different fractions of humus. *J. Indian Chem. Soc.* 48, 279–287.
- Delpla, I., Jung, A.-V., Baures, E., Clement, M., Thomas, O., 2009. Impacts of climate change on surface water quality in relation to drinking water production. *Environ. Int.* 35, 1225–1233.
- Deshmukh, A.P., Pacheco, C., Hay, M.B., Myneni, S.C.B., 2007. Structural environments of carboxyl groups in natural organic molecules from terrestrial systems. Part 2: 2D NMR spectroscopy. *Geochim. Cosmochim. Acta* 71, 3533–3544.
- Edzwald, J.K., Tobiasson, J.E., 1999. Enhanced coagulation: USA requirements and a broader view. *Water Sci. Technol.* 40 (9), 63–70.
- Egeberg, P.K., Christy, A.A., Eikenes, M., 2002. The molecular size of natural organic matter (NOM) determined by diffusivity and seven other methods. *Water Res.* 36, 925–932.
- Eikebrokk, B., Vogt, R.D., Liltved, H., 2004. NOM increase in Northern European source waters: discussion of possible causes and impacts on coagulation/contact filtration processes. *Water Sci. Technol.* 4 (4), 47–54.
- Escobar, I.C., Randall, A.A., 2001. Assimilable organic carbon (AOC) and biodegradable dissolved organic carbon (BDOC): complementary measurements. *Water Res.* 35, 4444–4454.

- Fabris, R., Chow, C.W.K., Drikas, M., Eikebrokk, B., 2008. Comparison of NOM character in selected Australian and Norwegian drinking waters. *Water Res.* 42, 4188–4196.
- Forsberg, C., Petersen Jr., R.C., 1990. A darkening of Swedish lakes due to increased humus inputs during the last 15 years. *Verh. Int. Ver. Limnol.* 24, 289–292.
- Fukano, K., Komiya, K., Sasaki, H., Hashimoto, T., 1978. Evaluation of new supports for high-pressure aqueous gel permeation chromatography: TSK-gel SW type columns. *J. Chromatogr.* 166, 47–54.
- Gjessing, E.T., 1965. Use of Sephadex gels for estimation of humic substances in natural water. *Nature (London)* 208, 1091–1092.
- Gjessing, E.T., 1970. Ultra filtration of aquatic humus. *Environ. Sci. Technol.* 4, 437–438.
- Gjessing, E.T., 1973. Gel- and ultramembrane filtration of aquatic humus: a comparison of the two methods. *Schweiz. Z. Hydrol.* 35, 286–294.
- Gjessing, E.T., Alberts, J.J., Bruchet, A., Egeberg, P.K., Lydersen, E., McGown, L.B., Mobed, J.J., Munster, U., Pempkowiak, J., Perdue, M., Ratnawerra, H., Rybacki, D., Takacs, M., Abbt-Braun, G., 1998. Multi-method characterization of natural organic matter isolated from water: characterization of reverse osmosis-isolates from water of two semi-identical dystrophic lakes basins in Norway. *Water Res.* 32, 3108–3124.
- Gjessing, E.T., Steiro, C., Becher, G., Christy, A., 2007. Reduced analytical availability of polychlorinated biphenyls (PCBs) in coloured surface water. *Chemosphere* 66, 644–649.
- Greenwood, P.F., Leenher, J.A., McIntyre, C., Berwick, L., Franzmann, P.D., 2006. Bacterial biomarkers thermally released from dissolved organic matter. *Org. Geochem.* 37, 597–609.
- Hay, M.B., Myneni, S.C.B., 2007. Structural environments of carboxyl groups in natural organic molecules from terrestrial systems. Part 1: infrared spectroscopy. *Geochim. Cosmochim. Acta* 71, 3518–3532.
- Her, N., Amy, G., Foss, D., Cho, J., Yoon, Y., Kosenka, P., 2002. Optimization of method for detecting and characterizing NOM by HPLC-size exclusion chromatography with UV and on-line DOC detection. *Environ. Sci. Technol.* 36, 1069–1076.
- Her, N., Amy, G., Chung, J., Yoon, J., Yoon, Y., 2008a. Characterizing dissolved organic matter and evaluating associated nanofiltration membrane fouling. *Chemosphere* 70, 495–502.
- Her, N., Amy, G., Sohn, J., Gunten, von, U., 2008b. UV absorbance ratio index with size exclusion chromatography (URI-SEC) as an NOM property indicator. *J. Water Supply Res. Technol.* 57 (1), 35–44.
- Howe, K.J., Ishida, K.P., Clark, M.M., 2002. Use of ATR/FTIR spectrometry to study fouling of microfiltration membranes by natural waters. *Desalination* 147, 251–255.
- Hua, G., Reckhow, D.A., 2007. Characterization of disinfection byproduct precursors based on hydrophobicity and molecular size. *Environ. Sci. Technol.* 41, 3309–3315.
- Huber, S.A., Frimmel, F.H., 1992a. A liquid chromatographic system with multi-detection for direct analysis of hydrophilic organic compounds in natural waters. *Fresenius J. Anal. Chem.* 342, 198–200.
- Huber, S.A., Frimmel, F.H., 1992b. A new method for the characterization of organic carbon in aquatic systems. *Int. J. Environ. Anal. Chem.* 49, 49–57.
- Hudson, N., Baker, A., Ward, D., Reynolds, D.M., Brunsdon, C., Carliell-Marquet, C., Browning, S., 2008. Can fluorescence spectrometry be used as a surrogate for the biochemical oxygen demand (BOD) test in water quality assessment? An example from South West England. *Sci. Total Environ.* 391, 149–158.
- Hur, J., Williams, M.A., Schlautman, M.A., 2006. Evaluating spectroscopic and chromatographic techniques to resolve dissolved organic matter via end member mixing analysis. *Chemosphere* 63, 387–402.
- Jacangelo, J., DeMarco, J., Owen, D., Randtke, S., 1995. Selected processes for removing NOM: an overview. *J. Am. Water Works Assoc.* 87 (1), 64–77.
- Jung, C., Son, H., 2008. The relationship between disinfection by-products formation and characteristics of natural organic matter in raw water. *Korean J. Chem. Eng.* 25 (4), 714–720.
- Kang, M.-G., Ku, Y.-H., Cho, Y.-K., Yu, M.-J., 2006. Variation of dissolved organic matter and microbial regrowth potential through drinking water treatment processes. *Water Sci. Technol.* 6 (4), 57–66.
- Kanokkantaopong, V., Marhaba, T.F., Panyapinyophol, B., Pavasant, P., 2006a. FTIR evaluation of functional groups involved in the formation of haloacetic acids during the chlorination of raw water. *J. Hazard. Mater.* B136, 188–196.
- Kanokkantaopong, V., Marhaba, T.F., Pavasant, P., Panyapinyophol, B., 2006b. Characterization of haloacetic acid precursors in source water. *J. Environ. Manage.* 80, 214–221.
- Kim, H.-C., Yu, M.-J., 2007. Characterization of aquatic humic substances to DBPs formation in advanced treatment processes for conventionally treated water. *J. Hazard. Mater.* 143, 486–493.
- Kim, H.-C., Yu, M.-J., Han, I., 2006. Multi-method study of the characteristic chemical nature of aquatic humic substances isolated from the Han River. *Korean Appl. Geochem.* 21, 1226–1239.
- Kim, J., Cai, Z., Benjamin, M.M., 2010. NOM fouling mechanisms in a hybrid adsorption/membrane system. *J. Membr. Sci.* 349, 35–43.
- Koprivnjak, J.F., Perdue, E.M., Pfomm, P.M., 2006. Coupling reverse osmosis with electrodialysis to isolate natural organic matter from fresh waters. *Water Res.* 40, 3385–3392.
- Korshin, G.V., Benjamin, M.M., Li, C.-W., 1999. Use of differential spectroscopy to evaluate the structure and reactivity of humics. *Water Sci. Technol.* 40 (9), 9–16.
- Korshin, G., Chow, C.W.K., Fabris, R., Drikas, M., 2009. Absorbance spectroscopy-based examination of effects of coagulation on the reactivity of fractions of natural organic matter with varying apparent molecular weights. *Water Res.* 43, 1541–1548.
- Krasner, S.W., Weinberg, H.S., Richardson, S.D., Pastor, S.J., Chinn, R., Scimmenti, M.J., Onstad, G.D., Thurston Jr., A.D., 2006. Occurrence of a new generation of disinfection byproducts. *Environ. Sci. Technol.* 40, 7175–7185.
- Kunenkov, E.V., Kononikhin, A.S., Perminova, I.V., Hertkorn, N., Gaspar, A., Scmitt-Kopplin, P., Popov, I.A., Garmash, A.V., Nikolaev, E.N., 2009. Total mass difference statistics algorithm: a new approach to identification of high-mass building blocks in electrospray ionization Fourier transform ion cyclotron mass spectrometry data of natural organic matter. *Anal. Chem.* 81, 10106–10115.
- Laborda, F., Ruiz-Beguería, S., Bolea, E., Castillo, J.R., 2009. Functional speciation of metal-dissolved organic matter complexes by size exclusion chromatography coupled to inductively coupled plasma mass spectrometry and deconvolution analysis. *Spectrochim. Acta B* 392, 392–398.
- Lankes, U., Lüdemann, H.-D., Frimmel, F.H., 2008. 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. *Water Res.* 42, 1051–1060.
- Lankes, U., Müller, M.B., Weber, M., Frimmel, F.H., 2009. Reconsidering the quantitative analysis of organic carbon concentrations in size exclusion chromatography. *Water Res.* 43, 915–924.
- Leenher, J.A., 1981. Comprehensive approach to preparative isolation and fractionation of dissolved organic carbon from natural waters and wastewaters. *Environ. Sci. Technol.* 15 (5), 578–587.
- Leenher, J.A., 1985. Fractionation techniques for aquatic humic substances. In: Aiken, G., McKnight, D., Wershaw, R., MacCarthy, P. (Eds.), *Humic Substances in Soil, Sediment and Water*. John Wiley & Sons, pp. 409–429.
- Leenher, J.A., Croue, J.-P., 2003. Characterizing dissolved aquatic organic matter. *Environ. Sci. Technol.* 37 (1), 18A–26A.
- Li, A., Hu, J., Li, W., Zhang, W., Wang, X., 2009. Polarity based fractionation of fulvic acids. *Chemosphere* 77, 1419–1426.
- Liu, R., Lead, J.R., Baker, A., 2007. Fluorescence characterization of cross flow ultrafiltration derived freshwater colloidal and dissolved organic matter. *Chemosphere* 68, 1304–1311.
- Liu, S., Lim, M., Fabris, R., Chow, C., Chiang, K., Drikas, M., Amal, R., 2008. Removal of humic acid using TiO_2 photocatalytic process – fractionation and molecular weight characterisation studies. *Chemosphere* 72, 263–271.
- Liu, S., Lim, M., Fabris, R., Chow, C., Drikas, M., Amal, R., 2010. Comparison of photocatalytic degradation of natural organic matter in two Australian surface waters using multiple analytical techniques. *Org. Geochem.* 41 (2), 124–129.
- Ma, H., Allen, H.E., Yin, Y., 2001. Characterization of isolated fractions of dissolved organic matter from natural waters and a wastewater effluent. *Water Res.* 35, 985–996.
- Malcolm, R.L., MacCarthy, P., 1992. Quantitative evaluation of XAD-8 and XAD-4 resins used in tandem for removing organic solutes from water. *Environ. Int.* 18, 597–607.
- Mao, J., Cory, R.M., McKnight, D.M., Schmidt-Rohr, K., 2007a. Characterization of a nitrogen-rich fulvic acid and its precursor algae from solid state NMR. *Org. Geochem.* 38, 1277–1292.
- Mao, J., Tremblay, L., Gagné, J.-P., Kohl, S., Rice, J., Schmidt-Rohr, K., 2007b. Humic acids from particulate organic matter in the Saguenay Fjord and St. Lawrence Estuary investigated by advanced solid-state NMR. *Geochim. Cosmochim. Acta* 71, 5483–5499.
- Marhaba, T.F., 2000. Fluorescence technique for rapid identification of DOM fractions. *J. Environ. Eng. Sci.* 126, 145–152.
- Marhaba, T.F., Van, D., Lippincott, R.L., 2000. Changes in NOM fractions through treatment: a comparison of ozonation and chlorination. *Ozone Sci. Eng.* 22, 249–266.
- Marhaba, T.F., Pu, Y., Bengraïne, K., 2003. Modified dissolved organic matter fractionation technique for natural water. *J. Hazard. Mater.* B101, 43–53.
- Marhaba, T.F., Borgaonkar, A.D., Punburananon, K., 2009. Principal component regression model applied to dimensionally reduced spectral fluorescent signature for the determination of organic character and THM formation potential of source water. *J. Hazard. Mater.* 169, 998–1004.
- Matilainen, A., Sillanpää, M., 2010. Removal of natural organic matter from drinking water by advanced oxidation processes. *Chemosphere* 80, 351–365.
- Matilainen, A., Iivari, P., Sallanko, J., Heiska, E., Tuhkanen, T., 2006. The role of ozonation and activated carbon filtration in the natural organic matter removal from drinking water. *Environ. Technol.* 27, 1171–1180.
- Matilainen, A., Vepsäläinen, M., Sillanpää, M., 2010. Natural organic matter removal by coagulation during drinking water treatment: a review. *Adv. Colloid Interface* 159, 189–197.
- Mawhinney, D.B., Rosario-Ortiz, F.L., Baik, S., Vanderford, B.J., Snyder, S.A., 2009. Characterization of fulvic acids by liquid chromatography-quadrupole time-of-flight mass spectrometry. *J. Chromatogr. A* 1216, 1319–1324.
- Messaoud, F.A., Sanderson, R.D., Runyon, J.R., Otte, T., Pasch, H., Williams, S.K.R., 2009. An overview on field-flow fractionation techniques and their applications in the separation and characterization of polymers. *Prog. Polym. Sci.* 34, 351–368.
- Moon, J., Kim, S.H., Cho, J., 2006. Characterizations of natural organic matter as nano particle using flow field-flow fractionation. *Colloid Surf. A* 287, 232–236.
- Nimmagadda, R.D., McRae, C., 2007. Characterisation of the backbone structures of several fulvic acids using a novel selective chemical reduction method. *Org. Geochem.* 38, 1061–1072.
- Odén, S., 1919. Die huminsäure. *Kolloidchem. Beiheft.* 11, 75.

- ÓLoughlin, E., Chin, Y.-P., 2001. Effect of detector wavelength on the determination of the molecular weight of humic substances by high-pressure size exclusion chromatography. *Water Res.* 35, 333–338.
- Park, J.-H., 2009. Spectroscopic characterization of dissolved organic matter and its interactions with metals in surface waters using size exclusion chromatography. *Chemosphere* 77, 485–494.
- Parsi, Z., Hartog, N., Górecki, T., Poerschmann, J., 2007. Analytical pyrolysis as a tool for the characterization of natural organic matter – a comparison of different approaches. *J. Anal. Appl. Pyrol.* 79, 9–15.
- Peiris, R.H., Hallé, C., Budman, H., Moresoli, C., Peldszus, S., Huck, P.M., Legge, R.L., 2010. Identifying fouling events in a membrane-based drinking water treatment process using principal component analysis of fluorescence excitation–emission matrices. *Water Res.* 44, 185–194.
- Peuravuori, J., Pihlaja, K., Välimäki, N., 1997. Isolation and characterization of natural organic matter from lake water: two different adsorption chromatographic methods. *Environ. Int.* 23, 453–464.
- Peuravuori, J., Ingman, P., Pihlaja, K., 2003. Critical comments on accuracy of quantitative determination of natural humic matter by solid state ^{13}C NMR spectroscopy. *Talanta* 59, 177–189.
- Pirkanniemi, K., Sillanpää, M., 2002. Heterogeneous water phase catalysis as an environmental application: a review. *Chemosphere* 48, 1047–1060.
- Pirkanniemi, K., Metsärinne, S., Sillanpää, M., 2007. Degradation of EDTA and novel complexing agents in pulp and paper mill process and waste waters by Fenton's reagent. *J. Hazard. Mater.* 147, 556–561.
- Posner, A.M., 1963. Importance of electrolyte in the determination of molecular weights by sephadex gel with specific reference to humic acids. *Nature (London)* 198, 1161–1163.
- Rämö, J., Sillanpää, M., 2001. The degradation of EDTA by hydrogen peroxide in alkaline conditions. *J. Clean. Prod.* 9, 191–195.
- Reemtsma, T., 2009. Determination of molecular formulas of natural organic matter molecules by (ultra-) high-resolution mass spectrometry – status and needs. *J. Chromatogr. A* 1216, 3687–3701.
- Reemtsma, T., These, A., 2005. Comparative investigation of low-molecular-weight fulvic acids of different origin by SEC-Q-TOF-MS: New insights into structure and formation. *Environ. Sci. Technol.* 39, 3507–3512.
- Reemtsma, T., These, A., Springer, A., Linscheid, M., 2006. Fulvic acids as transition state of organic matter: Indications from high resolution mass spectrometry. *Environ. Sci. Technol.* 40, 5839–5845.
- Reemtsma, T., These, A., Springer, A., Linscheid, M., 2008. Differences in the molecular composition of fulvic acid size fractions detected by size-exclusion chromatography-on line Fourier transform ion cyclotron resonance (FTICR) mass spectrometry. *Water Res.* 42, 63–72.
- Richardson, S.D., Plewa, M.J., Wagner, E.D., Schoeny, R., DeMarini, D.M., 2007. Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: a review and roadmap for research. *Mutat. Res. – Rev. Mutat.* 636, 178–242.
- Richardson, S.D., Fasano, F., Ellington, J.J., Crumley, F.G., Buettner, K.M., Evans, J.J., Blount, B.C., Silva, L.K., Waite, T.J., Luther, G.W., McKague, A.B., Miltner, R.J., Wagner, E.D., Plewa, M.J., 2008. Occurrence and mammalian cell toxicity of iodinated disinfection byproducts in drinking water. *Environ. Sci. Technol.* 42, 8330–8338.
- Ritchie, J.D., Perdue, E.M., 2008. Analytical constraints on acidic functional groups in humic acids. *Org. Geochem.* 39, 783–799.
- Roccaro, P., Vagliasindi, F.G.A., 2009. Differential vs. absolute UV absorbance approaches in studying NOM reactivity in DBPs formation: comparison and applicability. *Water Res.* 43, 744–750.
- Rodrigues, F.J., Núñez, L.A., 2009. Characterization of aquatic humic substances. *Water Environ. J.* 23, 1–8.
- Rosario-Ortiz, F.L., Snyder, S.A., Suffet, I.H., 2007. Characterization of dissolved organic matter in drinking water sources impacted by multiple tributaries. *Water Res.* 41, 4115–4128.
- Sarathy, S.R., Mohseni, M., 2007. The impact of UV/H₂O₂ advanced oxidation on molecular size distribution of chromophoric natural organic matter. *Environ. Sci. Technol.* 41, 8315–8320.
- Seredynska-Sobecka, B., Baker, A., Lead, A., 2007. Characterisation of colloidal and particulate organic carbon in freshwaters by thermal fluorescence quenching. *Water Res.* 41, 3069–3076.
- Sharp, E.L., Jarvis, P., Parsons, S.A., Jefferson, B., 2006. Impact of fractional character on the coagulation of NOM. *Colloid Surf. A* 286, 104–111.
- Simpson, A.J., Simpson, M.J., Kingery, W.L., Lefebvre, B.A., Moser, A., Williams, A.J., Kvasha, M., Kvelleher, B.P., 2006. The application of ^1H high-resolution magic-angle spinning NMR for the study of clay-organic associations in natural and synthetic complexes. *Langmuir* 22, 4498–4503.
- Singer, P.C., 2006. DBPs in drinking water: additional scientific and policy considerations for public health protection. *J. Am. Water Works Assoc.* 98 (10), 73–80.
- Singer, P.C., Bilyk, K., 2002. Enhanced coagulation using a magnetic ion exchange resin. *Water Res.* 36, 4009–4022.
- Soh, Y.C., Roddick, F., van Leeuwen, J., 2008. The impact of alum coagulation on the character, biodegradability and disinfection by-product formation potential of reservoir natural organic matter (NOM) fractions. *Water Sci. Technol.* 58 (6), 1173–1179.
- Song, H., Orr, O., Hong, Y., Karanfil, T., 2009. Isolation and fractionation of natural organic matter: evaluation of reverse osmosis performance and impact of fractionation parameters. *Environ. Monit. Assess.* 153, 307–321.
- Specht, C.H., Frimmel, F.H., 2000. Specific interactions of organic substances in size-exclusion chromatography. *Environ. Sci. Technol.* 34, 2361–2366.
- Spencer, R.G.M., Bolton, L., Baker, A., 2007. Freeze/thaw and pH effects on freshwater dissolved organic matter fluorescence and absorbance properties from a number of UK locations. *Water Res.* 41, 2941–2950.
- Stenson, A.C., 2008. Reversed-phase chromatography fractionation tailored to mass spectral characterization of humic substances. *Environ. Sci. Technol.* 42, 2060–2065.
- Swietlik, J., Dabrowska, A., Raczky-Stanislawski, U., Nawrocki, J., 2004. Reactivity of natural organic matter fractions with chlorine dioxide and ozone. *Water Res.* 38, 547–558.
- Templier, J., Derenne, S., Croué, J.-P., Largeau, C., 2005. Comparative study of two fractions of riverine dissolved organic matter using various analytical pyrolytic methods and a ^{13}C CP/MAS NMR approach. *Org. Geochem.* 36, 1418–1442.
- Tercero Espinoza, L.A., ter Haseborg, E., Weber, M., Frimmel, F.H., 2009. Investigation of the photocatalytic degradation of brown water natural organic matter by size exclusion chromatography. *Appl. Catal. B – Environ.* 87, 56–62.
- Thorn, K.A., Cox, L.G., 2009. N-15 NMR spectra of naturally abundant nitrogen in soil and aquatic natural organic matter samples of the International Humic Substances Society. *Org. Geochem.* 40, 484–499.
- Thurman, E.M., 1985. *Organic Geochemistry of Natural Waters*. Martinus Nijhoff/Dr. W. Junk Publishers, Dordrecht, The Netherlands.
- Thurman, E.M., Malcolm, R.L., 1981. Preparative isolation of aquatic humic substances. *Environ. Sci. Technol.* 15, 463–466.
- Toor, R., Mohseni, M., 2007. UV-H₂O₂ based AOP and its integration with biological activated carbon treatment for DBP reduction in drinking water. *Chemosphere* 66, 2087–2095.
- Tuutijärvi, T., Lu, J., Sillanpää, M., Chen, G., 2009. As(V) adsorption on maghemite nanoparticles. *J. Hazard. Mater.* 166, 1415–1420.
- Uyguner, C.S., Suphandag, S.A., Kerc, A., Bekbolet, M., 2007. Evaluation of adsorption and coagulation characteristics of humic acids preceded by alternative advanced oxidation techniques. *Desalination* 210, 183–193.
- Vilhunen, S.H., Sillanpää, M.E.T., 2009. Ultraviolet light emitting diodes and hydrogen peroxide in the photodegradation of aqueous phenol. *J. Hazard. Mater.* 161, 1530–1534.
- Warton, B., Heitz, A., Allpike, B., Kagi, R., 2008. Size-exclusion chromatography with organic carbon detection using a mass spectrometer. *J. Chromatogr. A* 1207, 186–189.
- Wei, Q., Feng, C., Wang, D., Shi, B., Zhang, L., Wei, Q., Tang, H., 2008. Seasonal variations of chemical and physical characteristics of dissolved organic matter and trihalomethane precursors in a reservoir: a case study. *J. Hazard. Mater.* 150, 257–264.
- Wong, S., Hanna, J.V., King, S., Carroll, T.J., Eldridge, R.J., Dixon, D.R., Bolto, B.A., Hesse, S., Abbt-Braun, G., Frimmel, F.H., 2002. Fractionation of natural organic matter in drinking water and characterization by ^{13}C cross-polarization magic-angle spinning NMR spectroscopy and size exclusion chromatography. *Environ. Sci. Technol.* 36, 3497–3503.
- Worrall, F., Burt, T.P., 2007. Trends in DOC concentration in Great Britain. *J. Hydrol.* 346, 81–92.
- Wu, F.C., Evans, R.D., Dillon, P.J., 2003. Separation and characterization of NOM by high-performance liquid chromatography and on-line three-dimensional excitation emission matrix fluorescence detection. *Environ. Sci. Technol.* 37, 3687–3693.
- Wu, F.C., Evans, R.D., Dillon, P.J., Cai, Y.R., 2007a. Rapid quantification of humic and fulvic acids by HPLC in natural waters. *Appl. Geochem.* 22, 1598–1605.
- Wu, F.C., Kothawala, D.N., Evans, R.D., Dillon, P.J., Cai, Y.R., 2007b. Relationships between DOC concentration, molecular size and fluorescence properties of DOM in a stream. *Appl. Geochem.* 22, 1659–1667.
- Yapsakli, K., Cecen, F., 2009. Use of an enriched inoculum for determination of biodegradable dissolved organic carbon (BDOC) in drinking water. *Water Sci. Technol.* 9 (2), 149–157.
- Zappia, L.R., Alessandrino, M., Garbin, S., Pringle, P., Heitz, A., Joll, C., Masters, D., Hiller, B., Capewell, S., Franzmann, P.D., Plumb, J.J., Von Eckstaedt, S.V., Cadée, K., 2008. Comparison of methods for the determination of biodegradable dissolved organic carbon in potable water supply: use of a novel biofilm. *Water Sci. Technol.* 8 (6), 633–641.
- Zhang, T., Lu, J., Ma, J., Qiang, Z., 2008. Fluorescence spectroscopic characterization of DOM fractions isolated from a filtered river water after ozonation and catalytic ozonation. *Chemosphere* 71, 911–921.
- Zhao, Z.-Y., Gu, D.-J., Li, H.-B., Li, X.-Y., Leung, K.M.-Y., 2009. Disinfection characteristics of the dissolved organic fractions at several stages of a conventional drinking water treatment plant in South China. *J. Hazard. Mater.* 172, 1093–1099.
- Zhou, Q., Cabaniss, S.E., Maurice, P.A., 2000. Considerations in the use of high-pressure size exclusion chromatography (HPSEC) for determining molecular weights of aquatic humic substances. *Water Res.* 34, 3505–3514.
- Zularisam, A.W., Ismail, A.F., Salim, R., 2006. Behaviours of natural organic matter in membrane filtration for surface water treatment – a review. *Desalination* 194, 211–231.