Development and optimization of analytical methods for the detection of 18 taste and odor compounds in drinking water utilities

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ABSTRACT

Taste and odor (T&O) issues have been a major concern among drinking water utilities as source waters are becoming increasingly vulnerable to compounds released during algal blooms as well as non-algal compounds. While most of the literature focuses on the two most common T&O compounds – 2-MIB and geosmin, there are other compounds that have the potential to cause T&O events. The aim of this study was to develop an advanced analytical method using solid phase microextraction (SPME) and gas chromatography-tandem mass spectrometry (GC-MS/MS) to identify 18 T&O compounds belonging to various odor classes. The developed method was optimized for the 18 analytes and implemented to determine the holding time of the compounds in raw and treated (distribution system point-of-entry or PoE) drinking water matrices. Compounds belonging to certain classes such as pyrazines and anisoles were found to be "stable" ($< 30\%$ loss) in all tested waters for up to two weeks, while aldehydes, ketones, esters and alkyl sulfides showed $> 30\%$ loss within 96 h in raw water. Preservation of samples at low pH (< 2) using hydrochloric acid increased the holding times and reduced losses within 96 h for aldehydes, ketones and esters. The paper also discusses the occurrence of these compounds with water utilities from the Midwest and Eastern US during the summer months. The study detected eight T&O compounds - 2-MIB, geosmin, β-cyclocitral, β-ionone, hexanal, indole, dimethyl disulfide and dimethyl trisulfide. While five compounds were detected above their threshold concentrations in the raw water, two of them (2-MIB and geosmin) were detected above threshold in the PoE samples.

1. Introduction

Semi-volatile and volatile organic compounds are released either naturally (e.g., cyanobacteria, algae and bacteria) or anthropogenically (e.g., chemical spills) into source waters and can cause taste and odor (T&O) issues in drinking water (Guo et al., 2016; Lu et al., 2012; Peter and Von Gunten, 2007). These compounds alter the characteristics of drinking water such as smell and taste, making the water unpleasant to drink, and are not always effectively removed during conventional treatment. This impacts customer confidence in water quality and poses a major problem to the water treatment industry (Zamyadi et al., 2015). Most laboratories in the US that conduct chemical analysis for T&O compounds

rely on the Standard Method 6040D that has been validated for detecting three T&O compounds – 2-MIB, geosmin and isopropyl methoxypyrazine (IPMP).

T&O events from algal blooms have been reported for decades, but there is an increase in their frequency that could be attributed to changes in climatic conditions and increasing agricultural run-offs carrying nutrients such as nitrogen and phosphorus (Anderson et al., 2002; Huang et al., 2018). In addition to 2-MIB and geosmin, several potential T&O compounds are released from blooms, chemical spills and wastewater effluents (Bruchet et al., 2007). It is important for drinking water utilities to identify and understand the stability and treatability of emerging non-MIB/geosmin compounds so that the utilities are prepared to respond to T&O events.

While a majority of T&O events are caused by compounds released from algal blooms and decay of dead matter in aquatic ecosystems, events have been reported to occur because of compounds that are formed during treatment, such as disinfection

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Table 1
Taste and odor compounds with odor description and corresponding threshold concentrations (determined for human nose)

Compound	Odor Description	Odor Threshold Concentration (ng/L)	Detection Limit (ng/L)
Earthy/musty			
2-methylisoborneol, 2-MIB	musty, earthy	2-15[a,j]	2.5
Geosmin	earthy	4[a]	0.5
2,4,6-trichloroanisole, 2,4,6-TCA	musty	0.1-2[a]	0.5
2,3,6-trichloroanisole, 2,3,6-TCA	musty, moldy, cork	0.1-2[b]	0.5
2,4,6-tribromoanisole, 2,4,6-TBA	musty, moldy, cork	0.1-10[a,b]	1
Earthy/green pepper			
isopropyl methoxy pyrazine, IPMP	earthy, potato bin	1-2[c]	0.5
isobutyl methoxy pyrazine, IBMP	earthy, green pepper	1-2[c]	0.5
Swampy/septic/feces			
dimethyl disulfide, DMDS	septic, putrid	30[d]	2.5
dimethyl trisulfide, DMTS	septic, putrid, garlic	10[d]	2.5
indole	feces (high concentration); jasmine (low concentration)	100[i] 370,000[e]	50
Medicinal/sweet			
2-ethyl-2-methyl dioxolane, EMD	medicinal, sickening sweet	10[f]	2.5
Grassy/woody/hay			
cis-3-hexen-1-ol, c3HO	grassy, sharp	70,000[a]	250
cis-3-hexenyl acetate, c3HA	grassy, sweet	1000-2000[g]	5
β-cyclocitral	woody (low concentration), tobacco-like (high concentration)	19,000[a]	1
Grassy/Fishy/rancid			
hexanal	grassy/vegetable	4500[h]	50
2,4-heptadienal, 2,4-HD	fishy/rancid	1000-5000[h]	5
Vegetable/fruity			
2,6-nonadienal, 2,6-ND	cucumber	20[a]	250
β-ionone	fruity	7[a]	1

[a] : (Peter and Von Gunten, 2007);
[b] : (Zhang et al., 2005);
[c] : (Sala et al., 2002);
[d] : (Huang et al., 2019);
[e] : (Godayol et al., 2011);
[f] : (Quintana et al., 2016);
[g] : (Chen et al., 2013);
[h] : (Furtula et al., 2004);
[i] : (Guo et al., 2015);
[j] : (Piriou et al., 2009).

byproducts (DBPs), and compounds that are formed within the distribution system (Watson et al., 2008; Zhang et al., 2012). Industrial spills and releases to the environment are another source of synthetic organic compounds that contribute to occasional T&O episodes. Compounds such as dioxanes and dioxolanes have been reported previously to have caused T&O events and were associated with effluents from resin manufacturing plants (Boleda et al., 2007; Bruchet et al., 2007; Quintana et al., 2016; Romero et al., 1998).

2-MIB and geosmin are earthy/musty compounds that have very low odor threshold concentrations (OTC) of 2-15 ng/L and 4 ng/L, respectively, and are detected in surface waters with algal, bacterial and phytoplankton growth (Table 1). Other compounds that cause T&O issues have been documented in various case studies where customers have reported swampy/septic, fishy, rancid, chlorinous and vegetable odors (Guo et al., 2019; Ma et al., 2011, 2013; Zhang et al., 2012; Zhao et al., 2013). Fishy/rancid odors have been reported to be caused by aldehydes, such as 2,4-heptadienal (2,4-HD), while cucumber odor is caused by 2,6-nonadienal (2,6-ND) and grassy/vegetable/lettuce odor by

hexanal (Zhao et al., 2013). Septic and swampy odors have been linked with hydrogen sulfide, dimethyl sulfide (DMS), dimethyl disulfide (DMDS), dimethyl trisulfide (DMTS) and indole that are formed primarily because of decaying biomass (Chen et al., 2010; Feng et al., 2018; Guo et al., 2019). Musty/corky flavors were observed during the formation of 2,4,6-trichloroanisole (2,4,6-TCA), 2,3,6-trichloroanisole (2,3,6-TCA) and 2,4,6-tribromoanisole (2,4,6-TBA) in the distribution systems from biomethylation of DBPs, chlorophenol and bromophenol (Byrd, 2017; Lee et al., 2017).

β-cyclocitral and β-ionone are algal and cyanobacterial metabolites and have been reported to co-occur along with toxins released by cyanobacterial species (Graham et al., 2010; Huang et al., 2018; Jones and Korth, 1995). Pyrazines, although less frequently detected than 2-MIB and geosmin, have been included in various T&O studies for their low threshold concentrations in the ng/L range (Chen et al., 2010; Deng et al., 2011; Peter and Von Gunten, 2007). Isopropyl methoxy pyrazine (IPMP) is a microbial metabolite released by *Actinomycetes* species while isobutyl methoxy pyrazine (IBMP) is commonly associated with the degradation of microbial biomass in natural waters (Khiari et al., 1997;

Peter et al., 2009). In addition, grassy odors have been identified in water sources caused by compounds such as cis-3-hexenyl acetate (c3HA) and cis-3-hexen-1-ol (c3HO), which have OTC values that are 3-5 orders of magnitude higher (Table 1) than pyrazines and anisoles (Khiari et al., 1999; Peter and Von Gunten, 2007; Suffet et al., 2004). As water temperature increases during the summer months, the odor threshold values might be lower than the OTCs reported in Table 1 (Whelton and Dietrich, 2004).

The most important tool needed for monitoring and preventing T&O issues is a robust analytical method for the detection of compounds near, or below, their OTC values (Table 1). The detection of T&O compounds is typically conducted using gas chromatography-mass spectrometry (GC-MS), olfactory-GC-MS, and sensory techniques such as flavor profile analysis and threshold odor number (Bruchet, 2019; Chen et al., 2013; Dietrich et al., 2003; Suffet et al., 2004). Although GC-MS has been widely used for chemical analyses, using tandem mass spectrometry (MS/MS) was shown to have greater sensitivity by reducing background noise and improving signal-to-noise ratios (Wang et al., 2019). For sample preparation, several extraction techniques have been used such as solid phase extraction, stir bar sorptive adsorption, closed loop stripping analysis, purge and trap, headspace sampling and solid-phase microextraction (SPME). Studies reported that headspace SPME showed minimal interferences compared to other techniques, thus, resulting in better reproducibility and high sensitivity in the ng/L range (Chen et al., 2013; Furtula et al., 2004; Godayol et al., 2011; Watson et al., 2000). Ma et al. (2011) developed a SPME method coupled with GC-MS to quantify six T&O causing aldehydes released in natural waters by algal cultures. Lu et al. (2012) studied the application of headspace SPME and GC with flame photometric detection to analyze hyper-eutrophic lake water samples and found five odorous sulfur compounds: hydrogen sulfide, methanethiol, DMS, DMDS and DMTS.

Numerous studies optimized SPME and GC-MS methods to improve the sensitivity and achieve lower detection limits. Ma et al. (2012) and Chen et al. (2013) developed and optimized a GC-MS method using headspace SPME to detect 2-MIB, geosmin, haloanisoles, pyrazines and aldehydes. Both studies focused on the optimization of the SPME method by studying the effects of different types of SPME fibers and determined that the most efficient fiber was divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS). The higher efficiency of this dual coated fiber compared to other commercially available single coated fibers was because of the high affinity of the DVB phase for small alcohols, the presence of the non-polar PDMS stationary phase for highly nonpolar compounds and the increased fiber surface area of highly porous CAR phase (Godayol et al., 2011; Ma et al., 2012; Watson et al., 2000). These results are corroborated by Zhang et al. (2005) who compared six commercially available SPME fibers and reported that the DVB/CAR/PDMS fiber had the highest extraction efficiency in achieving method detection limits in the pg/L range for 10 T&O analytes.

Though there have been several studies on identifying non-MIB/geosmin compounds, very few of them focused on a wide range of compounds from various odor classes. Furthermore, there is a paucity of mechanistic studies to understand the stability of these compounds (or lack thereof) in environmental water matrices. Hence, the aim of this study was to i) develop and optimize an expanded and semi-automated analytical method that can detect T&O compounds across various odor classes having different odor thresholds ranging from ng/L to µg/L, ii) conduct holding time and preservation studies to understand the stability of these compounds in different water matrices and iii) conduct an occurrence study with drinking water utilities across the Midwest and Eastern US during the Summer and Fall months.

2. Experimental

2.1. Chemicals and Materials

Analytical standards (>98% purity) of 2-methylisoborneol, geosmin, 2-isopropyl methoxypyrazine (IPMP), 2-isobutyl methoxypyrazine (IBMP), 2,4,6-trichloroanisole (2,4,6-TCA), 2,4,6-tribromoanisole (2,4,6-TBA), β-cyclocitral, β-ionone, cis-3-hexenyl acetate (c3HA), cis-3-hexen-1-ol (c3HO), dimethyl disulfide (DMDS), dimethyl trisulfide (DMTS), 2,6-nonadienal (2,6-ND), 2,4-heptadienal (2,4-HD), 2-ethyl-2-methyl-1,3-dioxolane (EMD), hexanal, indole, naphthalene-d8 (N-d8) and 2,4,6-trichloroanisole-d5 (2,4,6-TCA-d5) were obtained from Sigma-Aldrich (St. Louis, MO, USA). 2,3,6-trichloroanisole (2,3,6-TCA) was purchased from Santa Cruz Biotechnology (Dallas, TX, USA). Stock and working standard solutions were prepared in methanol ($\geq$99.9% purity, Sigma-Aldrich, St. Louis, MO) and were stored at 4°C. Reagent grade sodium chloride (NaCl) was purchased in bulk (12 kg plastic drum) from EMD Millipore (Burlington, MA, USA).

For SPME, 1 cm dual-coated (50/30 µm) DVB/CAR/PDMS fibers were purchased from Supelco (Bellefonte, PA, USA). GC inlet liners that are compatible with SPME fibers were purchased from Agilent Technologies (Santa Clara, CA, USA). 20 mL amber headspace screw-top vials with PTFE/silicone magnetic caps were used for holding 10 mL samples for GC-MS/MS analysis (Agilent Technologies, USA).

2.2. Solid-phase microextraction (SPME)

A semi-automated method based on headspace SPME was developed using CTC PAL sample preparation and injection system (CTC Analytics, Switzerland) with an agitator module for heating and a conditioning station. SPME extractions were conducted after conditioning the fibers for 6 hours at 270°C. The fiber was also conditioned for 1 min before each extraction and 5 min after desorption. The sample was first heated at 55°C for 4 min in the agitator module at 500 rpm. Following this, the analytes were extracted from the sample by exposing the fiber in the headspace of the vial for 15 min while the sample was continuously heated and agitated at 55°C and 500 rpm. The fiber was then desorbed for 2 min at 250°C in the injection port.

2.2.1. SPME Optimization

The optimal SPME conditions were determined after studying the effect of various factors on compound extraction such as: salt content in the samples, extraction time, extraction temperature, desorption time and desorption (GC inlet) temperature. The conditions were optimized one at a time by testing a range of values for each parameter: extraction time 5-20 min, extraction temperature: 45°C-75°C, desorption time: 1-6 min, and desorption (GC inlet) temperature: 225-265°C, and six values were tested for salt content: 10-60% *w/v*.

2.3. Gas chromatography – tandem mass spectrometry (GC-MS/MS)

Compound analysis was carried out on an Agilent 7890B gas chromatograph (Santa Clara, CA, USA) coupled with an Agilent 7000 tandem MS (Santa Clara, CA, USA). Compounds were separated on an Agilent J&W HP-5ms ultra inert GC column (30 m x 250 µm x 0.25 µm). The split/splitless injection port was equipped with an Agilent straight splitless SPME liner with an inner diameter of 0.75mm. The initial oven temperature was 60°C that was held for 1 min; then ramped up to 150°C at 20°C/min and then up to 270°C at 30°C/min where it was held for 0.5 min. Total GC run time was 10 min. The carrier gas (helium) flow rate was maintained at 2 mL/min and the collision gas (nitrogen) flow was at

1.5 mL/min. The front inlet temperature was 250°C with a septum purge flow at 3 mL/min, while source temperature and transfer line temperatures were 230°C and 280°C, respectively. The optimized MS/MS parameters are shown in the Supplemental Information (Table S1).

2.4. Sample Preparation

Samples and calibration curves were prepared by adding 10 mL sample volume to the GC vial with 40% *w/v* NaCl and then were spiked with 25 ng/L of internal standards (ISTDs), N-d8 and 2,4,6-TCA-d5. Lab control standards were prepared with 25 ng/L of ISTDs in 10 mL Milli-Q® water and lab-fortified matrix spikes were prepared with 25 ng/L ISTDs and 25 ng/L of T&O compounds in 10 mL samples. External calibration curves were used for 15 compounds, while for 2,4,6-TCA, 2,3,6-TCA and 2,4,6-TBA, internal calibration curves were used with isotopically labelled 2,4,6-TCA-d5. All the compounds were calibrated over a range of 0.5 – 250 ng/L, except for five compounds with lower sensitivities (hexanal, c3HO, c3HA, 2,6-ND and indole) that were calibrated over a range of 50 – 25,000 ng/L.

2.5. Holding Time Study

A preliminary set of experiments were designed and conducted to study the effect of holding time on the stability of the selected 18 T&O compounds in three different matrices – lab-grade water (Milli-Q®, referred to as "control"), surface water from the Mississippi River collected at the intake of a local water utility (referred to as "raw"), and the treated water collected post-disinfection at the entry point into the distribution system (referred to as point of entry or "PoE"). The utility has a conventional treatment train. The raw water has an average pH of 8.3; turbidity (average): 50 NTU; alkalinity: 140-180 mg/L as $CaCO_3$; total organic carbon (TOC): 5-6 mg/L, while PoE has an average pH of 7.5; turbidity: < 0.3 NTU; alkalinity: 130 – 160 mg/L as $CaCO_3$; TOC: 3-4 mg/L. Water samples were collected 1-2 hours prior to the start of the experiments in amber glass bottles. Sodium thiosulfate was added at a concentration of 75 mg/L to quench chlorine disinfectant residual in the water samples. Compounds with lower sensitivity (c3HO, c3HA, hexanal, 2,6-ND and indole) were spiked at 2,500 ng/L, while the others were spiked at 100 ng/L. After spiking, the samples were transferred into 40-mL amber glass vials without headspace.

2.5.1. Effect of holding time

To study the impact of storage on the stability of the compounds, a range of holding times were selected that are typical for utilities and laboratories during sampling and storage, ranging from short to long periods: 0 h, 24 h, 48 h, 72 h, 96 h, 168 h (1 week) and 336 h (2 weeks). Samples at each time point were analyzed in triplicates.

2.5.2. Effect of preservatives

To study the effect of different preservation techniques, pre-salting and acid preservation were tested. For these experiments, raw and PoE samples were spiked at concentrations mentioned in Section 2.5 and stored in vials with preservatives: 16 g of NaCl for pre-salting (to maintain salt concentration at 40% *w/v*) and 4-5 drops 1:1 HCl for acid preservation (pH < 2) per 40 mL vial. Samples were analyzed in triplicates at set holding times as mentioned in Section 2.5.1. Acidified samples were neutralized with 3% *w/v* of sodium bicarbonate prior to analysis on the GC-MS/MS.

2.6. Occurrence Study

For the occurrence study, raw and PoE samples were collected over a period of four months in 2019 from 13 drinking water

Table 2
Utilities that participated in the occurrence study and their source water types

Utility	State	Source Type
Utility A	KY	Reservoir
Utility B	KY	River
Utility C	IL	River
Utility D	NJ	Reservoir
Utility E	NJ	Reservoir
Utility F	MO	River
Utility G	MO	River
Utility H	WV	River
Utility I	IN	Lake
Utility J	TN	River
Utility K	VA	River
Utility L	KS	Reservoir
Utility M	KS	River

utilities (Table 2). Samples were collected bi-weekly, shipped to the laboratory overnight, and stored at 4°C until analysis. Samples were analyzed within 72 h whenever possible to minimize the holding time. To determine the effect of water quality on compound recoveries, lab-fortified matrix spikes were prepared as described in Section 2.4 for every raw and PoE sample analyzed.

3. Results and Discussion

3.1. Method Optimization

The method precision was determined from triplicate analyses during the holding time study and the average relative standard deviation (RSD) was between 2-20%. Method detection limits for most compounds were below their corresponding odor threshold concentrations with the optimized SPME and GC-MS/MS method (Table 1). The compound peak responses were evaluated for determining optimum values of each of the SPME parameters tested – salt content, extraction time, extraction temperature, desorption time and desorption temperature. The optimum values for individual T&O compounds are shown in SI (Table S2).

3.1.1. Salt Content

One of the most significant factors for extraction efficiency was the salt content of the sample as demonstrated in this study as well as previous SPME studies (Furtula et al., 2004; Ma et al., 2012; Watson et al., 2000). Peak responses of all the 18 compounds increased proportionally with an increase in the salt concentration from 0% to 40% *w/v* (SI Fig. S1). Chen et al. (2013) and Lu et al. (2012) reported similar increase in recoveries resulting from the increase in the ionic strength of the sample, thus, reducing the solubility of the compounds by increasing their partition coefficients. However, a further increase from 40% *w/v* to 60% *w/v*, led to a decrease in the peak responses of six compounds (β-ionone, indole, DMDS, DMTS, c3HA and EMD) by 25-62%. Ma et al. (2012) reported a decrease in compound recoveries at salt concentrations higher than 30% *w/v* and hypothesized that the undissolved NaCl under saturated conditions might adsorb the compounds. Hence, for the compounds in this study, 40% *w/v* NaCl was the optimum concentration.

3.1.2. Extraction time

The peak responses for all 18 compounds increased with extraction times up to 15 min, and slightly increased at 20 min. Chen et al. (2013) showed that extraction time had a lesser impact on SPME efficiency than extraction temperature, salt content, or agitation rate. Hence, to keep the sample run time as short as possible, an extraction time of 15 min was chosen for the rest of the study.

3.1.3. Extraction temperature

The change in peak responses with temperature (from 45-75°C) varied among the compounds. The peak responses decreased rapidly with increasing temperature for volatile compounds, such as dimethyl sulfides (i.e., DMDS and DMTS), while semi-volatile compounds, while compounds such as β-cyclocitral, β-ionone, indole, geosmin and pyrazines showed an increase in peak responses with temperature up to 65°C (Table S2). Godayol et al. (2011) and Chen et al. (2013) reported that high extraction temperatures might have a negative effect on recovery of highly volatile compounds as the fiber starts desorbing. To maximize peak responses and minimize losses of highly volatile and semi-volatile compounds, the final extraction temperature was set at 55°C.

3.1.4. Desorption Time

The effect of desorption time was studied at 1, 2, 4 and 6 min. The peak responses remained consistent with a low variation (±15%) between 1 and 6 min. To keep the sample run time short, the desorption time was set at 2 min.

3.1.5. Desorption Temperature

The desorption temperature (GC inlet temperature) is a critical parameter that impacts the partition of compounds from the solid phase (fiber coating) into the gaseous phase. Out of the four temperatures tested (225°C, 235°C, 250°C and 265°C), the optimum temperature was found to be 250°C (Table S2). Except for a few compounds such as β-ionone, c3HO, EMD, hexanal and indole, all the other compounds had maximum peak responses at 250°C, hence this temperature was used for the rest of the study.

3.2. Holding Time Study

The optimized method was used to study the stability and holding times of the T&O compounds as described in Section 2.4. The raw and PoE samples spiked with T&O compounds showed varying stability over time depending on the physical and chemical properties of the compounds. Compound recoveries between 70-130% were considered acceptable in accordance with the Standard Method guidelines for lab-fortified sample matrices (Method 6040D, Standard Methods for the Examination of Water and Wastewater. https://www.nemi.gov/methods/method_summary/5720/). The holding times for the compounds determined in this study based on acceptable recoveries are summarized in Table 3.

3.2.1. Stability of Compounds in Raw Water

The holding time study with raw water resulted in acceptable recoveries (> 70%) for compounds such as geosmin, 2,6-ND, c3HO, indole, β-cyclocitral and β-ionone for the first 96 h but the recoveries decreased later in the 1-week and 2-weeks samples (Fig. 1). Compounds such as DMTS had acceptable recoveries only at 0 h and decreased below 70% thereafter, while hexanal had acceptable recoveries up to 8 h and 2,4-HD and c3HA up to 24 h (Fig. 1). Very few studies discuss the behavior of aldehydes, esters and dimethyl sulfides in natural water matrices and the possible reasons for their losses. Some suggest that the reactive carbonyl group (C=O) present in these compounds could participate in nucleophilic addition reactions in the presence of hydroxide (OH⁻) ions in mildly alkaline waters, resulting in the hydrolysis of the compounds (Chen et al., 2013; Sugaya et al., 2004). Sugaya et al. (2004) indicated that the reactivity of the carbonyl group increases as the alkyl group size decreases. The faster loss of 2,4-HD with time compared to more stable 2,6-ND (Fig. 1) in this study was consistent with the observations by Sugaya et al. (2004).

The reactions involving carbonyl groups in esters and aldehydes are often pH and temperature dependent.

Khiari et al. (1999) showed the degradation of c3HA in alkaline surface waters during storage even at 4°C. It is hypothesized that hydrolysis in alkaline pH could be the cause for degradation of 2,4-HD and hexanal observed in our study. The alkyl sulfide DMTS experienced higher losses than the aldehydes and esters, with a 50% loss within 24 h. Han et al. (2017) showed that the dimethyl sulfides can undergo hydrolysis in natural water matrices. However, DMTS showed a similar loss in the control sample as well, suggesting that the compound is susceptible to loss in water regardless of pH and the presence of natural organic matter (NOM).

The haloanisoles (2,4,6-TCA, 2,3,6-TCA and 2,4,6-TBA) showed consistent recoveries of above 90% for up to two weeks. These compounds contain an ether functional group which is not susceptible to hydrolysis like the carbonyl group. Compounds such as 2-MIB, IPMP, IBMP and DMDS were stable for the duration of the study (Fig. 1). Geosmin was stable up to one week with a loss of only 12% observed in the 1-week samples, which was similar to the losses reported in the studies by Korth et al. (1992) and Zhang et al. (2010) on stability of geosmin in water samples. Both 2-MIB and geosmin are tertiary alcohols that are less vulnerable to nucleophilic attacks in alkaline waters compared to compounds such as aldehydes and ketones. Methoxypyrazines, IPMP and IBMP, are also very persistent compounds which makes their removal difficult in the wine industry where they are frequently detected (Reynolds, 2010).

3.2.1a. Effect of Acid Preservation

Samples preserved with acid (1:1 HCl) showed higher stability for esters, aldehydes, alcohols and ketones such as hexanal, c3HO, 2,4-HD, c3HA, β-cyclocitral, indole, geosmin and β-ionone (Fig. 2). While the holding time of 2,4-HD was only 24 h in the non-preserved raw water, it increased up to 1 week in acidified raw water (Fig. 2). Similarly, there was an increase in holding times of c3HA, 2,4-HD and hexanal, which had recoveries above 90% up to 1 week. The recoveries of compounds c3HO, geosmin, β-cyclocitral and β-ionone also increased by 10-50% in the 2-week samples of acidified raw water compared to the non-acidified raw water (Fig. 2).

The impact of acid preservation on the stability of esters, aldehydes and sulfides has been discussed in previous studies such as with c3HA and DMDS (Han et al., 2017; Khiari et al., 1999). As the studies showed faster degradation of the two compounds with increasing pH, decreasing the pH, thus, may hinder the hydrolysis and extend their holding times. The only compound out of acceptable recovery range in both non-preserved raw and acidified raw water was DMTS, which showed 50% loss within 24 h in both the cases (Figs. 1 and 2). While acid preservation improved the recoveries of most compounds, 2-MIB and EMD were negatively impacted (Fig. 2). Previous studies that reported loss of 2-MIB at low pH had attributed it to the dehydration of the tertiary alcohol in acidic environments (Bu et al., 2017; Hsieh et al., 2012). Similarly, acid catalyzed hydrolysis mechanisms were discussed in the case of dioxolanes, which could be the cause of loss of EMD (Fife and Natarajan, 1986). While a few other compounds such as geosmin, IPMP and IBMP were also impacted by acid addition, the reactions were reversed after neutralizing the acidified samples with sodium bicarbonate.

3.2.1b. Effect of Pre-salting

Effect of pre-salting was also studied during a separate experiment, to understand the impacts of salt as a preservative in the raw water. Recoveries in pre-salted samples of spiked raw water, i.e., the samples stored with 40% (w/v) NaCl, increased the recovery of DMTS by 60% compared to non-preserved raw water. However, the compound recovery still did not exceed 70% (data not shown).

Table 3
Holding times for T&O compounds in different water matrices

	Raw		PoE		Control (Milli-Q®)	
	Sample pH	Low pH (<2)	Sample pH	Low pH (<2)	Sample pH	Low pH (<2)
Earthy/musty						
2-MIB	2 w	< 8 h	2 w	0 h	2 w	< 8 h
geosmin	1 w	2 w	2 w	2 w	2 w	2 w
2,4,6-TCA	2 w	2 w	2 w	2 w	2 w	2 w
2,3,6-TCA	2 w	2 w	2 w	2 w	2 w	2 w
2,4,6-TBA	2 w	2 w	2 w	2 w	2 w	2 w
Earthy/green pepper						
IPMP	2 w	2 w	2 w	2 w	2 w	2 w
IBMP	2 w	2 w	2 w	2 w	2 w	2 w
Swampy/septic/feces						
DMDS	2 w	2 w	2 w	96 h	2 w	2 w
DMTS	< 8 h	0 h	24 h	< 8 h	24 h	< 8 h
Indole	96 h	1 w	2 w	2 w	2 w	2 w
Medicinal/sweet						
EMD	2 w	0 h	2 w	0 h	2 w	0 h
Grassy/woody/hay						
c3HO	1 w	2 w	2 w	2 w	2 w	2 w
c3HA	24 h	1 w	2 w	1 w	2 w	2 w
β-cyclocitral	1 w	2 w	2 w	2 w	2 w	2 w
Grassy/Fishy/rancid						
hexanal	8 h	2 w	2 w	2 w	2 w	2 w
2,4-HD	24 h	1 w	2 w	1 w	2 w	2 w
Vegetable/Fruity						
2,6-ND	96 h	24 h	2 w	8 h	24 h	< 8 h
β-ionone	96 h	2 w	2 w	2 w	2 w	2 w

w = week; h = hour
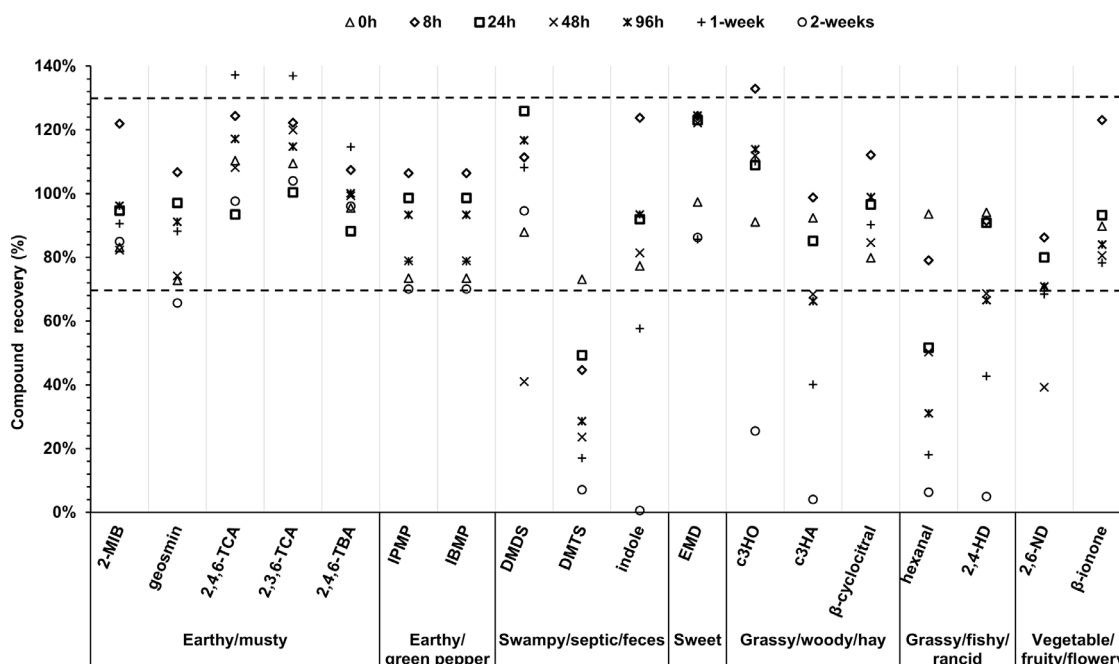
Fig. 1. Compound recoveries (%) in the raw water after holding times 0 h, 8 h, 24 h, 48 h, 96 h, 1 week and 2 weeks without any preservatives (dotted lines represent the acceptable recovery range, 70-130%).

The impact of pre-salting on the recoveries of other compounds was negligible. Satchwill et al. (2007) evaluated pre-salting of natural waters and reported no improvement in stability of T&O compounds.

3.3.2. Stability of Compounds in PoE Water

Most compounds that had low recoveries in raw water had greater recoveries in the PoE samples with minor losses in the range of 2-20% even after 2 weeks (SI Figs. S2 and S3). However, the recovery of DMTS dropped below 70% after 48 h, while 2,6-ND was above 70% for only up to 1 week. Other compounds including

the aldehydes and ketones, such as hexanal, c3HA, c3HO, 2,4-HD and 2,6-ND were stable for 2 weeks with recoveries above 80%. The average pH of PoE water from the drinking water treatment plant was 7.5. The near neutral pH of the PoE water and negligible matrix effects could be the reason for increased stability of compounds that experienced losses in mildly alkaline and NOM-rich raw water. The results from the PoE samples showed a similar trend to those observed in the control water for most compounds, with the exception of 2,6-ND. Of the 18 compounds tested in the control water, 17 compounds had recoveries greater than 70% for 2
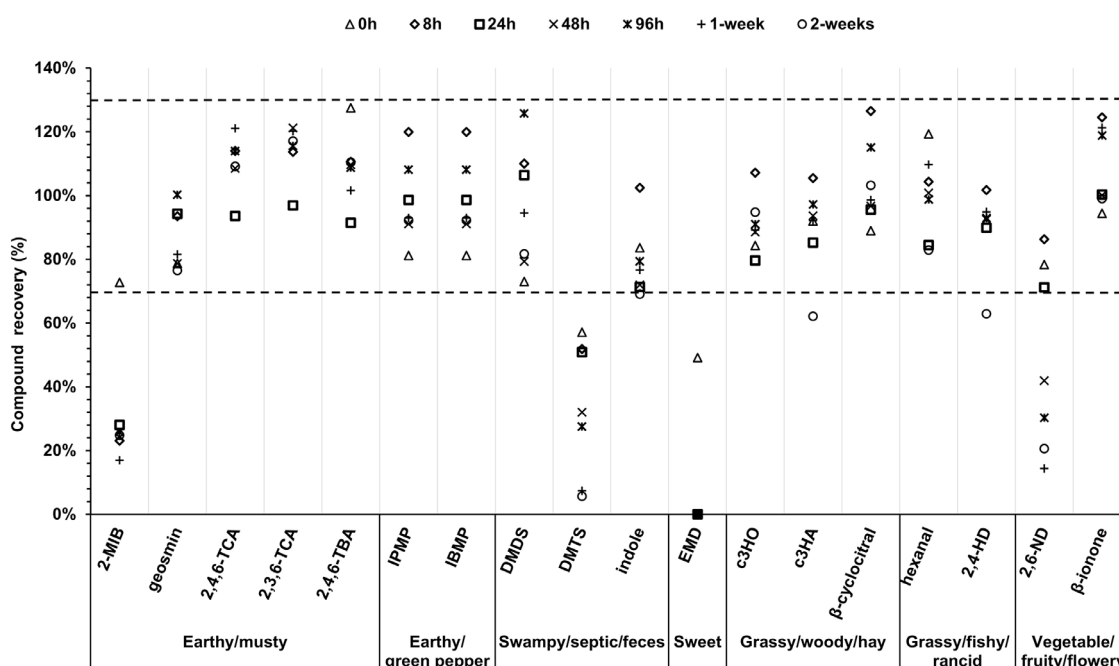
Fig. 2. Compound recoveries (%) in the raw water with acid as preservative (pH < 2) after holding times 0 h, 8 h, 24 h, 48 h, 96 h, 1 week and 2 weeks (dotted lines represent the acceptable recovery range, 70-130%).

Table 4

Compounds detected during occurrence study in the raw and PoE samples from utilities where concentrations were above odor threshold concentrations (OTCs)

Compound name	Detected in Utility	Sample Type	Concentration (ng/L)	Odor Activity Values
2- MIB	Utility A	Raw	17	8.5
	Utility B	Raw	136	68
		PoE	111	55.5
geosmin	Utility B	Raw	70	17.5
		PoE	15	3.8
	Utility E	Raw	98	24.5
	Utility J	Raw	5	1.3
	Utility D	Raw	6	1.5
	Utility I	Raw	7	1.8
		PoE	7	1.8
β-cyclocitral	Utility E	Raw	1300	0.07
DMDS	Utility A	Raw	432	14.4
DMTS*	Utility A	Raw	102	10.2
	Utility E	Raw	22	2.2

* Concentrations are estimated as the method is semi-quantitative for this compound

weeks, while the only compound (DMTS) showed significant losses within 96 h (similar to the observations in PoE water). The acidification of PoE water and control water did not show any improvement in the recovery of DMTS (SI Fig. S3).

3.4. Occurrence Study

The raw and PoE samples collected from different treatment utilities across the Midwest and Eastern US were detected with non-MIB/geosmin T&O compounds such as β-cyclocitral, β-ionone, DMDS and DMTS and occasionally indole and hexanal (Table 4). Most compounds detected above OTCs in raw samples were from reservoir and lake sources: 2-MIB exceeded its OTC in the reservoir at Utility A, geosmin in 3 reservoirs (Utilities A, D and E), a lake (Utility I) and a river (Utility J), β-cyclocitral in a reservoir (Utility E), DMDS in a reservoir (Utility A) and DMTS in two reservoirs (Utilities A and E). Only two compounds, 2-MIB and geosmin, were

detected above their OTCs in PoE samples. 2-MIB was detected in the PoE samples of Utilities A and B with its highest concentration reaching 111 ng/L at Utility B in October (136 ng/L in the corresponding raw sample), while geosmin was detected at a concentration up to 15 ng/L at Utility A in July (70 ng/L in the corresponding raw sample). The odor activity values of detected compounds were calculated from ([detected concentration]/[odor threshold concentration]) to determine the intensity of odors with respect to their threshold values (Wang et al., 2020).

Co-occurrence of T&O compounds with toxin-producing cyanobacterial species has been documented by various studies on Midwestern lakes and reservoirs (Graham et al., 2010; Loftin et al., 2016; Shang et al., 2018; Watson et al., 2008). While 2-MIB and geosmin are produced by various cyanobacteria, algae, diatoms and *Actinomycetes* bacteria (such as *Streptomyces*), β-cyclocitral is a metabolite mainly produced by *Microcystis*, a cyanobacterial species (Huang et al., 2018; Jüttner and Wat-

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son, 2007; Lee et al., 2017). *Microcystis* also produces harmful cyanotoxins called microcystins that can have severe impact on human and animal life upon consumption. In our study, raw samples from a reservoir (Utility E) with high concentrations of β-cyclocitral (up to 1,300 ng/L) also contained elevated concentrations of microcystins in the range of 0.4-5 µg/L, above the 10-day EPA health advisory levels (infants: 0.3 µg/L; adults: 1.6 µg/L, http://water.epa.gov/drink/standards/hascience.cfm). Another river source (Utility B) was detected with high levels of both β-cyclocitral (1,255 ng/L) and microcystins (0.7 µg/L). β-cyclocitral was suggested as a "biomarker", thus a potential indicator, for the presence of toxin-producing cyanobacterial species (Jones and Korth, 1995; Watson et al., 2008). However, further research is needed to establish the statistical significance if a correlation between the occurrence of β-cyclocitral and microcystins exists.

4. Conclusions

Based on the results of this study, the following conclusions were drawn.

- An advanced analytical method was developed based on SPME and GC-MS/MS to detect 18 T&O compounds including 2-MIB and geosmin, which can be implemented by water utilities to monitor for T&O events. The method detection limits were near or below OTCs for most compounds except for 2,6-ND. The method was quantitative for 17 compounds and semi-quantitative for DMTS.
- Sample preparation and SPME method were optimized by studying the impact of salt content, extraction time, extraction temperature, desorption temperature and desorption time. A 40% *w/v* of salt with 15 mins of extraction time at 55°C and 2 mins of desorption at 250°C were chosen as optimum SPME conditions for maximizing recoveries.
- The compounds were studied for their stability in raw and PoE water matrices. For the raw water, the holding time for certain aldehydes, ketones and esters was less than 96hours, while for pyrazines and anisoles it was 2 weeks. 2-MIB and geosmin had acceptable recoveries at least up to 1 week. The results and published literature suggest that hydrolysis is the major reason for the degradation of most of the compounds. Preservation of samples using acid (HCl) extended the holding times of aldehydes, ketones and esters.
- The occurrence study conducted with 13 drinking water utilities provided valuable insights into frequently occurring T&O compounds other than 2-MIB and geosmin including β-cyclocitral, β-ionone, DMDS, DMTS, indole and hexanal. Five of the compounds were present at concentrations above their OTCs in the raw water while two of them (2-MIB and geosmin) were detected above OTCs in the PoE samples.

Declaration of Competing Interest

None.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.wroa.2021.100099.

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