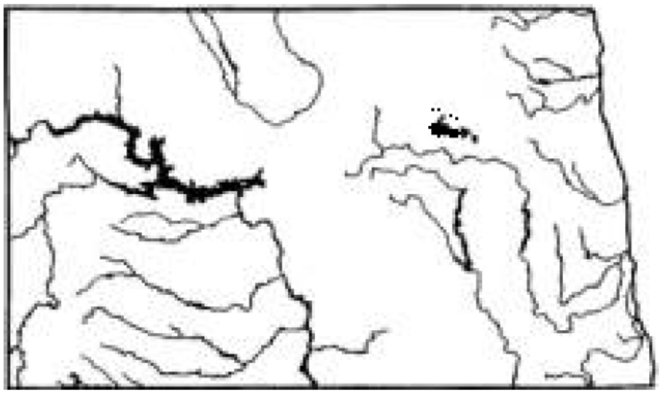

Technical Report No: ND08-03

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ABSTRACT

For the first time, natural organic matter (NOM) in the Red River, MN (RRNOM) and water from the Moorhead Water Treatment Plant (MWTP) were separated into six fractions: hydrophobic acid, hydrophobic base, hydrophobic neutral, hydrophilic acid, hydrophilic base, and hydrophilic neutral. A novel NOM fractionation technique using a series of solid phase extraction cartridges (three Bond Elute® ENV cartridges, one Strata™X-C cartridge, and one Strata™X-AW cartridge) was used. The technique requires only 6 hours of fractionation time, which is much faster than traditional fractionation techniques (24 hours). Hydrophobic acid and hydrophilic neutral were the two major fractions accounted for 36% and 25% of RRNOM, respectively. The six NOM fractions of RRNOM were further characterized using Fourier transformed infrared spectroscopy and solid state ^{13}C nuclear magnetic resonance spectroscopy. The hydrophobic acid and hydrophilic neutral fractions contained mainly carboxylic acids and primary amines, respectively. The fractionation results of finished water at MWTP revealed that hydrophilic neutral fraction was the highest (45% of NOM). This study provides valuable information on NOM composition in the Red River water and efficiencies of treatment units at MWTP for removal of different NOM fractions. With this information, appropriate operational adjustments on treatment processes can be made to minimize problematic NOM fractions that deteriorate drinking water quality.

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BACKGROUND

Natural organic matter (NOM) is commonly found in ground and surface waters. In the drinking water field, the presence of NOM is a concern because it can cause several impacts on water quality and treatment processes. NOM not only creates aesthetic problems such as color, taste and odor but also forms carcinogenic disinfection byproducts (DBP), such as trihalomethanes and haloacetic acids, upon reacting with chlorine. In addition, NOM can lead to other problems, such as increasing coagulant demand, membrane fouling, and bacterial regrowth in the distribution system.

NOM is a broad range of heterogeneous organic compounds derived from the decomposition of plants and animals. The composition of NOM includes humic substances (humic and fulvic acids), low molecular weight (hydrophilic) acids, proteins, carbohydrates, carboxylic acids, amino acids, fats, waxes and hydrocarbons (Thurman, 1985). The reactivity of NOM is closely related to its physicochemical properties such as molecular weight, aromaticity, elemental composition, and functional group content (Maurice et al., 2002). However, it is not well understood due to heterogeneous properties of bulk NOM. To overcome the complexity of NOM, isolation or fractionation is often required in order to obtain more uniform material for further characterization as well as to provide better understanding between NOM properties and its behavior when subjected to treatment processes.

Resin fractionation is one of the techniques used to isolate NOM into different subgroups of compounds that have similar properties. This technique has been used to investigate which NOM fractions have potential to form carcinogenic byproducts (Leenheer et al., 2000; Marhaba and Van, 2000; Buchanan et al., 2006). Furthermore, it has been used to determine the susceptibility of NOM fractions under different treatment processes, such as coagulation (Chow et al., 2004; Sharp et al., 2004), ozonation (Dickenson and Amy, 2000; Świetlik et al., 2004), and UV oxidation/biotreatment (Buchanan et al., 2005). Kwon et al. (2005) have employed a resin fractionation technique to investigate NOM fractions that cause bio-fouling of membranes.

NOM fractions can be operationally defined based on the types of resins used for fractionation. The two traditional and well known protocols for NOM fractionation were developed by Leenheer (1981) and Aiken et al. (1992). The method of Aiken et al. (1992) uses XAD-8 and XAD-4 resins in tandem. This method can only fractionate NOM into three fractions; hydrophobic (retained on XAD-8), transphlilic (retained on XAD-4), and hydrophilic (not retained on both resins). The method developed by Leenheer (1981) can provide more information on NOM fractions by isolating NOM based on polarity and charge into six fractions: hydrophobic acid (HPOA), hydrophobic base (HPOB), hydrophobic neutral (HPON), hydrophilic acid (HPIA), hydrophilic base (HPIB), and hydrophilic neutral (HPIN). It employs three columns separately containing XAD-8 resin, AG-MP-50 resin (cation), and DUOLITE A-7 resin (anion).

During the past decade, the two fractionation methods have been modified by several numbers of researchers to suit their needs (Leenheer et al. 2000; Goslan, 2003; Marhaba et al., 2003; Chow et al. 2004). Therefore, it is difficult to compare the results among different fractionation methods. Although resin fractionation techniques are useful, they all are laborious and time consuming in both resins clean up and fractionation steps. At least 24 hours are required to segregate the six NOM fractions (Leenheer, 1981; Marhaba et al., 2003).

In the past few years, the uses of pre-packed hydrophobic solid phase extraction (SPE) sorbent such as C-18 to isolate NOM have been examined (Kaiser et al., 2003; Kim et al., 2003; Schwede-Thomas et al., 2005). The advantages of this SPE technique include less time consumption and simple setups. However, this current technique can only isolate NOM to hydrophobic and hydrophilic fractions. At present, there is no fractionation protocol using pre-packed sorbents to fractionate NOM into six fractions analogous to the most widely used method of Leenheer (1981). Recently, the fellow and his mentor have developed a new NOM fractionation procedure using pre-packed SPE sorbents to fractionate NOM into six fractions analogous to the methods of Leenheer (1981). With this novel technique, the fractionation time could be reduced to about 6 hours. This report presents the application of the novel SPE technique for fractionating NOM in the Red River. Fourier transform infrared spectroscopy (FTIR) and solid state ^{13}C nuclear magnetic resonance (NMR) were used to characterize the isolated NOM fractions for functional group and carbon structure, respectively. In addition, water samples along a treatment train, that uses the Red River as a raw water source, were fractionated to investigate the removal of each NOM fraction by different treatment units.

DESCRIPTION OF THE CRITICAL STATE OR REGIONAL WATER PROBLEM INVESTIGATED

The Moorhead Water Treatment Plant (MWTP) uses the Red River water as a primary source to produce drinking water for residents of the City of Moorhead, MN. Understanding the characteristic and composition of NOM in the drinking water source is helpful for the identification of the problematic NOM fractions (the NOM fractions that have potential to form carcinogenic disinfection byproducts). Currently, the fractionation and characterization of NOM from the Red River have never been investigated. Total organic carbon (TOC) is used to measure the performance of NOM removal at different treatment stages at MWTP. However, the TOC values of bulk water can only indicate the organic content but do not provide information on the treatability of the different types of organic molecules in NOM. The NOM fractionation could elucidate the effect of water treatment processes at MWTP on NOM composition.

SCOPE AND OBJECTIVES

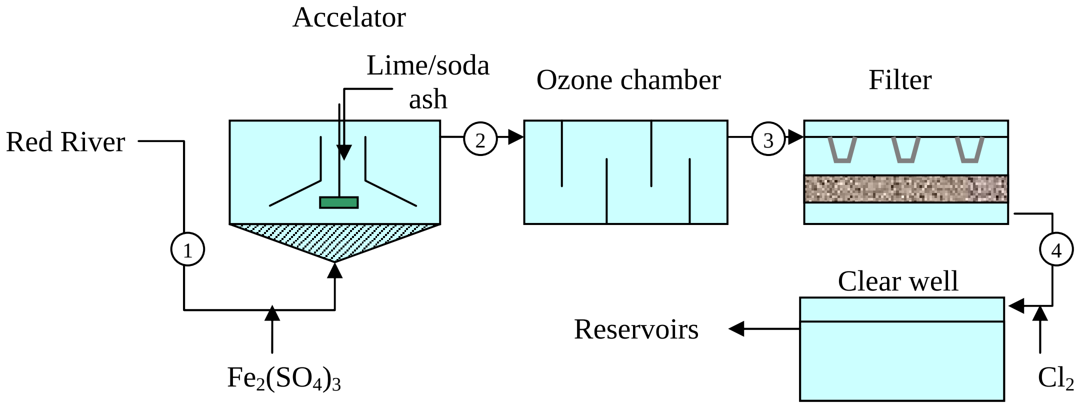
The main scope of this study includes fractionating and characterizing NOM from the Red River, and investigating the removal of each NOM fraction along the treatment train of MWTP. The specific objectives of the study are as follows:

1. To fractionate NOM in water from the Red River;
2. To characterize the isolated NOM fractions by ^{13}C NMR, and FTIR for structural groups, functional groups, respectively; and
3. To investigate the effect of water treatment processes at MWTP on NOM composition.

MATERIALS AND METHODS

Samples

The Red River and three water samples along a treatment train were collected from the MWTP and then filtered through a pre-rinsed GF/C filter and a 0.45 μm cellulose nitrate membrane filter. A schematic diagram of MWTP and the sampling locations are shown in Figure 1.



Sampling locations: 1) Red River, 2) Accelator effluent, 3) Ozone effluent, 4) Filter effluent

Figure 1. Schematic diagram of MWTP and sampling locations.

NOM Fractionation Setup and Procedure

A fractionation procedure was developed to differentiate NOM into six fractions based on polarity and acid/base/neutral properties. The fractionation system consists of three cartridges of Bond Elute® ENV (Varian, Inc., CA, USA), one cartridge of strong cation exchange Strata™X-C (Phenomenex, CA, USA), and one weak anion cartridge Strata™X-AW (Phenomenex, CA, USA) (Figure 2). All cartridges contain one gram of sorbents. The properties of the SPE sorbents are listed in Table 1.

The fractionation procedure is as follows. First, all cartridges are cleaned with 10 mL of methanol (MeOH). Then, Strata™X-C and Strata™X-AW catridges are conditioned with 10 mL of 1 N HCl. Next, all catridges were rinsed with ≥ 1 L of deionized distilled water (DDW) or until dissolved organic carbon (DOC) of the rinsate is less than 0.1 mg/L. One liter of water sample is adjusted to pH 7 and then drawn through the first ENV cartridge. The organic fraction retained in the first column is defined as HPON. Then, the water sample is adjusted to pH 10 using 1 N NaOH and loaded to the second ENV cartridge. The HPOB is captured in this second ENV cartridge. The sample after the second ENV cartridge is adjusted to pH 2 using concentrate H_2SO_4 and drawn through the third ENV cartridge in which HPOA is retained. Next, the water sample is drawn through the Strata™X-C cartridge without pH adjustment. The NOM fraction retained by Strata™X-C is defined as HPIB. The water sample after the Strata™X-C cartridge is adjusted to pH 7 and then drawn through the Strata™X-AW cartridge. The HPIA remains in this cartridge. The organic fraction that is not retained by all five cartridges is considered as HPIN.

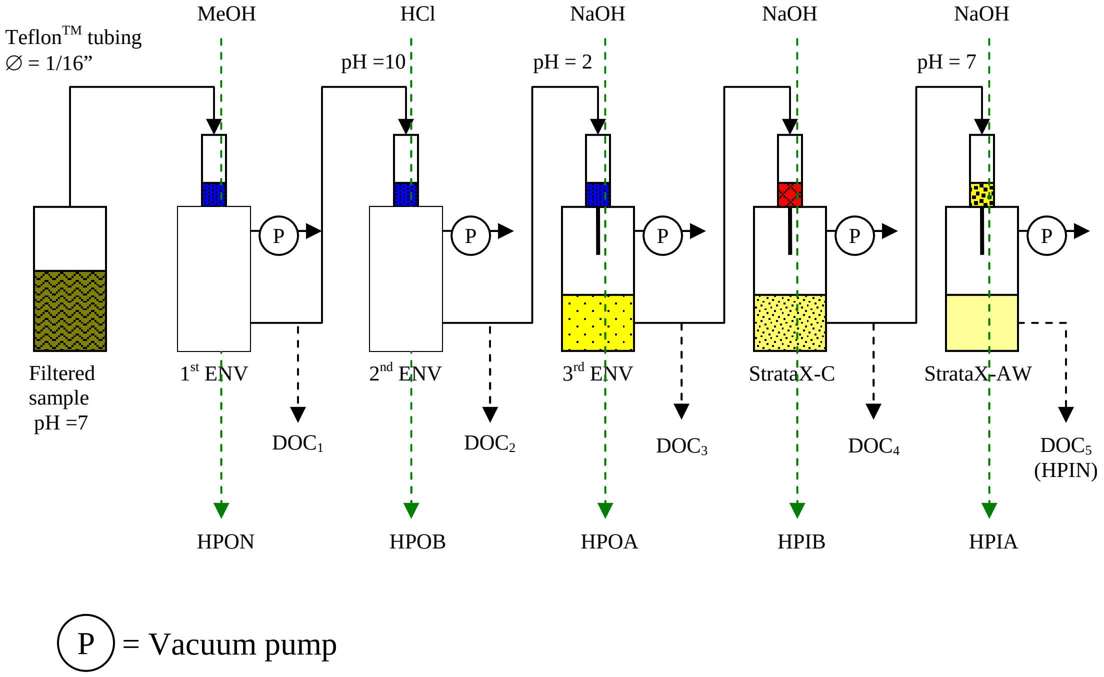


Figure 2. SPE fractionation setup and procedure.

Table 1. Physical properties of SPE sorbents.

Sorbent	**Category**	**Functional group**	**Surface area (m^2/g)**	**Particle size (μm)**	**Mean pore size (Å)**	**pKa**	**Mean capacity (meq/g)**
Bond Elute® ENV	Nonpolar	Styrene divinyl benzene	N/A	125	450	N/A	N/A
Strata™ X-C	Cation exchanger	Benzene sulfonic acid	705-825	31	89	< 1.0	1.1
Strata™ X-AW	Anion exchanger	Primary and secondary amines	705-825	31	88	9.8	0.54

The water sample is drawn through all cartridges under 10 mmHg vacuum pressure. The observed flow rates of water through Bond Elute® ENV, Strata™X-C, and Strata™X-AW are 35, 15, and 45 mL/min, respectively. Forty milliliters of the water samples after passing through each cartridge are collected for DOC analysis. The DOC values of the water sample after passing the first, second, third ENV, Strata™X-C, and Strata™X-AW cartridges are designated as DOC_1, DOC_2, DOC_3, DOC_4, and DOC_5, respectively. The organic carbon content of each fraction is the difference in DOC values before and after each cartridge except the HPIN fraction:

$\text{HPON} = \text{DOC of water sample} - \text{DOC}_1$ (1)
$\text{HPOB} = \text{DOC}_1 - \text{DOC}_2$ (2)
$\text{HPOA} = \text{DOC}_2 - \text{DOC}_3$ (3)
$\text{HPIB} = \text{DOC}_3 - \text{DOC}_4$ (4)
$\text{HPIA} = \text{DOC}_4 - \text{DOC}_5$ (5)
$\text{HPIN} = \text{DOC}_5$ (6)

Effect of NOM Concentration on Capacity of SPE Cartridges

An experiment was carried out to determine whether the capacities of SPE cartridges were exceeded during the fractionation of RRNOM. Different DOC levels of the RRNOM samples were employed. If the organic carbon loading was over capacity of SPE cartridges, a substantial change of the percent distribution of each NOM fraction should be observed. Two DOC concentrations of RRNOM (3.87 and 8.44 mg/L) were fractionated. Note that the two RRNOM concentrations were of diluted and original samples, respectively.

Sample Preparation for FTIR and ^{13}C NMR Characterization

In order to obtain sufficient mass of NOM fractions for solid state ^{13}C NMR, 54 L of RRNOM sample were fractionated (1 L at a time). The NOM fractions sorbed on each cartridge were eluted as follows. The HPON fraction was eluted from the first ENV cartridge using 10 mL of MeOH (JT Baker, HPLC grade, CA, USA). The isolate was evaporated to dryness at 60ºC to remove MeOH (Roubeuf et al., 2000). Next, the residue of HPON was redissolved in DDW. The HPOB fraction in the second ENV cartridge was extracted using 10 mL of 0.1 N HCl. The HPOA, HPIB, and HPIA fractions were eluted from the third ENV, Strata™X-C, and Strata™X-AW, respectively, by using 10 mL of 0.1 N NaOH.

The solutions of HPOA, HPIA and HPIB eluted by NaOH were passed by gravity through AG-MP-50 cation exchange resin to remove sodium. The solution of HPIN was passed through AG-MP-50 cation exchange resin and WA-10 anion exchange resin, respectively. Then solution of all NOM fractions were freeze dried. The amount of AG-MP-50 cation exchange resin (Leenheer, 1981) and WA-10 anion exchange resin (Marhaba et al., 2003) used in this step is described elsewhere. This prevents the formation of sodium bicarbonate (through the reaction between sodium and atmospheric carbon dioxide), which interferes with FTIR spectra (Leenheer, 2007; Cabaniss, 2007), and removes other trace metals that interfere with NMR spectra (Kaiser et al., 2003).

Analytical Methods

DOC was analyzed according to Standard Methods (APHA et al., 1998) using an ultraviolet/persulfate oxidation TOC analyzer (Phoenix 8000, Tekmar Dohrmann, OH, USA). DOC of each sample was measured twice. The TOC analyzer was calibrated according to the instrument manual. Ultraviolet absorbance at 254 nm (UV_{254}) was determined using a spectrophotometer (Genesys^{TM} 10 UV-Vis, Thermo Spectronic, NY, USA). Specific ultraviolet absorbance (SUVA), an indicator of relative unsaturated carbon amount, is determined by dividing UV_{254} by DOC.

The FTIR analysis was performed using a Nicolet 8700 FTIR spectrometer. Freeze dried NOM samples were mixed with potassium bromide at a ratio of 1:100 to form pellets. The data were acquired at a wave number range of 400-4000 cm^{-1} and 100 scans were obtained for each spectrum at a resolution of 4 cm^{-1}.

The samples were characterized by quantitative ^{13}C NMR, using the technique described by Mao et al. (2000). This procedure utilizes direct-polarization magic-angle spinning (DPMAS) at a high rotational speed (13 kHz), combined with a T_1^C correction obtained from a CP/T_1 - TOSS experiment. The recycle delays used for DPMAS were determined for each sample and were between 6 and 10 second. The number of scans recorded ranged between 5,000 and 35,000. The samples were packed in a 4-mm-diameter zirconia rotor with a Kel-F cap. Spectra were acquired at 75 MHz on a Bruker ASX300 spectrometer. The ^{13}C NMR spectra were integrated according to the following chemical shift regions: 0-60 ppm for aliphatic carbon, 60-90 ppm for heteroaliphatic carbon, 90-165 ppm for aromatic carbon, 165-190 ppm for carboxylic carbon, and 190-220 ppm for ketone/quinine (Pomes et al., 2000). The distribution among these major carbon types was calculated by integration using software supplied with spectrometer operating system. It is noted that the spectrum of HPIN was acquired qualitatively and cannot be integrated since the recycle delay time of 1 second was used in which actual spin-lattice relaxation time was not obtained.

RESULTS AND DISCUSSION

NOM Composition of the Red River

The fractionation results of RRNOM are shown in Table 2. The two major fractions of RRNOM were HPOA at 36% and HPIN at 25%. Base fractions (HPOB and HPIB) were small, which was typical for natural waters (Korshin et al., 1997; Marhaba et al., 2000; Świetlik et al., 2004). SUVA < 3 indicates large proportions of nonhumic material (Edward and Van Benschoten, 1990). DOC concentrations did not have much effect on the percent distribution of each NOM fraction. Only small differences were observed. The results indicated that organic carbon loadings were not over the capacities of SPE cartridges.

Table 2. NOM composition of the Red River.

River	DOC (mg/L)	SUVA (L/mg C.m)	Fractions (%) HPOA	HPOB	HPON	HPIA	HPIB	HPIN
Red River	3.87	2.64	36.05	1.79	13.59	20.79	2.72	25.06
	8.44	2.41	35.43	2.59	15.68	17.95	3.44	24.91

Fourier-Transform Infrared Spectra

The FTIR spectra of the NOM fractions of RRNOM are presented in Figures 3. A carboxylic character of NOM was found in the HPOA, HPIA, and HPIB fractions of RRNOM (an O-H band at 3400-3300 cm^{-1} and a C=O band at 1730-1700 cm^{-1}). Primary amines were found in HPOB and HPIN fractions of RRNOM (two peaks of N-H at 3500-3300 cm^{-1}). The HPON fraction mostly consisted of aliphatic alcohols and carbohydrates as shown by a strong O-H band (3400 cm^{-1}), a -CH- band (3000-2800 cm^{-1}), and a C-O band (1150 cm^{-1}).

Solid State ^{13}C Nuclear Magnetic Resonance Spectra

The DPMAS ^{13}C NMR solid state spectra for selected RRNOM samples, and carbon type distribution are shown in Figures 4 Table 3, respectively. The ^{13}C NMR spectra of HPOB and HPIB of RRNOM could be not obtained due to insufficient amounts of solid samples. The HPOA and HPIA fractions mainly consisted of carboxylic acids. The HPOA fraction of RRNOM had a higher percentage of aliphatic carbon than the HPIA fraction while the HPIA fraction was richer in the percentage of carboxylic acids. The spectrum of HPON fraction clearly indicates that this fraction was high in aliphatic carbon (60-0 ppm) and low in carboxylic acid carbon (190-165 ppm). Also, it contained more heteroaliphatic carbon (90-60 ppm) than the HPOA and HPIA fractions. The carbon type of HPON falls into the description of aliphatic alcohol as reported by Świetlik et al. (2004). The HPIN fraction contained high aliphatic carbon. The peak at chemical shift of 55-45 ppm indicates C-N bond which is part of protein compounds.

Removal of NOM fractions in water treatment plant

Figure 5 presents the profile of NOM fractions along the treatment train of MWTP. For Accelator™ (coagulation/softening processes in one unit), the reduction of all NOM fractions was observed. The HPON, HPOA, and HPIA fractions were significantly removed (> 50%), while HPIN fraction was removed only 24%. The lower percent removal of HPIN fraction might be due to its hydrophilicity and less charge density (Carrol et al., 2000). Due to low DOC concentrations of HPOB and HPIB fractions, the reduction of these two fractions was negligible through the entire treatment train.

Ozonation decreased HPON and HPOA fractions by 72% and 34%, respectively but increased HPIA and HPIN fractions by 50% and 28%, respectively. The increases of HPIA and HPIN fractions were due to the transformation of HPOA and HPON fractions, that were oxidized by ozone to become more hydrophilic. This is confirmed by the reduction of SUVA after ozonation because unsaturated aliphatic and/or aromatic compounds tend to be hydrophobic (Dickenson and Amy, 2000). It is likely that the increases of HPIA and HPIN concentrations were from the production of low molecular weight of acids, aldehyde and ketones (Swetlik et al., 2004). Filtration was found to affect HPIN fraction greatly (33% removal) but to cause only small changes for the other five fractions. The removal of HPIN fraction could be from biodegradation. Ozone prior filter could render the filter to be biologically active. The removal of biological dissolved organic carbon (Museus and Khan, 2006) and ozonation byproducts (Hurley, 2001) was observed in the filtration system at MWTP. Small DOC reduction (20%) and a slight change of SUVA suggested that organic compounds removed during filtration were likely nonaromatic.

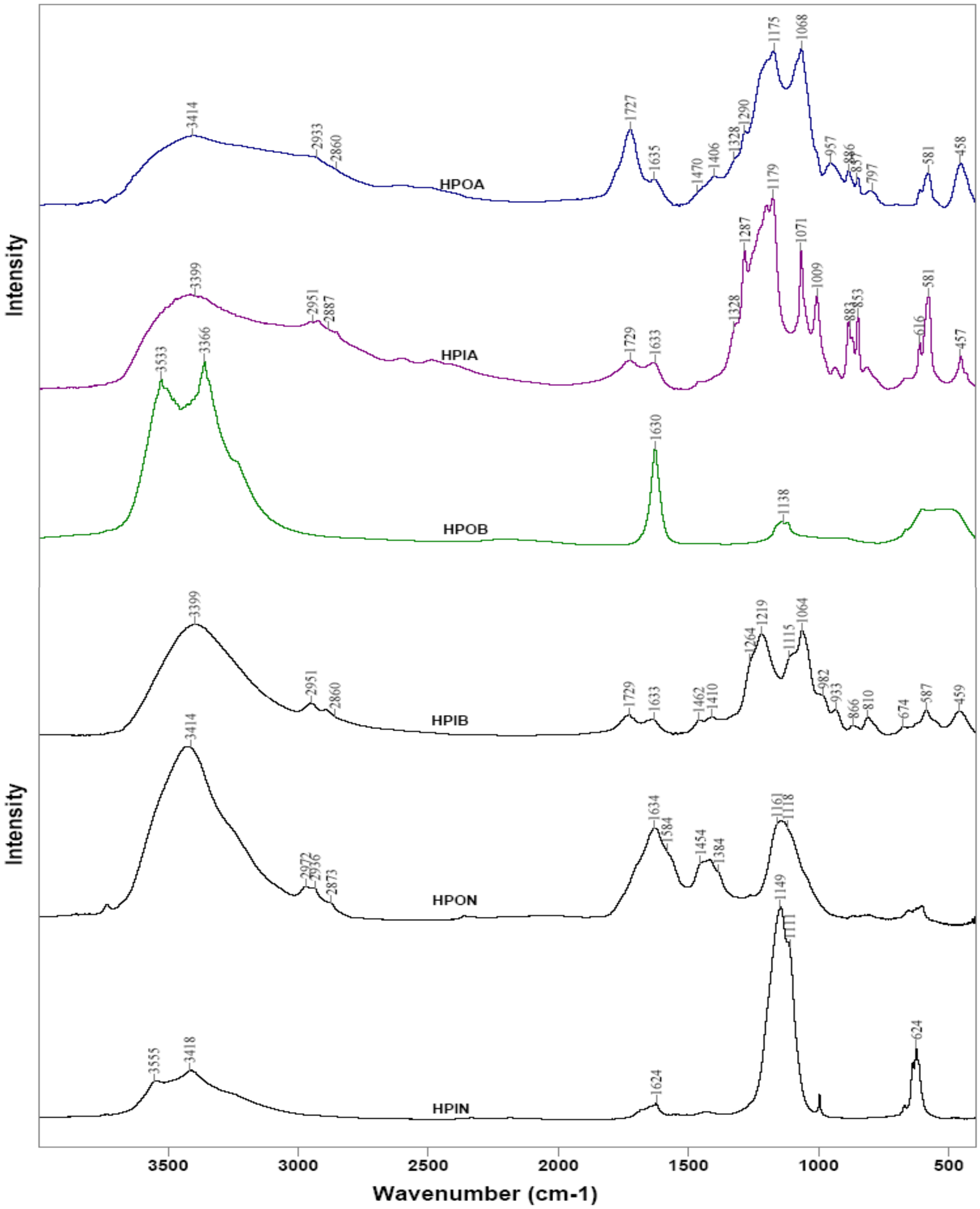


Figure 3. FTIR spectra of NOM fraction from the Red River.

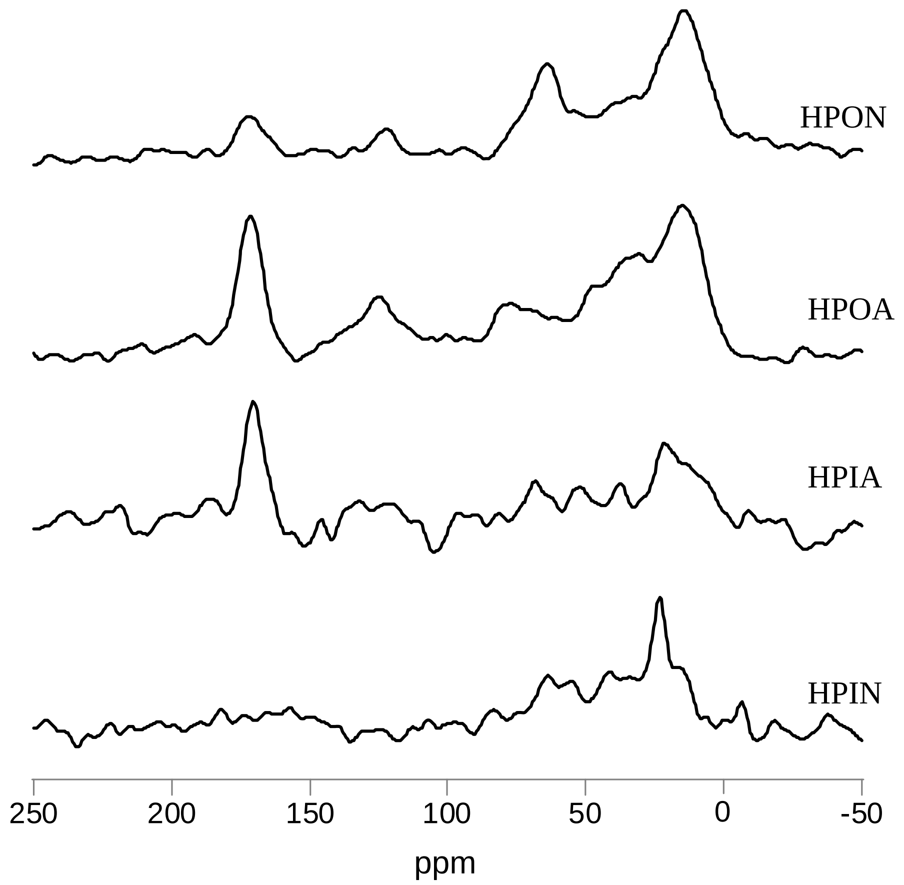


Figure 4. DPMAS ^{13}C NMR spectra of NOM fraction from the Red River.

Table 3. Carbon-type distribution of the Red River NOM (%).

NOM fractions	Ketone/ quinone 220-190 ppm	Carboxylic acid/ ester/amide 190-165 ppm	Aromatic 165-90 ppm	Heteroaliphatic 90-60 ppm	Aliphatic 60-5 ppm
HPOA	0.3	17.4	16.5	11.7	54.1
HPIA	0.5	23.8	18.9	11.7	45.0
HPON	0.2	6.9	8.3	17.9	66.7

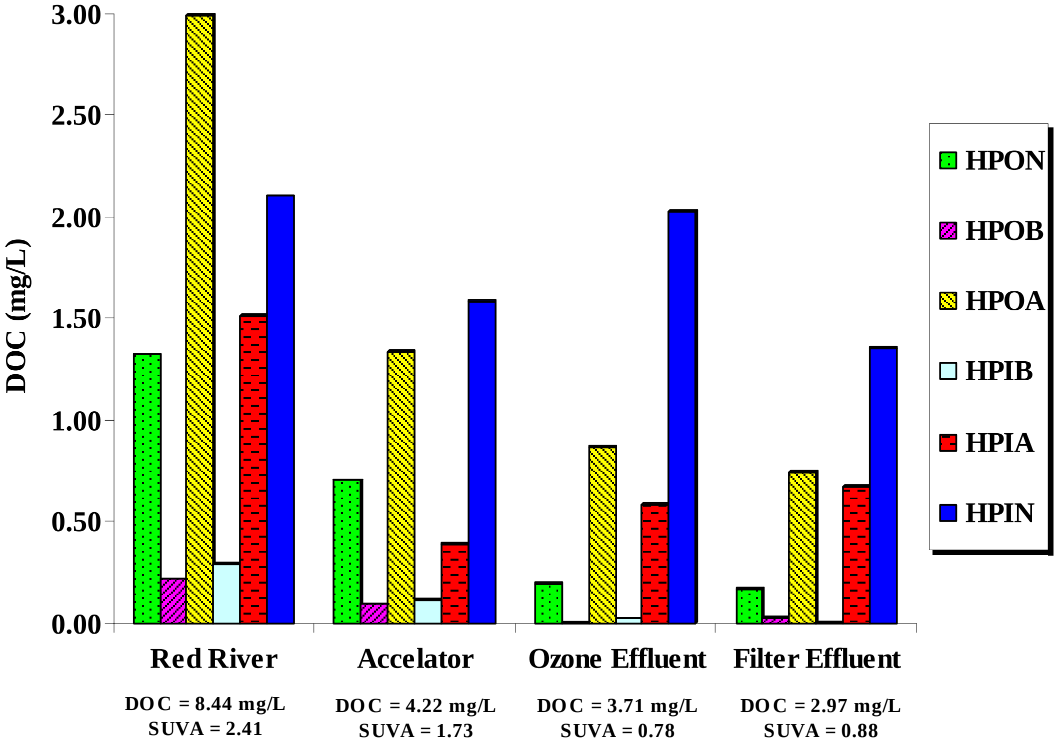


Figure 5. NOM distribution of water samples from MWTP.

CONCLUSIONS

This research investigates NOM fractions from water in the Red River water and Moorhead water treatment plant using a novel rapid NOM fractionation technique. Fourier-transform infrared spectra and ^{13}C NMR results of RRNOM fractions were agreeable and provided insight characteristics of organic constituents of NOM fractions. These results combined with the fractionation results suggested that RRNOM has a variety of organic contents. Approximately 56% of RRNOM was contributed by organic acids while about 40% was from neutral fractions that were made up of carbohydrates, alcohols, aldehydes and ketones. The results of NOM composition at MWTP revealed the treatability of NOM fraction at different treatment stages. Ozonation resulted in increasing HPIA and HPIN fractions. The HPIN, HPOA, and HPIA were the major fractions in water after filtration. It is not known whether or which of these fractions would form carcinogenic byproducts upon reacting with chlorine. A more detailed study is needed to determine chlorination byproduct formation potential of NOM fractions. Then, adjustments in operation of treatment process units can be made to minimize the reactive NOM fractions.

REFERENCES

Aiken, G. R.; McKnight, D. M.; Thorn, K. A.; Thurman, E. M. (1992) Isolation of hydrophilic organic acids from water using nonionic macroporous resins. *Org. Geochem.*, **18** (4), 567-573.

APHA; AWWA; WEF (1998) *Standard Methods for the Examination of Water and Wastewater*. 20th ed.: Washington, D.C.

Buchanan, W.; Roddick F.; Porter, N. (2006) Formation of hazardous by-products resulting from the irradiation of natural organic matter: Comparison between UV and VUV irradiation. *Chemosphere*, **63** (7), 1130-1141.

Buchanan, W.; Roddick, F.; Porter, N.; Drikas, M. (2005) Fractionation of UV and VUV pretreated natural organic matter from drinking water. *Environ. Sci. Technol.*, **39** (12), 4647-4654.

Cabaniss, S. E. (2007) personal communication.

Carroll, T.; King, S.; Gray, S. R.; Bolto, B. A.; Booker, N. A. (2000) The fouling of microfiltration membranes by NOM after coagulation treatment. *Water Res.*, **34** (11), 2861-2868.

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 SRT-AQUA*, **53** (2), 85-92.

Dickenson, E. R. V.; Amy, G. L. (2000) Natural organic matter characterization of clarified waters subjected to advanced bench-scale treatment processes. In *Natural Organic Matter and Disinfection By-Products;* Barrett, S. E., Krasner, S. W., Amy, G. L., Eds.; ACS Symposium Series **761**; American Chemical Society: Washington, DC; pp 122-138.

Edzwald, J. K.; Van Benschoten, J. E. (1990) Aluminum coagulation of natural organic matter. In *Chemical Water and Wastewater Treatment*; Hahn, H. H., Klute, R., Eds.; Springer-Verlag: Berlin; pp 341-359.

Goslan, E. H. (2003) *Natural Organic Matter Character and Reactivity: Assessing Seasonal Variation in a Moorland Water*, Eng. D. Thesis, Cranfield University: Cranfield, U.K**.**

Hurley, S. (2001) *An Investigation of the Disinfection Byproduct Formation and Removal at the Moorhead Water Treatment Plant*. M. Sc. Thesis, North Dakota State University: Fargo, N.D.

Kaiser, E.; Simpson, A. J.; Dria, K. J.; Sulzberger, B.; Hatcher, P. G. (2003) Solid-state and multidimensional solution-state NMR of solid phase extracted and ultrafiltered riverine dissolved organic matter. *Environ. Sci. Technol.*, **37** (13), 2929-2935.

Kim, S.; Simpson, A. J.; Kujawinski, E. B.; Freitas, M. A.; Hatcher, P. G. (2003) High resolution electrospray ionization mass spectrometry and 2D solution NMR for the analysis of DOM extracted by C_{18} solid phase disk. *Org. Geochem.*, **34** (9), 1325-1335.

Korshin, G. V.; Benjamin, M. M.; Sletten, R. S. (1997) Adsorption of natural organic matter (NOM) on iron oxide: effects on NOM composition and formation of organo-halide compounds during chlorination. *Water Res*., **31** (7), 1643-1650.

Kwon, B.; Lee, S.; Cho, J.; Ahn, H.; Lee, D.; Shin, H. S. (2005) Biodegradability, DBP formation, and membrane fouling potential of natural organic matter: Characterization and controllability. *Environ. Sci. Technol.*, **39** (3), 732-739.

Leenheer J. A.; Croué J. P.; Benjamin, M.; Korshin G. V.; Hwang C. J.; Bruchet A.; Aiken G. (2000) Comprehensive isolation of natural organic matter for spectral characterization and reactivity testing. In *Natural Organic Matter and Disinfection By-Products*; Barrett, S. E., Krasner, S. W., Amy, G. L., Eds.; ACS Symposium Series **761**; American Chemical Society: Washington, DC; pp 68-83.

Leenheer, 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.

Leenheer, J.A. (2007) personal communication.

Mao, J. D., Hu, W. G., Schmidt-Rohr, K., Davies, G., Ghabbour, E. A., and Xing, B. (2000) Quantitative Characterization Of Humic Substances By Solid-State Carbon-13 Nuclear Magnetic Resonance. *Soil Sci. Soc. Am. J.* **64**, 873-884.

Marhaba, T. F.; Pu, Y.; Bengraine, K. (2003) Modified dissolved organic matter fractionation technique for natural water. *J. Hazard. Mater.*, **101** (1), 43-53.

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** (3), 249-266.

Marhaba, T. F.; Van, D. (2000) The variation of mass and disinfection by-product formation potential of dissolved organic matter fractions along a conventional surface water treatment plant. *J. Hazard. Mater.*, **74** (3), 133-147.

Maurice, P. A.; Pullin, M. J.; Cabaniss, S. E.; Zhou, Q.; Namjesnik-Dejanovic, K.; Aiken, G. R. (2002). A comparison of surface water natural organic matter in raw filtered water samples, XAD, and reverse osmosis isolates. *Water Res.*, **36** (9), 2357-2371

Museus, T.; Khan, E. (2006) *A study of microbial regrowth potential of water in Fargo, North Dakota and Moorhead, Minnesota*; North Dakota Water Resources Research Institute Technical Report No. ND06-01; North Dakota State University: Fargo, N.D.

Pomes, M. L.; Larive, C. K.; Thurman, E. M.; Green, W. R.; Orem, W. H.; Rostad, C. E.; Coplen, T. B.; Cutak, B. J.; Dixon, A. M. (2000) Sources and haloacetic acid/trihalomethane formation potentials of aquatic humic substances in the Wakarusa River and Clinton Lake near Lawrence, Kansas. *Environ. Sci. Technol.*, **34** (20), 4278-4286.

Roubeuf, V.; Mounier, S.; Benaim, J. Y. (2000) Solid phase extraction applied to natural waters: Efficiency and selectivity. *Org. Geochem.*, **31** (1), 127-131.

Schwede-Thomas, S. B.; Chin, Y. P.; Dria, K. J.; Hatcher, P.; Kaiser, E.; Sulzberger, B. (2005) Characterizing the properties of dissolved organic matter isolated by XAD and C-18 solid phase extraction and ultrafiltration. *Aquatic Sci.*, **67** (1), 61-71.

Sharp, E. L.; Parsons, S. A.; Jefferson, B. (2004) The effects of changing NOM composition and characteristics on coagulation performance, optimisation and control. *Water Sci. Technol.: Water Supply*, **4** (4), 95-102.

Świetlik, J.; Dąbrowska, A.; Raczyk-Stanisławiak, U.; Nawrocki, J. (2004) Reactivity of natural organic matter fractions with chlorine dioxide and ozone. *Water Res.*, **38** (3), 547-558.

Thurman, E. M. (1985) *Organic Geochemistry of Natural Waters,* Martinus Nijhoff/Dr. W. Junk Publishers: Dordrecth, Netherlands.