The impact of alum coagulation on pharmaceutically active compounds, endocrine disrupting compounds and natural organic matter
Sabrina Diemert and Robert C. Andrews

ABSTRACT
This study assessed the impact of chemical coagulation using alum on the removal of three endocrine-disrupting compounds (EDCs; bisphenol A, clofibric acid and estriol) and nine pharmaceutically active compounds (PhACs; acetaminophen, carbamazepine, diclofenac, gemfibrozil, ketoprofen, naproxen, pentoxifylline, sulfamethoxazole and sulfachloropyridazine). The impact on natural organic matter (NOM) fractions as determined using liquid chromatography–organic carbon detection (LC–OCD; total dissolved organic carbon (DOC), hydrophobic DOC, biopolymers, humic substances, building blocks, low molecular weight neutrals and acids) was also examined. Three test surface waters were included: Lake Ontario, Grand River and Otonabee River water (Ontario, Canada). Gemfibrozil concentrations were reduced in both Otonabee and Grand River waters. Reductions were noted for carbamazepine and (inconsistently) for acetaminophen, and estrone appeared to increase in concentration in Grand River water with increasing alum doses. NOM removal was primarily attributed to the humic fraction, with small reductions in biopolymers in all of the waters studied.

Key words | coagulation, drinking water treatment, endocrine disrupting compounds, LC–OCD, natural organic matter, pharmaceuticals

INTRODUCTION
Environmental levels of many pharmaceutically active compounds (PhACs) and endocrine-disrupting compounds (EDCs) are currently unregulated, but their presence in source waters used by drinking water treatment plants (Kleywegt et al. 2011) has piqued public interest. Additionally, a number of these compounds have been recommended for inclusion in future environmental regulations in the United States (USEPA 2009); thus, it is prudent to evaluate the performance of low-cost water treatment processes for their EDC/PhAC removal efficiency, such as chemical coagulation.

Coagulation is a common unit process used in conventional drinking water treatment to reduce natural organic matter (NOM). Aluminum sulfate (alum) is the most commonly used chemical coagulant (Matilainen et al. 2010). While NOM removal performance is well documented for coagulation (Edzwald & Tobias 1999; Matilainen et al. 2010), questions still remain regarding its EDC/PhAC removal efficiency. Previous studies of conventional treatment involving bench-, pilot-, and full-scale tests indicate that the effect of coagulation on PhAC/EDC removal varies, with removal often falling below 50% (Ternes et al. 2002; Carballa et al. 2005; Vieno et al. 2006; Thuy et al. 2008; Huerta-Fontela et al. 2011). The current hypothesis that EDC/PhACs are removed during coagulation by first adsorbing or complexing with NOM in the raw water, which then interacts with the coagulants has been supported in several investigations (Ballard & MacKay 2005; Westerhoff et al. 2005; Vieno et al. 2006; Thuy et al. 2008). As such, the extent of EDC/PhAC removal is affected by the
quantity of NOM in source waters. However, little research has been conducted to link NOM characteristics (size or chemical attributes) with EDC/PhAC removal. Additionally, NOM is a complex mixture of organic chemicals and its composition varies widely between source waters and seasons (Sharp et al. 2006). Therefore, the present study aimed to investigate the impact of the chemical characteristics of NOM on the removal of organic micropollutants during coagulation.

New analytical techniques can provide detailed information regarding NOM characteristics. Liquid chromatography–organic carbon detection (LC–OCD) provides quantitative measurements of NOM, both as a total dissolved organic carbon (DOC) value and as fractions based on size and chemical properties. These fractions are comprised of hydrophobic DOC (compounds which are retained on the size exclusion chromatographic (SEC) column) and five hydrophilic DOC fractions: biopolymers (polysaccharides, proteins and colloids), humic substances, building blocks (fragments of humic substances), low molecular weight (LMW) organic acids and low molecular weight neutrals (alcohols, aldehydes, ketones, sugars, amino acids). Additionally, this technique provides information regarding the molecular weight and aromaticity of the humic substances via an ultraviolet (UV) detector (Huber et al. 2011). The application of LC–OCD to monitor NOM chemical characteristic changes during coagulation for EDC/PhAC removal has not been previously reported in the literature.

The objective of this study was to explore the links between EDC/PhAC removal and NOM fraction changes during coagulation, which can provide more information on the interactions between NOM and emerging micropollutants. To investigate concurrent NOM and EDC/PhAC removal, trials were conducted using replicated experimental design incorporating jar tests to model coagulation at bench-scale. NOM and EDC/PhAC removal with the addition of alum was examined in three different source waters to treatment facilities in Canada. NOM in raw and coagulated water was characterized using LC–OCD. Concentrations of EDCs and PhACs were analyzed using a solid-phase extraction procedure followed with liquid chromatography/ion trap mass spectrometry (LC/MS/MS).

METHODS

Analytical methods

Three EDCs (bisphenol A, clofibric acid and estriol) and nine PhACs (acetaminophen, carbamazepine, diclofenac, gemfibrozil, ketoprofen, naproxen, pentoxifylline, sulfamethoxazole and sulfachloropyridazine) were selected for the alum study and analyzed via LC/MS/MS. These compounds were chosen due to their occurrence in source and treated waters, their potential health effects, and their wide range of physical and chemical characteristics such as size, solubility, hydrophobicity, charge and acidity (Table 1). Estriol is currently being considered for regulation in the USEPA’s Contaminant Candidate List 3 (USEPA 2009). Additionally, all compounds excluding pentoxifylline and estriol have been recently detected in at least one Canadian source or treated drinking water sample, with maximum concentrations between 2 ng/L (sulfamethoxazole) to 749 ng/L (carbamazepine) (Kleywegt et al. 2011). EDCs and PhACs were extracted (using solid-phase extraction techniques) and analyzed by a method based on the Ontario Ministry of the Environment (MOE) method EOP-E3454, version 2.0 (MOE 2008). Analyses were conducted at the University of Toronto using a Varian 212 LC and 500-MS (Agilent Technologies, Mississauga, ON). The LC was equipped with a Metaguard Pursuit guard column (2.0 mm) and Pursuit XRs Ultra 2.8 C18 analytical column (100 × 2.0 mm) (Agilent Technologies, Mississauga, ON). Neat standards were purchased from Sigma-Aldrich Inc. (Oakville, ON), surrogates (d4-acetaminophen, d10-carbamazepine, d4-clofibric acid, d4-gemfibrozil, d7-naproxen) and internal standards (d16-bisphenol A for negative mode, 13C6-sulfamethazine phenyl for positive mode) were purchased from CDN Isotopes (Pointe-Claire, QC). Refer to Supplementary Information for method detail (available online at http://www.iwaponline.com/ws/013/145.pdf).

NOM components were analyzed at the University of Waterloo, ON, Canada, using LC–OCD. The system is described in detail by Huber et al. (2011). Briefly, samples are filtered via an inline 0.45 μm PES filter (Sartorius, Germany, #16557) and then enter a SEC column (250 mm × 250 mm, TSK HW 50S, 300 theoretical plates, Tosoh, Japan). After
chromatographic separation, the sample enters a UV detector (UVD 254 nm, type S-200, Knauer, Berlin, Germany) followed by an organic carbon detector (OCD). DOC is determined via a bypass stream diverted around the column. The DOC which does not elute from the column is calculated as the hydrophobic DOC. Proprietary software was used for data acquisition and processing (ChromCalc, DOC-LABOR, Karlsruhe, Germany).

UV absorbance at 254 nm (UV254) was determined using a CE 3055 Single Beam Cecil UV/Visible Spectrophotometer (Cambridge, UK) with a 1 cm quartz cells (Hewlett Packard, Mississauga). Specific UV absorbance at 254 nm, or SUVA, is calculated using the UV254 value (multiplied by a factor of 100) divided by the DOC value of the water (mg/L). pH was measured using a pH meter Model 8015 (VWR International, West Chester, PA).

**Bench-scale experiments**

Single batches of raw, untreated water were collected between October 3 and December 6, 2011 from three water utilities in Ontario, Canada: Lake Ontario water from Ajax Water Supply Plant (Ajax, ON), Otonabee River water from the Peterborough Water Treatment Plant (Peterborough, ON) and Grand River water from Mannheim Water Treatment Plant (Waterloo, ON). These waters may potentially be impacted by wastewater and rainfall. They were chosen as test matrices as they collectively serve as sources for drinking water for millions of consumers and represent a range of organic carbon types, SUVA content and alkalinities.

For each test, raw water equilibrated to room temperature (22 °C) was spiked to a nominal concentration of 1,000 ng/L EDCs/PhACs using an acetonitrile-based solution (50 μg each EDC/PhAC per mL acetonitrile; this solvent-based EDC/PhAC solution was used for ease and precision of spiking and for increased stability of the analytes). Following a 24 hour mixing period, the water was divided in 2 L aliquots into acrylic square jars (Phipps and Bird, VA). Alum was dosed into individual jars, and jar testing was conducted using a PB-700 Standard Jar Tester paddle stirrer (Phipps and Bird, VA): water samples were subjected to 90 seconds of rapid mixing.

**Table 1**  PhACs and EDCs analyzed via LC/MS/MS

<table>
<thead>
<tr>
<th>Compound (Formula)</th>
<th>Classification</th>
<th>Molecular weight (g/mol)</th>
<th>Water solubility (g/L)abc</th>
<th>Log $K_{ow}$</th>
<th>Log $D_{ow}$ @ pH 8abc</th>
<th>$pK_a$</th>
<th>MDL (ng/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetaminophen (C₈H₉NO₂)</td>
<td>PhAC (NSAID/antipyretic)</td>
<td>151</td>
<td>15</td>
<td>0.48</td>
<td>0.47</td>
<td>9.86</td>
<td>62</td>
</tr>
<tr>
<td>Bisphenol A; BPA (C₁₅H₁₆O₂)</td>
<td>EDC (plasticizer)</td>
<td>228</td>
<td>0.071</td>
<td>3.64</td>
<td>3.64</td>
<td>10.29</td>
<td>37</td>
</tr>
<tr>
<td>Carbamazepine (C₁₅H₁₂N₂O)</td>
<td>PhAC (antiepileptic)</td>
<td>236</td>
<td>0.022</td>
<td>1.89</td>
<td>1.89</td>
<td>13.94</td>
<td>10</td>
</tr>
<tr>
<td>Clofibric acid (C₁₀H₁₁ClO₃)</td>
<td>EDC (herbicide)</td>
<td>214</td>
<td>100</td>
<td>2.43</td>
<td>2.43</td>
<td>3.18</td>
<td>46</td>
</tr>
<tr>
<td>Diclofenac (C₁₂H₁₂Cl₂NO₂)</td>
<td>PhAC (NSAID)</td>
<td>296</td>
<td>2.3</td>
<td>4.55</td>
<td>4.55</td>
<td>4.18</td>
<td>66</td>
</tr>
<tr>
<td>Estriol (C₁₈H₂₄O₃)</td>
<td>EDC (natural hormone)</td>
<td>288</td>
<td>0.029</td>
<td>2.53</td>
<td>2.53</td>
<td>10.25</td>
<td>49</td>
</tr>
<tr>
<td>Gemfibrozil (C₁₅H₂₂O₃)</td>
<td>PhAC (lipid regulator)</td>
<td>250</td>
<td>11</td>
<td>4.30</td>
<td>4.30</td>
<td>4.75</td>
<td>41</td>
</tr>
<tr>
<td>Ketoprofen (C₁₆H₁₄O₃)</td>
<td>PhAC (NSAID)</td>
<td>254</td>
<td>5.8</td>
<td>2.91</td>
<td>2.91</td>
<td>4.23</td>
<td>26</td>
</tr>
<tr>
<td>Naproxen (C₁₄H₁₂O₃)</td>
<td>PhAC (NSAID)</td>
<td>230</td>
<td>1.5</td>
<td>2.88</td>
<td>2.88</td>
<td>4.84</td>
<td>23</td>
</tr>
<tr>
<td>Pentoxifylline (C₁₂H₁₈N₄O₃)</td>
<td>PhAC (vasodilator)</td>
<td>278</td>
<td>9.2</td>
<td>0.15</td>
<td>0.15</td>
<td>0.50d</td>
<td>9</td>
</tr>
<tr>
<td>Sulfamethoxazole (C₁₀H₁₁N₃O₃S)</td>
<td>PhAC (antibiotic)</td>
<td>253</td>
<td>2.8</td>
<td>0.66</td>
<td>0.66</td>
<td>5.81</td>
<td>15</td>
</tr>
<tr>
<td>Sulfachloropyridazine (C₁₀H₉ClN₄O₂S)</td>
<td>PhAC (antibiotic)</td>
<td>285</td>
<td>22</td>
<td>0.68</td>
<td>0.68</td>
<td>5.90</td>
<td>19</td>
</tr>
</tbody>
</table>

bWater solubility at pH 7, 25 °C.
c$\text{p}K_a$ refers to acid $\leftrightarrow$ conjugate base (AH $\leftrightarrow$ A$^-$$+$$H^+$) unless indicated (Snoeyink & Jenkins 1980).
d$\text{p}K_a$ for these compounds refers to conjugate acid $\leftrightarrow$ base (AH$^+$ $\leftrightarrow$ A$^-$$+$$H^+$).
$\log K_{ow}$ = Octanol-water partition coefficient (neutral species only).
$\log D_{ow}$ = Octanol-water partition coefficient (ionized and neutral species).
NSAID = Non-steroidal anti-inflammatory drugs.
$\text{p}K_a$ = Acid dissociation constant.

MDL = Method Detection Limit (determined by multiplying the standard deviation of 7 replicates in Milli-Q®, prepared in the same order of magnitude as the expected MDL (50–100 ng/L) by the single-sided Student’s t-test at a significance level of 0.01 (99% confidence level).
Coagulant doses were chosen based on total organic carbon (TOC) reduction targets as described in the USEPA Enhanced Coagulation Guidelines (USEPA 1999), based on the organic carbon content and alkalinity of the water. DOC reduction was targeted instead of TOC reduction; jar tests are appropriate for assessing the chemistry of coagulation using DOC as it is independent of scale, while TOC concentrations may be impacted by scale-dependent factors such as settling (Edzwald & Tobaison 1999). Additionally, since LC-OCD analysis requires 0.45 μm filtering, DOC was tracked over coagulation for consistency. To select the coagulant dose, first the DOC reduction targets were chosen for each water type according to the raw water alkalinity and DOC, as dictated by the Enhanced Coagulation Guidelines (USEPA 1999). Next, preliminary tests were run in which the test waters were subjected to jar tests with a range of alum doses. The alum dose that attained the targeted DOC reduction was determined from the jar test results and selected as the ‘target alum dose’. Subsequent alum doses were chosen as ±20%, and ±40% from the ‘target alum dose’ to provide a reasonable variation of operational conditions within a treatment plant.

The pH was not controlled in this study in order to simulate typical treatment conditions; most conventional water treatment plants only control pH through the dosage of the coagulant, and thus this will vary according to the dose and type of coagulant. Even when a target pH is selected, this is generally to depress the pH to a more optimal range for coagulation, rather than to hold the pH constant throughout the coagulation process (Budd et al. 2004).

A separate two-way analysis of variance (ANOVA) was applied to experimental results to assess the effects of alum and acetonitrile concentration on the response factors; this was done to screen for potential effects of the acetonitrile solvent used to spike the EDCs/PhACs into the raw waters. None of the EDCs or PhACs were significantly affected by the acetonitrile concentration, while LMW neutrals and hydrophobic DOC were shown to increase with the addition of the solvent. It was concluded that acetonitrile does not significantly affect coagulation processes, as the NOM fractions it affected appear to play no significant role during coagulation (i.e. alum dose does not have a significant impact on their concentrations). Refer to the Supplementary Information for more data on these tests (available online at http://www.iwaponline.com/ws/013/145.pdf).

### Statistical analysis

A statistical ANOVA was applied at a confidence level of 99% to determine if the alum dose had a significant effect on the response factors (EDC, PhAC, or individual NOM fractions). ANOVA calculations and experimental design were completed using statistical software Design Expert 8.0.7.1 (Minneapolis, MN). See Supplementary Information for details regarding ANOVA calculations (available online at http://www.iwaponline.com/ws/013/145.pdf). A higher level of confidence was chosen (99%) in order to minimize Type I errors. This allows for some flexibility due to noise in EDC/PhAC measurement, and better allows for identification of physically significant trends as opposed to random variation in analytical detection. While this has the effect of decreasing the power of the experiment and increasing the probability of Type II errors, this was considered a lesser priority for the present study.

As ANOVA testing only indicates which response variables are significantly affected by alum dose but provides no insight into trends, Tukey’s Honestly Significant Difference (HSD) post-hoc test, was applied after the ANOVAs were calculated. In the HSD test, all sample means are compared pairwise to determine which sets of samples vary significantly from each other (Sokal & Rohlf 1995). The Tukey HSD was applied to the EDCs, PhACs and NOM fractions for which alum dose was identified as significant through the one-way ANOVA. HSD at 95% confidence is calculated as:

\[
HSD = Q_{0.05, k, df} \sqrt{\frac{MSE}{n}}
\]

where \( Q \) = the studentized range critical value (Sokal & Rohlf 1995), \( k \) = number of factor levels (6), \( df \) = degrees of freedom for error (obtained from Design Expert), \( n \) = number of replicates in means (for EDCs/PhACs and pH \( n = 3 \), for NOM \( n = 2 \)), \( MSE \) = mean squared error (obtained from Design Expert).

The response variable means can be plotted with the 95% confidence intervals as error bars (calculated as \( \frac{1}{2} \) HSD); any points that do not have overlapping error bars.
are significantly different. This test allows for determination of the type of effect that alum has on the response factors.

RESULTS AND DISCUSSION

Water quality

Water quality characteristics are listed in Table 2. For all waters, the DOC values comprised $>95\%$ of the total organic material measured as TOC. The three waters exhibit very different NOM fraction compositions. Lake Ontario is an example of a water with low DOC (<2 mg/L) and SUVA (<2 L/mg C/m), technically falling below requirements for USEPA’s treatment guidelines as prescribed by the Disinfection Stage 1 Rules (USEPA 1999). As such, coagulation is not required nor expected to remove large amounts of organic carbon. This hypothesis is additionally supported by its low concentration of humic substances (0.81 mg/L); this NOM fraction is generally well removed in coagulation (Huber et al. 2011), and water with lower concentrations of humic substances is less amenable to coagulation (Chow et al. 2008). It was included in the study as an example of a ‘low DOC and SUVA’ water and its DOC reduction target (25%) was chosen by ‘rounding up’ the raw water DOC value to 2 mg/L.

Otonabee River and Grand River waters have very similar DOC levels. However, the Grand River has a higher SUVA (3.36 compared to Otonabee River’s 2.05) indicating the higher hydrophobic NOM character (Edzwald & Tobiason 1999). A measure of unsaturation in the humic fraction only (in contrast with the overall SUVA, which considers all types of DOC) is reflected in the humic SUVA value, calculated as the specific UV absorbance at 254 nm for the humic peak (detected using the LC-UVD), divided by the humic substance concentration (detected using the LC–OCD). Lake Ontario water has a low humic SUVA (<2 mg/L), indicating that the humics present in the water are likely to be more hydrophilic in character compared to the river waters, which both have higher humic aromaticity (3.70 and 4.09 for Otonabee and Grand River water, respectively) (Huber et al. 2011).

It should be noted that the hydrophobic DOC fraction refers to organic matter which is retained on the SEC column in the LC–OCD or not eluted within the run time (120 minutes); thus, while the content is considered hydrophobic in relation to the column resin, it is not of the same character as resin-fractionated hydrophobic NOM reported in other characterization studies (such as Sharp et al. 2006)). Additionally, this fraction tends to be detected with low precision (see Supplementary Information, available online at http://www.iwaponline.com/wst/013/145.pdf) and is often ignored during investigations (Haberkamp et al. 2007; Baghoth et al. 2009).

NOM, EDC and PhAC concentration changes over coagulation

The compounds which were identified as being significantly affected by alum (using ANOVA) are listed as follows. The degree of significance for each factor is demonstrated by the $p$-value: for example, a compound with a $p$-value ($p$) of

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Lake Ontario</th>
<th>Otonabee River</th>
<th>Grand River</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>8.2</td>
<td>8.0</td>
<td>8.1</td>
</tr>
<tr>
<td>DOC (mg/L)</td>
<td>1.89</td>
<td>6.12</td>
<td>6.21</td>
</tr>
<tr>
<td>TOC (mg/L)</td>
<td>1.92</td>
<td>6.20</td>
<td>6.48</td>
</tr>
<tr>
<td>Alkalinity (mg/L as CaCO₃)</td>
<td>116</td>
<td>100</td>
<td>260</td>
</tr>
<tr>
<td>SUVA (L/mg DOC/m)</td>
<td>1.09</td>
<td>2.05</td>
<td>3.36</td>
</tr>
<tr>
<td>Hydrophobic DOC (mg/L)</td>
<td>0.15</td>
<td>0.80</td>
<td>0.35</td>
</tr>
<tr>
<td>Biopolymers (mg/L)</td>
<td>0.20</td>
<td>0.53</td>
<td>0.28</td>
</tr>
<tr>
<td>Humic substances (mg/L)</td>
<td>0.81</td>
<td>3.02</td>
<td>4.16</td>
</tr>
<tr>
<td>Building blocks (mg/L)</td>
<td>0.41</td>
<td>0.95</td>
<td>0.88</td>
</tr>
<tr>
<td>Low molecular weight acids (mg/L)</td>
<td>0.09</td>
<td>0.18</td>
<td>0.16</td>
</tr>
<tr>
<td>Low molecular weight neutrals (mg/L)</td>
<td>0.22</td>
<td>0.64</td>
<td>0.39</td>
</tr>
<tr>
<td>SUVA of humic fraction (L/mg humic C/m)</td>
<td>1.61</td>
<td>3.70</td>
<td>4.09</td>
</tr>
<tr>
<td>Humic molecular weight (g/mol)</td>
<td>569</td>
<td>608</td>
<td>696</td>
</tr>
<tr>
<td>USEPA Enhanced Coagulation TOC reduction target (1999)%</td>
<td>25%&lt;sup&gt;a&lt;/sup&gt;</td>
<td>35%&lt;sup&gt;a&lt;/sup&gt;</td>
<td>25%&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Alum dose required to meet DOC target (mg/L)</td>
<td>25.0</td>
<td>38.0</td>
<td>25.0</td>
</tr>
</tbody>
</table>

<sup>a</sup>Calculated using LC–OCD software as UV254 absorbance for the humic fraction divided by the concentration of humic substances.

<sup>b</sup>Calculated in ChromCalc via retention time calibration for humic OC peak with Suwannee River standards.

<sup>c</sup>DOC was used instead of TOC in present study.

<sup>d</sup>Lake Ontario water has low organic carbon content and SUVA (<2 mg/L) and <2, respectively), thus it is exempt from USEPA guidelines. For inclusion in the experiments, it was approximated to the nearest appropriate treatment category based on alkalinity.

Table 2 Water characteristics for alum coagulation tests
0.01 can be described as ‘experiencing a significant impact due to alum at a significance level of 99%’.

- Lake Ontario: humic substances ($p = 0.0043$), biopolymers ($p = 0.0008$)
- Otonabee River: gemfibrozil ($p = 0.0082$), humic substances ($p = 0.0009$), biopolymers ($p < 0.0001$)
- Grand River: gemfibrozil ($p = 0.0023$), carbamazepine ($p < 0.0001$), acetaminophen ($p < 0.0001$), estriol ($p = 0.0017$), humic substances ($p = 0.0007$), biopolymers ($p = 0.0035$).

Of the EDCs/PhACs, none were significantly affected by alum coagulation in Lake Ontario water, and only gemfibrozil was affected in Otonabee River water. All significantly-affected compounds were subjected to the Tukey HSD test and plotted in Figure 1 for NOM fractions and Figure 2 for EDCs/PhACs.

HSD analysis indicates that the concentrations of humic substances and biopolymers in coagulated water were not statistically different between individual doses, but are significantly smaller than the initial (uncoagulated) concentrations of these NOM fractions (Figure 1). Percentage decreases were fairly consistent between water types: 43–63% reduction in humic substance concentration and 57–72% reduction in biopolymer concentration. On a concentration basis, a smaller amount of humics was removed in Lake Ontario water (0.35 mg/L) when compared to...

![Figure 1](https://iwaponline.com/ws/article-pdf/13/5/1348/415088/1348.pdf)
Grand and Otonabee River waters (1.93 and 1.77 mg/L, respectively). Biopolymer removal was small (<0.3 mg/L) for all water types, but considered statistically significant using Tukey’s HSD test. Additional removal at higher coagulant doses was not observed over the narrow, but operationally realistic, alum dose ranges examined. The same water types and alum doses were used in another recent study which focused on links between the characteristics of NOM and subsequent emerging disinfection by-product (DBP) formation potential, yielding similar NOM removal rates (Diemert et al. 2013). Comparable humic substance and biopolymer removals have also been reported in previous coagulation experiments, including a 54% humic substance reduction in bench-scale coagulation tests of Otonabee River water (Wassink et al. 2011) and up to 80% reduction in biopolymer concentrations with iron and aluminum coagulants in waste water secondary effluent (Haberkamp et al. 2007). Hydrophobic DOC, building blocks, LMW acids and neutrals were not significantly affected by coagulation and have been consistently considered to be recalcitrant (Soh et al. 2008; Baghoth et al. 2009; Huber et al. 2011).

No clearly evident trend between EDC/PhAC properties (log \( K_{ow} \), log \( D_{ow} \), \( pK_a \)) and their concentration changes was observed with increasing alum doses. Acetaminophen is considered ‘highly hydrophilic’ (Log \( D_{ow} \) < 1), while carbamazepine, gemfibrozil and estriol are compounds with ‘medium mobility’ into hydrophobic phases (1 < log \( D_{ow} \) < 4) (Wells 2006). According to the \( pK_a \) values, gemfibrozil will be negatively charged, as will a small concentration of acetaminophen molecules according to the ‘two units rule of thumb’ for pH and molecule ionization (Wells 2006), while carbamazepine and estriol will remain neutral. Other negative or uncharged molecules with mid-to-low hydrophobicities were not significantly removed during coagulation.

ANOVA was also applied to the pH data observed at each coagulant dose; for each water type, alum dose had a significant negative effect on the filtered water pH at 99% confidence. The NOM fraction chemistry may change due to protonation of the phenolic groups (which ionize between pH 8 and 12) and carboxylic acid functional groups (which ionize at pH < 8; Ritchie & Perdue 2005). The lesser charge density from these now-neutral phenols and carboxyl...
groups may limit the removal of NOM by the cationic metal hydroxide polymers at higher alum doses. The pH fluctuation is displayed graphically in Figure 3.

Gemfibrozil concentrations decrease with alum application in both Otonabee and Grand River waters (see Figure 2). Similar maximum removals were observed in both waters: 37% reduction in Otonabee River and 31% in Grand River. Gemfibrozil, with its negative charge, might be removed through charge neutralization mechanisms with the cationic aluminum polymers. Also, as pH decreases, gemfibrozil’s tendency to partition into organic phases increases with its increasing Log $D_{ow}$ values, changing from 1.81 at pH 8 to 2.07 at pH 7 (Sci Finder Scholar 2012); the pH depression observed in Otonabee River water due to alum addition may have contributed to gemfibrozil removal (see Figure 3). It may be more likely that gemfibrozil is being removed through association with NOM which is then removed through coagulation, as opposed to charge neutralization mechanisms: no significant changes in gemfibrozil concentration was noted in Lake Ontario water, which has lower concentrations of the highly conjugated humic substances which are easily coagulated in the river waters. A previous study by Rahman et al. (2010) using a water matrix with similar NOM levels and characteristics (Lake Huron) also yielded low (<10%) removals of gemfibrozil using a polyaluminum chloride coagulant.

Carbamazepine, which exhibited a maximum of 32% reduction in Grand River water, has been noted for its recalcitrance to coagulation in previous studies. No significant removal was noted in Milli-Q®, lake water, and synthetic surface water composed of Aldrich humic acid when coagulated with alum or ferric sulfate (Vieno et al. 2006). Nor was carbamazepine concentration affected in primary sewage treatment of wastewater using ferric chloride, aluminum sulfate and PACls (Carballa et al. 2005), in bench- and full-scale ferric chloride coagulation optimized to remove turbidity (Ternes et al. 2002), or in jar tests using river waters with alum and ferric chloride doses designed to meet the USEPA Interim Enhanced Surface Water Treatment Rule (Westerhoff et al. 2005), similar to the doses in the present study. However, carbamazepine adsorption tests with silica have indicated that while the PhAC is not affected by humic and fulvic acids (Suwannee River), its sorption is significantly decreased by the presence of Suwannee River NOM (Bui & Choi 2010); potentially, this is due to carbamazepine becoming associated (i.e. through hydrogen bonding) with soluble organic compounds of a more hydrophilic nature. Therefore, carbamazepine removal may be orchestrated through interactions with other non-humic components of NOM, such as biopolymers in the Grand River water (which are then reduced substantially through coagulation).

Acetaminophen in Grand River water exhibits an inconsistent concentration pattern: the concentrations at alum conditions $\geq$20 mg/L are significantly smaller than that at 15 mg/L alum dose, but not significantly different from the raw water acetaminophen concentration. Physically, this may indicate that acetaminophen desorbs slightly from NOM to increase its concentration in the aqueous phase at alum doses <20 mg/L by approximately 9%. However, studies have indicated that acetaminophen sorbs negligibly to charged and organic sorbents (Lorphensri et al. 2006), and as the increase in acetaminophen concentration...
is quite small, it is possible that the increased acetaminophen concentration detected at 15 mg/L alum may be an outlier.

Estriol, contrary to the other compounds, exhibits a positive trend in Grand River water with increasing alum doses; the upper two alum doses (30 and 35 mg/L) yield concentrations which are significantly higher than the initial concentration (Figure 2). This might indicate that estriol, which could potentially adsorb or partition into NOM, is disassociating from the NOM at higher coagulant doses. Estrogenic hormones similar in structure to estriol and estriol are known to partition into humic substances (Yamamoto & Liljestrand 2003), and their sorption to activated sludges has been shown to vary with solution pH (Schäfer et al. 2002). It has been hypothesized that NOM undergoes conformational changes in the presence of cations (such as those from alum), alternating from a stretched linear conformation at low ionic strength to coiled structures at higher ionic strengths. After this conformational change, previously accessible hydrophobic cavities will be inaccessible to hydrophobic compounds (Döring & Marschner 1998), potentially making NOM-organic contaminant interactions more reversible (Devitt et al. 1998) and may result in higher aqueous concentrations of the free EDCs and PhACs (Comerton et al. 2009). However, care should be taken when interpreting this data due to high variability (95% confidence intervals are ±185 ng/L).

**CONCLUSIONS**

This study explored the removal of EDCs and PhACs through chemical coagulation with alum and the concurrent removal of NOM fractions from three waters: Lake Ontario, Otonabee River and Grand River water. EDC/PhAC fate during coagulation is complex and was shown to be highly dependent on the water matrix and NOM characteristics. While some compounds may be removed through NOM sorption or charge neutralization with cationic coagulant metal hydroxides, others may undergo reversible interactions with NOM and partition into the aqueous phase at higher concentrations with coagulation addition. NOM-compound complexes are likely to be responsible for the behavior reported for EDCs/PhACs during coagulation, however little information is known regarding the mechanisms behind these interactions. Further studies should aim to explore these sorption mechanisms.

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