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Characterizing Ohio River NOM Variability and Reconstituted-Lyophilized NOM as a Source Surrogate

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Abstract

Natural organic matter (NOM) was collected, concentrated, and lyophilized on a monthly basis for 15 months to create a temporal NOM library and assess seasonal variability of untreated Ohio River water. Using fluorescence spectroscopy with parallel factor analysis, similar spectral components for both the ultrafiltered source water (UF1X) and reconstituted lyophilized NOM were observed in a two-component model throughout the study, with overall average emission and excitation wavelengths of 418 nm and 270 nm, respectively, for component 1 and 482 nm and 370 nm, respectively, for component 2. Fluorescence spectroscopy, high-pressure liquid chromatography–size exclusion chromatography, and elemental analysis indicated that the NOM was humic-like during the study with only small seasonal changes. Data from these analyses also demonstrated similarity between results for UF1X, reverse osmosis–concentrated NOM, and reconstituted- lyophilized NOM, validating the use of the reconstituted- lyophilized NOM as a surrogate for its source.

Keywords

fluorescence; humic; lyophilization; NOM; reverse osmosis; TOC

Drinking water sources contain natural organic matter (NOM), a complex mixture of organic material produced by animals, plant life, soils, and effluent from industrial and public services. NOM chemistry, concentration, and structure vary over time and are heavily dependent on biological sources and surrounding soil (Leenheer & Croue 2003). Surrogates

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ENDNOTES

have been used to more easily quantify and characterize NOM; these commonly include odor, taste, total organic carbon (TOC), and ultraviolet light absorbance at 254 nm (UV₂₅₄) (Thurman 1985). Seasonal changes can be observed by characterizing source water NOM over periods of time using common surrogates and additional advanced techniques that include flow field-flow fractionation (Baalousha & Lead 2007), high-performance liquid chromatography (HPLC) (Her et al. 2002), elemental analysis (Maurice et al. 2002), fluorescence spectroscopy (Pifer et al. 2011), molecular weight fractionation (Hua & Reckhow 2007), and nuclear magnetic resonance (Aiken et al. 1992). In addition to studying the seasonal changes in NOM, a standardized library of concentrated NOM, which would be beneficial to drinking water and health effects studies, can be created and characterized using these various surrogate methods.

Reverse osmosis (RO) is one technique capable of producing highly concentrated, aqueous NOM whole mixtures advantageous for drinking water and toxicological research (Perdue & Ritchie 2003). Previous drinking water-related research efforts used UV₂₅₄ and TOC surrogates for NOM characterization in addition to evaluating whole mixtures of disinfection by-products (DBPs) in RO-concentrated NOM (Pressman et al. 2010). However, the limited shelf-life of aqueous NOM samples hinders research efforts because the organic matter degrades over time and must be produced before each research effort, adding to the time and complexity of experimentation. Shelf-life and NOM degradation issues in aqueous concentrate can be overcome by lyophilization (freeze drying), which produces a solid that can last for decades and is easier to store and ship for analysis purposes (Koprivnjak et al. 2006). The lyophilization process removes the remaining water from concentrated NOM, resulting in a solid that can be easily reconstituted back to an aqueous state (McCurry et al. 2012). Lyophilization and reconstitution methods were developed for concentrated NOM resulting in 101% TOC and 91% UV₂₅₄ recovery (McCurry et al. 2012). Subsequently, the DBPs formed from chlorinating concentrated and lyophilized- reconstituted NOM were shown to be representative compared with the DBPs formed in the original source water, which promoted the creation of a standardized library of solid NOM for drinking water research (Pressman et al. 2012). However, despite these advances in NOM research, there is a lack of advanced seasonal characterization of RO-concentrated NOM beyond UV₂₅₄ and TOC surrogates. Techniques such as fluorescence spectroscopy, HPLC, and elemental analysis would not only add to the robustness of TOC and UV₂₅₄ characterization of source water NOM, but also further validate the RO concentration, lyophilization, and reconstitution processes by characterizing NOM after each treatment stage. Changes in NOM characterization, along with potential losses due to NOM fractionation, may be evident using more advanced characterization methods.

Using previously developed methods for NOM concentration and lyophilization, a library of drinking-water-relevant lyophilized solid can be created. Such a library of well-characterized NOM from all seasons and conditions, including weather events that a treatment plant may experience, would be beneficial to the drinking water industry. The library would allow treatment and removal studies to be conducted in order to modify treatment processes for seasonal conditions as well as conduct health-related DBP research (Narotsky et al. 2013). In another example, research is ongoing for using a lyophilized NOM source for benchmarking granular activated carbon (GAC) evaluations with various GAC sources.

Furthermore, extending the library to additional water sources would allow the drinking water industry to compare treatment technologies across multiple standardized water sources. However, neither a temporal nor a multi-source, drinking-water-relevant NOM library has yet been created.

The primary objectives of this research were to create a library of lyophilized NOM collected monthly from the Ohio River for at least one year and to characterize the NOM library using methods including fluorescence spectroscopy with parallel factor analysis (PARAFAC), high-performance liquid chromatography–size exclusion chromatography (HPLC–SEC), and elemental analysis in addition to UV₂₅₄ and TOC surrogates. The characterization techniques will allow for the observation of seasonal variations in the source water NOM along with the validation of RO concentration, lyophilization, and reconstitution processing of NOM compared with the source water NOM for the creation of the NOM library.

MATERIALS AND METHODS

Ultrafiltered source water (UF1X) and RO concentrate collection.

Ohio River NOM was concentrated approximately one week per month starting April 2010 through July 2011 in Cincinnati, Ohio. Raw water was processed through a 200- μ m cloth bag filter, ultra-filtration (two ceramic 0.02- μ m membranes¹), cation exchange resin columns (hydrogen-form²), and RO (three membranes in series³) following previously established methods (Pressman et al. 2010). The RO equipment was operated such that an approximate 165 $\times$ volumetric concentration factor was maintained throughout NOM concentration that resulted in an approximate 150 $\times$ UV₂₅₄ and TOC concentration factor. Water quality analyses were conducted for raw source water, UF1X, ion exchange effluent, RO concentrate, and the effluents of the three RO membrane permeates. These included hourly UV₂₅₄ analyses as well as TOC, ion chromatography (IC), and inductively coupled plasma (ICP) samples collected every 5 h of operation; these were sufficient to assess potential changes in source water and RO concentrate during field collection (Pressman et al. 2010).

UF1X and RO concentrate storage and post-processing.

Approximately 150 L of RO concentrate was collected each month and stored in high-density polyethylene (HDPE) carboys⁴ at 4°C for approximately four days until post-processing. UF1X was collected in small 1.0-L aliquots every 5 h and batched into a 20-L HDPE carboy⁴ that was stored at 4°C for subsequent analysis. The batched UF1X represented conditions throughout the period of concentrated NOM collection. Sulfate in the raw water was concentrated within the RO system along with the NOM. Dissolved sulfate negatively affects lyophilization by producing an NOM solid mixed with sulfuric acid (Pressman et al. 2010, Koprivnjak et al. 2006); therefore, sulfate was removed via

¹19P37–30 Membralox 0.02- μ m, Pall Corp., Port Washington, N.Y.

²Ambersep 200H hydrogen-form, Rohm and Hass, Philadelphia, Pa.

³Filmtec BW30–4040, Dow, Midland, Mich.

⁴Nalgene Thermo Fisher Scientific, Waltham, Mass.

precipitation with barium chloride (BaCl_2).⁵ A 0.86 molar ratio of barium to sulfate (Ba^{2+} to SO_4^{2-}) was used to avoid over-applying barium in the first precipitation stage when sulfate concentrations were highest and required dilution to perform analytical analysis. TOC, IC, and UV_{254} samples were collected after precipitation for subsequent analysis. The supernatant was stored in 33-gal HDPE drums,⁶ and the precipitated barium sulfate solid was discarded. Each month required two or three precipitation stages to remove sulfate to a target concentration of 10 mg/L in the RO concentrate. After the first stage, subsequent BaCl_2 precipitation stages used a 1:1 Ba^{2+} to SO_4^{2-} molar ratio because the lower sulfate concentrations allowed direct analytical measurement without dilution and resulted in greater analytical accuracy and precision. RO concentrate was filtered with pre-rinsed, 0.45- μm cartridge filters⁷ and stored at 4°C in a 33-gal HDPE drum for four to six weeks until lyophilization. IC, ICP, TOC, fluorescence, and UV_{254} samples were collected after the final stage of precipitation and filtration.

Concentrate lyophilization and reconstitution.

RO concentrate was then lyophilized in a pilot-scale freeze dryer⁸ following a previously developed procedure (McCurry et al. 2012). Solid NOM was collected and stored in amber glass bottles, one for each month, in a light-free cabinet along with silica gel packets to absorb excess moisture. Lyophilized NOM was reconstituted for experiments with ultra-pure deionized water ($r = 18 \text{ M}\Omega\text{-cm}$), pH adjusted to 10 with 6 N sodium hydroxide (NaOH)⁹ and mixed for a 24-h period (McCurry et al. 2012). The resulting liquid was filtered with pre-rinsed, 0.45- μm polyethersulfone (PES) disc filters.¹⁰ The volumetric mass-to-volume ratio from lyophilization was used to determine the amount of NOM solid to mix with ultra-pure water. TOC, ICP, UV_{254} , fluorescence, and HPLC samples were collected after reconstitution and filtration.

Water quality parameters, measurement procedures, and instrumentation.

UV_{254} was measured following Method 5910 for UV- absorbing organic constituents (*Standard Methods* 2012) with a UV spectrophotometer.¹¹ ICP analysis was conducted using an inductively coupled plasma optical emission spectrometer¹² according to US Environmental Protection Agency (USEPA) method 200.7 (USEPA 1994). TOC was analyzed following USEPA method 415.3 (USEPA 2005) using a combustion catalytic TOC analyzer.¹³ The TOC is representative of dissolved organic carbon (DOC) because all samples are taken after ultrafiltration (0.02 μm) or filtration with cartridge/PES disc filters (0.45 μm). IC analysis was performed using an optical ion chromatography instrument¹⁴ according to USEPA method 300.1 (USEPA 1997). HPLC–SEC was conducted with a chromatography oven,¹⁵ an absorbance detector set to UV_{254} ,¹⁶ an 8- μm column,¹⁷ a gel

⁵Certified ACS, Thermo Fisher Scientific, Waltham, Mass.

⁶Thermo Fisher Scientific, Waltham, Mass.

⁷AquaPrep 600, Pall Corp., Port Washington, N.Y.

⁸VirTis Virtual EL, SP Industries, Warminster, Pa.

⁹N.I.S.T. Traceable, Aqua Solutions, Deer Park, Tex.

¹⁰Supor-450 PES, Pall Life Sciences, Port Washington, N.Y.

¹¹Nicolet Evolution 300, Thermo Fisher Scientific, Waltham, Mass.

¹²iCAP 6000 spectrometer, Thermo Fisher Scientific, Waltham, Mass.

¹³TOC-Vcph, Shimadzu Corp., Columbia, Md.

¹⁴Metrohm-Peak 761 IC, Metrohm-USA, Riverview, Fla.

filtration standard,¹⁸ and a mobile phase (0.01 M potassium phosphate and 0.025 M sodium sulfate pH adjusted to 7.5 with NaOH at a flow rate of 1 mL/min. Elemental analysis was conducted by Huffman Laboratories Inc. (Golden, Colo.).

Fluorescence spectroscopy was conducted using a fluorometer¹⁹ with excitation wavelengths of 240–450 nm (5-nm step), emission wavelengths of 300–600 nm (2-nm step), and a 5-nm slit width for both aspects. Preliminary fluorescence analysis was conducted using smaller step increments with larger wavelength ranges and varying slit widths (data not shown). These expanded settings did not reveal additional component locations and required significantly longer measurements times (approximately 3 h/sample versus 30 min/sample). The settings used for fluorescence measurements were the best compromise between excitation–emission matrix (EEM) resolution and time. Fluorescence data were corrected for sample UV absorbance, Raman integration, Rayleigh scattering removal, and instrumentation settings, and peak EEM intensities were normalized by sample TOC concentrations using mathematical software²⁰ and the FDOMcorr toolbox (Murphy et al. 2010). Following data corrections, PARAFAC was used to analyze the data and compare corrected fluorescence EEMs. PARAFAC implements a series of EEMs modeled after the source multi-way data. The model with the lowest error was selected and illustrated the locations of peaks within a set of EEMs, which were then used to characterize the NOM. PARAFAC analysis was conducted according to a previously established method using the DOMFluor toolbox (Stedmon & Bro 2008) for the mathematical software. The analysis included split-half validation in which individual EEMs were randomly split into four separate data sets. Model component locations for the emission and excitation wavelengths were mathematically compared by the toolbox using Tucker congruence coefficients, as demonstrated by Lorenzo-Seva and Berge (2006), to the four split data sets. The toolbox then identified whether a model was validated against the randomly split sets of EEMs. Visual comparisons of the model component locations, against the corrected EEMs, were generated by the toolbox and used as a secondary validation.

Preliminary fluorescence evaluation showed that TOC concentration and concentrate pH had no effect on peak locations within corrected EEMs (data not shown), although there were minimal saturation effects in areas around the peak locations in samples with higher TOC concentrations. Thus, all RO concentrate and reconstituted NOM samples were volumetrically diluted to approximate UF1X concentrations and were pH adjusted to match the UF1X prior to fluorescence analysis. Fundamentally, 1 mL of RO concentrate or reconstituted NOM was added to 164 mL of ultra-pure water, adhering to the average RO volumetric concentration factor of 165×. TOC samples were analyzed after dilution, and the fluorescence EEM peak intensities were corrected for the TOC dilution factor. The corrected fluorescence EEMs were analyzed for 15 months of UF1X as one sample set, RO concentrate as one sample set, reconstituted NOM as one sample set, and as a combined

¹⁵Dionex LC30, Thermo Fisher Scientific, Waltham, Mass.

¹⁶Dionex AD20, Thermo Fisher Scientific, Waltham, Mass.

¹⁷PL aquagel-OH 30, Agilent Technologies, Santa Clara, Calif.

¹⁸Bio-Rad Laboratories, Hercules, Calif.

¹⁹Fluorolog3, HORIBA Instruments Inc., Edison, N.J.

²⁰MATLAB Release 2011b, The Mathworks Inc., Natick, Mass.

sample set using PARAFAC. The corrected EEMs of the UF1X for each month were further analyzed using manual peak picking in order to observe seasonal variations in source NOM. Corrected EEMs produced by the FDOMcorr toolbox were exported into individual spreadsheets for the manual peak picking process.

RESULTS AND DISCUSSION

Initial water quality parameters were measured in the UF1X and RO concentrate (Table 1). TOC recovery during concentration with RO varied from 87 to 100% on a month-to-month basis, and UV₂₅₄ recovery, during concentration with RO, varied from 97 to 99%, which is typical of concentrating NOM through RO (Pressman et al. 2010, Perdue & Ritchie 2003). While concentration factors varied for both TOC and UV₂₅₄ for the RO concentrate (Table 1), the average concentration factor following barium precipitation for both TOC and UV₂₅₄ over the course of the study was 130×. Comparing UV₂₅₄ and TOC, the concentration factors for TOC were slightly higher following RO but were the same after barium precipitation because of small differences in the losses between RO and barium precipitation. These small differential losses have not resulted in measurable effects in previous studies, and the overall TOC and UV₂₅₄ losses were typical of those observed in previous studies (McCurry et al. 2012, Pressman et al. 2010). As expected, silicon and sulfate were concentrated with RO in addition to the source NOM (McCurry et al. 2012). Barium precipitation reduced sulfate in the concentrate to 4.97–60.33 mg/L, acceptable levels for lyophilization, and silicon was decreased after lyophilization and reconstitution to 3.00–58.14 mg/L across the duration of the study. Higher than expected concentrations of some metals were detected and may be explained by possible leaching of metals from the concentration or barium mixing systems and/or non-ideal dilutions during inductively coupled plasma-atomic emission spectroscopy (ICP–AES) analysis (McCurry et al. 2012).

Figure 1 shows seasonal variations for the TOC in both the UF1X and the post-barium precipitated RO concentrate (Figure 1, part A) in addition to similar variations for UV₂₅₄ (Figure 1, part B). The TOC and UV₂₅₄ in both the UF1X and RO concentrate generally decreased during the winter season (December 2010–March 2011) and increased in the spring until peaking in the summer (July 2010–August 2010). Notable exceptions include April 2010 shortly following late-March precipitation and May 2010 in which NOM was concentrated during precipitation events. Samples were not collected in June 2011 because of resource limitations.

Fluorescence spectroscopy was used to characterize the NOM with principle components produced by PARAFAC analysis. The collected NOM was assessed in four groups: 15 months of UF1X, 15 months of RO concentrate, 15 months of reconstituted NOM, and all three sources combined as one sample set. Figure 2 shows that the PARAFAC analysis of the fluorescence EEMs revealed two peak components for the UF1X (Figure 2, part A), RO concentrate (Figure 2, part B), reconstituted material across 15 months of collection (Figure 2, part C), and for the composite sample (Figure 2, part D). Multiple PARAFAC models, with one to 10 components, were constructed by the DOMFluor toolbox. Models with three or more components failed split-half validation and were not representative of the source fluorescence data. The sub-peak in component 2 of the sample sets (at approximately 270

nm excitation and 490 nm emission) was not segregated as a third individual component but rather part of component 2. Table 2 suggests that the two components are in similar locations for the separate groups of NOM and the composite sample. Thus, concentrating NOM with RO, lyophilizing the resulting aqueous solution, and reconstituting the solid material does not appear to alter the NOM character with respect to the PARAFAC components. Because of the similar peak locations for the UF1X, RO concentrate, and reconstituted NOM, all three NOM sources were analyzed as one sample set using PARAFAC. The same two principle components were observed, resulting in the same characterization of the NOM when all sets were analyzed together (Figure 2, part D and Table 2).

Both components identified in the PARAFAC analysis are representative of humic-like NOM, falling within the range of excitation and emission wavelengths of previously analyzed humic acids and humic-like NOM (Hall & Kenny 2007). The locations of the components indicate the predominance of humic acid-like organics in the Ohio River, a primary constituent of soil (Stevenson 1994). Component 1 is further classified as UV humic-like because the peak falls between previously identified excitation and emission ranges for UV humic-like NOM (Stedmon et al. 2003). Component 2 expressed a longer emission wavelength compared with component 1, for every sample, suggesting that it contains slightly more conjugated fluorescence molecules (Cory & McKnight 2005). Component 2 is additionally characterized as visible humic-like NOM (Stedmon et al. 2003), which contains an excitation peak in the visible light region. In comparing the fluorescence components of RO concentrate and reconstituted NOM with that of the UF1X water, the similarity suggested performance of lyophilized NOM in drinking water research would be analogous to the source NOM. Thus, the addition of fluorescence spectroscopy added an important new characterization tool to those previously used (i.e., TOC, UV₂₅₄, DBP formation) with these lyophilized and reconstituted materials (McCurry et al. 2012; Pressman et al. 2012, 2010).

Figure 3 presents several EEM regions developed for NOM characterization resulting from the analysis of various fluorescent compounds including humic and fulvic acids, proteins, and microbial by-products (Chen et al. 2003). Superimposing the principle components of the Ohio River NOM on Figure 3 showed that both components are within Region V, which has been identified as being humic acid-like. The locations of components 1 and 2 are correlated to allochthonous, soil-influenced NOM (Coble & Timperman 1998, Mopper & Schultz 1993). Biological sources, such as microorganisms, do not appear to be significant components of these Ohio River NOM samples because of the lack of peaks found in Regions I, II, and IV. Rather, the samples in this research appear primarily influenced by the soil and decay of organic material within the riverbed and surrounding watershed.

Additional analysis was performed on the fluorescence EEMs to calculate the fluorescence index (FI) and the humification index (HI) for the UF1X, RO concentrate, and reconstituted NOM from each month. The HI correlates to dissolved organic matter (DOM) characterization based on the humic levels of the organic content (Ohno 2002) and was calculated using corrected fluorescence intensities (*I*) at a single excitation wavelength of 254 nm and multiple emission wavelengths:

$$HI = \frac{\sum I_{435 \rightarrow 480}}{\sum I_{300 \rightarrow 345} + I_{435 \rightarrow 480}} \quad (1)$$

Figure 4 represents the HI (Figure 4, part A) and FI (Figure 4, part B) for the monthly samples of the UF1X, RO concentrate, and reconstituted NOM. The HI values for the three sources of NOM during the study range from 0.80 to 0.89 (Figure 4, part A) and correlate to previously established HI data for humic-like NOM (Ohno 2002). Small variations occurred in the HI data that may possibly be due to seasonal variations. The FI is a ratio of corrected fluorescence intensities at 370 nm:450 nm and 370 nm:500 nm (excitation:emission) and correlates to DOC organic aromaticity (McKnight et al. 2001). The FI values for the UF1X, RO concentrate, and reconstituted NOM ranged from 1.44 to 1.57 (Figure 4, part B). These small fluctuations, generally not considered significant (Johnson et al. 2011), indicated little sequential variability in the DOC of the UF1X, which agreed with earlier results from PARAFAC analysis of the UF1X EEMs. Additionally, the FI range observed in the study compared well with previous FI data for predominantly allochthonous, terrestrially derived organic matter from second-order or larger streams (noting the Ohio River is an eighth-order stream) (Johnson et al. 2011, McKnight et al. 2001). The fluctuations in both the HI and FI data generally followed the same trend in the UF1X, RO concentrate, and reconstituted NOM, demonstrating that the concentration, lyophilization, and reconstitution processes have little effect on the fluorescence characterization of the NOM.

To evaluate the potential for seasonal variation in the fluorescence response on a month-to-month basis, manual peak picking was used with corrected UF1X EEMs for each month. Figure 5 shows the locations of the monthly excitation and emission peaks. As with the PARAFAC analysis, there were two peaks observed in each sample. Overall, the excitation location for peak 1 ranged from 260 to 270 nm while the emission location for peak 1 ranged from 410 to 425 nm. The peak 2 excitation location ranged from 360 to 380 nm, and the emission location from 462 to 488 nm. These fluorescence excitation and emission values were remarkably similar to those determined in the PARAFAC analysis, resulting in similar findings on the humic nature of the samples. Observation of the minimal variability in the excitation/emission peaks over the 15 months of samples does not seem seasonal in nature because such trends are not apparent in the data.

HPLC–SEC analysis was conducted for UF1X and reconstituted NOM from the 15-month collection period. Figure 6 shows two sets of HPLC–SEC elution time graphs for the UF1X and reconstituted NOM. One single peak was observed for both the UF1X (Figure 6, part A) and reconstituted NOM (Figure 6, part B) starting at around 8 min of elution time and ending at 10 min for all months. While a second minor peak is visible in the reconstituted NOM at around 10 min (Figure 6, part B), this peak was correlated to a change in pressure and volume caused by the instrument feed pump and is not believed to reflect a separate peak. The HPLC–SEC pump experienced issues providing constant steady pressure/volume through the gel column and UV₂₅₄ detector, specifically around the 10-min mark when the sample volume was expended, which resulted in the elevated UV readings. Changes in pressure/volume were more visible with the reconstituted NOM because the TOC and

UV₂₅₄ were approximately 150× that of the UF1X. The similarity between the 15 months of UF1X and reconstituted NOM data shows that any potential NOM losses that may have occurred during RO concentration, post-processing, lyophilization, and reconstitution did not target specific NOM size fractions but rather the NOM as a whole mixture. Knowing that potential losses through processing do not appear to create new NOM size distributions or affect the overall NOM size distribution is an important result that enables future uses of the freeze-dried materials as standardized sources representing the original UF1X source.

The lyophilized solid NOM collected during the 15-month period was analyzed using elemental analysis as shown in Table 3. All values are reported as percentages and were corrected using lab-measured oxygen content. Small monthly variations in the composition of the NOM are evident in the amounts of measured carbon, hydrogen, nitrogen, oxygen, and sulfur. The carbon composition of the lyophilized-concentrated NOM varied between 49 and 57% with an average of 53% across the 15 months of collection. These values agree well with Ohio River elemental analysis carbon data reported by Metz et al. (2012) (50–53%) and Westerhoff et al. (1998) (55.5%). The composition of oxygen was between 35 and 41% with an average of 37%, which also agreed with previous analysis by Westerhoff et al. (1998) (35.9%). Furthermore, the oxygen-to-carbon ratios (0.62–0.84) were within range of previously identified freshwater humic-like soil-based NOM (Rice & MacCarthy 1991). The resulting characterization of the NOM from elemental analysis compared well with results from the other characterization methods described earlier in this article.

The NOM was overwhelmingly described as humic-like and allochthonously influenced with small fluctuations in the data parameters observed during different months, possibly due to seasonal variability. Over the course of the study, the humic-like NOM characterization did not change following RO concentration, sulfate removal, lyophilization, and reconstitution. The lyophilized-reconstituted NOM compared closely with the source UF1X and RO concentrated NOM by all of the methods applied in this research. The characterization results developed in this research, combined with previous research efforts (McCurry et al. 2012, Pressman et al. 2012), validated the lyophilized-reconstituted NOM compared with the original source, allowing the use of the temporal NOM library as a standardized source for benchmarking drinking water research. With these results, the NOM from this 15-month library may now be shared with other researchers in the water industry.

CONCLUSIONS

The general humic-like characterization of the Ohio River did not change during the 15-month study. Peak positions within corrected fluorescence EEMs, component locations from PARAFAC analysis, the FI and HI values, HPLC–SEC data, and elemental analysis indicated that the NOM was humic-like throughout the study. Small NOM variability was evident in the TOC, UV₂₅₄, elemental analysis, FI and HI values, and HPLC–SEC peaks. However, these small fluctuations were not sufficient to change the overall NOM character, and only limited seasonality was observed in some parameters, including TOC and UV₂₅₄.

Overall, RO concentrate and lyophilized-reconstituted NOM compared closely with the source UF1X in all measured parameters. Responses in fluorescence spectroscopy and the

NOM size distribution as measured with HPLC–SEC were remarkably similar. Adding these new techniques to previous methods (i.e., TOC, UV₂₅₄, DBP formation) for validating that lyophilized-reconstituted NOM remains similar to its source provided additional evidence that any losses in NOM appear to affect the entire mixture, as opposed to specific fractions. A unique library of Ohio River NOM was created over 15 months. The temporal collection of well-characterized, standardized Ohio River NOM is the first of its kind and is expected to benefit drinking water treatment and research studies. Pending funding, future research will characterize and expand the NOM library to multiple drinking water sources.

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FIGURE 1.

TOC (A) and UV₂₅₄ (B) for the RO concentrate (post-barium precipitation) and UF1X during the 15-month study. RO—reverse osmosis, TOC—total organic carbon, UF1X—ultrafiltered source water, UV₂₅₄—ultraviolet light absorbance at 254 nm. Concentrate values are on the left ordinate and UF1X values are on the right ordinate for both panels. Concentrate axes approximately normalized by the average concentration factor (130×) compared to UF1X axes.

FIGURE 2.

Principle component EEMs for the UF1X (A), RO concentrate (B), reconstituted NOM (C), and all three sources analyzed as one data set (D) produced by PARAFAC EEMs—excitation-emission matrixes, NOM—natural organic matter, PARAFAC—parallel factor analysis, RO—reverse osmosis, TOC—total organic carbon, UF1X—ultrafiltered source water

All samples were pH adjusted to match the UF1X for each month and normalized by TOC concentration. The dark-red centers of the EEMs represent the locations of each principle component. The secondary peak in the EEMs for component 2 is not a principle component and is therefore ignored.

FIGURE 3.

The locations of each component from the single data set (all sources) analysis illustrated in previously established EEM regions^a

EEM: excitation-emission matrix, Region I-aromatic protein, Region II-aromatic protein II, Region III-fulvic acid-like, Region IV-soluble microbial by-product like, Region V-humic acid-like

The excitation range extends down to 200 nm to show Regions I-III even though peaks were not detected below 260 nm in this research.

^a Adapted from Chen et al. 2003

FIGURE 4.

Humification index (A) and fluorescence index (B) results for the UF1X, RO concentrate, and reconstituted NOM over the 15-month study. NOM—natural organic matter, RO—reverse osmosis, UF1X—ultrafiltered source water

FIGURE 5.

Locations of the two peaks in corrected EEMs for individual months. EEMs-excitation-emission matrixes

Figure 6.

High-performance liquid chromatography with UV₂₅₄ detection for the UF1X (A) and reconstituted NOM (B). NOM—natural organic matter, TOC—total organic carbon, UF1X—ultrafiltered source water. All reconstituted NOM samples were pH adjusted to match respective UF1X levels. The TOC of the reconstituted NOM is approximately 150× that of the UF1X; it was not diluted to 1× conditions for analysis.

TABLE 1.

Initial water quality parameters (minimum–maximum) for the UF1X and concentrate over 15 months

	UF1X	RO Concentrate
pH	7.0–7.7	1.0–1.7
UV ₂₅₄ — <i>cm⁻¹</i>	0.044–0.086	5.75–10.4
UV ₂₅₄ concentration factor	—	118–145
Average UV ₂₅₄ RO recovery—%	—	97–99
TOC— <i>mg/L</i>	1.77 – 2.86	260–499
TOC concentration factor	—	122–178
Average TOC RO recovery—%	—	87–100
Aluminum— <i>mg/L</i>	<0.004–0.012	0.001–2.87
Antimony— <i>mg/L</i>	<0.003–0.020	<0.003–0.315
Arsenic— <i>mg/L</i>	<0.004–0.019	<0.004–0.599
Barium— <i>mg/L</i>	0.029–0.070	<0.001–0.047
Beryllium— <i>mg/L</i>	<0.005	<0.005–0.011
Cadmium— <i>mg/L</i>	<0.001	<0.001–0.035
Calcium— <i>mg/L</i>	19.0–44.0	<0.010–7.39
Copper— <i>mg/L</i>	0.020–0.128	0.001–0.168
Iron— <i>mg/L</i>	<0.001–0.650	0.008–6.31
Lead— <i>mg/L</i>	<0.002	<0.002–0.129
Lithium— <i>mg/L</i>	<0.005–0.010	<0.005–0.369
Magnesium— <i>mg/L</i>	5.85–14.9	<0.005–0.646
Manganese— <i>mg/L</i>	<0.001–0.020	<0.001–0.064
Nickel— <i>mg/L</i>	<0.001–0.002	0.001–0.902
Phosphorus— <i>mg/L</i>	0.010–0.030	0.042–4.84
Potassium— <i>mg/L</i>	1.37–3.91	<0.300–4.80
Sodium— <i>mg/L</i>	9.40–44.9	<0.03–16.0
Sulfate— <i>mg/L</i>	10.5–114	4,980–13,200 ^a
Silicon— <i>mg/L</i>	0.060–2.93	118–423 ^b
Tin— <i>mg/L</i>	<0.001–0.004	<0.001–0.254
Zinc— <i>mg/L</i>	<0.001–0.004	<0.001–0.307

RO- reverse osmosis, TOC—total organic carbon, UF1X—ultrafiltered source water, UV₂₅₄- ultraviolet light absorbance at 254 nm

Dashes indicate parameters that are not relevant in UF1X.

^a After barium precipitation, sulfate range in the concentrate was 4.97– 60.33 mg/L.^b After reconstitution of lyophilized NOM, silicon was reduced to 3.00–58.14 mg/L.

TABLE 2.

Principle components for each NOM source and all sources analyzed as a single data set

Sources	Component 1		Component 2	
	Emission <i>nm</i>	Excitation <i>nm</i>	Emission <i>nm</i>	Excitation <i>nm</i>
UF1X	418	270	482	370
RO concentrate	416	275	482	365
Reconstituted NOM	416	275	482	375
All sources	418	270	482	370

NOM—natural organic matter, RO—reverse osmosis, UF1X—ultrafiltered source water

TABLE 3.

Elemental analysis of the lyophilized NOM solid

Sample Date ^a	Composition—%					O:C Ratio
	C	H	N	O	S	
April 2010	49	5.2	2.7	41	2.1	0.84
May 2010	57	4.4	2.2	35	1.5	0.62
June 2010	51	4.3	3.0	39	2.2	0.76
July 2010	52	4.0	2.8	39	2.4	0.74
August 2010	55	4.0	2.9	36	2.0	0.66
September 2010	52	4.2	3.1	35	2.9	0.63
October 2010	54	4.5	3.2	35	2.8	0.66
November 2010	54	4.4	3.4	35	2.8	0.65
December 2010	54	5.2	2.5	37	1.5	0.67
January 2011	50	5.0	2.9	38	3.5	0.76
February 2011	53	5.3	2.5	37	2.2	0.69
March 2011	52	4.6	2.5	39	2.7	0.75
April 2011	53	5.6	2.4	38	2.0	0.71
May 2011	54	4.7	2.9	36	1.9	0.62
July 2011	55	4.1	3.1	36	2.5	0.84

C—carbon, H—hydrogen, N—nitrogen, NOM—natural organic matter, O—oxygen, S—sulfur

All values are corrected for dry conditions and adjusted using measured oxygen.

^a Samples were not collected in June 2011 because of resource limitations.