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Odorous Compounds in Municipal Wastewater Effluent and Potable Water Reuse Systems

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S Supporting Information

ABSTRACT: The presence of effluent-derived compounds with low odor thresholds can compromise the aesthetics of drinking water. The potent odorants 2,4,6-trichloroanisole and geosmin dominated the profile of odorous compounds in wastewater effluent with concentrations up to 2 orders of magnitude above their threshold values. Additional odorous compounds (e.g., vanillin, methylnaphthalenes, 2-pyrrolidone) also were identified in wastewater effluent by gas chromatography coupled with mass-spectrometry and olfactometry detection. Full-scale advanced treatment plants equipped with reverse osmosis membranes decreased odorant concentrations considerably, but several compounds were still present at concentrations above their odor thresholds after treatment. Other advanced treatment processes, including ozonation followed by biological activated carbon and UV/H2O2 also removed effluentderived odorants. However, no single treatment technology alone was able to reduce all odorant concentrations below their odor threshold values. To avoid the presence of odorous compounds in



drinking water derived from wastewater effluent, it is necessary to apply multiple barriers during advanced treatment or to dilute wastewater effluent with water from other sources.

INTRODUCTION

In many regions facing freshwater scarcity, municipal wastewater effluent constitutes a considerable part of the potable water supply. Over the past two decades, the practice of subjecting wastewater effluent to advanced treatment—including reverse osmosis, activated carbon adsorption and chemical oxidation has become more commonplace. The even more widespread practice of obtaining potable water supplies from effluentimpacted surface waters is also growing as population pressures place further stress on freshwater supplies.

Despite the increasing importance of potable water reuse and intensified attention being given to wastewater-derived trace organic contaminants, little effort has been directed at compounds that could cause taste and odor problems in drinking water. Previous research has demonstrated that potent odorants in lakes, rivers and water distribution systems ¹⁻⁶ frequently result in consumer complaints. Odorous compounds in drinking water have often been attributed to algae or bacteria in the source water or fungi in biofilms on pipe surfaces (see Supporting Information (SI) Table S1). For example, geosmin and 2-methylisoborneol have been identified as the sources of earthy odors in numerous surface waters ⁶⁻⁸ while the musty odor of 2,4,6-trichloroanisole has been detected in rivers and water distribution systems.^{3,4,7} Due to the potency of these odorants, sensitive

analytical methods with gas chromatography coupled with mass spectrometry or olfactometry are often needed to identify $^{9-11}$ and quantify these compounds in drinking water supplies.^{12,13}

Municipal wastewater effluent also contains odorants but most previous studies on wastewater-derived odors have focused on nuisance air pollution produced by wastewater treatment processes (e.g., reduced sulfides in sludge thickening).^{14–16} These studies have been useful in the assessment of commonly applied control measures, such as biofilters, activated carbon, and chemical oxidants,¹⁷ but they have not provided insight into the potential for wastewater-derived odorants to compromise potable water supplies. Through experience, engineers have learned that it is often necessary to use activated carbon during drinking water treatment to minimize taste and odor issues in effluent-impacted sources but few attempts have been made to quantify the wastewater-derived compounds responsible for taste and odors.

To assess the occurrence and fate of odorants in potable water reuse systems, analytical techniques developed by researchers

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studying taste and odors in drinking water and the food and beverage industry were applied to reclaimed water systems. Quantitative analysis of known potent odorants was accomplished by gas chromatography/mass spectrometry (GC/MS) while other compounds were analyzed by GC/MS-Olfactometry (GC/MS-Olf) and flavor profile analysis (FPA). To characterize the occurrence and fate of odorants, samples were collected at different stages of treatment from six full-scale advanced treatment plants. The removal of the most potent odorants was then evaluated in pilot- and bench-scale studies of different treatment processes under controlled conditions.

MATERIALS AND METHODS

Chemical Standards. 2-Methylisoborneol, 2,3,4-trichloroanisole and 2,4,6-tribromoanisole were purchased from Dr. Ehrenstorfer Gmbh (Augsburg, Germany). 2-Bromophenol, 2,6dibromophenol, 2,4,6-trichloroanisole, 2,4,6-trichlorophenol, 2,4,6-trichloroanisole, 2,3,6-trichloroanisole, β -ionone, and iodoform were purchased from Aldrich (St Quentin Fallavier, France) and Sigma-Aldrich (Saint Louis, MI). Deuterated surrogate standards (d5-geosmin and d5–2,4,6-trichloroanisole) were purchased from Cambridge Isotopes (Andover, MA). All other solvents and reagents were purchased at the highest level of purity available from Sigma-Aldrich and Merck KGaA (Darmstadt, Germany). Ultrapure deionized water ($R \ge 18.2 \text{ M}\Omega$ -cm) was produced in-house with a Milli-Q purification system.

Sample Collection. Samples were collected from six full-scale potable water reuse systems between September 2009 and February 2011 (SI Table S2). The plants had design capacities ranging from 60 to 200 ML d⁻¹. Five rounds of bimonthly samples were collected at Plants A–D while Plants E and F were sampled twice. All six advanced treatment plants received effluent from municipal wastewater treatment plants employing secondary biological treatment.

In full-scale Plants A-D, incoming nitrified effluent was chlorinated with an initial concentration of approximately 2 mg/L Cl₂ prior to microfiltration and reverse osmosis. The chlorine contact time between oxidant addition and the dechlorination point upstream of the reverse osmosis membrane was approximately 30 min. Plants E and F employed similar pretreatment trains except the wastewater entering the advanced treatment plants was not nitrified. After reverse osmosis, ultraviolet (UV) disinfection was employed at Plants A–D at fluence values of approximately 80 mJ/cm². UV/H₂O₂ was employed at Plants E and F with a fluence of approximately 500 mJ/cm² and an initial H₂O₂ concentration of approximately 5 mg/L. In Plant A, ozonation (2 mg/L dose, 10 min contact time) was applied to a portion of the water after UV disinfection.

Samples were also collected at a pilot plant treating denitrified municipal wastewater effluent with biological activated carbon filter (BAC) as detailed in Reungoat (2010).¹⁸ Pilot plant samples were collected during February and April 2010 before and after passage of the water through three different treatment columns: BAC without ozonation, ozonation followed by BAC, and ozonation followed by sand filtration. Before it was applied to the columns, wastewater effluent was ozonated (2 mg/L initial concentration) and subjected to coagulation, flocculation and aeration. For the two columns employing ozonation, an initial concentration of 5 mg/L O₃ and a 15 min contact time was employed.

All samples were collected in 1 L amber glass bottles with minimal headspace, shipped in iced coolers with overnight express service and extracted within 48 h of receipt. Samples were stored at 4 °C and were filtered (0.45 μ m) prior to extraction. Field blanks, matrix spike samples and duplicates were included for analysis in all sampling rounds.

Benchscale Experiments. Benchscale experiments were performed to assess the treatment efficacy of UV, UV/H_2O_2 , chlorination, and chloramination. Secondary wastewater effluent or reverse osmosis permeate samples collected from Plants A and C were amended with target odorants at concentration approximately ten times higher than their lowest reported odor thresholds. Concentrated spiking solutions contained methanol because a number of commercial standards were only available in this solvent. Less than 50 μ L of methanol was added to each 4 L sample prepared for the bench-scale experiments. Under these conditions, the steady-state concentrations of OH• are estimated to be reduced by methanol by approximately 90% and 20% in reverse osmosis permeate and secondary effluent, respectively (see SI).

UV and UV/H₂O₂ treatments were assessed in a tubular stainless steel flow reactor (2.6 L, 15 cm o.d.) with helical internal baffles. Other than a 10-cm segment of Tygon tubing attached to the peristaltic pump, steel tubing was used to minimize losses of odorants via sorption. No loss of compounds was observed in control experiments without UV light. The reactor was equipped with two Puritec immersible low-pressure UV lamps (OSRAM, Munich, Germany) installed laterally in the center of the reactor. UV fluence was estimated from the average hydraulic residence time and photometer reading taken at quartz portholes located along the reactor. H₂O₂ was quantified in water flowing in and out of the reactor by KMnO₄ titration.¹⁹

For chlorination and chloramination experiments, secondary effluent samples were dosed in 1-L amber glass bottles at initial concentrations of 5 and 15 mg/L as Cl_2 typically applied in effluent chlorination with contact times up to 120 min. Free chlorine was added from a standardized stock solution of sodium hypochlorite. Premixed chloramine dosing solutions were made fresh daily by slowly adding sodium hypochlorite with NH₄Cl at elevated pH.²⁰ Free chlorine and monochloramine were determined using DPD colorimetric kits with a Hach DR 3800 spectrophotometer (Loveland, CO). Controls without free chlorine and chloramine indicated negligible losses of compounds. Experiments were carried out in triplicate. At the end of the experiments, excess oxidant was quenched by sodium bisulfite.

Analytical Methods. Solid phase extraction of 0.45 μ mfiltered samples was performed using a hydrophobic/hydrophilic polymeric resin (Oasis-HLB by Waters) conditioned with 5 mL methanol, 5 mL dichloromethane and 10 mL Milli-Q water. Sample pH values were adjusted to 4–5 with HCl to ensure that the weakly acidic bromophenols (pK_a 7–9) and weakly basic methoxypyrazines (pK_a ~3) were present in their neutral forms. Samples were amended with 5 ng of d5-geosmin and d5–2,4,6trichloroanisole prior to extraction. Analytes were eluted from the cartridge with 10 mL dichloromethane. A sample preconcentration factor of 1000 yielded optimal instrument sensitivity while minimizing loss of the most volatile analytes. Sample extracts were concentrated to a final volume of 500 μ L using a 40 °C circulating water bath and a gentle stream of ultrapure N₂.

Analysis was carried out with an Agilent 7890A series GC system with flow equally split between a mass spectrometer and

an olfactory detector port (ODP). The 5975C series mass spectral detector (Agilent, Santa Clara, CA) was operated in selected ion monitoring (SIM) mode with chromatographic conditions as described in Zhang et al. (2006).¹² Olfactometry was conducted with a Gerstel ODP3 (Mülheim an der Ruhr, Germany). Sample from Plants E and F were analyzed using a Quattro micro GC triple quadrupole tandem mass spectrometer (Waters, Milford, MA) under similar chromatographic conditions.

Olfactometry and flavor profile analysis (FPA) were also employed to identify other odorous compounds as described elsewhere.²¹ Briefly, olfactory analysis was carried out for 15 min beginning one minute after the solvent peak while, simultaneously, mass spectra were collected in full-scan mode between m/z 40 to 550. Each sample was analyzed by three members of a team of eight analysts who had been trained using reference standards and blind testing. Peak intensities of odorous compounds were classified on a scale of 0 to 4, with 4 being the strongest odor intensity. Only peaks eliciting a response of 3 (moderate intensity) or greater in 75% of the secondary effluent samples were evaluated further. Odor descriptors were categorized according to the wastewater odor wheel.²²

Compounds associated with the most frequently detected odors were identified using several tools. Mass spectra were compared with the NIST mass spectral library (Agilent, Santa Clara, CA). Odor descriptions and retention times also were compared with data for compounds reported in peer-reviewed publications and public databases. Finally, compounds identified by these screening methods were compared with mass spectra, reference times and olfactometry data obtained from reference standards.

Whole sample odor was assessed by sensory panels taken from the eight trained analysts using the flavor profile analysis method described in Standard Method 2170B.²³

RESULTS AND DISCUSSION

Odorous Compounds in Municipal Wastewater Effluent. Twelve of the 15 target odorants were detected at least once in secondary effluent at concentrations up to approximately 100 ng/L (SI Table S3). The median concentrations of 2-methylisoborneol (2MIB, 11 ng/L), geosmin (27 ng/L), 2,6-dibromophenol (26DBP, 2.8 ng/L) and 2,4,6-trichloroanisole (246TCA, 9.5 ng/L) in secondary effluent were between 2 and 100 times higher than their respective odor thresholds. Another notable odorant, 2,4,6-tribromoanisole (246TBA) was detected in 40% of the secondary effluent samples at concentrations up to 6.6 ng/L.

To express the concentration of odorants relative to their odor intensity, the measured concentrations were divided by the lowest reported odor thresholds (SI Table S1). This ratio, referred to as the relative odor intensity, indicates that the compounds of greatest concern detected in secondary effluent were 2,4,6-trichloroanisole and geosmin (Figure 1). The characteristic earthy and musty odors of these compounds were repeatedly detected during flavor profile analysis of secondary effluent. 2,4,6-trichloroanisole and geosmin were detected during olfactometry as strong odors—consistently scoring between 3 (moderate) and 4 (strong) during olfactometry runs—at retention times corresponding to those observed for authentic standards.

The relative concentrations of the dominant target odorants in secondary effluent exhibited considerable intraplant variability



Figure 1. Relative odor intensity (ROI) of common odor compounds detected in secondary effluent from municipal wastewater treatment plants.



Figure 2. Intraplant variability of common odor compounds in secondary effluent. Standard deviation was not calculated for locations E, F, and G because only two rounds of sampling were performed.

(Figure 2). 2,4,6-trichloroanisole was the dominant odorant at Plants A, B, F, and G while geosmin contributed significantly to the overall odor at Plants B, C, and D. Geosmin was the dominant odorant at Plant E, which was the only treatment plant employing a trickling filter. The intraplant variability may have been influenced by precursor concentrations in the raw sewage or by the microbial community in the biological treatment systems.

Primary effluent samples collected between November 2009 and June 2010 indicated that biological wastewater treatment was a potential source for geosmin and 2,4,6-trichloroanisole (SI Table S3). In surface water supplies, geosmin is produced by a wide variety of microbes which also are commonly found in activated sludge, including *cyanobacteria, actinomycetes*,⁷ *actinobacteria*,²⁴ and *anabaena*.²⁵ Odors attributed to 2-methyl-isoborneol and geosmin have been reported in effluent from activated sludge plants treating wastes from pulp mills.²

Biological wastewater treatment was the main source of 2,4,6trichloroanisole. While primary effluent samples rarely contained the odorant (median concentration <0.38 ng/L), the compound was present in secondary effluent at a median concentration of 9.5 ng/L. 2,4,6-trichlorophenol, a potential precursor to 2,4,6trichloroanisole, was consistently detected in primary effluent. The decrease in concentration of 2,4,6-trichlorophenol during biological wastewater treatment in Plants A–D was correlated with the concentration of 2,4,6-trichloroanisole detected in the secondary effluent ($r^2 = 0.851$, SI Figure S1). Previous research has demonstrated that halophenols can be converted into haloanisoles in rivers ^{2,7} and in drinking water distribution systems.³ Fungi that biomethylate halophenols in biofilms of water distribution systems ^{3,7} are also present in many activated sludge microbial communities.²⁶ To test the hypothesis that halophenols served as precursors for haloanisoles during biological wastewater treatment, batch activated sludge experiments were conducted using ¹³C-labeled 2,4,6-trichlorophenol and 2,4,6-tribromophenol (SI Figure S2). During a 24 h incubation period, a molar yield of 5% was observed for conversion of halophenols into their respective haloanisoles, which is consistent with observations from the full-scale municipal treatment systems. While we did not identify microbes responsible for halophenol methylation, it is evident that haloanisoles were formed during biological wastewater treatment process.

The concentrations of brominated compounds such as 2,6dibromophenol, 2,4,6-tribromoanisole, and 2,4,6-tribromophenol in secondary effluent were correlated with effluent conductivity. Highest concentrations of brominated compounds were detected in Plant D, E, and F (conductivity $800-1800 \ \mu\text{S/cm}$, $<500 \,\mu$ S/cm in other treatment plants). Converting conductivity to Br⁻ concentration by assuming salt composition identical to seawater, we estimated Br⁻ concentrations of 160 to 1000 μ g/L in Plant D, E, and F which is the range where brominated disinfection byproducts start to become important in chlorinated water.^{27,28} The water supply for Plant D includes a tidally influenced river and desalinated seawater. Water supplies at Plants E and F include a local aquifer with known seawater intrusions and bromide-rich imported water. On the basis of these results, we surmise that the halophenols may be formed when chlorine is used during sewage treatment or in household applications.

In addition to the earthy/musty odors from geosmin, 2-methylisoborneol and 2,4,6-trichloroanisole, odors classified as rancid, sulfide, soapy, and fishy also were detected frequently during flavor profile analysis of secondary effluent. Characterization of secondary effluent by olfactometry yielded 15 odorous compounds which were consistently present at intensities comparable to geosmin and 2,4,6-trichloroanisole. During GC-MS/Olf, the earthy/musty odors characteristic of 2-methylisoborneol, geosmin and 2,4,6-trichloroanisole were detected at the expected retention times, confirming the identity of these three compounds. Other compounds identified during olfactometry of secondary effluent by comparison of authentic standards included 2-pyrrolidinone, methylnaphthalene isomers, hydroxyvanillin and vanillin.²¹ Methylnaphthalenes have recently been identified as an off-flavor in popular breakfast cereal²⁹ and vanillin has been reported in influent and effluent from wastewater treatment plants.³⁰

Fate of Odorous Compounds during Reverse Osmosis Treatment. Reverse osmosis treatment resulted in substantial reductions in the concentrations of potent odorants in full-scale treatment plants. Concentration of odorants quantified by GC/MS decreased by 78 to 97%, depending on the compound (SI Table S3). For compounds analyzed by GC/olfactometry, intensity scores decreased by 1 to 3 intensity units (e.g., from an average score of 3.7 to 3.0 for 2,4,6-trichloroanisole; from 3.7 to 0.7 for xylene isomers) depending on the abundance and threshold of the compounds. Although a relatively high average rejection of 86% was observed for 2,4,6-trichloroanisole, the compound and its musty odor were still observed during GC-MS, flavor profile analysis and GC/Olf due to its abundance in

feedwater and its extremely low odor threshold. Quantitative analysis indicated that the concentration of 2,4,6-trichloroanisole was 10–70 times higher than the odor threshold after reverse osmosis. For geosmin, the permeate contained concentrations close to the odor threshold. Several of the compounds identified by olfactometry—including 2-pyrrolidinone, methylnaphthalenes, vanillin, and hydroxyvanillin—also were detected in the reverse osmosis permeate. In the full-scan chromatograms, peak areas for these compounds decreased by 30–80% after reverse osmosis.

Previous research indicates that low-molecular weight and neutral compounds are often not completely removed during reverse osmosis treatment.³¹⁻³³ For example, removal of N-nitrosodimethylamine (NDMA, MW = 74 Da) ranged from 10 to 50% in full-scale plants with thin film composite membranes³ and 25 to 55% in benchscale systems with composite polyamide membranes.³⁵ Monitoring of odorants before and after reverse osmosis at the treatment plants indicated average rejection of 90% and 95% for 2-methylisoborneol (MW = 168 Da) and geosmin (MW = 182 Da), respectively. Meanwhile, 2,4,6-trichloroanisole (MW = 212 Da) and 2,6-dibromophenol (MW = 252 Da) only decreased by an average of 86% and 76%, respectively. The lower removal efficiency for 2,6-dibromophenol was consistent with previous studies indicating that the phenolic moiety can enhance passage of organic compounds through reverse osmosis membranes.³² Other neutral low-molecular weight compounds detected by GC-Olfactometry (e.g., 2-pyrrolidinone, MW = 85 Da and methylnaphthalenes, MW = 108 Da) did not exhibit evidence of substantial removal during reverse osmosis treatment.

Fate of Odorous Compounds during Oxidative Treatment. Oxidants used for disinfection or in advanced oxidation processes have the potential to remove odors from water.^{36–38} Transformation reactions produce changes in molecular structures that alter the affinity of the compounds for olfactory receptors. In some cases, such as oxidation of sulfides, oxidation eliminates the odor of the compounds. To assess the potential for removal of odorous compounds during disinfection or oxidative treatment, chlorination, ozonation, and an UV/H₂O₂ advanced oxidation process were evaluated (SI Table S4).

Chlorine and chloramine are capable of transforming many organic compounds under the conditions employed in drinking water treatment.³⁹ Based on the apparent reaction rate constants under circumneutral pH conditions, free chlorine (as HOCl or OCl⁻) should oxidize certain compounds with carbonyl groups (i.e., β -ionone, nonadienal, lactones), and to a lesser extent, phenolic groups (i.e., halophenols, vanillins). Free chlorine is not expected to be strong enough to oxidize alcohols (i.e., geosmin, 2-methylisoborneol) or haloanisoles. Chloramine is a weaker oxidant than free chlorine and could potentially react with compounds that are oxidized by chlorine at a slower rate.

Samples collected from full-scale treatment plants that applied chlorine prior to reverse osmosis did not exhibit significant removal of the five frequently detected odorants (p < 0.05). However, in approximately 25% of the samples from advanced treatment plants where effluent was denitrified prior to free chlorine addition (Plants A–D), the concentration of bromophenols increased. Bench-scale chlorination experiments conducted with free chlorine and NH₂Cl at doses ranging from 50 to 1800 mg/L·min confirmed these observations (SI Table S4). Only bromophenols, β -ionone, and nonadienal were transformed during free chlorine treatment. During chloramine bench-scale experiments, only nonadienal exhibited a measurable

decrease in concentration (by 40%) after a dose of 1800 mg/ L·min. The flavor profile panel reported that odors of free chlorine or chloramines masked the odors of other odorants in the wastewater effluent. GC-Olfactometry of treatment plant and benchscale experiment samples also indicated that chlorination or chloramination did not lower the odor intensity of odorous compounds in wastewater effluent.

Poor removal of odorous compounds is also expected for UV treatment at recommended germicidal doses ($60-100 \text{ mJ/cm}^2$), as practiced at Plants A–D. UV treatment has previously been documented to be ineffective in the removal geosmin and 2-methylisoborneol, even at doses up to 30 times higher than the germicidal dose.³⁶ Odorous compounds with conjugated bonds (i.e., halophenols, haloanisoles, β -ionone, and non-adienal) might be more reactive during UV treatment. Furthermore, indirect photolysis enhanced by effluent organic matter might also contribute to removal of odorous compounds.⁴⁰

Full-scale UV disinfection at Plants A–D, at a dose of 80 mJ/ cm², applied to permeate containing 2,6-dibromophenol, geosmin and 2,4,6-trichloroanisole did not produce detectable decreases in the concentrations of odorous compounds (p < 0.05). Similarly, flavor profile analysis and GC-olfactometry results did not show loss of any of the dominant odorants in the permeate during UV disinfection. To further evaluate the potential of UV treatment to remove odorants, wastewater effluent and reverse osmosis permeate spiked with target compounds were subjected to UV irradiation at up to 20 times the germicidal dose. As expected, the concentrations of halophenols, haloanisoles, β -ionone, and nonadienal decreased by >70% in reverse osmosis permeate after a fluence of 1000 mJ/cm² (Figure 3). Slightly faster removal of these compounds was observed when UV treatment was conducted in secondary effluent. For 2-methylisoborneol and geosmin, removal by direct UV photolysis in permeate was minimal (<5% loss at fluence values of 1000 mJ/ cm^2) while the concentration of 2,4,6-trichloroanisole decreased by approximately 20% at the same fluence. Slightly higher removal of 2-methylisoborneol, geosmin, and 2,4,6-trichloroanisole were observed in secondary effluent, presumable due to indirect photolysis. During GC-Olfactometry, the intensity of strong odor peaks (mean intensity 4) only decreased to moderate-strong levels (mean intensity 3.4) after application of 1000 mJ/cm^2 for a few odorants (including 5-hydroxyvanillin and vanillin). All other odorants were unaffected by UV treatment.

Addition of H₂O₂ to the UV reactor should increase the removal of odorants through the production of hydroxyl radicals. In a previous study with geosmin and 2-methylisoborneol, UV treatment in ultrapure water resulted in a decrease of approximately 10% for both odorants. Due to the presence of methanol in the spiking solution, the rates of contaminant disappearance observed in the bench-scale studies are slower than those expected in the treatment plant, especially in RO permeate. After addition of H₂O₂, concentration of the compounds decreased by more than 70% at the same UV fluence.³⁶ At plants that employed UV/H₂O₂ treatment (E and F), only 2-methylisoborneol and 2,4,6-trichloroanisole were detected after reverse osmosis, at concentrations up to 1.9 ng/L and 3.4 ng/L, respectively. These compounds were not detected above their method detection limits after UV/H2O2 treatment. During benchscale experiments with reverse osmosis permeate (Figure 4), nearly complete (>95%) removal of all odor compounds was observed at fluence of 1000 mJ/cm² and an initial H_2O_2 concentration of 10 mg/L. As predicted by the 4-fold increase in the OH[•] sink terms in secondary effluent (SI Table S7), the removal of odorants was noticeably slower in secondary effluent relative to reverse osmosis permeate.

GC/Olfactometry results indicated that UV/H_2O_2 treatment was effective in reducing the concentration of most odorant compounds below their threshold levels. For potent odorants in wastewater effluent, the intensity score decreased by at least 2 intensity units (e.g., from a mean of 3.3 to 0.3 for 2,4,6trichloroanisole, Table 1).

Previous research has demonstrated the removal of odorous compounds 37,38 and halophenols 41 during ozonation. Only β -ionone, 2,6-(E,Z)-nonadienal and halophenolate anions (present at high pH) react quickly with O₃ [$k_{\rm O3}$ >10⁴ $M^{-1}s^{-1}$]. 38 Geosmin, 2-methylisoborneol, and haloanisoles are transformed during ozonation mostly by OH*, making the process less effective in wastewater effluent where more OH* scavengers are present.

Ozonation at Plant A (initial O_3 concentration 2 mg/L, contact time 10 min) was applied on reverse osmosis permeate



Figure 3. UV treatment of odor compounds observed during benchscale experiment of spiked secondary effluent and reverse osmosis permeate at fluence $0-2000 \text{ mJ/cm}^2$. Initial concentration $C_o = 50 \text{ ng/L}$.



Figure 4. UV/H_2O_2 treatment of odor compounds observed during benchscale experiment of spiked secondary effluent and reverse osmosis permeate at UV fluence $0-2000 \text{ mJ/cm}^2$ and $10 \text{ mg/L} H_2O_2$ dose.

containing geosmin, 2,4,6-trichloroanisole and 2,6-dibromophenol at concentrations up to 50 times the respective odor thresholds. Under these conditions, ozonation decreased the concentrations of odorants to levels below their GC-MS detection limits. The strong earthy/musty odors present in the permeate (intensity >3) were not reported by panelists in flavor profile analysis or GC-Olfactometry with the exception of 2-pyrrolidinone, which was present at a weak intensity (\sim 1). At the biofilter pilot plant (Plant G), preozonation (5 mg/L, 15 min) was applied to wastewater effluent that contained geosmin, 2-methylisoborneol, 2,4,6-trichloroanisole, 2,3,4-trichloroanisole, 2,4,6-tribromoanisole at concentrations up to 50 times higher than the respective odor thresholds. Under these conditions, the concentration of 2-methylisoborneol decreased by between 60 and 90% and the haloanisole concentrations decreased by approximately 40%. The odors of geosmin, 2-pyrrolidinone and lactones were still detected by the panelists during GC-olfactometry of the ozonated effluent.

Fate of Odorous Compounds during Activated Carbon Treatment. Historically, granular and powder activated carbon have been used to eliminate taste and odor caused by geosmin and 2-methylisoborneol.^{42,43} Other odorous compounds identified in wastewater effluent generally have a similar or higher affinity for activated carbon to geosmin and 2-methylisoborneol, indicating a high potential for removal. BAC has previously been shown to remove a variety of pharmaceuticals with log K_{ow} values above 3¹⁸ with better removal observed for more readily biodegradable and hydrophobic compounds.

At the BAC pilot treatment system, 2,4,6-trichloroanisole, 2-methylisoborneol and geosmin as well as 10 other odorants were detected by olfactometry in the column influent. Without ozone pretreatment (SI Table S6), BAC treatment reduced the concentration of geosmin (51 and 61%) and 2-methylisoborneol (60 and 53%). It also reduced the concentration of 2,4,6trichloroanisole from about 4 ng/L to below the method detection limit (<0.22 ng/L). When ozone was applied prior to the biofilter in Plant G, complete removal of all odor compounds (>95%) was observed. No significant odor was detected during GC-olfactometry of samples from the outlet of biofilter pretreated with ozone, while at least eight odorants (including 2-pyrrolidone, methylnaphthalene isomers, and alkyl acids) were still detected at weak intensity in BAC samples without ozonation.

Dilution and Volatilization of Odorous Compounds in Surface Waters. In many situations, secondary effluent is discharged to surface waters that serve as potable water supplies. As indicated previously, at least 15 odorants are typically present in secondary effluent at concentrations above their odor thresholds. The dilution of secondary effluent with water free from odorous compounds could eliminate aesthetic problems downstream of the outfalls. For example, effluent containing 10 ng/L of 2,4,6-trichloroanisole (i.e., the median concentration detected in effluent samples) would need to be diluted until effluent accounted for less than 1% of the total flow before the concenontration of the compound in the source water would no longer exceed the odor threshold. Application of flavor profile analysis to diluted wastewater effluent from Plants A and C (11 and 27 ng/L 2,4,6-trichloroanisole, respectively) indicated that a weak earthy/musty odor could still be detected by panelists when effluent accounted for 3% of the sample volume. At this dilution factor, odors of 2,4,6-trichloroanisole and geosmin (intensity 2.0-3.0) were confirmed by GC-Olfactometry. In addition, weak odors at retention times corresponding to those of 2-pyrrolidinone and vanillin were detected in the diluted effluents. Assuming little removal downstream of treatment plant, the odorous compounds could pose aesthetic problems for many downstream water supplies.

Volatilization of odorants during storage or downstream transport could reduce the concentrations of odorous compounds. Previous research has yielded predictive models for the fate of volatile organic compounds in rivers based on a twofilm model with or without turbulence.⁴⁴ Similarly, a fugacitybased model has been developed to predict volatilization potential in reservoirs.45 In both models, the Henry's Law constant $(K_{\rm H})$ is an indicator of volatilization potential (SI Table S5) with actual volatilization rates dependent on site-specific characteristics such as water and wind velocity, depth, temperature,⁴⁴ hydraulic residence time, surface area and mixing.⁴⁵ Assuming conditions typically encountered in rivers, compounds with $K_{\rm H}$ > 10¹ Pa m³/mol are predicted to exhibit a decrease of approximately an order of magnitude during 25 km flow downstream in a river and a decrease of approximately 2 orders of magnitude during an 18-month storage period in a reservoir. Among the odorous compounds detected in wastewater effluent, the haloanisoles, crotyl mercaptan and 2,6-dibromophenol have the

Table 1. Key GC-MS/Olfactometry Odor	Peaks Detected in RO-Ozone, RO, UV/	//Peroxide and Ozone-BAC Treatment Trains
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GC-Olf Descriptor	sulfide	rancid	chemical	amine	fragrant	earthy ^a	chemical	woody	plastic	musty ^b	rancid	fragrant	earthy ^c	fragrant	waxy
Tentative ID	mercaptans	alkyl aldehydes	xylenes	2-pyrrol	<i>y-lactones</i>	2MIB	chlorophenol	unknown	methyl naphthalenes	246TCA	alkyl acids	vanillin	geosmin	50Hvanillin	unknown
RT (min)	7.0	7.2	7.7	12.0	12.5	14.0	14.3	15.2	16.3	17.0	18.0	18.2	18.5	20.5	21.4
2° Effluent	1 2 2	2 2 0	3 4 3	3 3 3	3 3 4	3 4 3	2 3 3	4 3 4	2 2 3	4 4 3	2 3 2	4 2 4	4 4 4	4 4 4	1 3 3
RO permeate	2 2 0	2 0 0	1 0 2	3 4 3	2 2 3	1 1 2	2 2 1	0 0 0	2 1 2	4 2 3	1 1 2	2 2 3	2 1 1	3 3 4	1 1 0
Ozone	1 2 0	1 0 0	1 0 1	0 2 0	2 0 0	1 0 0	0 0 1	0 0 0	0 1 0	1 2 0	1 0 0	2 0 1	0 2 0	0 2 1	1 1 0
2° Effluent	4 4 3	3 0 0	4 4 3	4 4 3	4 3 4	2 3 3	2 4 2	3 3 4	2 4 3	3 4 3	0 3 2	2 3 4	3 3 4	0 4 2	2 4 2
RO permeate	2 3 0	0 3 0	1 1 0	3 3 3	2 3 1	2 2 1	2 1 3	1 2 0	2 2 3	3 3 3	0 2 3	2 2 2	2 3 1	3 1 2	1 0 0
UV- H ₂ O ₂	0 1 2	2 0 2	0 2 1	1 0 1	2 2 1	0 0 1	1 0 1	1 0 1	1 1 0	0 0 1	0 0 0	0 2 0	1 0 0	1 1 1	1 1 1
2° Effluent	3 3 3	0 2 2	4 4 3	4 3 4	3 2 4	3 2 3	2 2 3	0 2 2	3 0 2	2 4 3	0 4 3	4 4 4	3 4 4	4 4 4	2 3 2
Ozone	0 0 0	0 0 0	3 2 3	2 3 2	2 3 2	0 1 2	1 2 1	0 0 0	0 0 0	0 0 0	1 0 1	0 0 0	2 3 1	0 0 0	1 0 0
BAC	0 0 0	0 0 0	1 0 0	2 1 2	0 0 0	0 0 0	0 0 0	0 1 1	0 0 0	0 0 0	2 0 0	1 0 0	0 1 1	0 0 0	1 2 1
NOTE: Columns represent odor descriptors and retention times of peaks in GC- Olfactometry. Rows represent triplicate runs for each sample. Intensity rating: 0 = None; 1 = Maybe; 2 = Weak; 3 = Moderate; 4 = Strong. Tentative identification is detail in (21). ^a 2-MIB; ^b 246TCA; ^c geosmin															

potential to undergo substantial losses through volatilization in surface waters (i.e., $K_{\rm H} > 10^1$ Pa m³/mol). However, 2-MIB, geosmin, 2-pyrrolidinone, vanillin, and hydroxyvanillin are unlikely to be substantially affected by volatilization.

There are other potential mechanisms through which odorants might be attenuated in surface waters. For example, biotransformation and phototransformation of pharmaceuticals occurred with half-lives of approximately one week in the Trinity River.⁴⁶ Limited information is available on the potential for odorants identified in wastewater effluent to undergo attenuation under similar mechanisms. For geosmin and 2-methylisoborneol, microbial transformation has been observed in reservoirs.⁸ Additional research is needed to make accurate predictions of the potential for these compounds to undergo biotransformation and photolysis in surface waters.

■ IMPLICATIONS

A suite of odorous compounds are present in wastewater effluent at concentrations well above their odor thresholds. While the presence of these compounds does not imply a health risk, their presence has the potential to pose challenges to potable water supplies. For surface waters that receive municipal wastewater effluent, substantial dilution coupled with long residence times are needed to reduce odorant concentrations to values below odor thresholds. Volatilization during storage or transit might be sufficient to remove haloanisoles but it will not remove less volatile odorants, such as geosmin, 2-pyrrolidone and hydroxyvanillin. To remove these odorants, downstream drinking water treatment plants may need to use activated carbon or an advanced oxidation process.

Advanced treatment of secondary effluent with multiple treatment barriers—as practiced in most potable water reuse systems—is needed to reduce the concentrations of odorants to values below threshold levels. Reverse osmosis is effective in removing odorants but several may be present at concentrations above their odor thresholds in the permeate. Ozonation or UV/H_2O_2 can eliminate these odors from the permeate. Advanced oxidation processes (i.e., UV/H_2O_2) or ozonation coupled with biological activated carbon also may provide a means for removing odorous compounds even in systems that do not employ reverse osmosis.

A summary of data from two full-scale advanced wastewater treatment plants and one pilot plant (Table 1) illustrates the ways in which GC-MS/Olfactometry of effluent coupled with GC/MS quantification of specific contaminants can be used to study the fate of odorants. As indicate by the olfactometry intensity scores, 2,4,6-trichloroanisole (RT = 17.0 min) and geosmin (RT = 18.5 min) are among the most persistent odorants in advanced treatment systems and can be used as indicators⁴⁷ of other odors thereby avoiding the need for labor-intensive olfactometry studies. After advanced treatment is completed, any remaining compounds can be identified and quantified using the approach described above.

ASSOCIATED CONTENT

Supporting Information. Additional figures, tables, calculations and method details are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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