Taste and odour problems generated in distribution systems: a case study on the formation of 2,4,6-trichloroanisole
Andreas Peter and Urs von Gunten

ABSTRACT
A taste and odour (T&O) episode in a Swiss town, where consumers complained about a musty odour in their drinking water, was investigated. The application of a combined organoleptic and instrumental method for T&O analysis allowed the identification of 2,4,6-trichloroanisole (TCA), with an odour threshold of 30 pg l$^{-1}$, in the drinking water in concentrations of up to 24 ng l$^{-1}$. The absence of this compound in the raw water and after treatment showed that it was formed in the distribution system. Experiments conducted in the laboratory showed that trichlorophenol as a potential precursor or chlorine as residual disinfectant played a key role in the formation of TCA, which was only formed in the presence of biofilms. Based on these results, appropriate counter-measures, such as water distribution without residual chlorine and maintenance of household particle filters, are suggested to mitigate this T&O problem.

Key words | biofilms, chlorination, drinking water, taste and odour, trichloroanisole

INTRODUCTION
Many taste and odour (T&O) problems in drinking water are provoked by algal metabolites (Suffet et al. 1999, 1996; Watson 2003). As surface water generally undergoes a multi-step treatment before it is distributed, many of these surface water-related T&O problems can be minimized with an optimal drinking water treatment (Hargesheimer & Watson 1996; Bruchet & Duguet 2004; Peter & von Gunten 2007). However, some T&O complaints cannot be related to the classical algal metabolites such as geosmin or 2-methylisoborneol (MIB), but are generated in the distribution system (Khiari et al. 1999). The causes of these T&O problems can mainly be subdivided into two categories. On the one hand, compounds that are leaching from plastic pipes and sanitary installations can impart flavours to the drinking water, which are often reported as plastic/rubber smells (Tomboulian et al. 2004). On the other hand, microbial activity in the distribution system (biofilms) can lead to the formation of a variety of T&O compounds (Skjevrak et al. 2004).

T&O problems generated in distribution systems are a major concern to water utilities because the respective T&O compounds cannot be retained through treatment, but are directly delivered to the customers. In these cases, it is of utmost importance to identify the compounds that cause the problems and also to track their origins and formation mechanisms. Only then can counter-measures be applied to mitigate the problem.

This study presents the case of a Swiss town which was confronted with consumer complaints. In this town, which is situated on the shore of Lake Zurich, the complaints started soon after the water utility had changed the drinking water treatment regime. Although the complaints declined over time, a few consumers kept complaining for more than a year about a musty odour in their drinking water. Finally, we were able to identify 2,4,6-trichloroanisole (TCA) as the compound that provoked these complaints. On the basis of this case, we illustrate a possible procedure for water utilities that are confronted with T&O complaints.

including the identification of the responsible T&O compound, its origin and the evaluation and design of counter-measures.

MATERIALS AND METHODS

Chemicals

T&O compounds which were used as external and internal standards in the quantitative analysis were obtained from Sigma-Aldrich (Buchs, Switzerland) in the highest purity available. Stock solutions (from 10 to 100 \( \mu \text{g} \text{l}^{-1} \)) were prepared in MilliQ-water. All other chemicals were reagent grade and used without further purification.

Water treatment plant (WTP)

The water utility investigated in this study treats water from Lake Zurich and distributes it to three municipalities with a total population of about 30,000 inhabitants. Lake Zurich (pH 7.7–8.6; DOC 1.4 mg l\(^{-1} \); alkalinity 2.5 mM) is mesotrophic and normally shows an annual lake turnover from December to March. Figure 1 gives a simplified overview of the treatment train that has been in operation since December 2005, which replaced the former four-step treatment train (flocculation–sand filtration–ozonation–activated carbon filtration). The consumer complaints started approximately one month after the water utility changed the drinking water treatment regime. Sodium hypochlorite was applied as residual disinfectant with a residual concentration of free chlorine of 0.02–0.06 mg l\(^{-1} \).

Sampling sites

Figure 2 shows the locations of the sampling sites in this case study. The sampling area comprised the raw water, the WTP as well as the distribution system. Sites 6 and 8 are hydrants in the vicinity of two homes with continuing consumer complaints; sites 7 and 9 are tap water samples inside the respective houses. If not indicated otherwise, these four sites were sampled after approximately five minutes of pre-flushing to allow the water temperature to stabilize. At site ‘f’, water was taken from a fountain where water was running constantly. Owing to the long transport stretch from the WTP, this point was a good representation for the average distribution system.

Analytical methods

Sensory analysis

Treated water (site 5; Figure 2) and water samples from several points in the distribution system were analysed on a bi-weekly to monthly basis by a sensory panel of the laboratory of the Canton of Zurich. The panel consisted of 4 to 6 persons who reported the organoleptic quality and the odour intensity.

Specific analysis of T&O compounds

For a specific screening of T&O compounds, SPME-GC-MS/ODP was applied. This method combined sensory analysis (ODP = olfactory detector port) with classical GC-MS-detection after pre-concentration with headspace-SPME. This method is described in detail elsewhere (Peter et al. 2009). Briefly, SPME (solid phase microextraction) was carried out using 1 cm long DVB-Carboxen-PDMS fibres (coating 50/30 \( \mu \text{m} \), Supelco, Bellfonte, PA).
mounted on a Combi PAL autosampler (CTC, Switzerland). The sample was first heated to 65°C and shaken during five minutes, followed by 30 minutes head-space extraction at 65°C. The SPME fibre was desorbed in a Split/Splitless Injector at 250°C during 3 minutes. GC-separation was done with a Trace GC 2000 (Thermo, Austin, TX) using a SLB-5MS column (length 30 m, i.d. 0.25 mm, film thickness 0.25 μm; Supelco, Bellfonte, PA) and helium as carrier gas. The GC was programmed from 50°C (constant temperature for 2 minutes) to 150°C (10° min⁻¹) and finally to 220°C (5° min⁻¹). The head pressure was held constant at 128 kPa. After the analytical column, the gas flow was split to the two detectors in a ratio of 1:1. This enabled a simultaneous detection of the T&O compounds at the MS (GCQ, Thermo, Austin, TX) and the olfactory detector port (ODP2, Gerstel, Germany). After successful identification of T&O compounds, the samples were analysed again together with external standards of the identified compounds for quantitative analysis. In this case, the MS was run in the SIM mode and IBMP (2-isobutyl-3-methoxypyrazine) was added to the samples as an internal standard at a concentration of 10 ng l⁻¹.

### Microbiological methods

Total cell numbers and the assimilable organic carbon (AOC), which is an indicator for the microbiological stability, were monitored during the investigation period. A detailed description of these flow cytometry-based methods can be found in the literature (Hammes & Egli 2005; Hammes et al. 2008).

### RESULTS AND DISCUSSION

#### Sensory analysis of drinking water

After the first complaints were received in December 2005, several samples were analysed by a sensory panel. While the treated water after the WTP (site 5, Figure 2)

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**Table 1** | Chronology of events and investigations

<table>
<thead>
<tr>
<th>Date</th>
<th>Event</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dec 2005/Jan 2006</td>
<td>Change in operation of WTP (Figure 1); first complaints after a few weeks</td>
</tr>
<tr>
<td>Dec 2005–Feb 2008</td>
<td>Sensory analysis of treated water on a bi-weekly to monthly basis</td>
</tr>
<tr>
<td>Nov 2006</td>
<td>Sampling at the WTP and T&amp;O screening with SPME-GC-MS/ODP (before lake turn-over)</td>
</tr>
<tr>
<td>Feb 2007</td>
<td>Sampling at the WTP and T&amp;O screening with SPME-GC-MS/ODP (during lake turn-over)</td>
</tr>
<tr>
<td>March 2007</td>
<td>Sampling at two homes and T&amp;O screening with SPME-GC-MS/ODP</td>
</tr>
<tr>
<td>May 2007</td>
<td>No further addition of residual disinfectant (NaOCl) at the WTP</td>
</tr>
<tr>
<td>June 2007</td>
<td>Sampling at two homes (the same ones as in March 2007) and T&amp;O screening with SPME-GC-MS/ODP</td>
</tr>
<tr>
<td>Nov 2007–Feb 2008</td>
<td>Experiments with particle filter from one of the investigated homes</td>
</tr>
</tbody>
</table>
exhibited a normal taste to most of the examiners, the majority of the panel confirmed the musty odour in the drinking water at the fountain (site ‘f’, Figure 2). Figure 3 summarizes the olfactory findings for these two sampling points.

It should be noted that most of the olfactory sensations at site 5 were not reported as musty, but as chlorinous. This can be traced back to the residual disinfectant, which—at that point—exhibited an active chlorine concentration between 0.02 and 0.06 mg l\(^{-1}\) (odour threshold: 0.025 mg l\(^{-1}\); Khiari et al. 1999). These first findings already indicated that the T&O problem was probably generated somewhere in the distribution system and not directly in the WTP. As a first hypothesis, it was argued that precursors which eventually led to the formation of the T&O compounds were not retained during drinking water treatment as efficiently as they were before the change in operation. Indeed, in the old treatment train the water was first subjected to filtration, whereas in the new process the raw water was directly ozonated without a pre-filtration step (Figure 1).

Figure 3(b) shows that the musty odour was detected by the sensory panel mainly in two periods, namely at the very beginning of the new operation scheme (December 2005–January 2006) and in summer–autumn 2006. A higher temperature in the distribution system (15–20\(^{\circ}\)C at certain sampling points in summer months compared with < 10\(^{\circ}\)C in winter months) is likely to have caused the latter incident. As for the first phase, it was also speculated that blooms of the cyanobacterium Planktothrix rubescens, which is abundant in the metalimnion of Lake Zurich in autumn (Peter et al. 2009), were involved in the T&O problem. In fact, the raw water, which is pumped at a depth of 40 m, was observed to exhibit high amounts of algal debris after ozonation during lake turn-over (generally from December to March). This negatively affected the performance of the WTP during this phase, which required frequent cleaning of the UF-membranes.

### Specific analysis for T&O compounds with GC-MS/olfactometry

In order to identify the T&O compounds that were responsible for the complaints, samples from several sampling campaigns were specifically analysed for T&O compounds with SPME-GC-MS/ODP. In two campaigns, the WTP at sites 1–5 (Figure 2) and a fountain (site ‘f’) were sampled. No T&O compounds could be detected in the first campaign, which was run in November 2006 before the turn-over of Lake Zurich. The second campaign, which was performed in February 2007 during the lake turn-over, revealed the presence of traces of the potent T&O compound 2-methylisoborneol (MIB) in the raw water. MIB exhibits a musty odour above a threshold...
concentration of 15 ng l\(^{-1}\) (Young et al. 1996). However, the MIB concentrations were already below the quantification limit (<2 ng l\(^{-1}\)) and the odour threshold in the raw water and not detectable after treatment. Therefore, MIB could not have been responsible for the musty odour in the tap water.

In a next step, samples were taken from two homes with continuing consumer complaints in March 2007. To verify whether the T&O compounds were present already in the distribution system or only formed in the house installations, two hydrants (sites 6 and 8, Figure 2) in the vicinity of the homes were sampled together with the tap water (sites 7 and 9, Figure 2) inside the houses. During this sampling campaign, another potent T&O compound could be detected. In both houses, the musty compound 2,4,6-trichloroanisole (TCA) was found at concentrations which were significantly higher than its odour threshold of 30 pg l\(^{-1}\) (Malleret et al. 2001). Table 2 shows the corresponding results of this investigation in March 2007 at the customers’ tap.

Table 2 clearly reveals the site-specific formation of TCA. The hydrant near home 2 was the only place where TCA had been detected in the distribution system. This might be due to the long water residence time in this area, which is exemplified by the higher water temperature (usually 3–5° C higher than in other parts of the distribution system during summer). As for home 1, a further inspection of the house installation revealed that the residents used a particle filter before the water was distributed in the house. This filter was heavily covered with biofilms (visual inspection) and could therefore have played a major role in TCA formation.

Hypothetical mechanism of TCA-formation

Figure 4 shows the hypothesized formation mechanism of TCA in the current study. It is assumed that phenolic precursors were chlorinated to 2,4,6-trichlorophenol (TCP), which was eventually transformed to TCA by microorganisms. The last step, namely the formation of TCA in the distribution system through the biomethylation of chlorophenols, has been described in the literature (Montiel et al. 1999). It is likely that this process led to the TCA that was observed in the two investigated homes.

We hypothesize that the chlorophenols were formed in a reaction between phenolic precursors and the residual disinfectant. 2,4,6-trichlorophenol is a likely transient reaction product because the activated ortho- and para-positions of the aromatic ring are appropriate sites for chlorination via an electrophilic ring substitution mechanism (Heasley et al. 2004). A complete chlorination with an eventual cleavage of the aromatic ring is suspected at substantially higher chlorine doses than used in the WTP (less than 0.1 mg l\(^{-1}\) active chlorine). To substantiate these assumptions, a kinetic model (Acuchem) was used to calculate the formation of chlorophenols (mono-, di- and tri-substituted) and non-aromatic products during the chlorination of phenols (Gallard & von Gunten 2002). The reactions of protonated phenols with HOCl are negligible at pH 8 and, therefore, were not taken into account for the calculations (Heasley et al. 2004). The kinetic data for the model are summarized in Table 3.

The calculated formation of TCP for varying initial chlorine doses and an assumed chlorine half-life of 5 hours in the WTP effluent water is shown in Figure 5.
The calculations revealed that chlorine doses between 0.05 and 0.5 mg l\(^{-1}\) Cl\(_2\) lead to the high levels of TCP. Stable TCP concentrations were achieved after approximately 20 hours. Higher chlorine doses resulted in a faster increase in the TCP concentrations and led to maximal TCP concentrations that were comparable to TCP end concentrations with lower chlorine doses. However, the TCP maximum was already achieved after 1 hour for a chlorine dose of 1 mg l\(^{-1}\) or 2 mg l\(^{-1}\). At that point, there was enough chlorine left to further (to a certain degree) oxidize TCP to non-aromatic products. While chlorine doses > 0.5 mg l\(^{-1}\) led to significantly lower final TCP concentrations than lower chlorine doses, they are likely to form undesired by-products, such as trihalomethanes (e.g. chloroform) (Gallard & von Gunten 2002).

### Table 3 | Second-order rate constants for reactions of HOCl \(^{p}\) with (chloro)phenols

<table>
<thead>
<tr>
<th>Compound</th>
<th>(pK_a)</th>
<th>(k) (M(^{-1}) s(^{-1})) (^{\dagger})</th>
<th>(k_{app}) (M(^{-1}) s(^{-1})) (^{\ddagger})</th>
<th>Oxidation products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td>10.0</td>
<td>30,000</td>
<td>297</td>
<td>80% 2-chlorophenol</td>
</tr>
<tr>
<td>2-chlorophenol</td>
<td>8.6</td>
<td>2,400</td>
<td>518</td>
<td>74% 2,6-dichlorophenol 26% 2,4-dichlorophenol</td>
</tr>
<tr>
<td>4-chlorophenol</td>
<td>9.4</td>
<td>2,600</td>
<td>93</td>
<td>2,4-dichlorophenol 2,4,6-trichlorophenol</td>
</tr>
<tr>
<td>2,4-dichlorophenol</td>
<td>7.9</td>
<td>300</td>
<td>176</td>
<td>2,4-dichlorophenol 2,4,6-trichlorophenol</td>
</tr>
<tr>
<td>2,6-dichlorophenol</td>
<td>7.0</td>
<td>190</td>
<td>173</td>
<td>2,4,6-trichlorophenol (and further reaction to non-aromatic products)</td>
</tr>
<tr>
<td>2,4,6-trichlorophenol</td>
<td>6.2</td>
<td>13</td>
<td>13</td>
<td>2,3,4,6-tetrachlorophenol (and further reaction to non-aromatic products)</td>
</tr>
</tbody>
</table>

\(^{\dagger}\)Only reactions of phenols with the protonated form of HOCl (\(pK_a\): 7.54) were considered.
\(^{\ddagger}\)Second order rate constants with deprotonated phenols (\(T = 23 \pm 2^\circ C\)) obtained from Gallard & von Gunten (2002) and Acero et al. (2005).

### Experiments with precursors and biofilms

To investigate the role of the assumed precursors and biofilms in TCA formation, the particle filter of home 1 was dismounted and used for laboratory experiments. In the first experiment, water from the WTP after ultrafiltration (site 4, Figure 2) was kept in the filter unit for one month. Subsequently, the experiment was slightly modified. In the second experiment, the suspected precursor (TCP) was spiked to the WTP effluent water at a concentration of 10 μg l\(^{-1}\). In a third and fourth experiment, chlorine was dosed to the WTP effluent water at a similar dose as in the WTP effluent (0.04 mg l\(^{-1}\) active chlorine) and at a much higher dose (2 mg l\(^{-1}\)) respectively. After the addition of chlorine, the water was stored for 4 hours before it was transferred to the filter unit. This period represented the transportation time in the distribution system. An additional experiment with 2 mg l\(^{-1}\) chlorine and a contact time of 40 hours was performed to check whether TCA was still formed after the expected complete oxidation of TCP (Figure 5). In all three experiments with chlorine addition, the residual chlorine was quenched with sodium thiosulfate (Na\(_2\)O\(_3\)S\(_2\)·5H\(_2\)O) at an excess concentration of 10\(^{-4}\) M before the solution was transferred to the filter in order to avoid negative effects on the biofilm.
Figure 6 shows the resulting TCA concentrations in the laboratory experiments with the household filter. No TCA formation could be observed with unspiked WTP-effluent water. The resulting TCA concentrations in the experiments with the assumed precursor TCP were similar to those detected in the first sampling campaign in this home (24 ng l\(^{-1}\)). This hints at the important role of this precursor and the biofilm-mediated transformation of TCP into TCA. The experiment with the addition of low chlorine doses, which also led to TCA formation, indirectly indicates the possible formation of TCP after the addition of the residual disinfectant. However, TCA formation was also observed with a high chlorine dose of 2 mg l\(^{-1}\) for two contact times (4 h, 40 h). This outcome is contrary to the kinetic calculation of chlorophenol formation (Figure 5), which predicted a complete oxidation of TCP at chlorine doses of 2 mg l\(^{-1}\) and contact times of more than 24 hours. Obviously, TCP is not the only precursor for TCA formation, but it is probable that other chlorinated aromatic compounds can lead to TCA after a microbiologically mediated transfer into phenolic compounds.

Hence, despite the obvious reactions of the investigated precursors (TCP and chlorine addition) to TCA, it remains unclear which kinds of precursor (phenolic/aromatic) were involved and where the actual phenolic precursors in the distributed water came from. Simple phenols in the raw water would be completely oxidized during ozonation. Hence, if the precursors were already present in the raw water, they must have been embedded in a more complex structure. Natural organic material (NOM), which is retained only to a minor degree in the presented treatment train (data not shown), is a possible source of the required precursors because it can be rich in polyphenolic moieties (Chen et al. 2002). Indeed, Figure 7 reveals that approximately one month after the change in operation (December 2005), the UV absorbance at 254 nm for the treated water started to rise. The UV\(_{254}\) is an indicator for the presence of aromatic compounds in the water. Obviously, the activated carbon filter could no longer completely retain the aromatic compounds after a few weeks of operation. The time of the breakthrough of the aromatic compounds (end of December 05) is consistent with the start of the consumer complaints. Alternatively, anthropogenic micropollutants might act as TCP-precursors. Although some of these compounds contain phenolic groups (e.g. the pesticide 2,4-D), their concentrations in Lake Zurich water are probably too low to be of importance (typically in the low ng l\(^{-1}\) range). Finally, a third possibility is that the precursors did not come from the raw water itself, but were leached from piping materials in the distribution system.

**Mitigation strategy**

According to our hypothesis (Figure 4), the addition of chlorine played a major role in the formation of TCA.
Hence, it was decided to stop residual disinfection in May 2007. The success of this measure was checked by analysing samples from the same two private homes, where TCA had been discovered, five weeks after the system was run without chlorine residual. In the meantime, the microbiological quality of the drinking water was monitored intensively. The absence of chlorine did not lead to an increase in the total bacterial cell numbers (data not shown), which can be explained by the low AOC-levels (assimilable organic carbon) of the treated water ($15–30 \mu \text{g l}^{-1}$). Hence, the microbiological requirements of tap water could be met even without the addition of a residual disinfectant.

As for TCA, this measure also proved to be successful. The June 2007 data in Table 2 show results for the system five weeks after stopping chlorine addition. TCA was no longer detected in the distribution system. Furthermore, the concentrations in the home with the particle filter (home 1) were also considerably lower than during the first sampling in March 2007. However, TCA was still present in the tap water of this house, although at detectable concentrations only in the first flush. Consistent results were obtained for the organoleptic quality of the tap water. The sensory panel had not reported a musty odour after May 2007 (Figure 3). As a consequence, consumer complaints declined, although they did not cease completely.

**CONCLUSIONS**

The presented case study confirms that it can be difficult to identify and solve the cause of T&O problems. In this case, it took several months to reliably identify the responsible T&O compound (TCA) and its origin. Finally, enough information had been gained to design counter-measures. However, parts of the puzzle remain unsolved. For example, it remains unclear where the precursors, which eventually led to TCA formation, came from.

Despite this incomplete picture, three main triggers that lead to enhanced TCA formation could be identified in the course of this investigation: (i) the availability of halogenated phenolic/aromatic precursors, mainly due to the addition of chlorine to the treated water; (ii) biofilms which mediate the formation of precursors into TCA; and (iii) long water residence time in the distribution system, which gives biofilms time to form TCA. The last factor is particularly pronounced in household installations with poor maintenance.

Hence, the following measures are suggested to prevent or at least minimize TCA formation:

- As the addition of chlorine as residual disinfectant is likely to favour the formation of TCA, distribution of the water without chlorine should be considered if the microbiological quality in the distribution system and drinking water regulations allow this measure. In this case, total bacterial cell counts are an ideal control parameter to monitor the microbiological water quality (Hammes et al. 2008). If a residual disinfectant is necessary, chlorine dioxide could be used as an alternative because it does not form chlorophenols.

- In order to prevent water from standing in the distribution system for a long time, dead ends or stretches with low water throughput should be avoided through constructive measures (e.g. ring systems).

- Plastic pipes and sealing materials, in particular, often contain plasticizers and polymer units that are easily bioavailable. Biofilms can quickly establish on the surface of materials which release these compounds. Only construction products that are designed to be in contact with drinking water and whose biomass production potential has been tested (e.g. according to the German method DVGW W270) should be used in distribution systems and in households.

- Particle filters that are used in households should be cleaned and maintained regularly. Otherwise, biofilms are likely to establish on such filters. It is impossible to completely avoid microbial growth in the distribution system, but hot spots with a high microbial activity such as the surface of filters should be avoided as much as possible.

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