

# A Tale of Two Treatments: The Multiple Barrier Approach to Removing Chemical Contaminants During Potable Water Reuse

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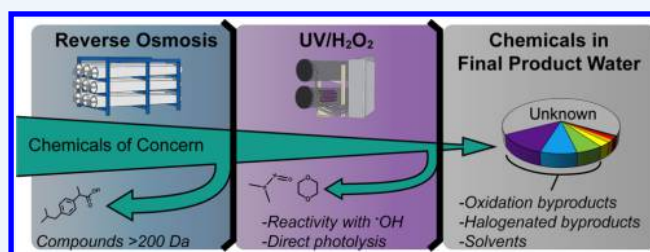
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**CONSPECTUS:** In response to water scarcity and an increased recognition of the risks associated with the presence of chemical contaminants, environmental engineers have developed advanced water treatment systems that are capable of converting municipal wastewater effluent into drinking water. This practice, which is referred to as potable water reuse, typically relies upon reverse osmosis (RO) treatment followed by exposure to ultraviolet (UV) light and addition of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>). These two treatment processes individually are capable of controlling many of the chemical and microbial contaminants in wastewater; however, a few chemicals may still be present after treatment at concentrations that affect water quality.

Low-molecular weight (<200 Da), uncharged compounds represent the greatest challenge for RO treatment. For potable water reuse systems, compounds of greatest concern include oxidation products formed during treatment (e.g., *N*-nitrosodimethylamine, halogenated disinfection byproducts) and compounds present in wastewater effluent (e.g., odorous compounds, organic solvents). Although the concentrations of most of these compounds decrease to levels where they no longer compromise water quality after they encounter the second treatment barrier (i.e., UV/H<sub>2</sub>O<sub>2</sub>), low-molecular weight compounds that are resistant to direct photolysis and exhibit low reactivity with hydroxyl radical (•OH) may persist. While attempts to identify the compounds that pass through both barriers have accounted for approximately half of the dissolved organic carbon remaining after treatment, it is unlikely that a significant fraction of the remaining unknowns will ever be identified with current analytical techniques. Nonetheless, the toxicity-weighted concentration of certain known compounds (e.g., disinfection byproducts) is typically lower in RO-UV/H<sub>2</sub>O<sub>2</sub> treated water than conventional drinking water.

To avoid the expense associated with managing the concentrate produced by RO, environmental engineers have begun to employ alternative treatment barriers. The use of alternatives such as nanofiltration, ozonation followed by biological filtration, or activated carbon filtration avoids the problems associated with the production and disposal of RO concentrate, but they may allow a larger number of chemical contaminants to pass through the treatment process. In addition to the transformation products and solvents that pose risks in the RO-UV/H<sub>2</sub>O<sub>2</sub> system, these alternative barriers are challenged by larger, polar compounds that are not amenable to oxidation, such as perfluoroalkyl acids and phosphate-containing flame retardants.

To fully protect consumers who rely upon potable water reuse systems, new policies are needed to prevent chemicals that are difficult to remove during advanced treatment from entering the sewer system. By using knowledge about the composition of municipal wastewater and the mechanisms through which contaminants are removed during treatment, it should be possible to safely reuse municipal wastewater effluent as a drinking water source.



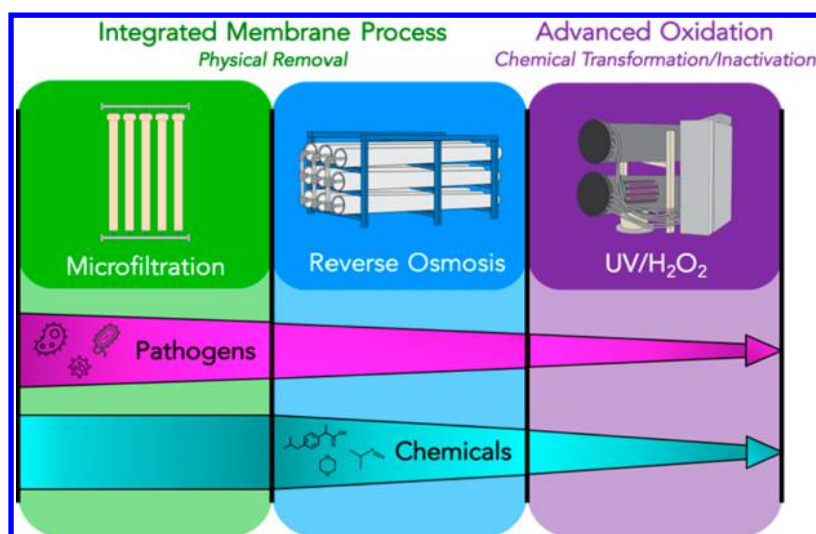
## INTRODUCTION

In the early 1900s, environmental engineers invented a means of treating source waters that were contaminated with waterborne pathogens.<sup>1</sup> The development of drinking water treatment systems meant that over approximately two decades, outbreaks of waterborne diseases like typhoid fever decreased, as lifespans were extended.<sup>2</sup> The system responsible for this

public health triumph typically involved a combination of physical removal of microbes by sand filtration followed by disinfection with chlorine. The term “multiple barrier,” which originally referred to watershed protection, water treatment,

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**Figure 1.** Advanced wastewater treatment for potable reuse employs microfiltration, RO, and UV/H<sub>2</sub>O<sub>2</sub>.

and addition of a chemical disinfectant after treatment, was adopted by researchers to describe this series of processes commonly employed during drinking water treatment.<sup>3</sup>

Although drinking water treatment was originally developed to address the risks of waterborne pathogens, it was extended to include removal of chemical compounds that impact aesthetics (e.g., geosmin, a compound with an organoleptic threshold of  $\sim 1$  ng/L<sup>4</sup>) and pose potential health risks (e.g., arsenic, which can cause cancer and other diseases<sup>5</sup>). To address the potential presence of chemical contaminants in drinking water, regulations developed in the 1970s and 1980s specified targets (e.g., maximum contaminant levels, MCLs) for chemicals known to impact human health, including synthetic organic compounds in source waters and toxic compounds formed during disinfection.

During this period, discharges of municipal wastewater effluent (i.e., treated sewage) were viewed as a potential risk to water supplies that could be mitigated through dilution of wastewater-impacted waters with water from cleaner sources. Over the past 50 years, expanding populations and decreasing availability of pristine water sources, coupled with advances in treatment technologies, have led to a gradual shift in attitude and practice.<sup>6</sup> Now, blending highly treated municipal wastewater into a source water (i.e., potable water reuse) is seen as a viable means of augmenting drinking water supplies.<sup>7</sup>

Around the time that potable water reuse systems were expanding, high-performance liquid chromatography-tandem mass spectrometry (LC-MS/MS) enabled the measurement of polar compounds that had rarely been detected in the aquatic environment. In particular, the discovery that trace concentrations (i.e.,  $< 5$  ng/L) of steroidal estrogens in wastewater were responsible for feminization of fish in effluent-receiving rivers,<sup>8–11</sup> coupled with detection of pharmaceuticals and personal care products in municipal wastewater effluent,<sup>10,12,13</sup> raised awareness of the issue of wastewater-derived contaminants.

There are currently  $\sim 25$  full-scale potable water reuse projects in operation worldwide.<sup>7</sup> Orange County (California) Water District's potable water reuse system was the first system to employ reverse osmosis (RO) and has served as a trendsetter, as the practice has expanded beyond Southern California. The project began in 1977 with the installation of

an advanced treatment plant that injected 57 000 m<sup>3</sup>/d of highly treated wastewater to counteract seawater intrusion caused by overpumping of groundwater. The facility originally treated half of the wastewater by RO to remove salts and chemical contaminants. Because of the high cost of early RO systems, the other half of the flow was subjected to granular activated carbon (GAC) filtration. Researchers studying these parallel physical treatment barriers reported that RO treatment resulted in lower concentrations of contaminants, such as ethylenediaminetetraacetic acid (EDTA) and dissolved organic carbon (DOC; i.e., after GAC and RO, DOC concentrations were 5.4 and 0.8 mg C/L, respectively).<sup>14,15</sup>

When the capacity of the system was expanded to 265 000 m<sup>3</sup>/d in 2008, an integrated membrane system with microfiltration and RO treated the entire flow. When the expansion was being designed, the toxic compounds *N*-nitrosodimethylamine (NDMA) and 1,4-dioxane were discovered in water produced by the first-generation treatment plant at concentrations exceeding levels known to pose chronic health risks. This discovery led to the installation of an additional chemical treatment barrier after RO: an advanced oxidation process (AOP) using UV and H<sub>2</sub>O<sub>2</sub>. The resulting advanced treatment plant, referred to as the Groundwater Replenishment System (GWRS), consisted of three sequential barriers to control waterborne pathogens: microfiltration, RO, and high-intensity UV light in the AOP. The system also combined physical (RO) and chemical (UV/H<sub>2</sub>O<sub>2</sub>) barriers to chemical contaminants (Figure 1). The GWRS currently operates with a flow of 379 000 m<sup>3</sup>/d. After its planned expansion to 492 000 m<sup>3</sup>/d in 2023, essentially all of the wastewater that can be recovered practically will be returned to the water supply. Research on the performance of this system is relevant worldwide, because the advanced treatment plant has operated longer than other projects that employ similar approaches, and it has been well-accepted by the community.<sup>16</sup> As a result, Orange County's multiple barrier treatment system has been replicated in potable water reuse projects in Texas,<sup>17</sup> Arizona,<sup>7</sup> Singapore,<sup>7</sup> and Western Australia.<sup>18</sup> Simply put, the GWRS potable reuse project has emerged as the "Gold Standard" to which proposed projects are compared.

Given the array of chemicals potentially present in wastewater, it would be difficult to validate their removal on

a chemical-by-chemical basis. A key assumption behind the “dual barrier” system is that physical (RO) and chemical (UV/H<sub>2</sub>O<sub>2</sub>) treatment systems will control chemical contaminants with different physical and chemical properties, and few chemicals will be insufficiently treated by the treatment sequence<sup>7,19</sup> (Figure 1). The veracity of this assumption is key to the performance of the dual barrier system.

### ■ REVERSE OSMOSIS AS A CHEMICAL BARRIER

Modern water reuse systems employ thin-film composite membranes for RO.<sup>20</sup> Dissolved solutes are excluded, because they diffuse through the polymer at rates that are much slower than that of the water molecules.<sup>21</sup> Other factors, such as electrostatic repulsion and van der Waals interactions, also affect solute removal during RO.<sup>22,23</sup> In general, uncharged compounds with molecular weights less than 200 Da are only partially rejected by RO membranes.<sup>24</sup> For charged compounds and larger compounds, concentrations typically decrease by over 95% during RO treatment under conditions employed in water reuse.<sup>25,26</sup>

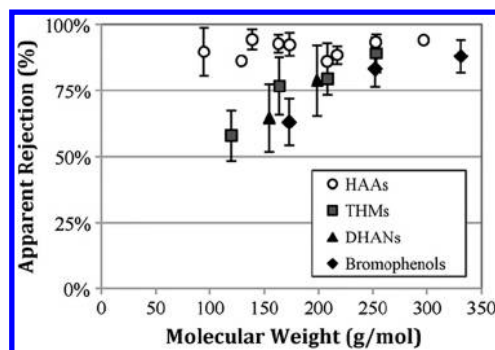
In contrast, compounds that pose the greatest challenges to the GWRS and similar facilities are uncharged, low-molecular weight compounds. NDMA (molecular weight = 74 g/mol) is a mutagenic and carcinogenic compound<sup>27</sup> (e.g., the notification level for NDMA in California is 10 ng/L<sup>28</sup>) that has been particularly problematic for potable water reuse systems. Early efforts to identify the source of NDMA implicated sewage (e.g., NDMA concentrations as high as 790 ng/L were detected in sewage<sup>29</sup>). NDMA was also formed when chloramines<sup>30,31</sup> or ozone<sup>32</sup> were applied upstream of microfiltration to control biological fouling on membrane surfaces. Precursors of NDMA include industrial chemicals<sup>33</sup> and chemicals present in domestic discharges, such as the wastewater from clothes washing.<sup>34</sup>

After NDMA was detected, efforts were made to control its formation and enhance its removal. Researchers discovered that minimizing the concentration of dichloramine—the chloramine species most responsible for NDMA formation—by using preformed monochloramine,<sup>35</sup> or by employing multiple introduction points for hypochlorite into ammonia-containing wastewater,<sup>36</sup> decreased NDMA formation. They also demonstrated that removal of NDMA during RO was affected by the type of membrane used,<sup>37</sup> the water temperature,<sup>38</sup> and the membrane age.<sup>39</sup>

Chloramination upstream of membrane processes can also produce low-molecular weight halogenated disinfection by-products (DBPs) through reactions with effluent organic matter.<sup>31,40</sup> These include a variety of toxic halogenated compounds (e.g., haloacetonitriles, haloacetamides, haloacetaldehydes, haloketones, and halonitromethanes).<sup>41,42</sup> Because of their small size (i.e., mostly <200 Da), these uncharged compounds are poorly rejected by RO membranes<sup>43,44</sup> (Figure 2).

When ozone is used as an oxidant upstream of microfiltration to reduce fouling,<sup>45</sup> the bulk organic matter in the wastewater effluent reacts with ozone and/or ·OH produced during ozone decomposition<sup>46</sup> to form aldehydes and ketones, such as formaldehyde and glyoxal.<sup>47</sup> Not only are many of these uncharged compounds poorly rejected during RO,<sup>48,49</sup> some exhibit high toxicity.<sup>50</sup>

In addition to oxidation products, there are compounds present in wastewater effluent that are poorly rejected by RO systems. Because most uncharged compounds are difficult to



**Figure 2.** Apparent overall rejection of select DBPs during RO, including charged haloacetic acids (HAAs) and uncharged trihalo-methanes (THMs), dihaloacetonitriles (DHANs), and bromophenols. Reproduced with permission from ref 43. Copyright 2010 Elsevier.

quantify by LC-MS/MS and are not monitored routinely, their presence has only come to the attention of researchers using sensitive gas chromatography-tandem mass spectrometry (GC-MS/MS) methods. For example, compounds with extremely low odor thresholds (i.e., 0.5–10 ng/L) are responsible for most consumer complaints about drinking water.<sup>51</sup> Odorous compounds, including 2,4,6-trichloroanisole (molecular weight = 211 g/mol), have been detected at concentrations up to an order of magnitude above their odor threshold after RO treatment.<sup>52</sup> Municipal wastewater also contains a variety of uncharged, low-molecular weight organic solvents (e.g., acetone, 1,4-dioxane). Concentrations of solvents in recycled water are usually below values developed for protection of public health.<sup>53,54</sup>

Despite their low frequency of detection in wastewater samples, solvents sometimes can pose serious problems for potable reuse systems. In 2001, at Orange County’s GWRS, 1,4-dioxane was detected prior to RO at up to 200 µg/L and in supply wells receiving recycled water at concentrations ranging from 4 to 20 µg/L<sup>55</sup> (the California notification level for the compound at the time was 3 µg/L). One significant 1,4-dioxane source was a manufacturer of cellulose acetate membranes (ironically, similar to membranes used in the facility).<sup>55</sup> In 2013, acetone was detected at the same facility at elevated concentrations for ~1 day<sup>56</sup> (Figure 3). Although solvents typically do not pose acute health risks at the concentrations detected after RO, such episodic events could result in taste and odor problems.

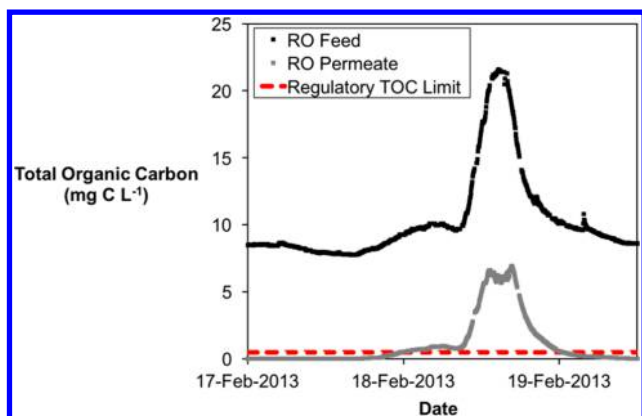
### ■ UV/H<sub>2</sub>O<sub>2</sub> AS A CHEMICAL BARRIER

When H<sub>2</sub>O<sub>2</sub> absorbs UV light, it undergoes homolytic cleavage to form ·OH (eq 1).



This process is particularly effective when it is used after RO due to the low concentrations of dissolved organic carbon (i.e., DOC <0.5 mg C/L), which typically serves as both a sink for ·OH and as a source of chromophores that compete for absorption of UV light. The steady-state concentration of ·OH ([·OH]<sub>ss</sub>) is a function of the rate of formation from photolysis of H<sub>2</sub>O<sub>2</sub> ( $R_{\text{form}, \cdot\text{OH}, \text{H}_2\text{O}_2}$ ), which can be reduced due to light screening from DOC and other chromophores, as well as by solutes that consume ·OH (eq 2). Steady-state ·OH concentrations typically range from  $1 \times 10^{-10}$  to  $1 \times 10^{-13}$  M when UV/H<sub>2</sub>O<sub>2</sub> is employed after RO in potable water reuse.<sup>57</sup>





**Figure 3.** Total organic carbon (TOC) online analyzer data at Orange County Water District GWRS. Immediate investigation as part of a source control program revealed that the increase was attributable to a pulse of acetone. The dashed line represents the TOC regulatory limit in California (0.5 mg C/L) for water produced in potable reuse. Raw data provided with permission from Orange County Water District and available from ref 56.

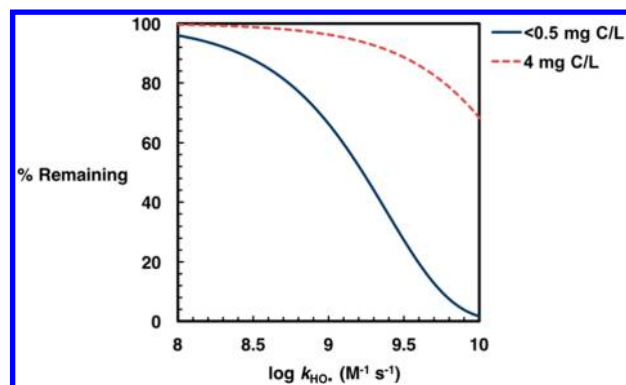
$$[\cdot\text{OH}]_{\text{ss}} = \frac{R_{\text{form}, \cdot\text{OH}, \text{H}_2\text{O}_2}}{\sum k_{\text{OH}, \text{C}_i} [\text{C}_i] + k_{\text{OH}, \text{H}_2\text{O}_2} [\text{H}_2\text{O}_2] + k_{\text{OH}, \text{DOC}} [\text{DOC}]} \quad (2)$$

Under typical operating conditions employed during UV/H<sub>2</sub>O<sub>2</sub> after RO treatment, an increase in DOC from 0.1 to 4 mg C/L will decrease [ $\cdot\text{OH}$ ]<sub>ss</sub> by approximately an order of magnitude.

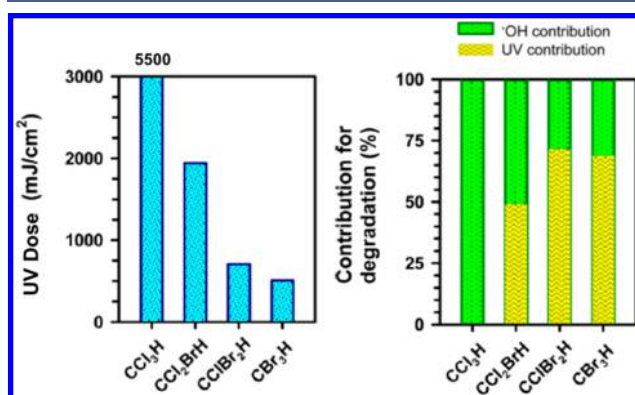
The transformation of a contaminant in UV/H<sub>2</sub>O<sub>2</sub> depends on its rate of photolysis and its reactivity with  $\cdot\text{OH}$  ( $k_{\text{HO}\cdot}$ ). Only compounds with high molar absorption coefficients and quantum yields (e.g., NDMA) are transformed to a significant extent by photolysis in UV/H<sub>2</sub>O<sub>2</sub> systems, and  $\cdot\text{OH}$  reacts with most organic compounds at nearly diffusion-controlled rates (i.e.,  $k_{\text{HO}\cdot} = (5\text{--}10) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ). The UV/H<sub>2</sub>O<sub>2</sub> process in advanced treatment is typically designed to achieve 1.2-log reduction (i.e., where a 1.2 log reduction corresponds to a 94.7% decrease in initial concentration or  $[\text{C}]/[\text{C}]_0 = 1 \times 10^{-1.2}$ ) in the concentration of NDMA (by direct photolysis) and 0.5-log reduction in the concentration of 1,4-dioxane (by  $\cdot\text{OH}$  oxidation). However, some of the same uncharged, low-molecular weight solvents and halogenated DBPs that are poorly rejected by RO also exhibit low reactivity with  $\cdot\text{OH}$  or do not undergo direct photolysis. For example, compounds like formaldehyde ( $k_{\text{HO}\cdot} = 1.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ) or chloroform ( $k_{\text{HO}\cdot} = 5.4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ) will not be removed to an appreciable extent (Figure 4).

Chloroform does not absorb UV light at 254 nm and exhibits low reactivity with  $\cdot\text{OH}$ . The UV dose needed for 50% removal of chloroform in a UV/H<sub>2</sub>O<sub>2</sub> system would be 5500 mJ/cm<sup>2</sup> (Figure 5).<sup>58</sup> The more toxic brominated trihalomethane species are better removed by both direct photolysis and to a minor extent by reaction with  $\cdot\text{OH}$  ( $k_{\text{HO}\cdot} = (6\text{--}10) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ), yet only 65% removal of bromoform would be expected under conditions used in most advanced treatment facilities (i.e., 750 mJ/cm<sup>2</sup> UV dose).

The design constraint of UV/H<sub>2</sub>O<sub>2</sub> in advanced treatment reflects the trade-off between system cost and the efficacy of the barrier. The less reactive, low-molecular weight compounds



**Figure 4.** Reactivity of compounds in UV/H<sub>2</sub>O<sub>2</sub> as a function of the log of the second-order rate constants of their reaction with  $\cdot\text{OH}$  (log  $k_{\text{HO}\cdot}$ ) assuming [ $\cdot\text{OH}$ ]<sub>ss</sub> =  $4 \times 10^{-10} \text{ M}$  (calculated based on 0.5-log removal of 1,4-dioxane,  $k_{\text{HO}\cdot} = 2.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ). The dashed line represents reactivity with a DOC concentration of 4 mg C/L under similar operating conditions.



**Figure 5.** UV dose (254 nm) needed to achieve 50% abatement of trihalomethanes (left) and the percentage contribution of direct photolysis or  $\cdot\text{OH}$  oxidation (right) in UV/H<sub>2</sub>O<sub>2</sub> with 3.4 mg/L H<sub>2</sub>O<sub>2</sub>. Adapted with permission from ref 58. Copyright 2016 American Chemical Society.

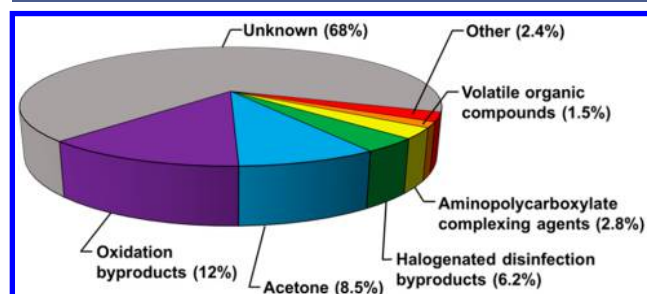
could be removed by increasing the size of the reactor. For example, 50% removal of chloroform through indirect photolysis could be achieved (Figure 5) but only by increasing the dose (and hence reactor size and energy consumption) by a factor of  $\sim 5$ .<sup>58</sup> Thus, oxidation of less-reactive contaminants, while theoretically possible, is too costly in practice.

When UV/H<sub>2</sub>O<sub>2</sub> or any other treatment process that relies upon oxidation is used, it is important to understand the potential formation of toxic byproducts. Although concentrations of target contaminants typically decrease during UV/H<sub>2</sub>O<sub>2</sub> treatment, oxidation processes mostly lead to compound transformation rather than complete mineralization.<sup>59</sup> For example, phenolic compounds can be transformed into products that are more toxic than the parent compounds (e.g., benzoquinones<sup>60</sup> and  $\alpha,\beta$ -unsaturated enedials and oxoanals<sup>61</sup>) during UV/H<sub>2</sub>O<sub>2</sub> treatment.

## ■ KNOWING THE UNKNOWN IN THE DUAL BARRIER SYSTEM

After close to three decades of research on chemical compounds in potable water reuse systems, it is evident that only a small subset of contaminants in wastewater effluent passes through RO membranes and resists oxidation by  $\cdot\text{OH}$  during UV/H<sub>2</sub>O<sub>2</sub> treatment. Under conditions typically

employed in advanced treatment plants, the final product water typically contains  $\sim 100 \mu\text{g C/L}$ .<sup>31,49</sup> Known organic compounds (mainly formaldehyde, acetone,<sup>49</sup> and halogenated DBPs<sup>31,54</sup>) account for  $\sim 35\%$  of the organic carbon present post-RO treatment (Figure 6). The remainder of the organic carbon ( $\sim 65 \mu\text{g/L}$ ) likely consists of other uncharged, low-molecular weight compounds.



**Figure 6.** Approximate contributions of select chemical contaminants to the DOC (assuming  $100 \mu\text{g C/L}$ ) post-RO treatment in potable water reuse. Data averaged and compiled from three different treatment facilities in refs 31, 49, and 54.

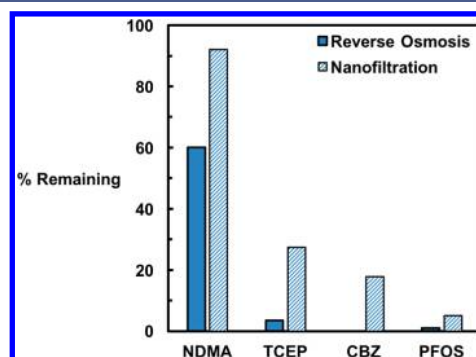
Because most of these neutral, low-molecular weight compounds are not amenable to quantification at these low concentrations by either GC-MS/MS or LC-MS/MS, it may be necessary to employ other approaches, such as bioanalytical tools, to assess the potential health risks associated with the residual constituents in product waters. A challenge for the application of bioanalytical tools to the problem is the significant concentration factor needed to obtain bioassay responses. Furthermore, the low-molecular weight, uncharged compounds are often lost during sample concentration due to their high volatility.<sup>62</sup> The National Research Council concluded that NDMA and DBPs likely pose the greatest chemical risks for consumers of recycled water.<sup>7</sup> However, it is important to note that these contaminants are present in source waters or can be formed during conventional drinking water treatment. When DBP concentrations from different types of waters are weighted by metrics of toxic potency, the total toxicity-weighted byproduct concentration is typically lower in recycled water produced by RO-UV/H<sub>2</sub>O<sub>2</sub> systems relative to conventional drinking water.<sup>31,63</sup>

### ■ POTABLE WATER REUSE WITHOUT REVERSE OSMOSIS TREATMENT

Under conditions typically employed during potable water reuse,  $\sim 15\%$  of the wastewater effluent is retained as RO concentrate.<sup>64</sup> Most communities that were early adopters of potable water reuse discharged their RO concentrate through existing ocean outfalls. However, discharge of RO concentrate is challenging for many inland communities, because zero-liquid discharge technologies<sup>65</sup> are expensive. As a result, many utilities are seeking alternatives to RO treatment.

Nanofiltration has been proposed as an alternative to RO, because tight nanofiltration membranes reject organic matter as well as microbes but allow monovalent salts to pass, resulting in a smaller volume of concentrate.<sup>66</sup> Another advantage is that nanofilters operating in place of RO membranes require less pressure, thereby reducing energy consumption and cutting electricity costs by up to 50%.<sup>66</sup> However, nanofiltration membranes are not as effective as RO

with respect to rejection of uncharged, low-molecular weight compounds (Figure 7). Furthermore, relative to RO, elevated concentrations of DOC after nanofiltration could reduce the efficacy of the UV/H<sub>2</sub>O<sub>2</sub> process by scavenging  $\cdot\text{OH}$  and absorbing UV light.



**Figure 7.** Percent remaining of NDMA, tris(2-carboxyethyl)-phosphine hydrochloride (TCEP), carbamazepine (CBZ), and perfluorooctanesulfonate (PFOS) after treatment by nanofiltration or RO. Data from refs 66–68.

Another alternative to RO employs the use of either powdered or granular activated carbon (PAC or GAC). For example, the Upper Occoquan Service Authority (Virginia) uses GAC to remove trace organic compounds and DOC prior to reservoir augmentation with recycled water.<sup>69</sup> Hydrophobic compounds tend to be well-removed by activated carbon, whereas charged compounds (e.g., naproxen, gemfibrozil, and ibuprofen) or hydrophilic compounds tend to be poorly removed under conditions typically employed during water treatment.<sup>26,70</sup> In addition, activated carbon is inefficient with respect to removal of perfluoroalkyl acids (PFAAs).<sup>71</sup> Finally, activated carbon must be regenerated more frequently when it is used to treat water with relatively high DOC concentrations, like municipal wastewater effluent.<sup>69</sup>

Another advanced treatment process involves use of ozone followed by sand filtration or filtration through GAC, which due to the presence of a biofilm is referred to as biologically activated carbon (BAC).<sup>72</sup> Combinations of ozone and BAC are currently being used in Switzerland to upgrade wastewater treatment plants discharging to sensitive aquatic ecosystems.<sup>73</sup> Compared to RO/AOP, combined ozone/BAC consumes less than half of the energy and costs approximately half as much to operate and maintain.<sup>74</sup> This approach does not remove compounds that exhibit low reactivity with ozone or  $\cdot\text{OH}$  (e.g., PFAAs). Furthermore, ozonation of wastewater can produce high concentrations of bromate,<sup>75,76</sup> a potential human carcinogen (MCL =  $10 \mu\text{g/L}$ ). Careful control of ozone doses during ozonation of wastewater can keep bromate concentration within an acceptable range.<sup>77</sup> In addition to wastewater treatment plant upgrades, combined ozone/activated carbon systems have also been used in existing and planned potable reuse systems, including surface water augmentation in Gwinnett County (Georgia)<sup>7</sup> and direct potable reuse in Windhoek (Namibia).<sup>18</sup>

### ■ THE THIRD BARRIER: CHEMICAL STEWARDSHIP TO SUPPORT POTABLE WATER REUSE

Industrial discharges were important sources of NDMA and 1,4-dioxane at Orange County Water District's GWRS, despite

a relatively modest number of industrial dischargers and a well-funded industrial source control program. Other examples of problematic compounds reported elsewhere include antyiel-  
lowing agents discharged by textile industries that produce high concentrations of NDMA upon ozonation<sup>78</sup> and resin manufacturing plants that discharge problematic amounts of odorous solvent 1,3-dioxane.<sup>79</sup> Consumer products like the insecticide fipronil, which is applied topically to dogs, has been detected in municipal wastewater at concentrations ranging from 13 to 88 ng/L.<sup>80</sup>

Ultimately, the dual barrier system may not provide adequate protection from all of the chemical contaminants present in wastewater. Rather than rely upon additional treatment processes, a third barrier may be necessary: robust source control programs that employ existing knowledge, as described in the previous sections, to identify and eliminate compounds that are not adequately removed in advanced treatment systems. The third barrier may be particularly important in systems that do not employ RO, where compounds like PFAAs and phosphate-containing flame-retardants like TCEP will not be well removed. Product substitution or better chemical stewardship could be much more cost-effective and sustainable than relying solely on treatment processes. This would also reduce exposure of aquatic ecosystems and downstream water supplies to these contaminants. The implementation of rigorous source control and chemical stewardship measures, coupled with research to identify problematic contaminants, will protect public health and provide confidence in potable water reuse as a viable path for communities worldwide.

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The authors declare no competing financial interest.

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