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## The Formation and Fate of Carbonyls in Potable Water Reuse Systems

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### Abstract

Low molecular weight, uncharged compounds have been the subject of considerable study at advanced treatment plants employed for potable water reuse. However, previously identified compounds only account for a small fraction of the total dissolved organic carbon remaining after reverse osmosis treatment. Uncharged carbonyl compounds (e.g., aldehydes and ketones) formed during oxidation have rarely been monitored in potable water reuse systems. To determine the relative importance of these compounds to final product water quality, samples were collected from six potable water reuse facilities and one conventional drinking water treatment plant. Saturated carbonyl compounds (e.g., formaldehyde, acetone) and  $\alpha,\beta$ -unsaturated aldehydes (e.g., acrolein, crotonaldehyde) were quantified with a sensitive new analytical method. Relatively high concentrations of carbonyls (i.e., above 7  $\mu\text{M}$ ) were observed after ozonation of wastewater effluent. Biological filtration reduced concentrations of carbonyls by over 90%. Rejection of the carbonyls during reverse osmosis was correlated with molecular weight, with concentrations decreasing by 33 to 58%. Transformation of carbonyls resulted in decreases in concentration of 10 to 90% during advanced oxidation, with observed decreases consistent with rate constants for reactions of the compounds with hydroxyl radicals. Overall, carbonyl compounds accounted for 19 to 38% of the dissolved organic carbon in reverse osmosis-treated water.

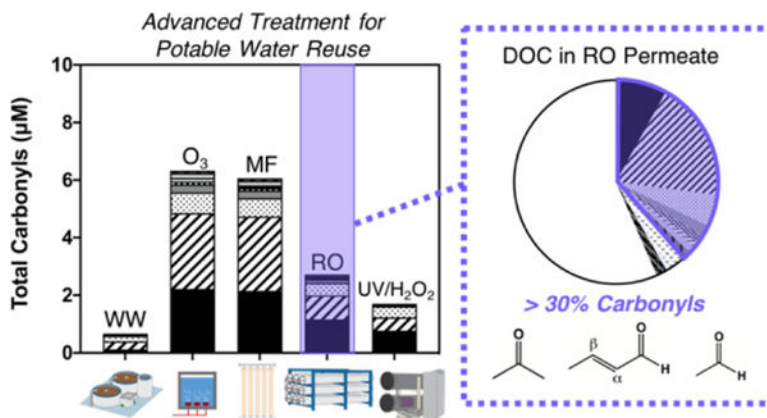
### Graphical Abstract

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Supporting Information

Details of analytical methods for analysis of carbonyl compounds, detailed information of treatment plants, water quality information and carbonyl compound concentrations for each sampling event, and LC-MS spectra from precursor ion scans using TSH.



## Introduction

Potable water reuse provides a reliable alternative water supply to communities facing water scarcity.<sup>1</sup> In many locations, this process involves the passage of municipal wastewater effluent through an advanced treatment plant equipped with microfiltration (MF), reverse osmosis (RO) and an advanced oxidation process (AOP), which most often employs ultraviolet light combined with hydrogen peroxide (i.e., the UV/H<sub>2</sub>O<sub>2</sub> process).<sup>2</sup> In some cases, additional oxidative treatment processes (e.g., ozonation) are also employed prior to microfiltration, with or without subsequent biological filtration.<sup>3,4</sup>

Uncharged, low molecular weight compounds, including halogenated disinfection byproducts (e.g., trihalomethanes, haloacetonitriles), *N*-nitrosamines, odorous compounds, and solvents have been detected after RO treatment in potable water reuse facilities.<sup>5–10</sup> Due to their potential impacts on human health and the aesthetic quality of drinking water, a considerable amount of effort has been directed at identifying and quantifying these compounds. Considering available data, we recently determined that these contaminants only account for about 5 to 10% of the 20 to 200 µg C L<sup>-1</sup> of dissolved organic carbon (DOC) typically observed in water produced by advanced treatment plants that employ RO.<sup>2</sup>

Carbonyl compounds have been detected after oxidants are employed in conventional drinking water and wastewater treatment plants.<sup>11–15</sup> In full and pilot-scale drinking water treatment plants that receive surface water, aldehydes (e.g., formaldehyde and acetaldehyde) and dialdehydes (e.g., glyoxal and methyl glyoxal) were produced during ozonation as well as during disinfection with chlorine or chlorine dioxide.<sup>16</sup> However, formaldehyde concentrations in treated water did not exceed 20 µg L<sup>-1</sup>, which is well below existing health-based guidelines (e.g., California has set a notification level of 100 µg L<sup>-1</sup> for formaldehyde<sup>17</sup> and New York has set a maximum contaminant level of 50 µg L<sup>-1</sup> for total aldehydes<sup>18</sup>). Higher concentrations of formaldehyde (i.e., up to 95 µg L<sup>-1</sup>) have been measured after ozonation of wastewater effluent.<sup>19</sup>

Carbonyl compounds are likely to be present in wastewater effluent due to industrial discharges, use in consumer products, and formation during effluent disinfection. They also may be produced when oxidants, such as ozone, are employed prior to microfiltration to

reduce organic fouling, or when chloramines are applied to reduce biological fouling.<sup>20</sup> Although these low molecular weight compounds are poorly rejected during RO treatment,<sup>21</sup> previous research on their occurrence is limited and has focused on only a few, easily measured saturated compounds (e.g., formaldehyde, acetaldehyde, and/or acetone).<sup>4,10</sup>

Laboratory-scale experiments have demonstrated the formation of  $\alpha,\beta$ -unsaturated carbonyls from the oxidation of phenolic compounds<sup>22–24</sup> and alkylated aromatic compounds.<sup>25</sup> Extending consideration of carbonyl compounds in advanced treatment systems beyond a few saturated aldehydes and ketones is important because all members of this chemical family elicit toxicity by forming covalent bonds with nucleophilic sites on biological targets.<sup>26,27</sup> The formation of these adducts has been associated with health outcomes such as cancer, neurodegenerative and cardiovascular diseases.<sup>28–31</sup> Furthermore, the double bond between carbons two and three in  $\alpha,\beta$ -unsaturated aldehydes substantially increases the electrophilicity, and therefore the toxicity of these compounds, compared to their saturated analogs.<sup>27,32–34</sup> For example, results from *in vivo* animal studies indicate that acrolein is over 100 times more toxic than its saturated analog, propionaldehyde.<sup>35</sup>

In addition to their possible human health effects, certain saturated aldehydes can adversely impact the aesthetics of drinking water.<sup>36,37</sup> For example, hexanal and butyraldehyde were detected at concentrations close to or above their organoleptic thresholds (4.5 and 9  $\mu\text{g L}^{-1}$ , respectively) when wastewater was ozonated.<sup>38–40</sup> The presence of odorous compounds in water produced by potable water reuse plants would be problematic because aesthetic issues are important to maintaining consumer acceptance of this new type of water source.<sup>41</sup>

Previous research on carbonyl compounds has focused on a few saturated compounds<sup>42,43</sup> in part due the lack of sensitivity in previously established analytical techniques, which were unable to detect  $\alpha,\beta$ -unsaturated aldehydes at concentrations relevant to advanced water treatment systems. Recent advances have made it possible to quantify a broader suite of carbonyl compounds, including  $\alpha,\beta$ -unsaturated aldehydes, ketones, and dialdehydes at lower limits of detection using *p*-toluenesulfonylhydrazine (TSH) as a derivatization agent with subsequent analysis via liquid chromatography/tandem mass spectrometry (LC-MS/MS).<sup>44</sup> To better understand the occurrence of carbonyl compounds in potable water reuse treatment trains, TSH derivatization was employed to study the formation and fate of six saturated aldehydes, seven  $\alpha,\beta$ -unsaturated aldehydes, and one ketone in six potable water reuse facilities and one conventional drinking water treatment plant. Results provide new insight into the formation, fate, and potential water quality impacts of these compounds in potable water reuse systems.

## Materials and Methods

Solutions were prepared with reagent grade chemicals using either 18.2 M $\Omega$  Milli-Q water from a Millipore system or LC-MS grade water (Millipore-Sigma). Chemicals and reagents were obtained at the highest purity available as detailed in the supplementary information (Text S1).

Triplicate grab samples were collected in 40-mL amber glass volatile organic analysis (VOA) vials without headspace. Samples and field blanks were collected from six advanced treatment plants (Plants A-F) and one conventional drinking water plant (Plant G). Grab samples were collected from the plant influent and after each major treatment process (from 5 or 6 locations depending on the facility). Samples were stored on ice and shipped to UC Berkeley by overnight courier. After receipt, the samples, field blanks, and laboratory blanks were stored at 4°C until carbonyl compound analysis, which typically took place within 12 hours. Each treatment facility was sampled twice, once between September and December 2018 and once between March and June 2019, with the exception of Plant G, which was sampled twice between March and June 2019.

Two of the six advanced treatment plants were full-scale facilities treating at least  $2.9 \text{ m}^3 \text{ s}^{-1}$  (i.e., > 65 millions of gallons per day) of municipal wastewater effluent. The remainder were pilot-scale plants (flows  $<0.05 \text{ m}^3 \text{ s}^{-1}$ ) used to assess the performance of different types of proposed advanced treatment trains. Plant G was a full-scale conventional drinking water treatment plant that received surface water and used ozone for taste and odor control. Plants A, B, C, and F received wastewater effluent that had not been subject to nitrification, Plant E received effluent that had been nitrified (i.e.,  $[\text{NH}_4^+] <0.07 \text{ mg L}^{-1}$  as N), and Plant D received effluent from two separate treatment plants (i.e., one that had been fully nitrified and the other non-nitrified;  $[\text{NH}_4^+] \sim 3 \text{ mg L}^{-1}$  as N in the combined effluent). With the exception of Plant F, all of the advanced treatment plants employed RO. At Plants C and D, sodium hypochlorite (NaOCl) was added prior to microfiltration or ultrafiltration while at Plants A, B, and E chloramines and ozone were added prior to microfiltration. Plant F applied ozone prior to biological filtration. Additional information on the treatment plants is included in Table S1.

Water quality parameters including pH, dissolved organic carbon (DOC), and UV absorbance at 254 ( $\text{UV}_{254}$ ) were measured for each sample within two days of collection. When available, online total organic carbon (TOC) measurements were also recorded at the time of sampling. Details related to the water quality analysis as well as data from Plants A-G are included in Text S2 and Tables S2A-G.

Samples were derivatized by adding at least a 200-fold excess of *p*-toluenesulfonylhydrazine (TSH), a derivatization agent that reacts selectively with aldehyde and ketone functional groups (Figure S1).<sup>44</sup> A suite of six saturated aldehydes, seven unsaturated aldehydes and one ketone (formaldehyde, acetaldehyde, acetone, acrolein, propionaldehyde, crotonaldehyde, butyraldehyde, 3-methylcrotonaldehyde, trans-2-pentenal, pentanal, 2,4-hexadienal, trans-2-hexenal, hexanal, and trans-2-heptenal) were analyzed via LC-MS/MS on an Agilent 1200 series HPLC system coupled to a 6460 triple quadrupole mass spectrometer. A Phenomenex Synergi Hydro-RP  $4\mu\text{m}$  column ( $150 \times 3 \text{ mm}$ ) was used for chromatographic separation. Details of derivatization, HPLC and multiple reaction monitoring (MRM) MS/MS methods, as well as representative chromatograms are included in Text S3, Tables S3-S4, and Figures S2-S3.

A 0.1 M stock solution containing a mixture of the analytes, prepared in methanol and kept in a freezer ( $-20 \text{ }^\circ\text{C}$ ) for a maximum of 3 months, was used to prepare standards. For

formaldehyde quantification, a freshly prepared 0.1 M solution was prepared in LC-MS grade water immediately prior to each set of samples and equilibrated for at least 12 hours at 4°C prior to use. A 0.1 M stock solution of TSH was prepared in acetonitrile and stored in the freezer (-20 °C) for a maximum of 1 month. TSH working solutions of either 2500 mg L<sup>-1</sup> (for the mixture) or 1000 mg L<sup>-1</sup> (for formaldehyde) were prepared in water from the 0.1 M stock daily.

Carbonyl compounds were quantified using standard addition with at least five points (Figure S4), and the highest concentration standard was at least two times higher than the detected concentration. Sample concentrations were corrected based on field and laboratory blanks processed in an identical manner. Analyte concentrations detected in blanks were usually below 10 ng L<sup>-1</sup> for all compounds except for formaldehyde, which was usually below 0.5 µg L<sup>-1</sup> (0.02 µM). For standard addition of the analyte mixture, samples (1 mL) were pipetted into HPLC vials, followed by the addition of 20 µL HCl (1 M), 10 µL TSH (from the 2500 mg L<sup>-1</sup> stock solution), and 20 µL of a known concentration of the analyte mixture (prepared in the sample matrix). Standard addition curves for formaldehyde were prepared and analyzed separately from all of the other analytes due to the higher likelihood of formaldehyde contamination from laboratory air (Figures S5). Formaldehyde samples were prepared in the same manner but without the addition of HCl, and with 10 µL of the 1000 mg L<sup>-1</sup> TSH stock solution. Derivatized mixture samples were equilibrated for at least 2 hours at room temperature and were analyzed by LC-MS/MS within 12 hours (Figure S6). Derivatized formaldehyde samples were analyzed within 2 hours to minimize the potential for laboratory contamination.

To assess the potential for carbonyl compound formation from the application of free chlorine to wastewater effluent, an initial concentration of 0.12 mM of NaOCl (8.5 mg L<sup>-1</sup> as Cl<sub>2</sub>; standardized by iodometric titration<sup>45</sup>) was added directly to 40 mL of the influent to Plant D to simulate conditions during the sampling event of 2019. The experiment was conducted in triplicate. After chlorination, samples were immediately derivatized and processed using the standard addition procedure described above.

## Results and Discussion

### Formation and Fate of Carbonyl Compounds

Total concentrations of the 14 carbonyl compounds detected at the treatment plants ranged from 0.18 to 7.4 µM (Figure 1). Similar carbonyl concentrations were observed in samples collected on two separate occasions at each treatment facility. Relative standard deviations were typically less than 20% between the two sampling events, with the exception of Plant A, which was likely a result of different applied ozone doses (i.e., the initial ozone concentration was 13 mg L<sup>-1</sup> in 2018 and 7 mg L<sup>-1</sup> in 2019). Individual compound concentrations from each event are included in Tables S5A–G and Figures S7A–G. Concentrations of total carbonyl compounds in the wastewater entering the advanced treatment plants ranged from 0.35 to 0.80 µM. Formaldehyde, acetaldehyde, and acetone together accounted for over 90% of the total carbonyl compounds and the α,β-unsaturated aldehydes accounting for approximately 0.3% of the total carbonyl compound concentration on a molar basis. After treatment, total carbonyl compound concentrations in final product

water ranged from 0.20 to 2.4  $\mu\text{M}$ . Formaldehyde dominated the carbonyl compound speciation (i.e., it accounted for an average of 40% of the total carbonyl compound concentration) and  $\alpha,\beta$ -unsaturated aldehydes accounting for approximately 2% of the total carbonyl compound concentration.

Overall, the highest total carbonyl concentrations (i.e., 1.4–7.4  $\mu\text{M}$ ) were observed after ozonation, which is consistent with the reaction of ozone with double bonds in organic matter to produce aldehydes and carbonyls.<sup>14</sup> After ozonation, formaldehyde and acetaldehyde accounted for approximately 80% of total carbonyl compound concentrations, while  $\alpha,\beta$ -unsaturated aldehydes accounted for approximately 1.5%. Acrolein and crotonaldehyde accounted for approximately 90% of the  $\alpha,\beta$ -unsaturated aldehydes on a molar basis. The concentrations of formaldehyde and acetaldehyde observed in this study were consistent with those reported in prior studies of ozonation of wastewater effluent and drinking water.<sup>15,16,19</sup>

The application of chlorine prior to microfiltration in Plants C and D also resulted in carbonyl compound production, but the total concentrations produced were only about 25% of those formed by ozonation. Formaldehyde and acetaldehyde were the predominant aldehydes produced by chlorination (i.e., they accounted for 70% of the carbonyl compounds on a molar basis), while  $\alpha,\beta$ -unsaturated aldehydes accounted for about 1% of the total molar yield of carbonyl compounds. Acrolein and crotonaldehyde accounted for an average of 95% of the  $\alpha,\beta$ -unsaturated aldehydes on a molar basis. The formation of carbonyl compounds when chlorine (i.e., NaOCl) is added to ammonia-containing municipal wastewater effluent has not been reported previously. In addition to ammonia, which reacts readily with free chlorine (i.e., HOCl) to form chloramines<sup>46</sup> (i.e.,  $k_1 = 4.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ ), wastewater effluent contains dissolved organic nitrogen species with functional groups (e.g., alkylamines) that can also react with free chlorine.<sup>47</sup> The reaction between chlorine and tertiary alkylamines also occurs quickly (i.e.,  $k_2 = 6.1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ), and the product (i.e., chlorinated trimethylamine) decays almost instantaneously to produce formaldehyde and dimethylamine.<sup>47</sup> Although organic amines are present in wastewater in low concentrations (i.e., <5% of the total nitrogen<sup>48</sup>) relative to ammonia, the overall rate of transformation by chlorine should be similar due to the relatively fast reaction kinetics. Therefore, reactions of free chlorine with organic nitrogen species, such as tertiary alkylamines, may explain the formation of carbonyl compounds observed during the chlorination of ammonia-containing wastewater effluent. However, without additional experiments, it is not possible to determine if free chlorine or chloramines were responsible for the formation of the carbonyl compounds.

Results from laboratory-scale chlorination experiments using wastewater effluent from Plant D yielded similar concentrations of formaldehyde (18.5  $\mu\text{g L}^{-1}$ , or 0.62  $\mu\text{M}$ ) and acetaldehyde (42.9  $\mu\text{g L}^{-1}$ , or 0.98  $\mu\text{M}$ ) as those detected in grab samples collected from the MF-feed (post-NaOCl application) at the facility (i.e., 19.2  $\mu\text{g L}^{-1}$  or 0.64  $\mu\text{M}$  formaldehyde, 41.6  $\mu\text{g L}^{-1}$  or 0.95  $\mu\text{M}$  acetaldehyde). Concentrations of other longer-chained saturated carbonyl compounds and  $\alpha,\beta$ -unsaturated aldehydes in the bench-scale experiment were also similar to those observed at the advanced treatment plant (i.e., less than 10% difference, Table S6), suggesting that the application of free chlorine to the

wastewater effluent was the source of the carbonyl compounds formed upstream of MF in Plants C and D.

Total carbonyl compounds concentrations decreased by over 90% when biofiltration was employed in Plants E and F (Figure 1). The data were consistent with previous findings from conventional drinking water treatment plants where the use of biologically active sand or biological activated carbon filters resulted in nearly complete removal of carbonyl compounds formed during ozonation of surface water and wastewater.<sup>40,49–52</sup> The increase in carbonyl compound concentrations in the final effluent (i.e., post-UV) of Plant F could have been due to a reaction involving UV light<sup>53</sup> or formation when chlorine was added immediately prior to the sample collection point. Carbonyl compounds were not removed to an appreciable degree during dual media (anthracite/sand) filtration at the conventional drinking water treatment plant (Plant G) because the operators of the facility added chlorine to control biological growth on the filters. This finding is consistent with data from other drinking water treatment plants where sand filtration was employed in a similar manner.<sup>16</sup>

Total carbonyl compound concentrations decreased by 32 to 58% during reverse osmosis treatment (Figure 1), with the concentrations of  $\alpha,\beta$ -unsaturated aldehydes decreasing by an average of 50%. Previous research has demonstrated a relationship between molecular weight and the rejection of uncharged organic compounds, with approximately 50% rejection of compounds with molecular weights of 100 g mol<sup>-1</sup> and rejections >90% for compounds with molecular weights greater than 200 g mol<sup>-1</sup>.<sup>6,21,54–56</sup> Our data also followed this relationship with 35% rejection of formaldehyde (MW 30 g mol<sup>-1</sup>) and 65% rejection of hexanal (MW = 100 g mol<sup>-1</sup>) (Figure 2). Although molecular weight was well correlated with rejection of uncharged species during RO, other physical and chemical properties (e.g., molecular volume, hydrophobicity, and polarity) also affect compound rejection.<sup>57</sup> For example, the significantly higher rejection (Mann-Whitney,  $p < 0.05$ ) of propionaldehyde compared to acetone (i.e., both compounds have molecular weights of 58 g mol<sup>-1</sup>) could be explained by the greater hydrophobicity and lower dipole moment of propionaldehyde (i.e., prop.) relative to acetone (e.g.,  $\log K_{ow,prop} = 0.59$ ,  $\log K_{ow,acetone} = -0.24$ ;  $\mu_{prop} = 2.72$  D,  $\mu_{acetone} = 2.91$  D).

Total carbonyl compound concentrations decreased by 27–45% when the treated water was subject to advanced oxidation processes (i.e., Figure 1; UV/H<sub>2</sub>O<sub>2</sub> for Plants A-D, UV/HOCl for Plant E). The transformation of a compound during advanced oxidation depends on the rate constant for its reaction with hydroxyl radical (HO<sup>•</sup>). Advanced oxidation processes for the potable water reuse facilities sampled as part of this study were designed to achieve at least 0.5-log removal (i.e., 68% removal) for 1,4-dioxane ( $k_{HO^{\bullet}} = 2.8 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>).<sup>58</sup> The reactivity of the carbonyl compounds with HO<sup>•</sup> spans a range of almost two orders of magnitude, with greater reactivity observed for the higher molecular-weight compounds and those compounds containing unsaturated carbon-carbon bonds (Table S7). Assuming that the potable reuse facilities were obtaining 0.5-log removal of 1,4-dioxane at the time of sampling and that reaction with HO<sup>•</sup> was the dominant transformation mechanism, it is possible to predict the amount of the compounds remaining after advanced oxidation.<sup>2</sup> Results from samples collected at the five treatment plants equipped with advanced oxidation processes were consistent with the expected relationship, with the least reactive



compound—acetone—decreasing in concentration by about 10% (Figure 3). Concentrations of formaldehyde and acetaldehyde decreased by approximately 35%, while concentrations of longer-chained saturated aldehydes (e.g., butyraldehyde, hexanal) decreased by approximately 70%. Concentrations of  $\alpha,\beta$ -unsaturated aldehydes, acrolein and crotonaldehyde, decreased by over 90% ( $\log k_{\text{HO}\cdot} = 9.8$  for both acrolein and crotonaldehyde; Figure 3).

### Implications for Water Quality

Although the presence of carbonyl compounds in drinking water has been known for over 30 years,<sup>11,59</sup> they have not been considered a priority with respect to water quality because individual compounds have not been detected at concentrations above thresholds for human health concerns or aesthetic impacts. For example, among the 12 measurements of formaldehyde in finished drinking water reported by Weinberg et al. (median concentration =  $5 \mu\text{g L}^{-1}$ ), none exceeded California's health-based notification level of  $100 \mu\text{g L}^{-1}$  or New York's maximum contaminant level (MCL) of  $50 \mu\text{g L}^{-1}$ .<sup>16</sup> The California health-based notification level for formaldehyde was derived based on a reference dose for chronic oral exposure of  $0.2 \text{ mg/kg-day}$ , assuming 20% of exposure is from drinking water.<sup>17</sup> Although details on the derivation of New York's MCL for total aldehydes are not readily available, it appears that a risk-based approach similar to the one applied for formaldehyde in California was used.<sup>18</sup>

Health-based guidelines are not available for any of the other saturated carbonyl compounds. Given the similarities in their structures and mode of action, for screening purposes, it is reasonable to assume that they would be approximately as toxic as formaldehyde and that an additive model could be used to represent their toxicity. If this were the case, none of the final product water from Plants A-G in this study would exceed California's notification level, but potable reuse Plants A, B, and F, as well as drinking water treatment Plant G would exceed New York's MCL (Figure 4).

Inclusion of the  $\alpha,\beta$ -unsaturated aldehydes in this analysis would raise additional concerns because they tend to be considerably more toxic than their saturated analogs.<sup>27,60</sup> This assertion is supported by data from *in vivo* exposure studies indicate that  $\alpha,\beta$ -unsaturated aldehydes acrolein and crotonaldehyde are approximately hundred times more potent than their saturated analogs, propionaldehyde and butyraldehyde, based on  $\text{LD}_{50}$  values for mice and rats.<sup>35</sup> Based on other animal studies, the reference dose for chronic oral exposure as determined for acrolein is 400 times lower than that of formaldehyde.<sup>61,62</sup> Even though this indicates that  $\alpha,\beta$ -unsaturated aldehydes might be more hazardous than their saturated analogues, their occurrence at substantially lower concentrations compared to their saturated analogues (Figure 4) might lead to a low overall risk. In addition,  $\alpha,\beta$ -unsaturated aldehydes are predicted to be rapidly metabolized to non-hazardous metabolites and/or quenched by glutathione.<sup>63</sup> Therefore, genotoxic effects detected in *in vitro* might not translate to *in vivo* toxicity. This is further supported by the fact that  $\alpha,\beta$ -unsaturated aldehydes used as flavoring agents, such as trans-2-hexenal, are generally recognized as safe for human consumption at low concentrations.<sup>63</sup> These findings should be interpreted with caution because previous studies have only focused on individual chemicals whereas this study

demonstrates that saturated and unsaturated aldehydes occur in mixtures. This emphasizes the need for additional toxicological data to fully assess the health-based implications. For drinking water, such assessments should be conducted with great care because low molecular weight compounds are often not amenable to pre-concentration by solid phase extraction and have the potential to volatilize during *in vitro* assays.<sup>64</sup>

In addition to impacting the overall safety of drinking water, carbonyl compounds can also compromise the aesthetic water quality. After the ozonation of wastewater effluent, individual carbonyl compounds (e.g., butyraldehyde and hexanal) were present at concentrations above their respective odor thresholds (e.g., 9 and 4.5  $\mu\text{g L}^{-1}$ ). Following treatment with BAC, butyraldehyde and hexanal concentrations were reduced to levels well below at which they would impact aesthetics (e.g.,  $<1 \mu\text{g L}^{-1}$ ). However, in Plants A and B, which employed of ozone without BAC, concentrations for hexanal exceeded its odor threshold in RO permeate; treatment with UV/H<sub>2</sub>O<sub>2</sub> was needed to lower the concentrations to concentrations below the odor threshold.

On the basis of the results of this study, advanced treatment plants that use ozone will produce concentrations of carbonyl compounds that could be problematic if biofiltration or advanced oxidation is not employed prior to distribution of the water. Although ozone is not employed frequently in advanced treatment plants equipped with RO, it is often used in potable water reuse systems that do not employ RO.<sup>65</sup> For example, two of the ten largest full-scale potable water reuse systems in the world (i.e., Upper Occoquan, VA and Gwinnett County, GA) employ ozone followed by activated carbon treatment without RO treatment.<sup>3</sup> In these systems, carbonyl compounds remaining after treatment are likely degraded in the reservoir or river where the treated water is stored prior to use. However, if this approach were to be adopted in systems without an environmental buffer (i.e., direct potable water reuse), exposure to carbonyl compounds could be a health concern.

### Contributions of Carbonyl Compounds to the Organic Carbon Content of Recycled Water

After RO treatment, recycled water typically contains between 20 and 200  $\mu\text{g C L}^{-1}$  of dissolved organic carbon. Excluding the carbonyl compounds measured in this study, compounds detected after RO treatment of municipal wastewater effluent (e.g., halogenated disinfection byproducts, *N*-nitrosamines, 1,4-dioxane) typically account for less than 10% of the measured DOC. Our measurements indicate that saturated carbonyl compounds and  $\alpha,\beta$ -unsaturated aldehydes account for between 19 and 38% of the dissolved organic carbon in Plants A-E (median = 33%, Figure 5). Given the mechanisms through which these compounds are produced during ozonation and chlorination, it is likely that some of the unidentified carbon also consists of other carbonyl compounds.<sup>22,23</sup>

During precursor ion scans of samples derivatized with TSH (Figures S8–S11) we observed approximately 10 peaks corresponding to carbonyl compounds for which analytical standards were not available. Peak areas of these unidentified carbonyl compounds prior to RO treatment were usually smaller than the areas measured for acetaldehyde and acetone in the chromatogram (Table S8). Assuming similar rejection during RO treatment for the masses identified (i.e., molecular weights 73–232  $\text{g mol}^{-1}$ , approximately 50–95% rejection), we estimate that these unidentified compounds accounted for less than 5% of the

unidentified dissolved organic carbon. Additional research is needed to identify and quantify these and other carbonyl compounds.

The remainder of the organic carbon likely consisted of other uncharged low molecular weight, hydrophilic compounds that are difficult to measure at these levels with existing analytical methods (e.g., alcohols, ethers). In addition, a fraction of the unidentified dissolved organic carbon could consist of compounds that are present at relatively high concentrations in wastewater effluent that are not completely removed during RO and UV/H<sub>2</sub>O<sub>2</sub> processes. For example, wastewater-derived contaminants like the antiviral acyclovir and the artificial sweetener sucralose have been detected in wastewater effluents at concentrations up to 0.2 µg C L<sup>-1</sup> and 13 µg C L<sup>-1</sup>,<sup>66,67</sup> respectively. Even if we assume high rejection (e.g., >90%) of these compounds during RO treatment due to their relatively high molecular weights, their presence could account for between 1 and 5% of the unidentified organic carbon assuming a total of 50 µg C L<sup>-1</sup> in the RO permeate. Despite our best efforts, it is likely that around half of the dissolved organic carbon in water from advanced treatment plants will not be amenable to identification with current analytical methods. If there are health risks associated with exposure to these additional unknown organic contaminants, they would have to be capable of causing adverse effects at concentrations in this range (i.e., <20 µg C L<sup>-1</sup>) assuming that only one compound accounted for all of the unknown carbon or if the unknown compounds affected the same biological targets.

## Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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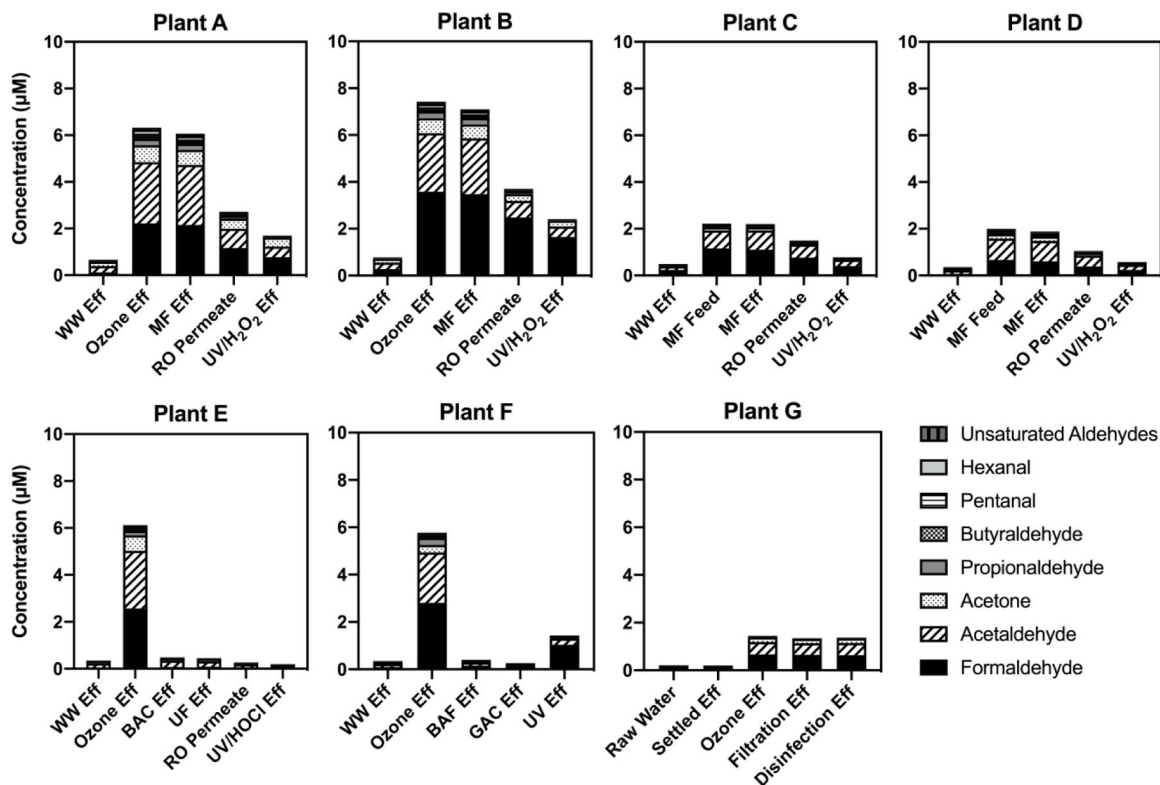
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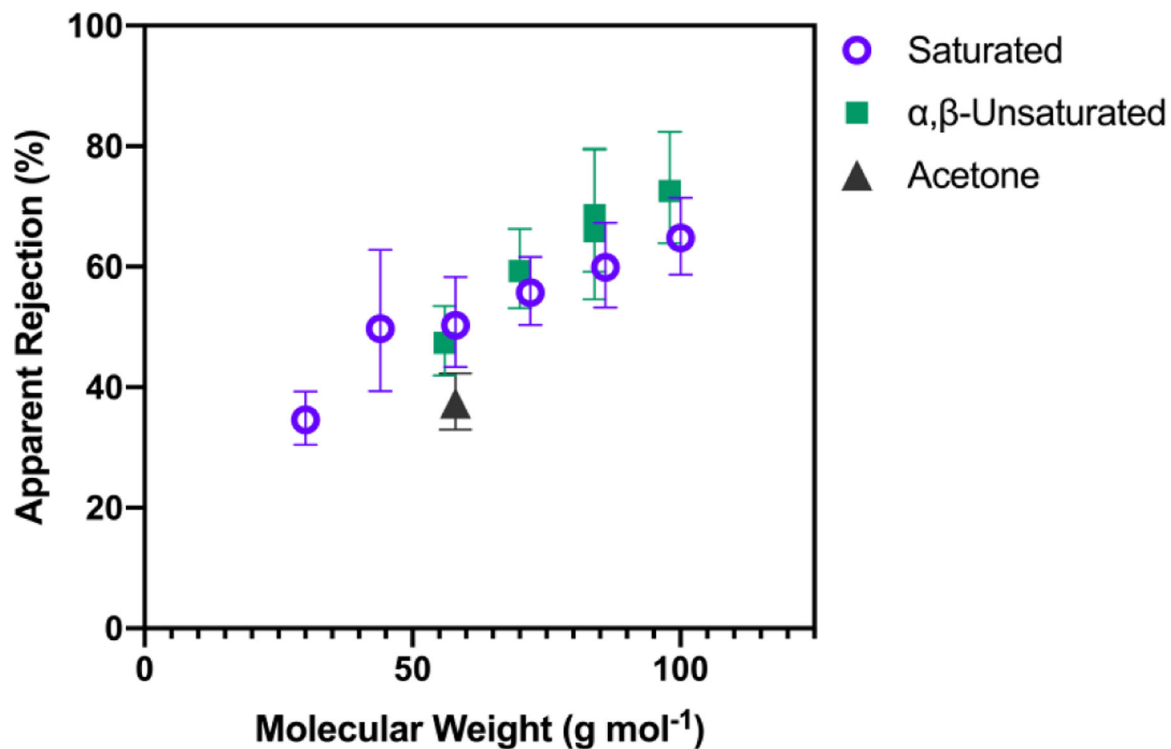
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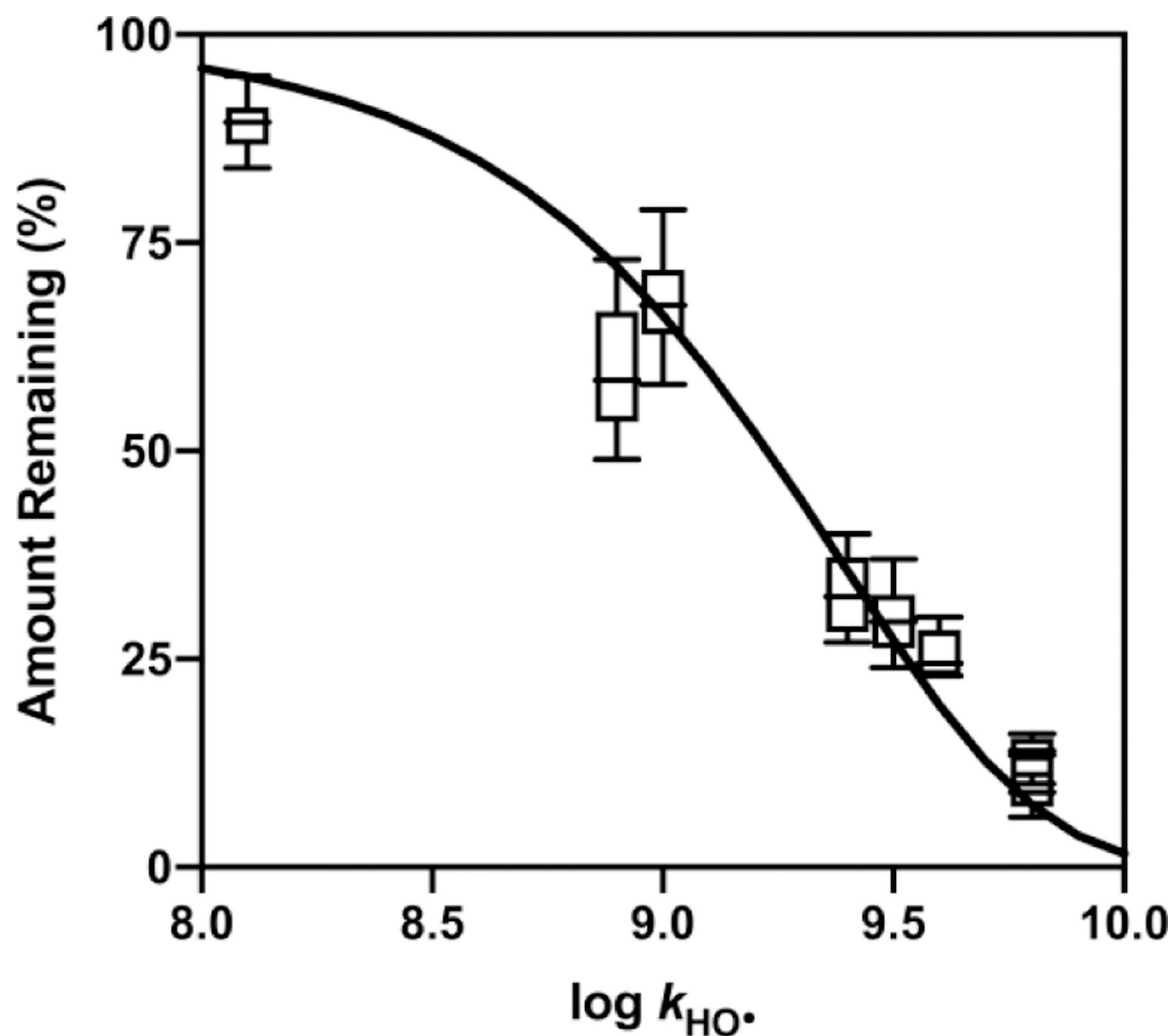
**Figure 1.** Concentrations of carbonyl compounds during each major treatment step. Data represent the median values from sampling events in 2018 and in 2019 (n=2, Tables S5A–G, Figures S7A–G). “WW” = wastewater; “Eff” = effluent; “MF” = microfiltration; “UF” = ultrafiltration; “RO” = reverse osmosis; “BAC” = biologically active carbon filtration; “BAF” = biological filtration; “GAC” = granular activated carbon filtration. Plants C and D applied NaOCl prior to the “MF Feed” point of sample collection.



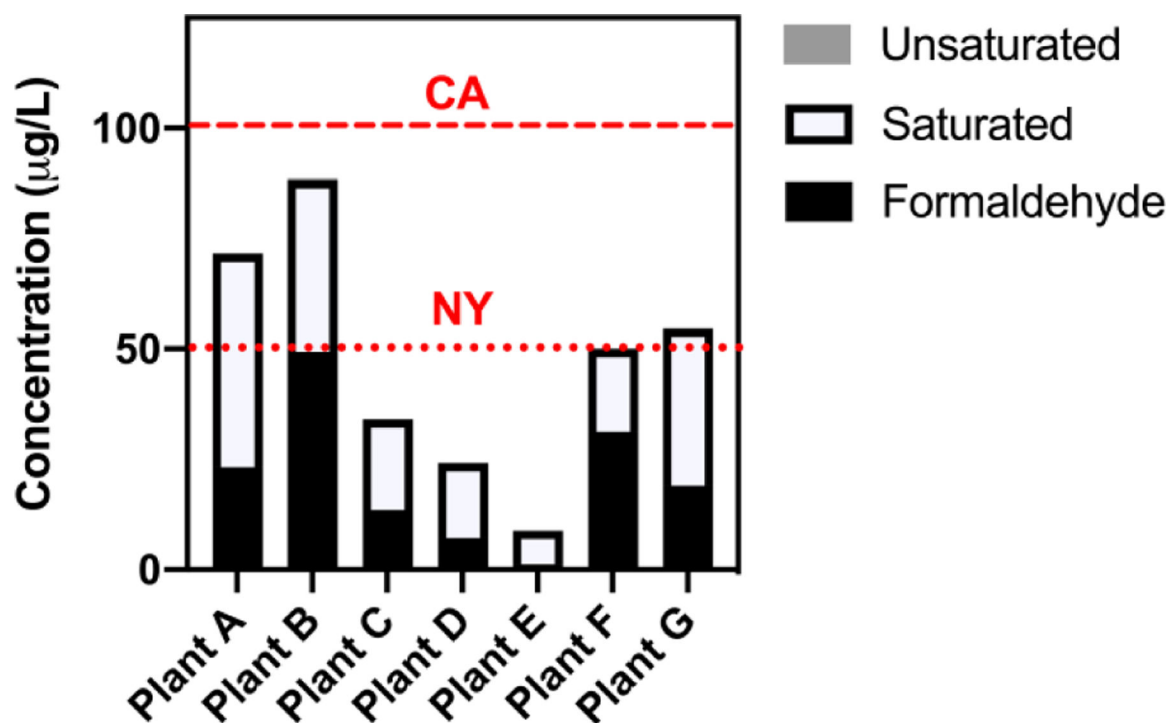


**Figure 2.**

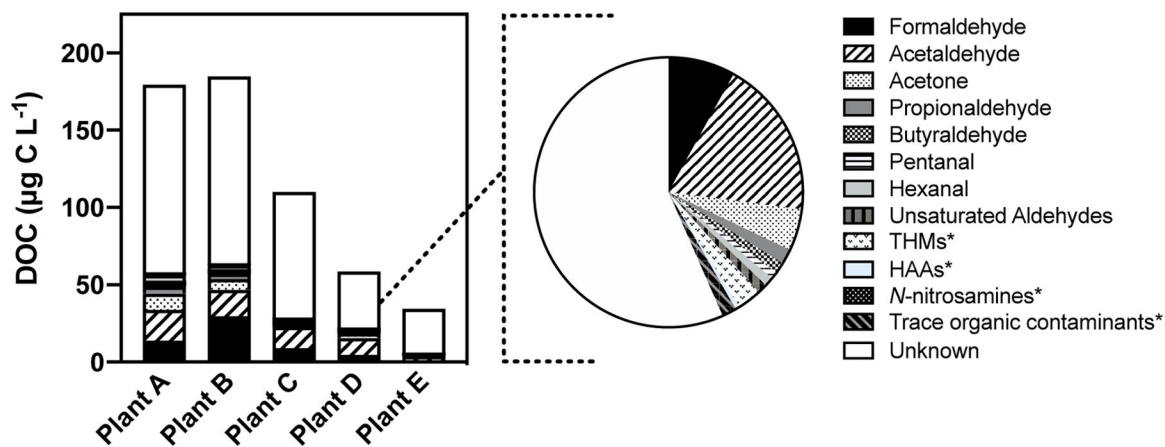
Apparent rejection ( $(1 - C_p/C_f) \times 100$  where  $C_p$  = permeate concentration and  $C_f$  = feed concentration) of compounds during RO treatment in Plants A-E as a function of molecular weight. Circles (saturated carbonyls,  $n=10$ ), triangles (acetone,  $n=10$ ) and squares ( $\alpha,\beta$ -unsaturated aldehydes,  $n=6$ ) represent the geometric mean across all treatment plants, and error bars represent 95% confidence intervals. Samples containing compounds at concentrations below limits of quantification were excluded from analysis.



**Figure 3.** Carbonyl compound percent remaining (%) after advanced oxidation as a function of the second-order rate constant of the compound with hydroxyl radical. The solid line represents predicted transformation assuming 0.5-log removal of 1,4-dioxane (adapted from Marron et al., 2019). Box and whisker plots represent observations of carbonyl compounds remaining after UV/H<sub>2</sub>O<sub>2</sub> in Plants A-E, which are plotted as a function of log  $k_{HO\cdot}$  for each compound (the box extends from the 25<sup>th</sup> to 75<sup>th</sup> percentile, whiskers from the 10<sup>th</sup> to 90<sup>th</sup> percentile, and the horizontal line within the box is plotted at the median). Samples containing compounds at concentrations below limits of quantification were excluded from analysis. See Table S7 for additional calculations.



**Figure 4.** Concentrations of carbonyl compounds in final product water from Plants A-G. Upper dotted line (CA) represents California's health-based notification level of  $100 \mu\text{g L}^{-1}$  and lower dotted line (NY) represents New York's MCL for total aldehydes of  $50 \mu\text{g L}^{-1}$ . Concentrations of unsaturated compounds are too low to be visible in the figure.



**Figure 5.**

Left, the contribution of carbonyl compounds to the total DOC concentration in RO permeate for Plants A–E. Right, a zoomed in distribution of compounds in the RO permeate from Plant D. Measurements for DOC and carbonyl compounds are median values from two sampling events ( $n=2$ ). \*Values for trace organic contaminants, as well as nitrogenous and halogenated disinfection byproducts, were not generated during this work and were taken from elsewhere for similar treatment trains.<sup>9,66</sup> Pie charts for Plants A–C and E can be found in Figure S12.