




## New production pathway of musty 2,4,6-tribromoanisole during raw water disinfection processes at a surface water treatment plant

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### ABSTRACT

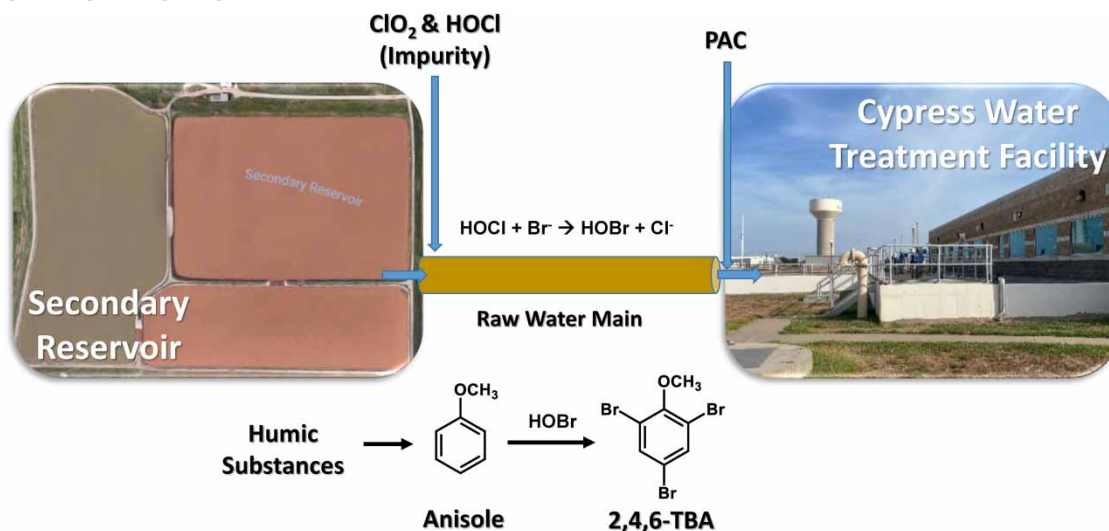
The City of Wichita Falls' Cypress Environmental Laboratory developed a comprehensive taste and odor (T&O) monitoring program to identify T&O compounds, their point of origin, and how to mitigate each T&O event to lessen its impact and maintain consumer confidence. In January 2023, a T&O compound was detected in the water system using sensory analysis with a threshold odor number (TON) of 3, guiding further analytical testing to identify for musty compounds. The unknown was confirmed to be 2,4,6-tribromoanisole (2,4,6-TBA) at a maximum of 9.86 ng/L. Its point of origin for production was tracked to a raw water line using chlorine dioxide as a primary disinfectant. Jar tests were performed to confirm that the mode of production was excess free chlorine from the generation of chlorine dioxide in the presence of bromide in raw water. The event was mitigated using powdered activated carbon in clarifiers to adsorb and settle out the compound, resulting in a non-detectable level (a TON of 1 and <5.00 ng/L for 2,4,6-TBA). This paper discusses the unique generation pathway within a full-scale treatment plant and how a monitoring and response program can be used to help detect a T&O event in early stages and aid mitigation processes.

**Key words:** anisole, bromide, chlorine, chlorine dioxide, T&O

### HIGHLIGHTS

- T&O monitoring programs can identify untargeted compounds.
- Sensory analyses are integral to an effective T&O monitoring program.
- 2,4,6-Tribromoanisole can be produced through disinfection processes.
- Powdered activated carbon is highly effective for adsorbing haloanisoles.
- Excess free chlorine dosing should be minimized when generating chlorine dioxide.

## GRAPHICAL ABSTRACT



## 1. INTRODUCTION

Taste and odor (T&O) issues are common in water utilities that rely on source water vulnerable to algal, cyanobacterial, and diatom blooms. Research has indicated that T&O compounds can also be formed during treatment processes and within the distribution system (Peter & Von Gunten 2007). These compounds impact the aesthetic quality of water by imparting taste and smell, thus causing issues with the public perception of water quality. The most commonly reported odors are earthy/musty followed by others such as grassy, swampy, and chlorinous odors (Khiari *et al.* 1999; Suffet *et al.* 2004; Peter & Von Gunten 2007). When T&O events occur at drinking water utilities, the major challenges are the unpredictability of such an event, including access to analytical methods and/or instruments that can identify the compounds causing the event and knowledge gap with the mitigation of T&O compounds that have not been studied enough. Recent advancements in analytical methods and treatability studies have explored compounds beyond 2-methylisoborneol (MIB) and geosmin and demonstrated the occurrence of several other compounds such as 2,4,6-tribromoanisole (2,4,6-TBA), dimethyl sulfides,  $\beta$ -cyclocitral and  $\beta$ -ionone in source and tap water samples at drinking water treatment plants (Pochiraju *et al.* 2021, 2022; Adams *et al.* 2022).

## 1.1. T&amp;O Monitoring and Mitigation at the City of Wichita Falls, Texas

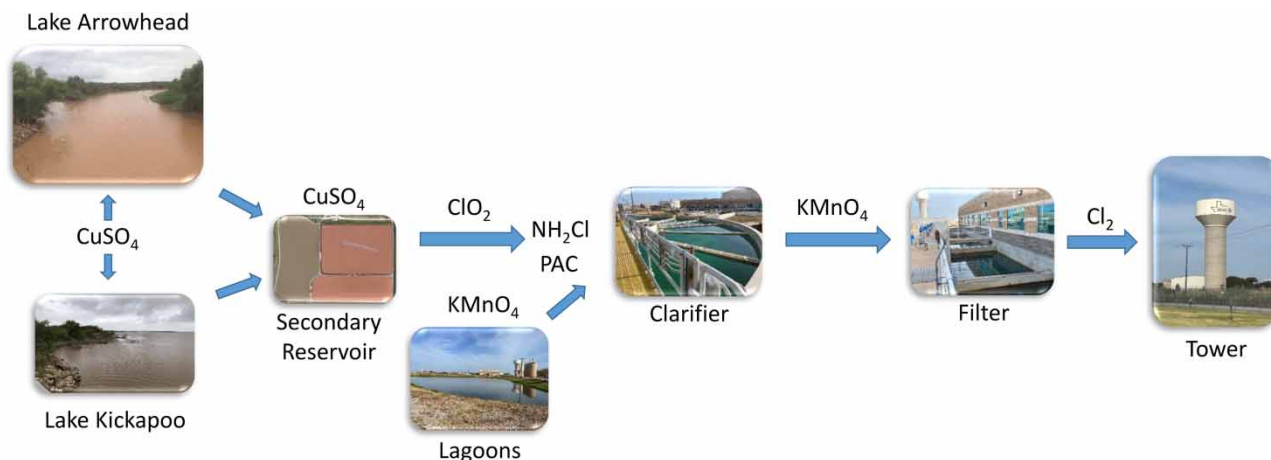
The City of Wichita Falls (CWF), Texas, has a surface water system with adjudicated rights to five water sources, four of which are used primarily for treatment: Lake Arrowhead, Lake Kickapoo, and the Lake Kemp/Lake Diversion system. The system has two water treatment facilities (WTFs) – Cypress WTF, which has one advanced and three conventional treatment plants, and Jasper WTF, which has two conventional treatment plants – and includes a water distribution system. After the highly successful production of odor-free drinking water through a direct potable reuse (DPR) project in 2014–2015 (Nix *et al.* 2021), where a blend of 50% conventionally treated raw water was mixed with 50% wastewater effluent treated by microfiltration/reverse osmosis, zero customer complaints were received during this time. It was determined that an odor-free drinking water was capable of being produced and that the Water Purification Division needed to make significant changes to its T&O monitoring and response programs.

After the termination of the DPR project, the CWF experienced a highly potent T&O event in 2016 where a *Dolichospermum* bloom produced above 1,700 ng/L of MIB in source water and above 250 ng/L in tap water (Adams *et al.* 2018). As a result, CWF's Cypress Environmental Laboratory (CEL) staff developed a monitoring program that uses field monitoring probes (sondes), microbiological analyses (algae/cyanobacteria enumeration and identification, and actinomycete culturing), general water quality parameter monitoring, sensory T&O analysis, and analytical detection of T&O compounds by gas chromatography–mass spectrometry (GC–MS) (Adams *et al.* 2021a). Over the last seven years, the program has detected and directed the mitigation and/or elimination of 15 T&O events, covering T&O produced in source water and produced

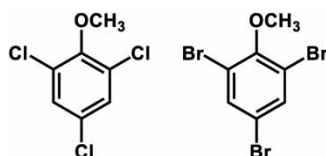
through the treatment process, as described in detail by Adams *et al.* (2021a, 2021b, 2022). The program creates an integrated network of analyses that complement each other and provide a more comprehensive water quality assessment than any single analysis if used by itself. The water system has the ability to switch sources between Lakes Arrowhead and Kickapoo if an event is localized. If a T&O event occurs in lakes or the holding reservoir, an algaecide treatment using 1.0 mg/L copper sulfate ( $\text{CuSO}_4$ ) for cell lysing and citric acid ( $\text{C}_6\text{H}_8\text{O}_7$ ) for chelation can be used to control the algal/cyanobacterial growth by applying directly to the lake from a boat. Once  $\text{CuSO}_4/\text{C}_6\text{H}_8\text{O}_7$  treatment in the source water is done, oxidants like chlorine dioxide ( $\text{ClO}_2$ ) and potassium permanganate ( $\text{KMnO}_4$ ) can remove certain T&O compounds. In addition, powdered activated carbon (PAC) is used, which is very effective at removing T&O compounds through adsorption (Figure 1).

However, during an event in 2021, the CEL staff identified halogenated anisole, 2,4,6-trichloroanisole (2,4,6-TCA;  $\text{C}_7\text{H}_5\text{Cl}_3\text{O}$ , molecular weight: 211.5 g/mol, Figure 2, left), which was produced by actinomycete colonies in filter media and produced a musty/moldy odor within the WTF (Adams *et al.* 2021b). 2,4,6-TCA has a geometric mean odor threshold concentration (OTC) of 0.9 ng/L (Young *et al.* 1996), which is substantially below the detection level of GC-MS analysis (5 ng/L). PAC is not a viable treatment if the T&O compounds are being produced after their dosing point in clarifiers, such as in filter media, water storage tanks/towers, or in the distribution system, so alternative mitigation methods were utilized, such as  $\text{KMnO}_4$ . This event showed that haloanisoles can be formed within the treatment process and spurred the modification of existing T&O monitoring programs and the CEL started screening for additional compounds contributing to musty and grassy odors.

In January 2023, a new odor event was detected by the CEL staff using sensory analysis that was believed to be the same compound that caused an event in winter 2022 that staff were unable to identify. In both cases, the odor was described as ‘musty/moldy’ and ‘fishy’ in a few cases. The production of 2,4,6-TCA was suspected but subsequently ruled out as the cause of this event after analyzing the water samples using the expanded T&O method from 2021. Instead, the production of another halogenated anisole, 2,4,6-TBA ( $\text{C}_7\text{H}_5\text{Br}_3\text{O}$ , molecular weight: 344.8 g/mol, Figure 2, right) was found to be responsible. 2,4,6-TBA has an OTC of 0.08 ng/L (Malleret & Bruchet 2002), which is below the detection limit (5 ng/L) by GC-MS.



**Figure 1** | Cypress WTF schematic and mitigation overview.



**Figure 2** | Chemical structures of two odorous haloanisoles (2,4,6-TCA [left] and 2,4,6-TBA [right]).

This paper investigates the production of 2,4,6-TBA within the treatment process, the T&O event timeline, and the steps taken by CEL staff to determine the unknown compound to be 2,4,6-TBA, including treatment changes and laboratory analyses, as well as mitigation to lessen the impact of the T&O event. These efforts resulted in a reduction of 2,4,6-TBA to the below analytical detection limits by GC–MS and demonstrated the possibility of this compound being produced in treatment plants as a byproduct of the disinfection process, which has not been reported previously.

## 2. MATERIALS AND METHODS

### 2.1. T&O compounds and analysis

Standard Methods: 2150 ‘Threshold Odor Test’, Standard Methods: 2170 ‘Flavor Profile Analysis (FPA)’ (APHA *et al.* 2022), and the T&O wheel described therein were utilized to investigate the unknown odorant. These sensory analyses allowed analysts to describe T&O compounds in a systematic way, whereby samples are dechlorinated with a 5.0 g/L ascorbic acid stock solution, stirred and heated to 60 °C, and analyzed by olfaction to assign an odor number and categorize the type of odor (muddy, musty, grassy, etc.). The strength of the odor was expressed by the threshold odor number (TON). Many compounds have lower OTCs than what can be detected by analytical means, such as GC–MS.

An expanded analytical method employing solid-phase microextraction (SPME, Standard Methods: 6040D) followed by GC–MS was developed for 2,4,6-TBA based on the previously described method for 18 T&O compounds by GC–tandem MS (GC–MS/MS) (Pochiraju *et al.* 2021). Water samples were analyzed by selected ion monitoring (SIM) using a Thermo Scientific (Waltham, MA) Trace 1310 ISQ LT GC–MS with a TraceGOLD-5MS column, with sample injection by a Supelco SPME fiber [divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS); Sigma #57329-U]. A Thermo Scientific TriPlus RSH autosampler was used with a three-position sample tool changer. High purity standards and SPME fibers are sourced from Sigma Aldrich (St. Louis, MO), and a calibration range of 5–200 ng/L was used and a method detection limit (MDL) of 2.2 ng/L was achieved for 2,4,6-TBA. Headspace vials (20 mL) with magnetic screw caps were used, with 3 g of sodium chloride, a 10 mL sample, and a 300 µL internal standard (2-isobutyl-3-methoxy pyrazine [IBMP]). Instrument conditions include a 5 min incubation time and a 30 min SPME extraction time at 65 °C, an 0.8 min SPME desorption time at 270 °C in a 50 mL/min splitless injection module using helium, a 1.5 mL/min column flow rate at 50 °C/1 min, 200 °C at 10 °C/min, 250 °C at 20 °C/min using helium as a carrier gas, 250 °C transfer line, 300 °C ion source, and 0.5 min SIM retention time window at 0.30 s SIM time.

### 2.2. Sampling during the T&O event in January 2023

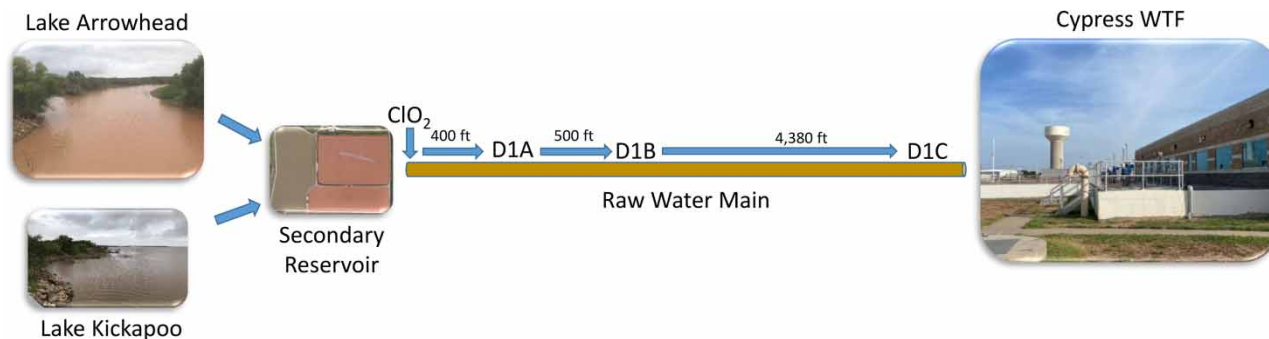
On January 9th, 2023, CEL staff noticed a slight musty odor in the tap water by sensory analysis, while all the routinely monitored compounds namely geosmin, MIB, 2-isopropyl-3-methoxy pyrazine, and 2,4,6-TCA by the SPME GC–MS analysis were non-detectable. Following sensory analyses during the January 2023 T&O event, samples were analyzed for the following week. Standards were chosen for the investigation of the event including 2,3,6-trichloroanisole and 2,4,6-TBA, which has been a known T&O compound in tap water since first detected in France (Malleret & Bruchet 2002), and has caused T&O issues in water systems previously (Bruchet *et al.* 2007). After confirming the odor of 2,4,6-TBA to be a positive match with the sensory analyses, general acquisition scans were run by GC–MS using a mass range of 50–400 amu with 0.2 s dwell time. Upon confirmation, a 2,4,6-TBA calibration curve was prepared (5–200 ng/L) and analyzed by SIM. Tap samples from the previous 2 weeks were then reanalyzed.

### 2.3. Sampling for investigating the source of 2,4,6-TBA

A series of water sampling events and analyses were conducted to determine the source of 2,4,6-TBA and its production mechanisms. Samples were collected from raw water, tap water, and at several sites within the distribution system. Samples were also collected from raw water post-ClO<sub>2</sub> addition at the disinfection zone 1 (D1C, Figure 3), post-chloramination in the treatment plant, and filter effluent. All the samples were analyzed using SPME GC–MS, and selected samples were also tested for actinomycetes using Standard Methods: 9250 ‘Detection of Actinomycetes’ (APHA *et al.* 2022). Additional sets of samples were collected on February 3rd, 6th, and 8th, 2023 and analyzed by sensory analysis and SPME GC–MS.

### 2.4. Bench-testing to confirm the production route

A temperature-controlled jar test was conducted to verify the 2,4,6-TBA formation where a recirculating water bath was used to simulate raw water temperature at 11.5 °C. Type 1 ultrapure water was used and added to three 2-L test jars. Each jar was



**Figure 3** | Schematic of Cypress D1C.

spiked with 0.30 mg/L bromide ( $\text{Br}^-$ , Ricca #R1180000-120A) to simulate the raw water concentration, two jars were spiked with 0.10 and 0.20 mg/L  $\text{Cl}_2$  to simulate excess dosages in the D1C, and one jar was not spiked with  $\text{Cl}_2$  to simulate no  $\text{Cl}_2$  addition. Jars were spiked with anisole at a concentration of 1.0  $\mu\text{g/L}$  (Sigma Aldrich #8014520500) to simulate humic anisoles in the raw water. Samples were rapidly mixed for 30 s and then slowly mixed for 1 h to simulate the detention time in the raw water pipe up to the D1C. Each jar was subsampled and analyzed by TON/FPA and SPME GC-MS.

To confirm that 2,4,6-TBA could be produced in the D1C raw water with naturally occurring concentrations of bromide and anisole and with the addition of  $\text{Cl}_2$ , a second temperature-controlled jar test was conducted to verify compound formation. Raw water from the D1C sample point was used and added to three 2-L test jars. Two jars were spiked with 0.10 and 0.20 mg/L  $\text{Cl}_2$  to simulate excess dosages in the D1C, and one jar was not spiked to simulate no  $\text{Cl}_2$  addition. Samples were rapidly mixed for 30 s and then slowly mixed for 1 h to simulate the D1C detention time. Each jar was subsampled and analyzed by TON/FPA and SPME GC-MS.

### 3. RESULTS AND DISCUSSION

#### 3.1. Timeline of unknown odor occurrence and mitigation measures

2,4,6-TBA was the only T&O compound detected, with the first confirmation in tap water at 5.57 ng/L on January 25th, 2023. Samples collected between January 9th and 23rd, 2023 were tested but showed no detection for 2,4,6-TBA. Actinomycete culturing confirmed that no colonies were present in tap water samples, and raw water samples never exceeded 100 CFU/100 mL, which is normal for CWF's raw water. Sensory analysis confirmed that the compound was still present but not detected by GC-MS. To remove the odorous compound, PAC was dosed at 10 mg/L prior to the clarifiers (Figure 1) at Cypress and Jasper WTPs on January 25th, 2023 as recommended by Pochiraju *et al.* (2022). Within the next 2–3 days, CEL staff noticed a marked reduction in odor by sensory analysis, indicating that the PAC was removing the compound being introduced into the system pre-clarification.

There was an interruption in the PAC feed system due to an ice storm between January 31st and February 1st, 2023, which resulted in a noticeable increase in the odor, and the analyses showed another detection of 2,4,6-TBA at 9.56 ng/L in tap water on February 2nd, 2023. The PAC systems were restarted on the same day. The full sample set collected through the treatment process to determine which disinfection process ( $\text{ClO}_2$  or chloramination) was causing the formation of the odor that was collected on February 3rd showed non-detectable levels for 2,4,6-TBA, while the odor was still detected by sensory analysis. This proved again that sensory perception can detect lower thresholds than GC-MS. The odor intensity lessened in the following days due to the addition of PAC and the second sample set collected on February 6th, 2023, and analyzed using TON/FPA, showed non-detectable levels except for D1C (Figure 3). The D1C site is post- $\text{ClO}_2$  and the sample had a strong musty odor. The SPME GC-MS results were all non-detectable levels as well except for the Cypress D1C, which had 9.86 ng/L of 2,4,6-TBA (Table 1). This led staff to consider the possibility that the disinfection with  $\text{ClO}_2$  was creating 2,4,6-TBA.

To test the hypothesis that the  $\text{ClO}_2$  disinfection process was causing the formation of 2,4,6-TBA in the raw water,  $\text{ClO}_2$  was shut off to the Cypress WTP on February 7th, 2023. To allow for the complete renewal of the raw water line, samples were collected after 4 h had elapsed since the  $\text{ClO}_2$  shutdown (the raw water line detention time: approximately 60 min). Sensory



**Table 1** | Sensory and GC–MS results of chlorine dioxide and PAC treatment

Sample site	Analysis	
	TON (#)/FPA (descriptor)	GC-MS (ng/L)
Secondary reservoir raw water	2, Muddy odor	<5.00
Chlorine dioxide monitoring point D1C	3, Strong musty odor	9.86
Post-chloramination	1, No odor	<5.00
Filter effluent	1, No odor	<5.00
Point of entry	1, No odor	<5.00

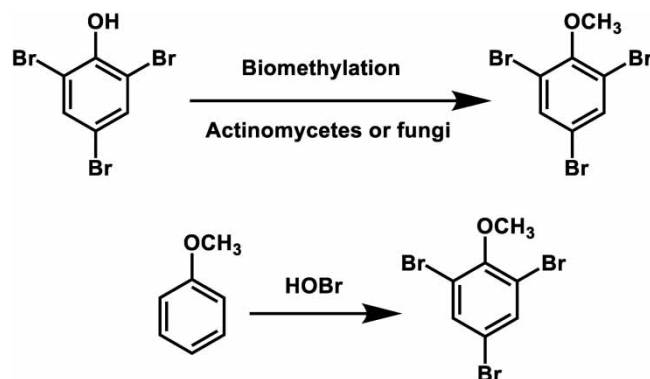
analysis yielded only earthy/muddy odors, with no musty odor. Results from SPME GC–MS were non-detectable for 2,4,6-TBA at levels <5.00 ng/L, which proved the hypothesis. Additional analyses conducted on February 8th, 2023 to confirm the results from previous sampling events showed non-detectable levels for sensory analyses as well as SPME GC–MS at <5.00 ng/L. When ClO<sub>2</sub> was turned on again the formation of 2,4,6-TBA returned, which strongly suggests that the musty/moldy 2,4,6-TBA was a product of the ClO<sub>2</sub> disinfection process.

It is well known that bromide is not oxidized by ClO<sub>2</sub> and will not form hypobromite, hypobromous acid (HOBr), bromoform, or bromate. However, it was surmised that 2,4,6-TBA is formed through the reaction of naturally occurring bromide and humic anisoles with excess free chlorine (Cl<sub>2</sub>), which could be present in measurable concentrations from the generation of ClO<sub>2</sub>. When ClO<sub>2</sub> is generated, Cl<sub>2</sub> is the target excess reactant, thereby limiting unreacted chlorite. When ClO<sub>2</sub> was turned off, 2,4,6-TBA remained non-detectable.

### 3.2. Possible pathways of 2,4,6-TBA production

It was found that 2,4,6-TBA could be produced by (1) the biochemical methylation of a bromophenol precursor by actinomycete colonies or fungus *Paecilomyces variotii* (Whitfield *et al.* 1997) or (2) in the reaction of anisoles in humic substances and bromide through disinfection (Acero *et al.* 2005; Melbye *et al.* 2006). The biological conversion of fungicide 2,4,6-tribromophenol (2,4,6-TBP) to 2,4,6-TBA (Figure 4(1)) is commonly known in packaged food and beverages (Whitfield *et al.* 1997; Jönsson *et al.* 2006; Giannikopoulos & Whitfield 2009). Also, Malleret & Bruchet (2002) hypothesized that the leaching of 2,4,6-TBP from tank coating followed by the biological conversion of 2,4,6-TBP caused the 2,4,6-TBA formation in their drinking water. However, in the current study, such biological activity was absent around D1C (Figure 3) where the 2,4,6-TBA formation was noticed.

Studies have been conducted previously to explore the pathway of bromination of anisole during chlorination in drinking water treatment facilities (Sivey *et al.* 2015; Zhang *et al.* 2016). These studies suggested that when bromide and anisole are present in source waters, HOBr and other brominating agents could form during chlorination and these brominating agents can then potentially attack the anisole compounds to form bromoanisoles (Figure 4(2)). Although ClO<sub>2</sub> used as a pre-oxidant

**Figure 4** | Two possible production pathways for 2,4,6-TBA: (1) biomethylation of 2,4,6-TBP and (2) bromination of anisole.

and primary disinfectant at the Cypress WTF does not produce HOBr, the small concentration of free  $\text{Cl}_2$  present from the generation of  $\text{ClO}_2$  (Figure 5(1)) could have been enough to react with the small concentration of bromide in the raw water to contribute to HOBr formation (Figure 5(2)) and form bromoanisoles (Figure 5(3)). This hypothesis was tested in the bench-scale testing as described in the following section.

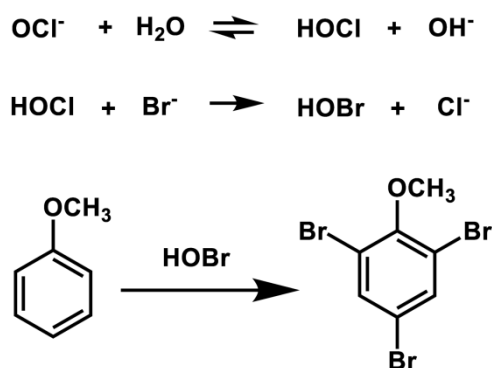
### 3.3. Bench-testing results

Results of the jar test with Type 1 ultrapure water show that in Jar 1, no odor was detected and that no 2,4,6-TBA was formed, which was spiked only with 0.30 mg/L  $\text{Br}^-$  and 1.0  $\mu\text{g/L}$  anisole. Jars 2 and 3 were each spiked with increasing concentrations of free  $\text{Cl}_2$ , and each had a noticeable increasing musty odor of 2,4,6-TBA and the compound was confirmed in Jar 3 (Table 2). These data support the production method observed during the monitoring of the treatment plant at the D1C, and that excess free  $\text{Cl}_2$  can cause the production of 2,4,6-TBA in the presence of  $\text{Br}^-$  and anisoles.

Results of the jar test with raw water show that in Jar 1, no musty odor was detected and that no 2,4,6-TBA was formed, which was not spiked with free  $\text{Cl}_2$ . Jars 2 and 3 were each spiked with increasing concentrations of free  $\text{Cl}_2$ , and each had a noticeable increasing musty odor of 2,4,6-TBA and the compound was confirmed in Jars 2 and 3 (Table 3). These data also support the production method observed during the monitoring of the treatment plant at the D1C, and that excess free  $\text{Cl}_2$  can cause the production of 2,4,6-TBA in the presence of naturally occurring  $\text{Br}^-$  and anisoles. Higher production in Type 1 ultrapure water can be attributed to the lack of organic  $\text{Cl}_2$  demand, as would be present in the raw water jar test.

### 3.4. Importance of monitoring $\text{ClO}_2$ yield and purity

The most common methods for monitoring  $\text{ClO}_2$  are Standard Methods: 4500-C and -E, which are amperometric titration methods that determine the concentrations of chlorine species, e.g.,  $\text{ClO}_2$ , free  $\text{Cl}_2$ , and chlorite ( $\text{ClO}_2^-$ ).  $\text{ClO}_2$  generators



**Figure 5** | Hypobromous acid formation pathway to contribute to 2,4,6-TBA formation: (1) production of hypochlorous acid in water; (2) production of hypobromous acid; and (3) bromination of anisole by electrophilic aromatic substitution.

**Table 2** | Bench test confirmation of 2,4,6-TBA production using Type 1 ultrapure water

Analysis type	Jar 1 – 0.00 mg/L $\text{Cl}_2$	Jar 2 – 0.10 mg/L $\text{Cl}_2$	Jar 3 – 0.20 mg/L $\text{Cl}_2$
TON/FPA	No odor	Very faint musty odor	Faint musty odor
SPME GC-MS	<5.00 ng/L	<5.00 ng/L	31.40 ng/L

**Table 3** | Bench test confirmation of 2,4,6-TBA production using raw water

Analysis type	Jar 1 – 0.00 mg/L $\text{Cl}_2$	Jar 2 – 0.10 mg/L $\text{Cl}_2$	Jar 3 – 0.20 mg/L $\text{Cl}_2$
TON/FPA	Earthy odor	Earthy/musty odor	Strong earthy/musty odor
SPME GC-MS	<5.00 ng/L	15.51 ng/L	22.91 ng/L

must be routinely monitored to ensure the yield and purity being produced. A high yield (>95%) ensures that enough  $\text{ClO}_2$  is being generated to meet disinfection requirements.

Some utilities do not strictly monitor the purity of  $\text{ClO}_2$  or check the concentration of free  $\text{Cl}_2$ . However, it is important to understand because chemical feed dosages need to be adjusted to achieve a desired amount of  $\text{ClO}_2$  while minimizing excess free  $\text{Cl}_2$  and  $\text{ClO}_2^-$ . In the United States, excess  $\text{ClO}_2^-$  must be minimized because the tap water U.S. EPA Maximum Contaminant Level is 1.0 mg/L. Excess free  $\text{Cl}_2$  must be minimized by careful operation of  $\text{ClO}_2$  generators to avoid the formation of unwanted disinfection byproducts, such as 2,4,6-TBA, in the treated water as this study shows. Overfeeding of free  $\text{Cl}_2$  to the generator can eliminate residual  $\text{ClO}_2^-$  and can produce a high yield of  $\text{ClO}_2$ . However, the excess  $\text{Cl}_2$  will result in a low purity, which is a signal for operators to increase the  $\text{Cl}_2$  feed rates, which possibly exacerbate the disinfection byproduct formation.

Yield and purity should be calculated as follows:

$$\text{Yield}(\%) = \frac{[\text{ClO}_2](\text{mg/L})}{\{[\text{ClO}_2](\text{mg/L}) + [\text{ClO}_2^-](\text{mg/L})\}} \times 100\% \quad (1)$$

$$\text{Purity}(\%) = \frac{[\text{ClO}_2](\text{mg/L})}{\{[\text{ClO}_2](\text{mg/L}) + [\text{ClO}_2^-](\text{mg/L}) + [\text{Cl}_2](\text{mg/L})\}} \times 100\% \quad (2)$$

To achieve a high yield (>95%), the dosage must be optimized to minimize  $\text{ClO}_2^-$ . To achieve a high purity (>90%), dosage must be optimized to minimize  $\text{ClO}_2^-$  and  $\text{Cl}_2$ . Too little  $\text{Cl}_2$  would cause an increase in  $\text{ClO}_2^-$  and a lower yield and purity, and too much  $\text{Cl}_2$  could result in little to no excess  $\text{ClO}_2^-$ , resulting in a high yield but potentially low purity of generated  $\text{ClO}_2$  due to excess  $\text{Cl}_2$ .

#### 4. CONCLUSIONS

By developing a multi-layered T&O monitoring program, CEL was able to detect a T&O event again by sensory methods prior to detection by SPME GC-MS. A target compound, 2,4,6-TBA, was chosen based on sensory results and the T&O wheel, which proved to be effective when samples were analyzed by SPME GC-MS. 2,4,6-TBA was confirmed to be present up to 9.86 ng/L and a TON of 3. To determine the likely mode of production, three possible sources of production of 2,4,6-TBA were tested. Actinomycetes and chloramination were ruled out, and it was found that 2,4,6-TBA was being produced in the raw water line post- $\text{ClO}_2$  addition, prior to treatment at the WTFs, through the reaction of excess free  $\text{Cl}_2$  from the  $\text{ClO}_2$  generation process with naturally occurring bromide and humic anisoles. PAC was effective in eliminating the T&O residual in the tap water, reduced 2,4,6-TBA to a non-detectable level of <5.00 ng/L, and achieved a TON of 1. The  $\text{ClO}_2$  generation process was turned off and the production of 2,4,6-TBA was eliminated. To the best of our knowledge, this is the first report describing the possible formation of 2,4,6-TBA in the drinking water treatment process in this manner.

CEL's T&O monitoring program continues to prove that sensory analysis is an integral part of an effective plan to detect unknowns. Proactive utilities should include sensory analysis in routine monitoring, especially if they do not have the capability to analyze samples by SPME GC-MS in-house. Future research is needed to continue to characterize T&O compounds, their routes of production, mitigation strategies, and the most effective means to identify them early to maintain consumer confidence. This research group is currently working to meet this need and has formed a Joint Task Group to expand SM 6040D and evaluate a suite of known T&O compounds that can be problematic for water systems (Adams *et al.* in preparation).

#### AUTHOR CONTRIBUTIONS

H.A. and M.S. performed conceptualization, designed the methodology, administered the project, wrote and edited the manuscript. S.P. performed conceptualization, designed the methodology, validated the study, wrote and edited the manuscript. K.I. performed conceptualization, designed the methodology, wrote and edited the manuscript. S.R. and E.A. validated the study, wrote and edited the manuscript. D.N. performed conceptualization, designed methodology, administered the project, validated the study, wrote and edited the manuscript.



## DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

## CONFLICT OF INTEREST

The authors declare there is no conflict.

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